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Subcontractor: Delphi Automotive Systems, LLC
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Points of Contact:
Administrative POC: Rodica Sibisan
Government Contracts Manager
Phone: 248-813-2106
Fax: 248-813-3251
Email: rodica.sibisan@delphi.com

Technical POC: Daniel Hennessy
Principal Investigator
Phone: 248-732-0793
Fax: 248-732-0496
Email: daniel.t.hennessy@delphi.com

Program Manager: Mike Rasmussen
Program Manager
Phone: 248-732-0681
Fax: 248-732-0495
Email : mike.e.rasmussen@delphi.com

Submitting Organization : Delphi Automotive Systems, LLC
5725 Delphi Drive
Troy, MI 48098

In Collaboration With: Battelle Memorial Institute, PNNL
Electricore, Inc
United Technologies Corporation

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SECA Final Scientific/Technical Report

1 EXECUTIVE SUMMARY

1.1 Introduction

Delphi Automotive Systems (“Delphi”) has been an active partner with the Department of Energy (“DOE”), under the Solid State Energy Conversion Alliance (“SECA”) program, since 1999. This final report will summarize the activity funded through DE-FC26-02NT41246.

The SECA program was originally conceived to have 3 distinct phases:

Phase 1: Proof of Concept: Development and Integration of Stack and Reformer technology into a demonstration system.

Phase 2: Cost reduction, power scale-up, system optimization, supplier development and manufacturing development.

Phase 3: Production engineering, validation and manufacturing scale-up for first commercial applications.

As a result of the work done under SECA, Delphi, partnered with Battelle-PNNL, was able to develop solid oxide fuel cell (“SOFC”) stack, reformer, and fuel cell system technology. Over the course of the program, Delphi was able to advance the technology from proof of concept to a commercial intent product. In 2008, Delphi was able to demonstrate a prototype SOFC Auxiliary Power Unit (“APU”) running on diesel fuel on a Peterbilt truck. In 2012, we will be installing the next generation power unit on a national fleet vehicle for a one-year on-road demonstration. The durability, performance, fuel economy, and emission information collected during this demonstration will prove the value proposition of a SOFC APU.

Stack advancements under this project contributed to Stationary Power Unit (“SPU”) development as well as military applications by Naval Undersea Warfare Center (“NUWC”) and National Aeronautics and Space Administration (“NASA”).

1.2 Summary of Delphi SECA activities by year:

1.2.1 2002:

At the outset, the SECA program added additional fuels to the gasoline focus Delphi was currently developing at the time. As a result of introducing natural gas, Delphi developed an integrated brazed, planar reformer/combustor/air preheater device which was capable of start-up, catalytic partial oxidation (“CPOx”) and autothermal operating modes. Delphi developed and tested catalyst washcoats for the reformer at its in-house

catalyst manufacturing division (ASEC Manufacturing in Tulsa, OK) using bench scale “single planar” reactors.

A Gen 2 stack was also developed: a cross-flow design. It used ferritic stainless steel interconnects incorporated into a “cassette” which also formed the gas inlet and outlet manifolds for cathode and anode flows. The cells were brazed into the repeating unit and then a glass seal was used between repeating units. The braze and glass materials and processes were developed by PNNL.

Stacks built in this time frame were small, with 1-6 cells. Most builds were with 7 x 7 cm active area cells. Durability was at about 1,000 h. Thermal cycling ability was initially very limited, with a notable loss of performance after even a single thermal cycle.

While the subsystem technologies were immature, Delphi was doing first designs of the tight packaging of hot zone, balance of plant and insulated enclosure components needed to make a functioning power system.

1.2.2 2003:

Systems development activities focused on developing plans and intermediate targets for all SOFC system subsystems. System mechanization schematics were developed for the current (Gen 2 APU) and next generation (Gen 3 APU and Gen 3 SPU) systems. Simulink and HYSYS models were developed in parallel with first generation control algorithms. Design changes were made to the first system in an SPU configuration. The first units with these changes were built and tested in 2004.

Reformer activities focused on fuel delivery and mixture preparation, sulfur tolerance and reformer operation mapping carbon formation regions. New techniques were developed to measure the onset of carbon formation in the reformer lab using an Inconel “cold finger”.

Stack development included evaluation of higher performance cathode materials and initial development of reinforcement of the glass seals (with ceramic fibers). By the middle of 2003 Delphi built a number of 15 cell stacks sized for the Gen2 system and these began to be routinely tested.

One key achievement in 2003 was the demonstration of a 2x15 cell stack module operating on coal gas at DOE’s Power System Development Facility in Wilsonville, AL. These stacks were mounted on an integrated stack manifold, as in the Gen 2 APU design. Another key achievement was the build and test of our first 30 cell stacks (**see Figure 1**).

Figure 1: Delphi Gen 3 stack on test

1.2.3 2004:

Delphi demonstrated 1.6 kW gross power in a Gen 2 APU. Solid model design geometry, Computational Fluid Dynamics (CFD), Finite Element Analysis (FEA), and Thermal analysis were completed for the Gen 3 APU.

The CPOx reformer (**see Figure 2**) was further developed with and both gasoline and methane testing completed. Endothermic reformer technology (using water or anode recycle) was being developed in parallel. This technology would be utilized in the SPU demonstration system.

Figure 2: Catalytic Partial Oxidation reformer, in the test lab.

Figure 3: Delphi Gen 3 cassette – exploded view

Gen 3 cassettes (repeating units for stack) were successfully fabricated and tested (**see Figure 3**). The Gen 3 cassettes have a 50% reduction in thickness and weight compared to Gen 2 cassettes. This allows 30 cells to be packaged in a space similar to the previous 15-cell stack prototypes. The Gen 3 cassettes were the first to be fabricated using high volume manufacturing processes like stamping, brazing and laser welding.

Over twenty Gen 2 stack sub-system were built and tested. Power densities of 420 mW/cm² at 0.7V/cell at 750°C were achieved in the stack laboratory with simulated recycle reformat. Thermal cycling tests in a furnace with 60 minutes heat-up from room temperature to 750°C demonstrated five thermal cycles with minimal degradation. Delphi's first 30-cell Gen 3 stacks were fabricated and tested. 2x30 cells was the intended production stack configuration for the 42 V gasoline APU.

1.2.4 2005:

The Gen 3 APU was adapted for use as a stationary power unit (SPU 1) by replacing the Gen 3.0 tubular gasoline CPOx fuel reformer with the new Gen 4.1 tubular CPOx natural gas fuel reformer. This design was the target for first system integration and test of a methane-fueled SPU.

Process Air Module ("PAM") components were built and tested on dynamometer and airflow stands. Since the PAM is a major contributor to parasitic power loss, particular attention is given to identifying the sources of the PAM losses. Test data is used to refine the Computational Fluid Dynamic ("CFD") analysis model so that alternative manifold design features can be studied to reduce the PAM power losses. Thermal testing of an instrumented motor and controller was completed at worst case ambient

temperature conditions so that the minimum airflow limit of the air-cooled PAM could be established. Durability testing of the motor and controller continued.

Prototype part fabrication of a third generation Integrated Component Manifold was completed. This design incorporated a new Gas Phase Combustor ("GPC"). Results from system tests indicated improved gas distribution, gas mixing, and reduced pressure drop in the manifold. Improved GPC light -off and sustained ignition was also achieved with this GPC design.

Reformer catalyst durability was demonstrated over 2,000 hours for steady-state partial oxidation of gasoline fuel, while meeting acceptable reformat quality. Modifications were made to the durability test to permit similar studies with natural gas or diesel fuels. The durability test was modified to match differing APU power requirements by cycling through five different sets of operating conditions. Catalyst formulations were identified for partial oxidation of low-sulfur diesel fuel, and appropriate processing regimes and catalysts were identified for processing of diesel fuel containing up to 50-ppmw sulfur. **Figure 4** shows a tubular reformer assembly of this generation. The section to the right of the flange contains mixing vaporization geometry, and the section to the left contains the reforming catalyst.

Figure 4: Tubular Reformer Assembly

Cathode development efforts have been focused on improving the long-term durability of (La,Sr)(Co,Fe)O₃ ("LSCF") cathodes for use in Cr-free operation. Interconnect development focused on improving cathode and anode contact as well as minimizing Cr interaction with the cathode. Stack results have demonstrated power densities of greater than 500 mW/cm² at 0.7 Volts and a 750°C operating temperature. Stacks have demonstrated greater than 2,000 hours continuous durability with less than 10% degradation (less than 1% in the last 1,000 hours). Thermal cycling tests have shown greater than 5 thermal cycles with no degradation in power.

1.2.5 2006:

2006 was a significant year for Delphi, meeting the systems goals of SECA phase 1:

- Peak Power Performance: Delphi's SECA demonstration system produced peak power of 4.24 kW on methane, achieving the goal of 3-10 kW.
- Peak Efficiency: Delphi's system demonstrated a peak efficiency of 37%, exceeding the phase 1 goal of 35 percent.
- Power Degradation: Delphi's demonstration system matched the durability goal with power degradation of just 7% over 1,500 hours of operation.
- Factory Cost: estimate of \$770 /kW, meeting the Phase 1 goal of \$800/ kW for the total power unit, in volume production.
- Fabrication: integration and testing of 30-cell stacks in the SECA Phase 1 demonstration system.

Figure 5: Testing of two SOFC systems

Delphi demonstrated stable reformer operation at the desired operating points of the system with natural gas fuel. **Figure 5** shows two SOFC power systems operating in the system test lab.

Delphi demonstrated cell power density in a 30-cell stack assembly of 700 mW/cm² at greater than 0.7 V/cell and operating conditions of 750°C nominal stack temperature, and 60% fuel utilization. The testing resulted in total power of 2.2kW for the 30 cell stack. The complete stack assembly has a mass of 9kg and volume of 2.5 L for mass specific power density of less than 4 kg/kW and volumetric power density of more than 0.9 kW/L.

Delphi's Balance of Plant ("BOP") component hardware was fabricated and tested for the SECA Phase 1. With the commencement of system durability testing, BOP design efforts focused on supporting system hardware builds and maintaining hardware currently on system test. Supplier sourcing activity during this period included identifying future prototype and production suppliers for Process Air Manifolds, and Cast Integrated Component Manifolds.

1.2.6 2007:

Having met the Phase 1 deliverables, Delphi continued SOFC development in support of the SECA Phase 2 initiatives.

Delphi SOFC conducted a system durability test using utility supplied natural gas and a TDA Research Inc. sorbent desulfurizer. This system logged over 2,400 hours of testing with a stack degradation rate of less than 1% per 500 hours.

A Delphi SOFC System was run to full power and it produced 2.2 kW net and 36% efficiency on methane with full-internal reforming. This system was then run for 470 hours at high load (50 amps, 1.8 kW net) with 75% internal reforming. The measured degradation on the stacks was 1.1 % per 500 hours. **Figure 6** shows the integrated SOFC system of this generation, fully enclosed, with the cover removed and with the top section of hot zone insulation removed.

Gen 5T Endothermic Reformer was modified for use with US07 ultra low sulfur diesel ("ULSD") fuel and evaluated with recycle based reforming. The advantages of this type of reforming are the improvement of reforming efficiency, reduced propensity to form carbon and the ability to have higher effective fuel utilization in the stack. For internal reforming of natural gas, a cracking catalyst was developed and evaluated with essentially 100% conversion of higher hydrocarbons and no selectivity to ethylene formation. Consequently, high methane content is retained, which is useful for stack cooling with internal reforming.

Figure 6 – Generation 3 SOFC System

Gen 3.2 cassettes were successfully fabricated. Based on the experience developed in producing Generation 3.1 cassettes, the new design was developed to reduce stresses within the cassette, allowing for a more robust cassette. An improved cassette to cassette glass seal was tested. Current seals would allow a stack to thermal cycle only 5 times. The new seal was developed that demonstrated 16 thermal cycles in the stack lab without leaks or degradation in power. A new, low-cost interconnect coating was developed which has low resistivity, blocks chromium ("Cr") effectively and most importantly, can be processed by high volume manufacturing processes. Avoiding Cr poisoning of the cathode is vital for long term stability of cathode performance.

Delphi developed and implemented a test for studying Cr vaporization in BOP components. The capability will enable Delphi to determine the level of Cr being released from completed assemblies and thereby understanding the system degradation mechanism.

1.2.7 2008:

Delphi successfully integrated a full-scale hot-reformate desulfurizer, diesel endothermic reformer, and SOFC stacks into an ULSD SOFC system. We demonstrated 50 thermal cycles on a Natural Gas SOFC System. The team designed and procured a heavy-duty vehicle application development chassis to enable system testing on a heavy duty truck.

Delphi designed a new air and fuel mixing approach that is expected to have benefits with respect to pre-combustion and fuel condensation / pyrolysis in the fuel reformer inlet. We prototyped a novel FeCrAlY-based honeycomb monolith that may be useful for chemical reactions requiring significant heat input.

Delphi successfully fabricated and integrated multiple 30-cell Generation 3.2 stack modules into the system. The team developed accelerated tests for cell and stack robustness.

Delphi sourced new Process Air Blowers and Recycle Pumps for the next generation system. The team initiated internal development on a more robust igniter to survive the aggressive thermal environment. The team also continued testing of Cr volatility from various materials.

1.2.8 2009:

No funded activities under the Delphi SECA contract.

Delphi continued to develop the small scale SOFC system, and reformer and BOP for truck APUs, funded internally and with other smaller DOE or DOD programs.

Figure 7: Comparison of SPU1 SOFC prototype with first truck APU design

Initial design and packaging was completed for the diesel truck APU configuration. This unit was designed for up to 5 kW and included a desulfurizer, a larger and more efficient endothermic reformer for diesel fuel and integrated power electronics. It was designed to fit in the same location as ICE-based APUs that are currently in the market.

1.2.9 2010:

Two 30-cell Gen 3.2 stacks incorporated with a natural gas CPOx reformer were built, tested, and delivered to NASA for their evaluation. The stacks performed very well at fuel utilizations of up to 80%. NASA used the Navy's NUWC facility to run tests on this hardware set with results reported at the 12th SECA Workshop, in July 2011 - <http://www.netl.doe.gov/publications/proceedings/11/seca/pdf/Thu%20PM/Burke%2C%20NUWC-NASA.pdf>.

Delphi's next generation, Gen 4 (large footprint) stack, was developed under the subsequent DOE SECA Coal Based Systems contract. The new stack utilized many of the advances developed under the initial SECA contract. Delphi provided stacks to United Technologies Corporation ("UTC") for system evaluation. Additionally, a pilot manufacturing process is being developed for this stack at Delphi's facility in Fenton, MI.

System testing continued in the lab and on test trucks (funded internally and with other small DOE or DOE programs). The "A" level APU system was shown publicly at the Hybrid Truck Users Forum conference in Dearborn, MI in September 2010 and at a number of other DOE, DOD or OEM customer events during the year (**see figure 8**).

Figure 8: SOFC APU installed on a PACCAR development truck

In addition to the stack and system development work described above, Delphi completed performance mapping tests with simulated coal gas reformat compositions with Gen 3.2 30-cell stacks. Delphi successfully completed the tests with the Gen 3.2 30-cell stack in co-flow and counterflow configuration. The testing included

performance evaluation of the stack as a function of different fuel compositions, different inlet temperatures and different fuel utilizations. Electrochemical performance, temperature distribution, in the plane of the repeating unit and within the height of the stack, and other stack outputs were mapped. The results provided a valuable understanding of the performance of the stack with coal gas reformat compositions.

1.2.10 2011:

No funded activities under the Delphi SECA contract. Stack scale-up and manufacturing development, heavy duty truck APU demonstration and military application development continued with other programs.

In January, Delphi's SOFC APU was placed on EPA's emerging technologies list, which is administered by EPA's National Clean Diesel Campaign program.

Figure 9: Current packaging of SOFC hot zone components

Figure 9 shows the current tight packaging of hot zone components in the truck APU B-level system, including a single, large footprint stack, an endothermic capable reformer with integral anode tail gas combustor and desulfurizer and heat exchanger components.

1.3 Conclusion:

Over the years of its SOFC development, Delphi has moved the technology from proof of technology, to proof of concept, to near commercial applications. Early systems did not generate enough power to support their own parasitic requirements. Today, we are investigating the opportunity to provide kW-scale power APUs to heavy duty commercial trucks while idling, as well as provide MW-scale power to large coal based power plants for regional power supply.

Delphi has worked through the technical development challenges and is now able to engage prospective customers in detailed conversations about how a SOFC power system can meet the necessity for clean, efficient, environmentally friendly power. Based upon current discussions, Delphi is building its business case to bring the technology to market.

Delphi has been able to develop the stack and supporting BOP components to be fuel flexible. To date, the team has proven that SOFC technology is compatible with gasoline, natural gas, hydrogen, and diesel. Future work will continue to expand this flexibility. Near term evaluation is planned for bio-diesel and bio-mass/waste fuels.

These gains would not have been possible without the support of DOE. The support provided by DOE during this period is greatly appreciated.

1.4 Recommendations

The SECA project has been very successful in developing Solid Oxide Fuel Cell capability in the US. The program needs to be continued to take advantage of the achievements. The focus needs to continue on cell and stack development in the near term, but should also include system integration activities, so that there is a path to market.

2 PROGRAM SUMMARY

2.1 Program History

The program history at Delphi is covered in detail in section 1.2.

2.2 Scope of Work

The overall objective is to develop a SOFC stack that can be economically produced in high volumes and mass customized for different applications in transportation, stationary power generation, and military market sectors. In Phase I, work will be conducted on system design and integration, stack development, and development of reformers for natural gas and gasoline. Specifically, Delphi-Battelle will fabricate and test a 5 kW stationary power generation system consisting of a SOFC stack, a steam reformer for natural gas, and balance-of-plant (BOP) components, having an expected efficiency of ≥ 35 percent (AC/LHV).

In Phase II and Phase III, the emphasis will be to improve the SOFC stack, reduce start-up time, improve thermal cyclability, demonstrate operation on diesel fuel, and substantially reduce materials and manufacturing cost by integrating several functions into one component and thus reducing the number of components in the system. In Phase II, Delphi-Battelle will fabricate and demonstrate two SOFC systems: an improved stationary power generation system consisting of an improved SOFC stack with integrated reformation of natural gas, and the BOP components, with an expected efficiency of ≥ 40 percent (AC/LHV), and a mobile 5 kW system for heavy-duty trucks and military power applications consisting of an SOFC stack, reformer utilizing anode tailgate recycle for diesel fuel, and BOP components, with an expected efficiency of ≥ 30 percent (DC/LHV). Finally, in Phase III, Delphi-Battelle will fabricate and test a 5 kW APU for mass-market automotive application consisting of an optimized SOFC stack, an optimized catalytic partial oxidation (CPO) reformer for gasoline, and BOP components, having an expected efficiency of ≥ 30 percent (DC/LHV) and a factory cost of $\leq \$400/\text{kW}$.

3 2002 TECHNICAL PROGRESS AND ACHIEVEMENTS

3.1 Task 1: System Development

The task provides for the overall system design, including product definition, conceptualization, system modeling, preliminary design, and system integration. Task 1 efforts were coordinated with subsystem development (Tasks 2 and 3) and provided for concept generation support for these tasks. Task 1 efforts were also coordinated with the system fabrication task. Inputs from the privately funded balance-of-plant components and manufacturing efforts will be key elements throughout the project.

3.1.1 Define System Requirements

3.1.1.1 General Requirements

The requirements for the 5 kW Auxiliary Power Unit (APU) were generated with the automotive (mobile) application as the focus. Progress towards the automotive requirements satisfied many of the stationary power plant requirements along the way. The general requirements of the power plant include the overall target volumetric and gravimetric power densities, overall conversion efficiency as well as the typical service life and duty requirements. These requirements are shown for prototype design levels (1-5 years) as well as target commercial levels (5-10 years). The requirements for the 5 kW automotive APU are summarized in **Table 3.1.1-1**.

Table 3.1.1-1: APU General Requirements

APU General Requirements:			
	Prototype	Commercial	Units
Net Electrical Output (VA)	3	5	kW
Response (10 to 90% load)	5000	500	msec
System Volume	75	44	Liters
	15	10	Liters/kW
System Mass	70	50	kg
Stack Volume	3	2	L/kW
Stack Mass	5	3	kg/kW
Service Duty <10% Power Degradation	>1000	>10000	hours
Service Life w/PM	3	10	years
Cold Start Duration	<20	<10	minutes
Start-Up Energy (at 12 V)	25	25	Ah
Cold Start Cycles <10% Power Degradation	>100	>7000	
Cooldown Thermal Time Constant	4	12	hours
Surface Temperature rise over ambient	40	30	deg C
Fuel Sulphur Content	<50	<50	ppm
Exhaust Emissions			
CO ₂	6000	600	g/kWh
CO	1	0.1	g/kWh
NO _x	0.1	0.01	g/kWh
HC	0.05	0.005	g/kWh
H ₂	0.5	0.05	g/kWh
PM	0.05	0.005	g/kWh

Of particular interest are the service life and service duty requirements. For automotive applications, regular service intervals may be required, as is typical with the powertrain and electrical systems, to achieve the intended service life. This would indicate that serviceability of the critical fuel cell componentry in the APU is required.

Response time requirements were estimated for the APU. Much of this requirement was dictated by the electrical system interfacing with the APU. For instances where the loads are fairly constant and slow changing, or where a storage battery is employed, the response time of the APU may be reasonably slow. Where this is not true, the APU response must necessarily be fast. This presents an engineering challenge to the design of the fuel cell system.

Since the SOFC APU has a relatively high operating temperature, start-up time and cool-down rate are important considerations. Ideally, the start-up time period would be as short as possible and the cool-down rate (shut-down) would be as long as possible. Unfortunately, these requirements are in opposition in that a short start-up time is aided by reducing heat capacity of the hot componentry, while a slow cool down rate is aided by increasing the heat capacity. Treating the system as a lumped thermal mass, the cool-down thermal time constant should be the product of the effective thermal resistance to ambient and the effective thermal capacitance of the hot components. Assuming that neither of these is a strong function of ambient temperature, large thermal resistance and large heat capacity is desirable for temperature maintenance. For start-up performance, thermal capacity must be minimized. Consequently, very high performance thermal insulation will be required to achieve adequate temperature maintenance.

The required time constant referenced in **Table 3.1.1-1** was targeted for the vehicle application where space for insulation is severely limited. The value of 12 hours for the time constant allows for approximately a 50% system temperature drop in an 8 hour period when no temperature maintenance cycle is employed. Indeed, in all applications, maximizing the thermal time constant is desirable. Insulation may be added where space is available for applications that require longer cool-down times. In stationary applications where start-up latencies are allowed to be longer in duration, both thermal capacity and insulation may be added to improve thermal performance.

3.1.1.2 Electrical Requirements

The electrical requirements are summarized in **Table 3.1.1-2**. Due to the implicit higher-voltage of a fuel cell stack, the requirements were tailored for a 42 V nominal voltage application. The minimum voltage output of 38V and the maximum output voltage of 50 V corresponded to the discharge voltage and maximum charge voltage respectively of a 42 V battery system. The minimum input voltage on the 42 V bus corresponded to the typical low charge condition. The requirements assumed the availability of a 12V bus.

Since one of the major advantages of a fuel cell APU is improved economy, the minimum electrical efficiency of the APU is specified as 25%. This is approximately 20-50% better than a typical gasoline powered generator system. While theoretical SOFC Stack efficiencies may be high, resultant system efficiencies are much reduced due to fuel conversion in the reformer, fuel utilization in the stack, parasitic electrical loads and losses, and electrical DC-to-DC or DC-to-AC conversions. The power budgets for both

POX reformer systems and anode recycle systems are shown in **Table 3.1.1-3**. For both systems, a 500 W maximum parasitic load was budgeted.

Table 3.1.1-2: APU Electrical Requirements

APU Electrical Requirements:				
	Minimum	Maximum	Nominal	Units
Net Electrical Output (VA)	0*	5**	3	kW
Electrical Efficiency (Full Power)	25	N/A	N/A	%
Maximum Electrical Parasitic Load	N/A	500	N/A	W
* Non-Isolated ** Continuous				
42 V Output	38	50*	42	V
42 V Input (Operation)	30	50*	42	V
42 V Input (Non-Destructive), 60 sec	-42	84	N/A	V
12 V Input (Operation)	9	16	12	V
12 V Input (Non-Destructive), 60 sec	-14	28	N/A	V
Ripple Voltage	0	2**	0	V
Quiescent current from -10 °C to +40 °C	N/A	0.1	N/A	mA
Electrical isolation @500 V	1	N/A	N/A	Mohm
* Including ripple ** Total amplitude				

Table 3.1.1-3: APU Power Conversion Budget

APU Fuel Conversion Budget:			
Fuel Conversion:	Anode Recycle		Units
	POX System	System	
Reformer Efficiency	76%	100%	
Fuel Utilization	76%	58%	
Stack Efficiency	50%	50%	
Elec Conditioner Efficiency	95%	95%	
Conversion Efficiency	27.5%	27.5%	
Net Elec Power	5	5	kW
Efficiency	25.0%	25.0%	
Fuel Power	20	20	kW
Allowable Electrical Parasitic Load	500	500	W

3.1.1.3 Environmental Requirements

The climatic requirements are summarized in **Table 3.1.1-4**.

A maximum operating altitude was specified. The concern with altitude is similar to any air-breathing power conversion device. At 3600 m (12000 ft), the air density is about 64% of that at sea level and for a constant volumetric flow, like that that would be provided by an air pump or blower at the same speed, the mass flow rate is reduced through the system. Naturally, additional capacity may be specified for the air pumps and blowers, however it was reasonable to expect either a degradation of power rating due to reduced mass flow, or a decrease in efficiency due to increased blower power. Due to space considerations, minimal excess capacity is desirable, so a reduced power rating target was specified.

The maximum inlet air temperature to the system was specified to be 45°C. This air is used for electronics cooling before it is ingested into the blower. The maximum ambient temperature acceptable to the electronics was 105°C. The operating temperature of the electronics should be no more than 125°C.

Table 3.1.1-4: APU Climatic Requirements

APU Climatic Requirements:				
	Minimum	Maximum	Nominal	Units
Ambient Temperature	-40	80	25	deg C
Inlet Air	-40	45	25	deg C
Relative Humidity @0-60 C	10	100	50	%
Operation Altitude	Sea Level	3600	Sea Level	m
	Or Below	20% Power Reduction		

3.1.1.4 Acoustic Requirements

The sound emission of the APU is important in the automotive application. The APU sound should not be notable when inside the vehicle under normal operation, nor outside the vehicle with respect to the background noise of the powertrain. The acceptable acoustic emission is detailed in **Figure 3.1.1-1**.

Figure 3.1.1-1: Acoustic Emissions

3.1.1.5 Vibration Requirements

The vibration profile is much more severe in an automotive environment than what is typical for a stationary application. This presented a special challenge to the stress-sensitive components like the SOFC stack and an emphasis on overall protection and isolation of the powerplant. The automotive APU was required to survive the vibration profile shown in **Table 3.1.1-5**.

Table 3.1.1-5: APU Vibration Profile

APU Vibration Profile:

(8 Hour Test)

Vertical Axis		Horizontal - Longitudinal Axis		Horizontal - Transverse Axis	
Center Frequency (Hz)	Power Density [(m/s ²) ² /Hz]	Center Frequency (Hz)	Power Density [(m/s ²) ² /Hz]	Center Frequency (Hz)	Power Density [(m/s ²) ² /Hz]
5	0.473	5	0.135	5	0.098
12	4.091	12	1.435	12	1.956
18	4.091	18	1.435	18	1.956
200	0.118	200	0.04	200	0.098

$$a_{rms} = 12 \text{ m/s}^2$$

(1.2 g)

$$a_{rms} = 6.8 \text{ m/s}^2$$

(0.69 g)

$$a_{rms} = 9.0 \text{ m/s}^2$$

(0.92 g)

3.1.1.6 Inlet Air Filtration Requirements

The APU requires an air filter because the quality of the ambient air is unknown. The air filter must demonstrate 99.5% efficiency per SAE J726C variable flow schedule procedure on SAE standard coarse and fine dust. At 14 g/sec, the filter must have a minimum retention of 28 grams of fine dust and 40 grams of coarse dust. At end-of-life, the filter should have no more than a 0.25 kPa pressure drop at 14 g/sec, 25 °C.

3.1.1.7 Fuel Filtration Requirements

The fuel filtration requirements were set per standard automotive application for gasoline.

3.1.1.8 Additional Typical Automotive Requirements

A typical automotive application has additional requirements pertaining to structural integrity and environmental protection. The details of these are highly dependent on application and vehicle installation. Both the structural and environmental protection requirements strongly influence the design of the APU package and enclosure. They may include the following:

Structural:

Drop test (20 cm) two axis each per 3 specimens

Crash worthiness (vehicle dependent)

Environmental protection:

Dust intrusion resistance
(fine Arizona dust per SAE J 726., DIN 40 050-9 test)
Hot water jet intrusion test (80 °C), 1cm/sec
Water immersion – 0 °C , 5% salt water
Salt spray exposure

Electro-magnetic Compatibility (EMC):

The requirements for EMC are typical per automotive standards. For reference, a listing of the typical tests is included in **Table 3.1.1-6**. Level 3 severity is specified for both Radio Interference Suppression and Interference Voltage Peak.

Table 3.1.1-6: Typical Automotive EMC Requirements

EMC tests according to GS 95002

Measurement required		No.	GS 95002		Type of Measurement
yes	no		Pt.	page	
x		1.	7.1.2	7	Emission of transients on power supply lines
x		2.	7.1.3	8	Immunity to transients on power supply lines
x		3.	7.1.3	8	Immunity to transients on signal, data and control lines
x		4.	7.2.1	9	Measurement of conducted interferences from electromechanical components; Interference suppression level 3; long term interference sources
x		5.	7.2.1	9	Measurement of conducted interferences from electromechanical components; Interference suppression level 1; short term interference sources
x		6.	7.2.2	10	Measurement of conducted interference from electronic components
x		7.	7.2.3	11	Measurement of radiated interference using a coupling clamp
x		8.	7.3.1	13	Measurement of radiated interference using a stripline
	x	9.	7.3.2	14	Measurement of conducted emissions using a current probe
x		10.	7.3.3	15	Measurement of radiated emissions from carsystems using an anechoic chamber
x		11.	7.4.1	17	Immunity tests using a stripline
	x	12.	7.4.2	19	Immunity tests from components and systems using a Anechoic chamber
	x	13.	7.4.3	20	Immunity tests using the BCI method
x		14.	7.4.4	20	Immunity tests using GSM modulation
x		15.	7.5	21	Component Immunity to electrostatic discharge (ESD)
	x	16.	7.6	21	Attenuation of audio frequencies on supply lines for audio systems
x		17.	7.7	22	Slew rate of voltages and currents on the vehicle electrical system

3.1.2 Develop Conceptual System Design

One of the most highly influential requirements in the pursuit of an automotive APU conceptual system design is the volumetric power density. For a typical vehicle installation, 10 liters/kW is the target. For the conceptual system design, a fixed package envelope was adopted as a starting point. While inconvenient, this fixed package envelope necessitated some initial concept system integration. In addition to the fixed package envelope, additional requirements were placed on the conceptual system design as enablers for serviceability and product function.

3.1.2.1 Conceptual Design Review

Two initial concepts were generated given the system requirements. The concepts were classified as the “T” and the “Square” based upon the general shape of the Hot-Zone-Module within the enclosure boundaries.

3.1.2.2 System Development Strategy (Plant Support Module and Hot Zone Module)

The low-temperature zone, or Plant Support Module (PSM), houses most of the Balance-of-Plant components, and had an anticipated temperature range of -40°C to 105°C . This is the common temperature range for components used in under-hood locations in mobile applications. While the requirements of this zone demanded rugged, durable subsystems, the devices and subsystems located in this area were adapted from conventional automotive technology.

The high-temperature zone, or Hot Zone Module, houses the “core” of the Solid Oxide Fuel Cell plant including Solid Oxide Fuel Cell stacks, Energy Recovery Unit heat exchangers, fuel reformer, gas burner, and manifolding. The expected temperature range for this zone is -40°C to 800°C (950°C in some locations). This zone was highly insulated from the Plant Support Module. The subsystems and components located in this zone were not considered conventional automotive technology and required unique materials, processes, and development activity.

Delphi’s system development strategy allowed for development of each system module, Plant Support Module and Hot Zone Module, as independent entities. This allowed for a “divide and conquer” approach to development. In addition, it served as an aid to system integration in that subsystems could rapidly be integrated into the system for “pull-ahead” evaluation without requiring full functionality of the entire system.

Figure 3.1.2-1: Auxiliary Power Unit Development Strategy

3.1.3 Develop System Mechanization (schematic)

The system mechanization featured several innovations that improved the potential system performance and packaging. The notable mechanization features included:

1. Integrated air/fuel preparation device, Non-Contact Vaporizer (NCV) and reformer start-up device (start-burner).
 This integration allowed for the elimination of a staged reformer strategy (micro-reformer transition to main reformer) and efficient packaging in the APU.
2. Electrically heated catalyst (EHC)
 Located at the APU exhaust, this device provided for low emissions during both cold start-up (electric power mode), and normal service.
3. Reformer with integrated air preheat function for NCV
 A small heat exchanger was integrated into the Reformer to provide air preheating for enhanced fuel vaporization quality in the NCV.
4. Catalytic Reformer combustor plates
 The catalyst treatment on the combustor acted as a clean-up catalyst for low emissions and complete heat release in the Reformer.

5. Inlet air cooling circuit
The inlet air of the APU was used to cool the blower motor and motor driver, as well as the control and power electronics.
6. Anode oxidation protection
Flow check valves and oxidation prone materials were used in the anode stream path to isolate and block oxygen from the SOFC anode during periods of APU inactivity.
7. Elimination of high-temperature control valves.
This provided a benefit to control and actuation reliability in the system, as well as a reduction in system complexity.
8. Anode recycle pump
This pump was optional in the mechanization, but it provided an increase in reformer and system efficiency. Other benefits included reduced carbon formation in the reformer due to higher O:C ratios.
9. Exhaust stream stack overwash
This improved stack warm-up performance as well as cooling of stacks during operation.
10. Reformate cooling heat exchanger
Hot reformate from the outlet of the reformer exchanged heat with cathode air stream before reaching the stacks. Advantages included preconditioning of reformate to reduce thermal shock to stacks and reduction of preheat requirement on cathode air. This allowed for lower-effectiveness heat exchangers to be used which may have reduced size and pressure drop.
11. Auxiliary burner cooling air circuit.
This feature allowed for the modulation of cathode air during warm-up to achieve high preheat temperatures without reducing system fuel flow. This improved heat exchanger function, and heat up performance.

3.1.4 Establish System Thermal Insulation Requirements

Thermal insulation is of special importance due to the high operating temperature of SOFCs. This is even more the case when the space available for insulation is reduced, as in the automotive SOFC APU. Additionally, issues of serviceability, ease of assembly and structural integrity must be considered in this application. **Figure 3.1.4-1** shows the two main concepts for APU insulation. Each had apparent advantages and disadvantages as referenced in the figure.

The top-loading shell concept was convenient for development work for its accessibility and flexible geometry. The package size constraint plays a large role in the choice of insulation technology. There is a large selection of commercial materials with alumina

and silica fibers or grains that have the capability to insulate a solid oxide fuel cell system.

Figure 3.1.4-1: Modular Thermal Insulation Concepts

For the same temperature rating, lower performing insulation may be used if thick thermal barriers could be tolerated in the design. With the automotive APU, and the aggressive target volumetric power density, thick thermal barriers could not be used, and the choice of thermal insulation was narrowed.

Figure 3.1.4-2 illustrates the required thermal conductivity of insulation material as a function of exterior surface temperature rise and panel thickness. For the requirement of no more than a 40°C rise over ambient temperature of the insulation surface, and a space budget limitation of 30 mm for insulation thickness, a target mean thermal conductivity is shown in the figure to be 17.5 (mW)/mK. This was the target that applied to a panel with mean temperature of 400°C assuming a linear temperature distribution.

Figure 3.1.4-2: Required Thermal Conductivity of SOFC Insulation

Figure 3.1.4-3 indicates typical thermal conductivity values for several types of high performance insulation as well as some dry air and CO₂ for reference.

Figure 3.1.4-3: Typical Insulation Thermal Conductivity

The clear choice for the application was evacuated fumed-silica insulation panels. Unfortunately, these panels require moderate vacuum containment, which was a challenge in high temperature applications, especially with the long service life expectations of the APU. Typically, vacuum insulation is found in cryogenic applications where polymer or thin metal foil bags contain the vacuum adequately for the application. In the SOFC system, these materials would not hold up at temperature and could not be used.

What was required were sheet metal barrier constructions of sufficient thickness, material and design to be robust to the vacuum requirements in service. This placed additional constraints on available insulation feature geometry such as pass-throughs and vias, welded joints and high stress concentration areas. For the automotive APU, initial development allowed for the use of non-evacuated insulation and the associated penalty in performance, but provisions were being made to adjust geometry and design to accommodate modular insulation shells that could be evacuated.

An example of the performance benefits of vacuum insulation is shown in **Figure 3.1.4-4**. Note the low surface temperature rise for a panel only 25 mm thick. With this performance, for a panel of 30 mm thickness, the predicted temperature rise is only 23°C over ambient and the APU would be able to achieve the required 12 hour cool-down thermal time constant assuming other losses to be minimized.

Figure 3.1.4-4: Vacuum Insulation Performance

3.1.5 Provide System Design Support for the Fuel and Air Delivery Systems

The system mechanization called for a single process air blower to source air to all of the individual circuit flows. The blower requirements, summarized in **Table 3.1.5-1**, were developed based upon modeling results.

Table 3.1.5-1: Process Air Blower Requirements

Process Air Pump Requirements			
Maximum ambient temperature			
Operation	85	C	
Storage	105	C	
Elevation	3600	m	
Maximum inlet temperature	45	C	
Maximum head pressure	15	kPa	148 mbar
			2.2 psi
Maximum capacity	19	g/sec	1035 L/min
			62 m ³ /h
		@45C	
			37 CFM
Noise Level	< 65	dB(A)	
Mass (pump + motor)	< 5	kg	
Adiabatic Air Power	248	W	
Target Overall Efficiency	> 50%		
(Pump + Motor)			
Parasitic System Loss	< 496	W	

Typically, the process air blower is the largest power consumer within the powerplant boundaries. In the development of these requirements, particular attention was paid to high efficiency so that system parasitic electrical loads would be minimized and higher net system efficiencies obtained. Because of package size restrictions and high operating temperatures (low gas densities), pressure drop in the SOFC APU was a concern. For a 5kW net powerplant, the flow rates drive pressure requirements exceed typical blower specifications.

In the requirements specified in **Table 3.1.5-1**, the head pressure requirement is 5 to 10 times greater than what is typical for most applications; however, the flow rates are about 5 to 10 times less than typical. The SOFC APU blower requirements fell into an application “hole” where the requirements for pressure are too high for a blower, but not high enough for efficient operation of most compressors, and the flow rates are too high for most compressors while much lower than most blowers produce efficiently. While the application is atypical, and commercial choices were limited, there were two technologies that offered promise for the automotive APU. They included the positive-displacement compressor and the high speed radial blower.

Performance curves for the two components evaluated are shown in **Figure 3.1.5-1** and **Figure 3.1.5-2**. Both units met flow and pressure requirements and target efficiencies were possible with some design optimizations. In the powerplant, additional considerations and evaluation criteria included reliability, noise output, attenuation potential, and size, mass, and cost.

Figure 3.1.5-1: Performance of Positive-Displacement Compressor

Figure 3.1.5-2: Performance of High Speed Radial Blower

While the blower provided the driving potential for flow through the system, in the system mechanization, it also provided cooling air to temperature sensitive components in the PSM. Specifically, the inlet air was ducted through a circuit that provided cooling for the blower motor, blower motor electric driver, system controller, and power conditioning module. In addition, it also provided for air exchange in the PSM airspace so that heat loss from the HZM did not create a high temperature condition in the PSM

3.1.6 Provide System Design Support for the Systems Control Development

A plant model with integrated controls was developed to jointly support system analysis and concurrent control strategy development. The system plant modeling and controls development was done in the MATLAB/ SimulinkTM environment. A small section of this model is shown in **Figure 3.1.6-1**. The figure depicts the cathode air preheat (CHEX) subsystem consisting of controllers, and dynamic heat exchanger and valve models. The model was used extensively to understand the complex system dynamics of the SOFC APU and develop control strategies. Additionally, model outputs allowed for better requirements and sizing estimates for Balance of Plant (BOP) components in the PSM and HZM (heat exchangers, valves and sensors).

The Simulink-based plant model was developed as a collection of functional modules that were checked, where possible, against expected results. The Simulink model was dynamic and had both plant elements and control elements integrated into a functional simulation. It was inherently limited in that it was all based upon lumped parameter physical elements and estimated properties. The model handled heat and mass balance relationships only.

Evaluations were made using the model to understand control strategy and mechanization enhancements to improve start-up time performance. Some of the findings proved to be both effective and also counter-intuitive. One example involved cathode air temperature and flow strategies during the warm-up phase. While maximum temperature gradient and maximum mass-flow were an obvious solution, it was not practical when heating a system with real devices and restrictions on capacity. For example, practical heat exchangers in this application are constrained by physical size and pressure drop considerations. Thermal effectiveness may be increased only so far until physical size and pressure drop are out of bounds for the system. For an effective system design, a good compromise or balance, must be found between competing objectives. An improved control strategy was developed to improve stack warm-up performance with the help of the dynamic system model.

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The system control architecture was one of distributed control responsibility with a central coordination point. The control environment was MATLAB/ Simulink™ within a Dspace micro-autobox™ hardware platform and Control Desk™ operator interface. **Table 3.1.6-1** summarizes the control environments.

Table 3.1.6-1: Control System Environments

Environment Name	Controller Hardware	Operator Interface	Sensors	Plant Support Module	Hot zone Module	Stack, Dc/Dc Converter, Power Conditioner, Battery
Desktop	PC	Simulink™ scopes or Control desk	virtual	virtual	virtual	virtual
Desktop / micro-autobox™	Micro - autobox™	Control desk	virtual	virtual	virtual	virtual
PSM development bench.	"	"	Real air meters and pressure sensors	Real blower and valves	virtual	virtual
Electric emulation bench	"	"	virtual	virtual	virtual	Emulated or real devices
Full Lab System	Micro - autobox™	Control desk	Real hardware	Real hardware	Real hardware	Real devices
Production Controller	DE controller	Canape	Real hardware	Real hardware	Real hardware	Real devices

3.1.7 Develop and Verify System Models

The system model was used to run many simulations of the 5 kW APU. An example of the model results are shown in **Figures 3.1.7-1 through 3.1.7-5**. The data describes a 5kW net output, gasoline SOFC APU undergoing a cold-start warm-up cycle followed by stepped APU electrical demand loads of 25 to 125 amps. Two cases were investigated. The first case was for straight POx reformer operation, and the second case featured anode tail gas recycling.

The basic warm-up cycle and subsequent stack temperature control is shown in **Figure 3.1.7-1**. Note that the control system did a good job regulating the flow and temperature of cathode air to regulate the stack temperature at 750°C. Additionally, the operation temperature of 750°C was reached in 20 minutes.

Figure 3.1.7-1: Overall System Performance Dynamic Simulation

The overall temperature regulation of the burner and reformer, as well as the flow circuit mass-flows, are shown in **Figure 3.1.7-2**. Of particular note was the fact that in POx mode, the reformer temperatures increased with increased fueling at high load, while with recycle, the challenge was to keep the reformer at the correct operating temperature. This was the expected behavior represented well dynamically in the system plant model. Note that the integrated control algorithms were regulating the plant parameters. This resulted in the transient response of flows and temperatures during step changes in electrical load.

Figure 3.1.7-2: System Characteristics

The reformer operational characteristics for the simulation period are shown in **Figure 3.1.7-3**. Anode recycle increased reformer O:C ratio and efficiency and consequently resulted in reduced gasoline fueling for a given electrical load point. This resulted in an increase in overall system conversion efficiency, as expected.

Figure 3.1.7-3: Reformer Characteristics

The stack characteristics for the simulation are shown in **Figure 3.1.7-4**. The controls drive the stacks to a predicted 60% fuel utilization operating point. On step load changes, the step fuel flow rate adjustments are easily observed. While the loads and stack behavior were identical between the two cases, in the POx case, system efficiency drops with increasing load due to reductions of stack efficiency. On the other hand, the introduction of anode recycle produces relatively flat and improved system efficiency throughout the load profile.

Figure 3.1.7-4: Stack Characteristics

The response of the process air blower throughout the simulation is shown in **Figure 3.1.7-5**. For the simulation, a constant manifold feed pressure was assumed for simplicity. Clearly, the case with anode recycle reduced system parasitic load throughout the load profile. This is partially due to the fact that at increased system efficiency, APU exhaust temperatures were reduced and less cathode airflow was needed to cool the stacks since the exhaust gas was allowed to externally cool the stacks. Another factor was that with the anode gas recycle, the reformer outlet temperature was lower which reduced the heat load on the stacks, hence less airflow was required at higher electrical loads. This effect can be most clearly seen in **Figure 3.1.7-6** where the heat transfer of various streams to the stack is displayed.

Figure 3.1.7-5: Blower Characteristics

Figure 3.1.7-6 compares results from a run in the desktop environment against an experimental run and demonstrates the control performance on the virtual plant model against real hardware. The model compared reasonably with the experiment on the overall start time of about 90 minutes.

Figure 3.1.7-6: Control Performance

There was relatively poor agreement between the stack temperature trajectory (T5) in the model and the experiment. Two contributing factors were: (1) the overly simple representation of the Integrated Component Manifold heat transfer, and (2) overall mass.

The Simulinktm system model included a high-fidelity stack performance model originally developed at PNNL. **Figure 3.1.7-7** is a plot of the measured versus predicted performance of this stack model. Good agreement is shown between predicted and measured performance.

Figure 3.1.7-7: Measured vs. Predicted Performance of Stack Model

The Aspen/Hysys system plant model was a steady state plant model used for system design. It contained heat release, heat exchange, mass transfer, thermodynamically determined composition at reactors (reformer, gas phase combustor), parasitic power consumption, and overall system efficiency determination. It was different from the Simulink[™] and Excel models in that it determined composition of reformat and exhaust products as a function of input reactant composition and reaction temperature by minimizing Gibbs free energy. In addition, the model also represented the closed loops inherent in the control system, so that as heat release changes with different operating loads, the needed amounts of air for temperature control respond accordingly. **Figure 3.1.7-8** shows example system outputs computed by the Aspen/Hysys model.

Figure 3.1.7-8: Aspen/Hysys Model Output

The Excel-based system model was used to compute heat transfer, heat release, and overall system efficiency. This model was also used for system design, and crystal ball

project management. It allowed for more flexibility with design parameters than either of the other two models and was compatible with other tools such as Crystal Ball[™]. However, it required more manual interaction than the other two to reset operating points as operating point changes. Each of these models was used for various different aspects of system design. They were compared against each other with good agreement. A summary of these models is contained in **Table 3.1.7-1**.

Table 3.1.7-1: Model Summary Table

	Simulink [™] / Matlab [™] Model	Aspen / Hysys Model	Excel System Model
Heat release	From LHV	From composition	From LHV
Heat transfer	Multi-element	Yes	Lumped parameter
Product composition	Assumed (gibbs planned)	Computed – gibbs minimization	Assumed (gibbs planned)
Dynamic	Yes	No/Yes	No
Controls	Actual	Simulated	Simplified
Integration with control model	Yes	No	No
Stack Model	Design, temperature, reformate flow / composition sensitive	Design, temperature, reformate flow / composition sensitive	Single voltage point assumed
Process air / Plant support module	Individual valves modeled	Simple	Simple
Carbon prediction	No	Yes	No
Power electronics models included	Yes	No	No
Overall System efficiency calculations	Yes - based on cycle efficiency	Yes – steady state	Yes – steady state
Ease of design iteration / model integration	Weak	Weak	Good – use for Crystal Ball
Hardware in loop emulation possible?	Yes	No	No

3.1.8 Perform System Integration

In the conceptual design phase, one of the requirements was to fix the target volumetric power density of the concept to that appropriate for an automotive SOFC APU. The integration of the subsystems into the APU product was undertaken in an engineering evaluation mock-up shown in **Figure 3.1.8-1**. While executed mainly as a packaging verification exercise, many functional parts were used.

Figure 3.1.8-1: APU System Integration (Engineering Mock-Up)

The emphasis on the end-product form factor produced a workable concept with achievable performance in a much smaller size than would normally have been attempted. **Figure 3.1.8-2** shows an early SOFC APU proof-of-concept, and for comparison, the Gen 2 design. The Gen 2 design had a higher power output, more internal content, and a much smaller size and mass than its predecessor.

Figure 3.1.8-2: APU System Integration Progress

3.1.8.1 Three Level System Integration Process

Delphi adopted a three level system integration strategy to facilitate the system integration process. This allowed for “pull-ahead” evaluation of initial subsystem

hardware, functional “shakedown” of basic system operation, and software and controls development. The three-level approach is shown in **Figure 3.1.8-3**.

Level I: In keeping with the system development strategy, the Hot Zone Module and Plant Support Module may be developed independently. This allowed for the evaluation and optimization of each module’s function without the added complexity, and requirements of function of the next level of integration. In addition, this level of integration allowed for a high implementation of instrumentation (thermocouples, pressure taps, gas sample ports, etc.) that became more intrusive and difficult to package at higher levels of integration.

Level II: This level represented the close coupling of the Hot Zone Module and Plant Support Module sub-modules developed at Level I. Full Auxiliary Power Unit functionality was represented at this level. This level allowed for the full evaluation of system performance issues, while still allowing for a high implementation of instrumentation, but avoiding complications caused by thermal management (heat leakage, high local temperatures etc.). This level of integration had the added benefit of improved accessibility over the next level of integration.

Level III: While the previous level of integration represented full Auxiliary Power Unit function, this level of integration represented full Auxiliary Power Unit function and packaging. At this level, implementation of instrumentation was necessarily reduced, accessibility was limited, and thermal management issues became very significant.

Figure 3.1.8-3: System Integration Levels

3.1.8.2 System Integration Status

Delphi progressed through all three levels of integration on a 5 kW Gasoline Auxiliary Power Unit using the first iteration of subsystem hardware. Basic function and control were demonstrated, however, the state of development for both subsystems and controls does not allow for robust operation of the Auxiliary Power Unit power plant, nor power output above break-even levels. A summary of the integration milestones is given in **Figure 3.1.8-4** and a list of resulting issues is presented in **Figure 3.1.8-5**.

Figure 3.1.8-4: System Integration Milestones

◆ **Level I: HZM**

- Improve seal gasket technology, difficult to seal stacks to ICM surface
- Improve start-up time by reducing heat capacity and component/control optimization
- Improve cycle durability and power density of SOFC stack (ISM)
- Improve control software for reformer and burner
- Eliminate carbon formation in reformer
- Validate anode oxidation countermeasures
- Development towards high reliability of temperature (RTD) and Igniter Components
- Development of reformer outlet gas composition sensor
- Improve cathode air heat exchanger characteristics at low flow rates

◆ **Level II: Close-coupled HZM + PSM**

- Further development of automatic control software (turn-key operation)
- Reduction of parasitic electrical loads
- Reduce blower noise
- Common calibration characteristic within sensor families
- Full deployment of product controller
- Deployment/development of power conditioning (DC to application) electronics
- Full deployment of safety and diagnostic software & hardware

◆ **Level III: APU**

- Need to reduce heat losses/leaks and adequately cool internal components
- Packaging and assembly improvement
- Improved component interfaces and seals
- Development of safety sensor (combustible gas leaks)
- Improvement of wiring harness routing and construction

Figure 3.1.8-5: System Issues and Needs

3.2 Task 2: Stack Development

This task focused on the development, fabrication, and demonstration of SOFC stacks, including all necessary design and development except for that pertaining to the electrical connectors used to draw the electrical energy from the stack to the outside load and to the frame and external shell for the stack.

3.2.1 Design Stack

3.2.1.1 Gen 2 Stack

The Delphi-Battelle Generation 2 stack was designed with anode supported cells, metallic interconnects and optimized manifolding to meet the stringent requirements of the transportation industry (**Table 3.2.1-1**).

Table 3.2.1-1: Stack Requirements for APU

Stack	Targets
Power	6 kW
Fuel	Gasoline based partial oxidation reformat
Durability (continuous)	5000 - 10000 hrs
Durability (thermal cycles)	> 5000
Fuel utilization	> 60%
Start up time	< 20 minutes
Weight	< 4 kg/kW
Volume	1 L/kW

One of the key features of this design was a robust cassette configuration as the repeating unit of the stack. The cassette involved a cell to cassette (ceramic to metal) bond that is pre-fabricated before the cassettes are assembled into a stack. (See **Figure 3.2.1-1**).

Figure 3.2.1-1: Gen 2 Cassette

Figure 3.2.1-1 shows the Gen 2 Cassette as a repeating unit (left); a 26-cell Gen 2 stack under test (center); and an Integrated Stack Module consisting of two multi-cell stacks in electrical series (right). The Gen 2 cassettes were successfully assembled into multi-cell stacks and tested. **Figure 3.2.1-1** (center) shows a picture of a 26-cell stack being tested in a furnace. Integrated Stack Modules were also designed, built and tested. An Integrated Stack Module consists of two stack modules in electrical series on a common base plate. It has integrated manifolding, load frame and current collectors. The Integrated Stack Module is a “stand alone” stack sub-system unit that can be mounted on the base manifold (Integrated Component Manifold) of the Auxiliary Power Unit and operated.

The stack design evolved in 2002 based on analysis and testing that provided valuable data for concept evaluation. Multiple concepts were considered for each individual sub-component of the stack. Some of them are listed below in **Table 3.2.1-2**.

Table 3.2.1-2: Design Features Under Consideration for Stack

SOFC Cells	Seals	Interconnect Metallic	Loading Mechanism	Cell Support	Manifolds air/fuel
Square/Rectangular	Compressive	Separator Plate with Mesh	None (if bonded)	Picture Frame	Rectangular Chimney
Other Shapes	Bonded Glass Brazing	Embossed Features	Load Frame with Compliant Member	Edge Cell	Multi Holes Chimney
		Etched Features	Load Frame without Compliant Member		Open Manifolds

3.2.1.2 Gen 3 Stack

The Delphi-Battelle team designed a Gen 3 cassette that has a lower mass and volume than a Gen 2 cassette (50% reduction in mass of cassette and thickness of cassette). It was made of metal components and uses processes more conducive to high volume production. It consists of two stamped metal components and the cassette was bonded together by laser welding. An anode-supported cell was brazed to the picture frame of the cassette before the cassette was assembled and bonded together.

Figure 3.2.1-2: Gen 3 Cassette

3.2.2 Model Stack Under Steady-State Conditions

By the beginning of this project, the SECA Core Technology program had developed Computational Fluid Dynamics (CFD) code that incorporated a stack electrochemistry module. The code is able to predict the temperature distribution within a stack operating under steady-state conditions. These calculations were performed for two stack design configurations, both of which are cross-flow arrangements, in which the flow direction of cathode/cooling air is orthogonal to the flow direction of the anode fuel gas. **Figure 3.2.2-1** shows typical steady state electrochemistry results for these designs. Each exhibited a hot spot in the lower right quadrant, which is caused by the presence of fresh, electrochemically active fuel on the anode juxtaposed to air on the cathode side that has already been warmed by flowing over the upper right quadrant. The total temperature difference was near 275°C for the thin interconnect design, whereas it was about 200°C for the thicker interconnect design.

Figure 3.2.2-1: CFD-Electrochemical Model Results of the Gen 2 Design

Computational Fluid Dynamics steady state modeling of the preliminary Delphi-Battelle Generation 3 stack was also conducted. The results indicated the flow channel height needed to be increased to minimize the pressure drop across the cell. **Figure 3.2.2-2** shows the cathode air velocity with the peak in the restricted region, which gave rise to an undesirable 7 MPa pressure drop. The analysis also showed that good flow distribution could be achieved on the anode side with a 2 kPa pressure drop.

Figure 3.2.2-3 shows the typical temperature distribution under high and low fuel utilization cases in a redesigned Generation 3 cassette with increased cathode flow channel height. The low fuel utilization case resulted in higher temperatures and a higher gradient, with a peak temperature of 855°C and a gradient of 200°C across the cell. The power density (current density) also decreased with increasing fuel utilization as shown in **Figure 3.2.2-4**.

Figure 3.2.2-2: Cathode Air Flow Velocity

Figure 3.2.2-3: Steady State Temperature Distribution

Figure 3.2.2-4: Effect of Fuel Utilization on Current Density

3.2.3 Model Stack Under Transient Conditions

Modeling was performed to simulate the temperature stress distributions generated during heating of various stack designs. Most of the stack heating is accomplished by blowing hot air through the cathode passages, although hot reformate is also assumed to be circulated through the anode passages. **Figure 3.2.3-1** shows transient modeling results for the thin interconnect design. At the left are the CFD model results showing temperature distribution on an anode within the stack at about 23 minutes into the heating cycle, just as the leading edge of the cell has reached 700°C. The trailing corners are still near 450°C. This is the moment when maximum stress occurred. As seen in the stress distribution at right, the maximum stress within the anode is 55 MPa.

Figure 3.2.3-1: CFD Model Results for the Thin Interconnect Design

Computational Fluid Dynamics and Finite Element modeling of the Generation 3 design were conducted to determine the thermal stress distribution generated during the start-up transient. The stack heating was achieved by blowing hot (1000 °C) air through the cathode passages and hot reformat on the anode side. The transient thermal analysis began at a uniform temperature of -40 °C. The stack reached an average temperature of 700°C in 17 minutes. Typical stress distributions for the anode and glass seals are shown in **Figure 3.2.3-2**. The peak anode stress of 38 MPa occurred at an average cell temperature of 230°C, while the peak seal stress of 68 MPa occurred at an average cell temperature of 530°C. Regions of the stainless steel separator plate that exceed the yield strength and will plastically deform can be observed by plotting the inverse safety as shown in **Figure 3.2.3-3**.

Auxiliary Power Unit system limitations, along with stack thermal stress limits, preclude the immediate application of the 1000°C air. An inlet air temperature controller was developed to maintain an optimum temperature gradient across the stack while maintaining the stack stress at an acceptable level. Start up time without the optimized controller was predicted to be 60 minutes for the Generation 2 design.

Variation in the frame-to-frame glass seal stress as a function of vertical thermal gradient was examined with Finite Element models. **Figure 3.2.3-4** illustrates the tensile stress that develops at the outside edge of the glass seal at the connection between cell frames. The edge stress dissipates in each interface higher up the stack. Modeling of the braze seal was also conducted. The braze stress was nominal, peaking at ambient room temperature.

Figure 3.2.3-2: Stress During Start-Up Transient

Figure 3.2.3-3: Separator Plate Inverse Safety Factor

Figure 3.2.3-4: Seal Stress

3.2.4 Develop High-Performance Cathode

In a typical cell, a five micron ceria barrier layer is screen printed and sintered to the electrolyte, followed by screen printing and sintering of the $(\text{LaSr})\text{FeO}_3$ (LSF) cathode. At the outset of this project, one inch diameter button cells with LSF based cathodes had exhibited power densities exceeding 0.6 W/cm^2 at 750°C , running on 50% hydrogen at 20% fuel utilization. However, these high levels of performance had not yet

been attained in larger stack tests. Also, a high degree of variability in cathode performance had been found in nominally identical cells. In addition, cell performance usually increased to a stable level over two to several days of “burn-in”. The objectives of this subtask were to:

- Understand the sensitivity of doped lanthanum ferrite to compositional, structural, and micro structural variables to increase reliability of cathode performance.
- Understand the burn-in process affecting cathode performance.
- Develop reliable, high performance cathode powder with a commercial powder vendor.
- Investigate alternate cathode materials to achieve desired power density and lifetime requirements.

Several cathode evaluation tests were performed on the intermediate-scale, single cell test stand. These cells have approximately 30 cm² active area. The commercially produced LSF cathode powder from one of the two vendors was found to have acceptable electrochemical activity in intermediate scale cell testing. Reliable commercial supply will require close interaction with the vendor to assure quality.

It was found that there is a trade-off between ceria barrier layer adherence and the subsequent performance of cells. Decreasing the sintering temperature of the ceria layer by 50 °C resulted in about a 40% increase in power density.

3.2.4.1 Cathode Test Stands

Cathode development also focused on bringing eight cathode test stands online. Initial testing of the stands, shown in **Figure 3.2.4-1**, focused on optimization of assembly procedures and variance testing with standardized materials sets.

Figure 3.2.4-1: Cathode Test Stands

3.2.5 Develop High-Performance Anode.

3.2.5.1 Bi-layer Development

At the outset of this project, both intermediate and full size bi-layers (anode/electrolyte composite) were being produced in limited quantities. However, bi-layers were warped, requiring a separate creep flattening procedure before cathode application. The process time for sintering and creep flattening was 72 hours. Creep flattened bi-layers had residual camber and relatively low strength. The objectives of this subtask are to:

- Decrease residual camber from electrolyte/anode TEC mismatch and increase the strength of the bi-layer.
- Determine the strength-porosity relationship for the current anode formulation.
- Decrease processing cycle times and improve yield.

Characterization was performed which established the room temperature biaxial flexure strength of baseline anode disks as 240 MPa. This is for the as-sintered (NiO-containing) anodes. The reduced (Ni metal containing) anodes had room temperature strength of 147 MPa, 8% std.dev., weibull 15.7.

Further process development during sintering of the bi-layers resulted in eliminating the separate creep flattening process. The resulting moderate camber is due to the remaining slight thermal expansion mismatch between the electrolyte and the anode. Efforts were initiated to partially substitute a lower thermal expansion materials for part of the YSZ in the anode.

3.2.6 Develop Cell Fabrication Techniques

The Cell Fabrication efforts focused on three major thrust areas; Camber reduction in anode supported cells, improved manufacturing techniques, and aqueous based production processes.

3.2.6.1 Camber Reduction in Anode-Supported Cells

In anode-supported cells, the thermal expansion differential between the thin, 8 μ m electrolyte (Thermal Expansion Coefficient 10.5 ppm/ $^{\circ}$ C) and the bulk NiO-Yttria-stabilized zirconia anode (12.5 ppm/ $^{\circ}$ C) creates a positive camber towards the electrolyte. In addition to making the subsequent processing operations on the bilayer more difficult, the camber of the ceramic part dictates the flatness of cell assemblies when the metal becomes sufficiently thin (300-500 μ m). In order to reduce this camber, several materials were investigated which could lower the Thermal Expansion Coefficient of the bulk anode without deleteriously impacting cell performance. An additive was found that successfully controlled camber. **Figure 3.2.6-1** shows the result of the additive on the camber induced into a GEN 3 cell assembly. Initial electrochemical validation testing was done on 1" diameter "button" cells containing the additive, which showed no performance degradation over 1000 hrs of operation, **Figure**

3.2.6 -2. In addition to the increased flatness, the cells also exhibit an increased flexural strength when compared to the base anode composition (**Figure 3.2.6-3**).

Figure 3.2.6-1: Effect of Additive on Cell Curvature

Figure 3.2.6-2: 1000 hr Test of Cell with Anode Containing Anti-Camber Additive

Figure 3.2.6-3: Bilayer Flexural Strength, As Oxide, Reduced and at 800 °C

3.2.6.2 Improved Manufacturing Techniques

Stresses created due to the difference in sintering kinetics of the anode and electrolyte layers during the co-sintering operation result in warpage of the bilayer structure. Removing this warpage required a secondary “creep flattening” operation in which the part was weighted during a heat treatment. In order to improve yield and reduce the number of high temperature firing operations, a constraining system was developed which enabled the desired part flatness to be achieved during the initial sintering operation. Microstructural analysis of these parts indicated no adverse reactions with the reusable constraint material. In addition to improving yield, the process increased the temperature-processing conditions under which the anode-supported cells could be fabricated.

3.2.6.3 Aqueous-Based Production Processes

Most ceramic processing techniques utilize organic solvents in order to prevent the formation of hydroxyl groups on the ceramic powder. However, the flammability and exposure limits of these organic solvents often prohibit safe and economic scale-up of these processes. Developments focused on: the replacement of the 2-propanol used in the anode milling operation with an aqueous based slurry; and developing an aqueous tape casting technique for the bulk anode composition to eliminate the MEK/Ethanol solvent system then used.

3.2.7 Develop Separator and Support Components.

Ferritic steel was chosen as the material of choice for initial separator plate development. It was discovered that glass seal strengths could be greatly improved by altering the sealing surface of the metal. A series of metal coating techniques were developed and tested. The most successful of these involves applying a slurry coating to the metal, followed by firing at near 1000°C. Metal components often require creep flattening after the coating step. In the case of the glass seal, application of the coating to metal A increases the rupture pressure by a factor of six.

3.2.8 Develop Gas Distribution Meshes

Two key components of the interconnect train are the anode and cathode gas distribution meshes. These structures reside within the gas distribution channels between the separator plate and the requisite electrode. They must allow access of fuel gas or air to the electrodes and, as well, must provide a low resistance pathway for electrical conduction. In particular, the development of the cathode mesh was challenging because it must survive at operating temperature in an oxidizing atmosphere. Several mesh design concepts were considered.

Figure 3.2.8-1 shows pressure drop data for the cathode gas distribution “feather” mesh design. The first plot shows pressure drop as a function of air flow rate for five flow channel heights with mesh “feathers” oriented parallel to the air flow direction. The second plot shows pressure drop as a function of flow channel height for one flow rate, 14 liters per minute, with mesh “feathers” oriented either parallel or perpendicular to the air flow direction.

Figure 3.2.8-1: Pressure Drop Data for Cathode “Feather” Mesh Design

3.2.9 Develop Mesh/Electrode Interface Materials

At the beginning of this project, stack testing was being performed exclusively with platinum interconnect components on the cathode side. Platinum mesh was welded to the stainless steel interconnect plate. The Pt mesh contacted the LSF cathode through a Pt bonding paste and a Pt grid, which had been screen printed and then pre-sintered onto the cathode surface. While this set up provided excellent oxidation resistance, it would have been prohibitively expensive for commercial applications. The objective of this subtask is to develop a cost-effective interconnect train that provides minimal electrical resistance.

A characterization device was developed, the Interconnect Resistance Unit (IRU), that measures the resistance of the cathode interconnect pathway over time at temperature. A schematic of the IRU is shown in **Figure 3.2.9-1**. Current at a density of 0.5 A/cm^2 is run through a double cathode “sandwich” as the specimen is heated at stack operating temperature in air. Various material combinations and configurations for separator plate, mesh, bonding paste and current collector grid were tested in the IRU. The Area Specific Resistance (ASR, ohm-cm^2) is calculated as $\frac{1}{2}$ the measured resistance multiplied by the surface area.

Figure 3.2.9-1: Interconnect Resistance Unit (IRU) Test Set-Up

3.2.10 Develop Glass and Glass-Ceramic Seals

At the beginning of this project, stack sealing was provided by a glass, “G18”, which joined Ferritic stainless to itself, or in the case of the cell-to-frame seal, to yttria stabilized zirconia. The G18 glass softens near 850°C as shown in **Figure 3.2.10-1**. The G18 glass had a coefficient of thermal expansion (CTE) of $11.7 \times 10^{-6}/^{\circ}\text{C}$ in the vitreous state. The G18 glass reacts with Cr_2O_3 on chromia-forming steels, yielding a barium chromate phase that exhibited a significant CTE mismatch with the underlying substrate and initiated cracking along the metal/glass interface.

Figure 3.2.10-1: Sealing Glass Viscosity Schematic

One of the objectives of this subtask was to conduct glass composition optimization studies focused on developing a glass ceramic with stable, matching CTE over thousands of hours at 750°C. Several candidate glass compositions were investigated in 2002.

A rupture strength test was developed to facilitate quantitative comparison of seal joint strengths. **Figure 3.2.10-2** shows a photo of the test specimen and a schematic of the pressurizing fixture. The metal washer is clamped into the fixture and air pressure is increased until the seal breaks and the ceramic bi-layer disk pops off. **Figure 3.2.10-3** shows several rupture strength results. The average rupture pressure for the bare Ferritic stainless steel type “A” glass sealed to bi-layer disks was 10 psi. Several factors affected the seal rupture strength. Choice of metal alloy (A, B, C or D) could result in up to a factor of four difference in rupture pressure, for seals to the bare metal surface. Pre-oxidation of metal B resulted in a slight increase in seal strength.

Figure 3.2.10-2: Seal Joint Rupture Strength Fixture and Test Specimen

Figure 3.2.10-3: Seal Joint Rupture Strength Test Results

During the work on the barium aluminosilicate G-18 glass, Delphi observed that when at operating temperature as crystalline phases form in the glass over time (**Figure 3.2.10-4a**), the CTE of the material decreased measurably (**Figure 3.2.10-4b**). This not only occurred in the bulk glass, but at the interface with the stainless steel used in the window frame. A two-prong approach was taken to correct this problem: (1) reformulation of the glass composition to improve long-term CTE stability in the bulk glass and (2) development of surface coatings on the stainless steel components in an effort to eliminate the formation of deleterious phases at the metal/glass interface.

Figure 3.2.10-4(a) Celsian Phase Formation

Figure 3.2.10-4(b): CTE Effects

3.2.11 Develop Alternative Seals

A silver-based braze was developed which appeared to be a viable alternative to the glass seal. The braze hermetically sealed a full-scale (~12 cm x 12 cm) bi-layer to a Ferritic stainless steel frame. Two braze compositions were tested using the seal rupture strength method. Braze #1 gave average rupture strengths of 46 and 52 psi, on coated metal A and on metal B, respectively. Braze #2 on coated metal A gave an average rupture pressure of 91 psi.

The silver-based braze developed performed well in rupture testing and was scaled up for use in stack testing. A commercial vendor supplied foils of the appropriate composition which were used to seal full-size cells to the Ferritic stainless steel window frames, as shown in **Figures 3.2.11-1 (a) and (b)**.

Figure 3.2.11-1 (a) Cell brazed & (b) SEM micrograph of frame joint.

3.2.12 Develop Gas Headers and Manifolds

Different concepts for loading the stack were developed, analyzed and tested. For glass sealed stacks a minimal load is required after the stack is sealed. A metal based "spring" was designed to provide this load after the sealing of the stack. Manifolding of the stack was also designed based on system requirements and ongoing CFD analysis.

3.2.13 Fabricate Developmental Stacks

Multiple stacks were built and tested. The stack tests can be classified into the following main categories:

- Stack tests with small active area cells
- Stack test with intermediate-size active area cells
- Stack tests with full sized cells

3.2.13.1 Stack Test with Small Active Area Cells

Multiple stacks were tested with cells of 4cm X 4cm dimension and cells of 7cm X 7cm dimension. Extensive experience was gained in the fabrication and testing of these stacks. Test data from small (4 cm x 4 cm) single cell stack is shown in **Figure 3.2.13-1**. After stable power was achieved the stack was maintained at this power for approximately three days. Some experiments were then undertaken to determine performance versus fuel utilization on concentrated hydrogen. Between 220 and 240 hours, the stack generated 0.4 W/cm² at 50% fuel utilization. At the end, the stack generated nearly 0.3 W/cm² at 74% utilization of hydrogen for 20 minutes.

Figure 3.2.13-1: Stack Test (4 cm x 4 cm Cell)

Data from stack testing with 7cmx7cm cells is shown in **Figure 3.2.13-2**. Extensive testing of these intermediate sized cells was carried out to understand and improve performance of the stack.

Figure 3.2.13-2: Cell Stack Test (7cm x 7cm Cell)

A 3-cell stack (with 7cm X 7cm cell) was run for 1000 hours on hydrogen at 0.7V/cell to evaluate durability. The degradation was less than 10% of its original electrochemical performance over this period of time. Most of this degradation was observed in the first 200 hours (**Figure 3.2.13-3**).

Figure 3.2.13-3: 1000 Hour Durability Test On 3-cell stack (with 7cm x 7 cm Cell)

3.2.13.2 Stack Test with Intermediate-Size Active Area Cells

The intermediate-sized tests were used to evaluate novel cell materials, cell processing parameters, new interconnect materials and designs, and alternate sealing techniques.

Screening tests and performance evaluations were performed using single-cell, intermediate-size tests.

Test data is presented in **Figure 3.2.13-4** for a single-cell intermediate-size stack test (I-16) that shows performance durability after four thermal cycles. The OCV after each thermal cycle was near the theoretical value of 1.09 V, indicating good performance by the glass seals. The initial power density for this stack was 0.43 W/cm^2 during the initial cycle. After four thermal cycles, the power density was 0.41 W/cm^2 , a net loss of 3% in power from the initial performance.

A demonstration of high-power density from an intermediate-size stack test is shown in **Figure 3.2.13-5**. With similar stack materials to test I-16, this test reached 0.65 W/cm^2 at 0.7 V and 750°C with 5 lpm air and 2 lpm of fuel (50/50 H_2/N_2). The stack components for test I-16 and I-17 did include Pt for the cathode current collector grid, paste and mesh.

Figure 3.2.13-4 : Intermediate-Size Stack Test w/ 5 Thermal Cycles

Figure 3.2.13-5: Intermediate-Size Stack Test w/High Power Density

3.2.13.3 Stack Tests with Full Sized Cells (12cmx12cm)

Extensive experience was gained in building stacks from full size cells. Multiple stacks with number ranging from 1-6 were built and tested. Testing of full size (~12cm X 12 cm) 1-cell stacks allowed Delphi to validate and optimize the design. **Figure 3.2.13-6** is an example of data obtained from a 1-cell stack test.

Figure 3.2.13-6: 1-Cell Stack Test (12 cm x 12 cm Cell)

Short stacks were also built and tested. Data shown in **Figure 3.2.13-7** is from a 6-cell stack using cells from a supplier. The stack was operated at 750°C and a series of electrochemical tests were carried out to study the stack performance. **Figure 3.2.13-7** shows the polarization curves for different compositions of reformat in the stack.

Figure 3.2.13-7: 6-Cell Stack (12 cm x 12cm Cell)

As expected, the 100% H₂ fuel performed the best, closely followed by the simulated reformat composition of 35% H₂, 40% CO, and 22% N₂. Maximum power density of 250 mW/cm² was achieved with hydrogen. The power density is comparable to the power density achieved with single cell stack tests with similar cells.

Complete stands to test stacks up to 5kW were purchased and installed for performance evaluation and durability testing. **Figure 3.2.13-7** below shows a picture of a typical Delphi stack test stand.

Figure 3.2.13-7: Test Stand for Electrochemical Stack Testing

3.2.14 Evaluate Stack Performance

3.2.14.1 Stack testing with Full-Sized Cells

Evaluation of performance with full sized Gen 2 single-cell stacks to multi-cell stacks (with ~11.5 x 11.5 cm cells) was carried out to validate the design and understand the performance characteristics. Multiple stack modules were built and tested. Multiple Integrated Stack Modules, stack sub-system (consisting of two stack modules in electrical series and manifolded in parallel) were built, tested and integrated into the Auxiliary Power Unit system.

3.2.14.2 1-Cell Cassette Stack

Full-size single cell stacks were tested to evaluate performance under different conditions. The IV curve in **Figure 3.2.14-1** shows the performance at 750°C with different reformat compositions. A maximum of 350 mW/cm² was achieved with hydrogen.

Figure 3.2.14-1: I-V curve from a 1-cell stack test at 750°C

Further, thermal cycling tests were performed on a full-size, single-cell stack test. **Figure 3.2.14-2** shows data on a stack being thermally cycled in a furnace from ambient to operating temperature. The temperature ramp rate was 3°C per minute. Leak rates were measured by pressurizing the stack to 3kPa with all outlets blocked. Open circuit voltages and power density at 0.5 V was measured in each cycle. The open circuit voltage and the power densities showed stable and encouraging performance. While the leak rate at room temperature increased over time, the leak rates at operating temperature were observed to be low throughout the test.

Figure 3.2.14-2: Thermal Cycling Test on Gen 2 Single-Cell Stack

3.2.14.3 26-Cell Cassette Stack

A 26-cell cassette stack was built and tested. The cassettes were pre-fabricated with the cells sealed in them and leak tested before assembly into a stack. The stack was then assembled with glass seal between the repeating units. Once the glass seal process was complete the cells were reduced in-situ and polarization curves were measured (see **Figure 3.2.14-3**). Hydrogen was used as a fuel (52 LPM) and Air (52 LPM) was used on the cathode side. Maximum power density of 350mW/cm² @ 15V (H₂) at 750°C was achieved.

Figure 3.2.14-3: IV Curve of 26-Cell Stack With Hydrogen at 750°C.

3.2.14.4 Integrated Stack Module

Multiple Integrated Stack Modules (two stack modules in electrical series) were built and tested. **Figure 3.2.14-4** shows a picture of a 2x15-cell Integrated Stack Module with load frame and current collectors integrated in the sub-system.

Figure 3.2.14-4: Integrated Stack Module

Figure 3.2.14-5: IV curve of a 2x15-cell Integrated Stack Module with Hydrogen at 750°C

Figure 3.2.14-5 is a polarization curve from a 2 x 15-cell Integrated Stack Module test. A maximum power density of 288 mW/cm² @ 17.6V was achieved (H₂, 750 °C). The amount of fuel flow was 60 LPM on the anode side and 60 LPM on the cathode side.

The Integrated Stack Module was integrated and operated in the Auxiliary Power Unit. This was a significant milestone in demonstrating the integrated functioning of an Auxiliary Power Unit. **Figure 3.2.14-5** shows the picture of the hot zone module in an Auxiliary Power Unit with integrated POx reformer and heat exchangers.

Figure 4.2.14-5: Integrated Stack Module Integrated in the Hot Zone of an Auxiliary Power Unit

For the first time, the Integrated Stack Module was heated by cathode air pre-heated in the system using the combustor and reformat from the reformer. The stacks were

heated to approximately 750°C. Open Circuit Voltages (OCV) came up to 30.8 V. POx reformat (from gasoline) flowing into the stack consisted of 21% H₂, 20% CO, 3% H₂O. Polarization curves were measured and shown in **Figure 3.2.14-6**. The stack produced 486 Watts @ 15.2V. This was the first result from a Gen-2 Auxiliary Power Unit producing power from gasoline. Further testing of Integrated Stack Modules in Auxiliary Power Unit and optimization of the startup and steady state operation is continuing.

Figure 3.2.14-6: IV Curve from Integrated Stack Module Integrated in the Auxiliary Power Unit (Hot Zone Module)

3.3 Task 3: Reformer Development

During Phase I, Delphi focused on two applications:

- (1) the stationary distributed power generation system fueled by pipeline natural gas, and
- (2) the gasoline-fueled automotive APU.

In 2002, Delphi focused the entire effort on the gasoline-fueled automotive APU. Major accomplishments that year included the following.

3.3.1 Development of Catalytic Partial Oxidation (CPO) Reformer

3.3.1.1 Requirements

The product development conducted on the Reformer subsystem was focused on evaluation of the current hardware versus a stated requirement, and to help understand the requirement itself. A general list of reformer requirements developed is given in **Table 3.3.1-1** which included a significant alteration from previous designs, mainly the elimination of “anode tail gas recycle” or simply “recycle” as a feature in the APU system.

Prior to 2002, Delphi had conducted modeling on several levels and showed the capability experimentally of the single planar reactor, in use at the time, to re-reform both H₂O and CO₂ present in anode tail gas. It is this re-reforming benefit and the second pass through the stack for increased fuel utilization that improves system efficiency and makes the recycle process so attractive. However, the complexity and effort required to design a pump to handle the 800°C gas was deemed too much for the current project objectives and therefore the reformer system would proceed as a Partial Oxidation (POx) system while the recycle pump was developed in parallel.

The impact of this decision is manifested in the reformer efficiency target being lowered to 70% (from ~110% with recycle) and new attention being focused on carbon formation due to the loss of the beneficial effects of water present in anode tail gas. The multi-plate planar reformer that was being designed, that included an integrated reformer / tail gas combustor, continued and added burden to show that a combustion process occurring on adjacent plates to the reforming exotherm could provide proper temperature management. The net result of the systems simplification was to make the reforming task potentially more difficult to make.

Table 3.3.1-1: Reformer Requirements

Requirement Name		Targets	
		Units	Simplified POx System
			5 kW net
Fuel			Carb ph 2
	sulfur - ppm	ppm	30
1 Reformate Quality			
	kW - LHV (H ₂ , CO, CH ₄)	kW	12.8
	Methane allowable - mole %	mole %	1/3 of H ₂ O mole%
	O ₂ allowable	ppm	1.0E-08
		atm	1.0E-14
	HC (C ₂ s and greater: wrt stack consumption)		C ₂ s < 0.1mole%
	HC (C ₃ H ₈ equiv) allowable - ppm	ppm	
2 Reformer Efficiency (LHV_{out}/LHV_{fuel in})			70%
	Recycle Fraction	%	0%
	Fuel In - gps	gps	
3 Tailpipe Emissions (Reformer + WER + EHC)			
	HC ppm	ppm	tbd (~2 est)
	CO ppm	ppm	tbd (~300 est)
	NO _x ppm	ppm	tbd (~7 est)
	CO ₂ @ SS max power (APU)	kg/kW _{hr}	
4 Start-up time: Reformer		min	~3 min
	Start-up time: APU System	min	<20 min
Reformer Turndown			
5 Carbon Avoidance			
6 Packaging			
	Volume	l	3.5 liters (20 x 12.5 x 14cm)
	Mass	kg	

3.3.1.2 Reformer System Concepts

While it was accepted that the reformer system reactor would be of a multi-plate planar construction, many of the other aspects of the reformer system were still undetermined relative to start-up devices and emission compliance features. Start time considerations, reformat quality during start-up, and tailpipe emissions were considered when deciding which of several system configurations to select.

Delphi had had some success with the cascaded reformer system used in the Proof of Concept unit where an electrically heated micro-reformer fed a main reformer. Because of this experience, this configuration became the baseline for evaluation against our requirements. The cascaded reformer system was dismissed in favor of combustion based heating devices due to concerns over the ability of this concept to meet size, start time targets, and power consumption limits. Coincidental with this decision, Delphi was also working on rapid start reformers for SULEV capable / H₂ enriched combustion vehicles. This program was having good success in bringing a ceramic foam substrate catalyst to light off in several minutes and it was felt this could be a viable approach for the SOFC Reformer system as well. Proper integration of a combustion heating process remained to be developed. Four (4) base configurations were considered. **Figure 3.3.1-1** shows a gas phase combustor (GPC) in several locations within the reformer mechanization. After much debate and weighing of trade-offs, configuration 1 was selected primarily on the strength of its simplicity.

Each of the configurations analyzed included an electrically heated catalyst (aka EHC or ATC – after treatment catalyst) as a guaranteed “catch all” for emissions. This was viewed as an emissions conservative approach (at the expense of power consumption) and was due to the fact that assessing emissions capability on immature and non-descript concepts would have been highly inaccurate.

Figure 3.3.1-1: Reformer Start Up GPC Location Configurations

3.3.1.3 Non-Contact Vaporizer (NCV) Development

Developments in air assisted vaporization allowed use of an inline fuel combustion process to provide heat for the start of reforming as well as delivery of the rich Air/Fuel mixture to the reformer during reforming. **Figures 3.3.1-2 and 3.3.1-3** show a Non-contact Vaporizer (NCV) design and design intent respectively. The approach was referred to as non-contact, in that instead of vaporizing fuel via heat addition due to contact with a heated surface, it is the rapid mixing with heated air that will fully vaporize the atomized injector spray. This approach avoids the fuel cracking deposits that form on heated surface vaporizers. **Figure 3.3.1-4** shows an example of the fuel and air mass distribution achieved with these devices using Planar Laser Induced Fluorescence, **Figure 3.3.1-5**.

Figure 3.3.1-2: Non-Contact Vaporizer

- **Fuel:** Injected via Delphi DI injector (350 kPa to 3 MPa) to control particle size and penetration.
- **Air / Recycle gas:** Introduced via an interchangeable director plate. Plates w/ multiple exit nozzles for each gas are used to form a controlled mixture: Convergence angle and swirl angle of flow.
- **Goal:** Create gas motion to suspend liquid fuel particles until vaporization is complete (non-contact vaporization) AND mix vapor w/ Air & Recycle to mixture homogeneity prior to catalyst introduction.

Experimental Air/Fuel/Recycle Gas
Mixture Fixture: Non Contact Vaporizer
(NCV)

Figure 3.3.1-3: Non-Contact Vaporizer – Design Intent

In Figure on left above vapor distribution of an 1st generation non contact vaporizer (NCV1) is shown. The light blue / white colored pixels represent vapor concentrations that fluoresce when hit with the sheet laser.

Figure on right shows results from 2nd generation vaporizer (NCV2) Note: NCV2 has a rectangular outlet but the circular pattern due to fuel injection is still evident

Figure 3.3.1-4: Vaporizer – Vapor Distribution

Figure 3.3.1-5: NCV Mixture Preparation Evaluation Fixture

3.3.1.4 Homogenous / Heterogeneous Combustor With and Without EHC

Comparison testing was conducted in order to better understand the emissions that might occur during start up and to help in the selection of an appropriate GPC approach. The start combustor and vaporizer used on Delphi's SULEV / H₂ enrichment program was compared with a production "cabin heater" combustor (aka Webasto) as this was felt to represent a state of the art clean heating device. While the NCV1 (non-contact vaporizer – generation 1) and start combustor represented a homogenous combustion process, the Webasto conversely is a heterogeneous combustion process with a diffusion flame zone and excess air added late in the combustion process. **Figure 3.3.1-6** shows an example of the test setup while **Table 3.3.1-2** shows both the relative emissions of these two configurations, as well as the benefit of using an EHC as the after-treatment strategy.

Figure 3.3.1-6:: NCV1 + Start Combustor

Table 3.3.1-2: Start Combustor Emissions

	Peak Values				Steady State Values					
	HC	Nox	CO	CO2	HC	Nox	CO	CO2	ATC Voltage	ATC Current
	ppm	ppm	ppm	mole %	ppm	ppm	ppm	mole %	Volts	amps
European Cabin Heater Emissions Limits (Heaters using liquid fuels)					<= 100	<= 200	1000			
Webasto	14874	51	25251	10	29	38	81	6.6	N/A	N/A
Webasto w/ ATC	2628	79	871	8.9	29	28	16	6.2	7	128
Benefit of ATC	12246	-28	24380	1.1	0	10	65	0.4		see note
NCV-1 + SULEV type Start Combustor	7140	47	123	10.9	38	14	25	10	N/A	N/A
NCV-1 + SULEV type Start Combustor w/ ATC	2672	23	73	8.8	10	10	22	7.8	12	155
Benefit of ATC	4468	24	50	2.1	28	4	3	2.2		
Based on the intended EHC being 0.66 the rated power of the tested EHC... And knowledge of the effect of flow (thermal load) on the EHC the steady state current draw of the intended EHC is estimated at ~100amps with <= 1 α/s flow										

3.3.1.5 NCV1 and Start Combustor Development

Based on the relative success of the start combustor testing, an NCV1 vaporizer and a H1 10 plate planar reformer were assembled together for testing (**Figure 3.3.1-7**). This test helped determine general start times (time to light off), emissions during start and run and better develop and optimize the controls strategy.

Figure 3.3.1-7: NCV1+H1 10 Plate (Partial Fixture)

The basic start sequence is charted in **Figure 3.3.1-8**. While not to scale, it shows how fuel delivery, flame initiation and quench, Reformer LO (Light-off) and GPC (Gas Phase Combustor) were sequenced. **Figure 3.3.1-9** shows the results of the initial testing on a minimum function fixture. The significant finding of this testing was that while the lead edge of the reformer can be brought to a LOT (light off temperature, 600°C for this discussion), it takes on the order of 20 minutes before the rear of the reformer is at or near LOT. This testing was only preliminary as no GPC was used to heat the reformer during most of the ramp to steady state.

Figure 3.3.1-8: Reformer Modes

Figure 3.3.1-9: NCV1 + Start Combustor + H1 SN 2

3.3.1.6

3.3.1.7 NCV1 + H1 on Full Fixture

Testing of NCV1 and H1 Reformers was continued with a new fully manifolded base fixture that provided a mounting of the GPC igniters. **Figure 3.3.1-10** shows the test setup used. **Figure 3.3.1-11** shows temperature and input data for a sample run from this testing. Lead edge temperatures rose quickly but areas downstream of the reformer inlet took considerable time to reach beneficial reforming temperatures (700°C and above). For the rear area of the plate temperature (T3), time to 700°C was approximately 11 minutes, while actual Reformate Out gas temperatures (T5) didn't reach 700°C until approximately 14 minutes. Additionally, the very slow rise of the air pre-heat for vaporization was a concern as it took nearly 45 minutes to reach 150°C. A portion of this time was attributed to the low performance of the lab insulation materials and techniques as compared to the APU configuration. However, the mass of the rear section of the reformer (cathode air pre-heat) presented such a large thermal sink that target air pre-heat temperatures and reformer outlet gas temperatures could not be rapidly achieved. These concerns were directly addressed in the design of the next generation (H2) reactor.

Figure 3.3.1-10: NCV1 + H1 10 Plate + Fixture

Figure 3.3.1-11: Temperatures: NCV1 + GPC

Gas compositions were also recorded during this testing and are found in **Figure 3.3.1-12**. Reformate quality was found to take 20 minutes to rise to levels approaching that required for stack consumption. Note that the latter part of this graph exhibits some variable behavior resulting from changing input conditions.

Figure 3.3.1-12: Gas Compositions: NCV1 + GPC

3.3.1.8 Develop Catalytic Partial Oxidation (CPO) Reformer - Reactor

The CPO Reformer Development was carried out on several reactor platforms covering a range from research level to application specific. Work carried out on each platform is discussed below.

3.3.1.8.1 1" Nominal OD Tubular Reactor (w/ foam substrate)

In general, reaction characterization is carried out on this type of reactor (**Figure 3.3.1-13**). Use of cylindrical foam substrates made for ease of wash coating and relatively quick change out. This work served as a baseline for reformation performance understanding.

Figure 3.3.1-13: 1" OD Lab Reactor

3.3.1.8.2 Single Plate Planar Reactor

Delphi concluded testing on this reactor (**Figure 3.3.1-14**) prior to the start of the DOE funded program, however, it is worthy of note as it confirmed key capabilities of a planar reactor. Data was collected that outlined general reformer behavior relative to temperature gradients, species gradients, space velocity capability and the viability of recycle. This information, as it was from a true “channel flow” reactor, was used to design the first generation (H1) reactor.

This reactor also provided our first experience with wash coating of a metal substrate in a reforming application (Delphi has other metal substrate wash coating experience, but for lower temperature exhaust catalysts).

Figure 3.3.1-14: Single Planar Reactor

3.3.1.8.3 Develop Catalytic Partial Oxidation Reformer – H1 Reactor

3D model concepts of two integrated reformers were completed. The H1 design (**Figure 3.3.1-15**) was selected as the concept to further develop based on the success with a similarly constructed Energy Recovery Unit built and tested earlier in the program.

Figure 3.3.1-15: H1 10 Plate Reformer

The basic functions of reforming, waste energy recovery, reformer air preheat, and cathode air heating was combined into a single multi-plate unit. **Figures 3.3.1-16** and **3.3.1-17** describe the two sides of a “reformer plate”. Initial construction involved double-sided etching and allowed unique flow path geometry on each face of the plate. **Figure 3.3.1-16** shows the three flow streams involved on the reformer / air heating side of the plate. Air and fuel vapor enter from the left move over a catalytic surface and are reformed before exiting to common manifolds. Cold air enters from one side and exits on the other after heating up due to heat exchange from the combustor side (and to a lesser extent proximity to the reforming section).

Figure 3.3.1-16 -- H1 Reformer/Air Heating Function

Figure 3.3.1-17: H1 Combustor Function

The H1 design saw considerable testing and generated important information. Initial testing employed a lab heated mixing inlet (**Figure 3.3.1-18**), but later an actual product intent NCV was used.

During the testing to determine maximum Gas Hourly Space Velocity (GHSV) for good conversion Delphi periodically encountered instances where repeat runs at the same conditions would not produce the same results in reformat quality. Carbon formation was suspected as the cause and consequently a series of runs were conducted in hopes of clarifying the relative merits of several burn-off methods as well as more clearly determining which data sets were impacted by carbon accumulation. Three particular burn-off methods were employed, referred to as:

- Dry Burn-off had been a technique used earlier in the development with some success, but the benefits of water addition had yet to be evaluated. Both methods employing water required that catalyst temperature (particularly the front edge) be maintained within limits via the test operator slewing in phi and steam/carbon ratios accordingly.

(NOTE: The suffix “corr3” refers to 3 levels of correction applied to raw data. Raw mole % data is first corrected for the water knockout that occurs prior to sample gas entering the Mass Spectrometer. The water mole% is estimated prior to the water knockout via a Dew Point sensor. The second correction is for misread between CO and N₂. Due to their identical molecular weights, the type of Mass Spectrometer employed for this testing can misread CO as N₂ and vice versa. Through mass balance on N₂ an expected N₂ mole % can be calculated and thus CO can be adjusted closer to its true value. The third correction is to back out the dilution effect of non-air N₂ that is frequently needed by the reformer to control lead edge temperatures.)

Figure 3.3.1-20: Burn-off Evaluation: HC, H₂O, CO₂

Figure 3.3.1-20 shows the chronology of burn-off data. Black arrows indicate spans in data that should be consistent as they represent repeat data points and/or averaging of many points. Red arrows indicate where a burn-off event occurred and changes in plotted variables in this span represent the potential effect of the burn-off event.

NOTE: Methane values were taken from a mass spectrometer with a calibration offset. The values are not accurate but still have resolution.

Both the 1Losyn/water post burn-off repeats and the 1Lostoich/water post burn-off repeats were not consistent. Data collecting at the time of this testing required periodic manual capture of Mass Spectrometer and specific control variables. As a way to minimize the impact of short-term fluctuations in response variables, data averaging of many minutes was employed and is indicated by ending with the 'avg' label. While this helped, variation was still unsatisfactory.

With respect to effectiveness, only the Lostoich/water showed significant impact. However, past experience had also shown the Dry Burn-off to be effective. This raised the possibility that the reformer states prior to burn-off were not consistent, such that a burn-off may or may not show the marked improvement indicative of it removing soot.

3.3.1.8.3.2 O₂ Getter Study

O₂ content of the reformat must be extremely low due to the damage that would result due to stack anode oxidation prior to the stack coming up to operating temperature. The system mechanization includes an 'oxygen getter' material that would remove limited amounts of oxygen present in the anode stream.

While it could be assumed that a reformation reaction should consume all the available oxygen and reformer out Mass Spectrometer shows indicated Oxygen at 0%, the resolution on the Mass Spectrometer cannot detect the low levels of O₂ that would be harmful to the stack. Because of this, Delphi conducted testing to indirectly measure O₂ levels in the reformat using both Oxygen getter material (nickel foam for this round of testing) and actual stack anode material.

Table 3.3.1-2 shows the conditions and results for four tests in this sequence. The first two tests employed actual H1 reformer hardware where the oxygen getter material was placed in the reformer outlet tubing. Tests three and four were conducted using a tube furnace with the oxygen getter material again located inside a tube but with heat provided via the furnace. Test one showed no evidence of oxidation. It did however show appreciable coke. Given that precautions were taken to expose this material to only steady state quality reformat (i.e., start-up was done off-line) it was necessary to find an explanation for the carbon deposition.

Table 3.3.1-2: Oxygen 'getter' Summary

Test #	1	2	3	4
TEST NAME	Preliminary	Lean correction	CO ₂ , no HC's	CO ₂ + HC's
HARDWARE	H1 SN5	H1 SN5	Tube in furnace	Tube in furnace
O/C	O/C=1.05	O/C=1.20	NA	NA
DATE	08/13/2002	08/23/2002	09/18/2002	10/01/2002
H ₂ O mol%	4.14	5.05	4.25	4.03
H ₂ mol%	20.87	19.22	19.12	11.36
CO mol%	19.86	19.25	22.62	11.47
CH ₄ mol%	0.82	0.68	0.00	1.09
Ethane mol%	0.05	0.02	0.00	0.00
Ethylene mol%	0.20	0.13	0.00	0.02
Propane mol%	0.00	0.00	0.00	0.008
Propylene mol%	0.00	0.00	0.00	0.008
CO ₂ mol%	2.35	2.45	2.32	0.76
N ₂ mol%	51.72	53.20	51.69	51.82
He mol%	0.00	0.00	0.00	19.44
Total mol%	100.01	100.00	100.00	100.00
Total Reformat Flow - slpm	32.8	27.0	18.0	19.0
Run Time	2hrs	3hrs	1hr 15min	1hr
Temp at "getters"	830 nom. 600 start	overtemp	770	770
Temp excursion?	possible (fuel oscill)	definite	None	None
Oxidation exposure	minimal / none	high degree	O ₂ flowback from vol change due to HVAC shutdown	O ₂ flowback from vol change due to HVAC shutdown
Upstream "getter"	coke, no oxide	NA	no coke	no coke
Fuel Cell mat	NA	NA	no coke, reduced	no coke, reduced
Downstream "getter"	NA	NA		no coke
Filter	NA	NA	NA	no coke

Test two was conducted in which O/C was increased to 1.2 as 1.05 was thought to be too aggressively rich. Due to a flow controller malfunction an overtemp condition was created and results were not useable.

Test three was conducted as a means of answering the question of whether the coke detected in test one was a result of in-stream reformat soot and soot pre-cursors or a result of CO reacting to form C and CO₂. Results indicated that the CO reaction was not a contributing factor.

Test four was conducted in an attempt to better simulate reformat by adding controlled amounts of hydrocarbons (HC's) to the reacting stream. Although no coke formed, it was felt that the test did not reasonably represent reformer outstream conditions.

3.3.1.8.3.3 External Mixing / Mixing Inserts

There were frequent concerns that combustor heat release was not uniform over the adjacent reforming layer contributing to increases in temperature gradients. Poor mixing was evident by the fact that the combustor outstream contained combustibles (H₂ and CO), which with good mixing should to be consumed given the temperature and excess O₂.

The first attempt to improve mixing involved pre-mixing the two flow streams (air and simulated anode tail gas) into a manifold external to the actual part and including a flame arrestor element. This method worked well and was used extensively from this point forward.

In parallel mixing inserts that fit inside the Gas Phase Combustor combustion manifold were designed and fabricated. Their design was intended to route air and anode tail gas in a way that would promote mixing by folding the two streams onto one another several times before entering into the plate combustor inlets. Limited testing of these inserts showed some improvement and by the time these improvements were realized it was concluded that the next generation reformer (H₂) would need a redesign of the combustor features.

3.3.1.8.3.4 Ethylene Climb Issue

A parameter of significant concern was the level of ethylene in the reformat. Ethylene is a key pre-cursor and intermediary in Poly Nuclear Aromatics / soot formation. **Figure 3.3.1-21** is data from 8/13/02 indicating an interesting Ethylene rise over the course of several hours of testing. Initial supposition was that O/C=1.05 is too rich and that ethylene formation could be a gradual result of carbon deposition.

Figure 3.3.1-21: Ethylene Climb at O/C = 1.05

A follow-up test using O/C of 1.2 indicated Ethylene level stable at approximately 0.13 mole % (**Figure 3.3.1-22**).

Figure 3.3.1-22: Ethylene Climb at O/C = 1.20

3.3.1.8.4 Reformer Efficiency

3.3.1.8.4.1 Combustor Ability to Control Reformer Plate Temperatures

The objective of initial H1 testing was to understand the ability to control reformer plate temperatures through the use of the GPC process. **Figure 3.3.1-23** shows a collection of various operating points plotted together showing the ability of the GPC to be run at an appropriate temperature to maintain reforming plate temperature at the desired range.

Figure 3.3.1-23: Combustor Control of Reformer Plate Temperature

3.3.1.8.4.2 Reactor Gas Hourly Space Velocity (GHSV) vs Conversion

Another area of investigation was the capacity of the reactor to assure that overall size of the design was adequate. **Figure 3.3.1-24** shows a “scale sweep” where fuel delivery increases along the X axis. The expected relationship is for conversion (i.e. reformer efficiency) to be constant at or below the maximum GHSV (plotted here as its inverse – residence time). Above the maximum GHSV, conversion would not be complete and would be seen in lower reforming efficiency.

While the data was not a modal as expected, the data points at 0.40 and 0.45 scale (0.25 and 0.28 grams per second, (gps) fueling respectively) show this change in conversion. As this was for a 10 plate assembly and an actual APU Reformer would have approximately 30 plates, this indicates that the reformer will have sufficient initial capacity for 5 kW APU (which would require approximately 0.6 gps to be converted to reformat at 75% reforming efficiency). It does point out that there is little durability margin and will need to be addressed in future designs.

Figure 3.3.1-24: H1 Scale Sweep

3.3.1.8.4.3 Lead Edge Temperature Management

H1 testing also uncovered a thermal management problem at the lead edge of the reformer. Delphi found that normal operating conditions resulted in temperatures in excess of 950 °C at thermocouples located near the entrance to the reactor. It was necessary to dilute the inlet feed stream with N₂ in order to control these temperatures and not damage the washcoat.

3.3.1.8.4.4 Combustor Emissions

Combustor capability was of interest in that ultimately the system would need to meet SULEV emissions levels without the assistance of an after treatment catalyst (ATC) downstream of the reformer (during run modes only). Initial testing of the H1 combustor performance can be found in **Table 3.3.1-3**. Several design weaknesses were found in the H1 design, including inadequate mixing and low/zero velocity areas in the combustor plate.

Table 3.3.1-3: Combustor Emissions

	time	Total HC ppm	Nox ppm	CO %	CO2 %	Source of Data
Ref Ramp up; combustor out	13:42	250	3	0.01	7.50	from Normal start w/ comb w/ emiss.xls (MG733C-15)
	13:44	2500	0	2.70	3.40	
	13:46	1000	0	0.18	6.93	
Steady State; combustor out	13:56	47	0	0.04	5.60	from Normal start w/ comb w/ emiss.xls (MG733C-15)
	13:57	226				

3.3.1.8.5 Develop Catalytic Partial Oxidation Reformer - H2 Reactor

The intent of the H2 design (**Figures 3.3.1-25 and 3.3.1-26**) was to remove the real and expected deficiencies in the H1 design. Coincident to its creation, revisions in the APU enclosure design and layout were also being considered. The primary thrust of the APU revision was to lower the surface area of the “hot zone” to reduce thermal losses. The H2 design allowed the revised APU hot zone enclosure to be “square” shaped as compared to the “tee” shaped hot zone required by the H1 design and thus allowed lower thermal losses to be realized. The key changes in H2 design as compared with H1 design included:

- Removal of the Cathode Air Heat Exchange function (the “square” hot zone design would use two separate heat exchangers mounted to each side of the reformer).
- A single combustor, centrally located with the combustor flow stream in crossflow with the reformer flow stream. This greatly simplified manifolding with only the combustor outlet having a duplicated port.
- Integration of the NCV2 vaporizer and start combustor.

Figure 3.3.1-25: H2 Reformer

Figure 3.3.1-26: Top Section – H2 Reactor

Several iterations of CFD modeling were conducted in order to achieve good distribution with the reforming and combustion plates. **Figures 3.3.1-27** and **3.3.1-28** show the distribution of the proposed H2 design which incorporated vertical manifolds at the lead edge to distribute recycle gas to each reformer layer (**Figure 3.3.1-29**). Additionally, the design incorporated a feature that uses reforming areas on both plates (reforming and combustor) for the initial 20mm of the reactor.

While Figures 3.3.1-27 and **3.3.1-28** show relatively good massflow distribution on both the reforming areas, this unfortunately did not translate to good massflow distribution where the two streams join (the portion of the reforming plate downstream of the transfer ports **Figure 3.3.1-29**). The cause of this was considerable massflow up and down the recycle chimneys. This feature was eliminated subsequently (as was the use of recycle in the system).

Figure 3.3.1-30 shows Total Assembly Pressure Drop plotted alongside Average Cell Pressure Drop. The difference in these values for a given design represents the manifold or chimney losses, which were minimized as the design was modified. Similar analysis was conducted on the combustor.

Figure 3.3.1-27: Reformer Massflow Imbalance - Master

Figure 3.3.1-28: Reformer Layer Outflow Balance

Figure 3.3.1-29: Recycle Chimney

Figure 3.3.1-30 Assembly versus Layer Average Pressure Drop

3.3.1.8.5.1 Fabrication Issues

Multi-plate planar reformer fabrication presented many issues, most of these were related to the braze. A successfully brazed assembly is defined by:

- **Final Height** being within specifications, the vaporizer has a fixed seal interface height and width that must seal to the H2 reformer face.
- **Seal Integrity** between each of three flow passages (reformer, combustor, air pre-heat) and seal to ambient.
- **Un-Restricted Flow Area** of each of the three flow passages.
- **Structural Squareness** allowing the ability to bolt the reformer assembly to manifold without significant enlargement to bolt holes to accommodate out-of-squareness.

Both pre-braze and post-braze heights were recorded for each assembly in an attempt to better predict the degree of braze settling. Predictability was moderate and sensitive to specifics of braze alloy, braze alloy application, braze cycle and burr conditions of the assembled parts (which impacts pre-braze height data collection).

Table 3.3.1-4 contains assembly and braze information on all braze attempts. The tables are divided at chronological points based on the material used for reformer fabrication during that period of braze development. These periods of specific material usage were a result of either material availability or concerns about the impact of material on braze success.

Table 3.3.1-4: H2 Inconel 600 Braze Configs: Index 6-8

Brazing Controls	H2 Reformer	H2 Reformer	H2 Reformer
Chronology Index	6	7	8
Identifier / Serial No.	B1 config	Braze Trial 0	B3 config (aka sn B2)
Date Sent to Brazer	?		?
Unsupported Shim Dimension (mm)	60.2/104.7 23.6/97.5 76.2/15.8	60.2/104.7 23.6/97.5 76.2/15.7	60.2/104.7 23.6/97.5 76.2/15.8
Channel Height; Ref / Comb	.75 / .94 (0.030" / 0.037")	.94 / .94 (0.037" / 0.037")	.94 / .94 (0.037" / 0.037")
Number of A/B etched Plates			
Number of Combustion Plates	25	5	24
Number of Combustion Shims			
Number of Reforming Plates	25	5	24 (w/ fingers)
Number of Reforming Shims			
Number of Generic Shims	49	11	47
Part Material	Inconel 600	Inconel 600	Inconel 600
Shim Thickness (mm)	0.010"	0.010"	0.010"
Braze Alloy 1st Braze	Nicrobraz 150 (BNi-9)	Nicrobraz 150 (BNi-9)	Nicrobraz 150 (BNi-9)
Braze Alloy 2nd Braze (Fittings)	N/A	N/A	Nicrobraz 150 (BNi-9)
Weight Applied During Braze Process (lb)	32?	32?	32?
Dimples in Shims (Yes/No)	No	No	Yes
Grafoil Shims Installed (Yes/No)	No	No	No
Shims Tack welded in place	No	No	No
Inconel tube inserts for squareness of assembly during braze	No	No	No
Wire EDM of locating bolt holess to 8.6 mm	No	No	No
Braze Application Method (Spray, Slather, Foil)	Spray Frames Only	Spray Frames Only	Spray Frames Only
Results (Good, Acceptable, Poor)	Poor (see .ppt file for photos)	Poor; still collapsing	OK after 1st braze; some collapsing after 2nd fitting braze; part in use

Table 3.3.1-4 covers the initial fabrication and braze of Inconel 600 H2 reformers. Inconel 600 was the first material used primarily due to its availability.

Haynes 214 was the preferred material, but as initial orders for H2 hardware were placed it became evident that lead times for Haynes 214 in the dimensions we desired would be longer than desirable. It was accepted that the Inconel 600 material did not have the properties to meet durability requirements but would allow more rapid testing of prototype geometry. The choice of Inconel did have some trade-offs. It was

advantageous in that it is slightly easier to machine than the Haynes 214 but more importantly, because it is a chromia former (forms chromium oxides when heated in an oxidizing environment) it can be brazed without any special treatments. While this is advantageous to the braze process, the alumina based washcoat does not adhere as well to a chromia former as it does to an alumina former. Haynes 214 on the other hand is an alumina former and as a result would have good washcoat adhesion performance but unfortunately requires Nickel plating in order to braze properly.

Table 3.3.1-4 shows braze trial #6 (following the relatively successful brazing of H1 serial numbers 1 through 5) had a poor result. Sectioning of the sample showed that significant shim collapsing had resulted. Braze trial #7 tried thicker reforming plates with similar results. Several theories were put forth on why this was occurring, including the suggestion that the reformer inlet edge of the shims which had a long unsupported length was the initiation point for the surface tension of accumulated braze to 'zipper' the shim together. Another theory suggested that the braze alloy was alloying with the base metal to further weaken the shims when at temperature. In general the notion of insufficient strength at temperature was a concern. The fact that Haynes 214 has substantially more strength at braze temperatures than does Inconel 600 was thought to improve the situation but the same phenomena was experienced with Haynes trials as well. Trials with both Bni3 and Bni9 brazes also experienced this problem.

The next trial used 'fingers' on the combustor plates that served to separate shims at the combustor level and hopefully provide a surface for braze to wick and attract the shim to prevent the reforming layer from collapsing. This proved marginally successful as Braze trial #8 yielded virtually no visible collapsed shims through the first braze. The subsequent braze cycle for attachment of top plate fittings resulted in some collapsing of shims but managed to yield the first viable part (serial number B2).

During this period, problems with the adhesion of the Nickel plating to the Haynes 214 was responsible for several assemblies failing leak check. This triggered work with several plating suppliers in order to produce parts capable of undergoing the braze environment without blistering. At one point, existing parts were screened based on the presence / absence of blisters after having been run through the braze cycle.

Despite the grouping by material, there were a number of other variables included in the many braze trials. Skew and hang-up were two problems that were primarily felt to be the result of fixturing. In order to provide low skew assemblies an internally guided braze fixture was employed (**Figure 3.3.1-31**). This involved four posts that were fixed to the fixture base plate. Over these posts were four loose fitting sleeves. Location of the posts and sleeves were on the centers of the four existing bolt holes found in each plate and shim. Parts were then placed over these sleeves allowing parts to slide on the OD of the sleeve during the braze process. The sleeves were sized such that the brazed assembly could be lifted off the fixture after braze and the sleeve could be machined away to return to the intended bolt hole diameter.

Figure 3.3.1-31: Initial Braze Fixture (no sleeves shown)

It was determined that this approach was too constrained to allow completely free and unbinding movement of the parts downward as the braze liquefied. Delphi had a number of trials that resulted in “hang ups” of portions of the braze stack. A number of increases in clearance and material changes were never completely successful and so a new fixture approach was adopted.

The second fixture (see **Figure 3.3.1-32**) was flexible in that several approaches could be tried. One approach involved guiding on a single part bolt hole diameter and using external guide rods on each of the two adjacent sides. This three-point guiding was presumed to allow the part to grow thermally without significant binding. Another approach used only external guiding in that two guide pins along each of two adjacent sides would be used. If brazed perfectly horizontally this idea would potentially allow the part to skew in a direction away from either of the guided sides. To prevent this, canted graphite blocks were made to tilt the fixture 5 degrees in each of the two guided directions. Additionally, canted blocks were used to support the braze weight. For this fixture, rods were polished ceramic to minimize friction (and potential hang up) with precision fits to the mating base fixture holes to minimize skew.

Figure 3.3.1-32: Second Braze w/ External Guides

While the tilted fixture approach did produce low skew assemblies, it had the unfortunate effect of directing excess braze alloy to collect at the rear of the reformer outlet passages as shown in **Figure 3.3.1-33**.

Figure 3.3.1-33: H2 Reformer A9 – Reformer Outlet

This was felt to ultimately be a result of excessive braze and a result of the spray application process. An evaluation was conducted to determine the mass of braze applied and its variability based on differing numbers of spray passes. See **Figure 3.3.1-34**.

Figure 3.3.1-34: Spray Braze Evaluation

This graphic describes the variation pattern in grams of spray on braze alloy deposited on both reforming plates ("R" designation) or combustion plates ("C" designation). These plates, along with shims that separate them, represent the repeating unit for constructing an H2 planar reformer. Two groups of parts were processed. The groups differ by the date they were sprayed. In each group six plates were positioned on the spray table in alternating fashion (i.e., C-R-C-R-C-R) from left to right to help block out

this effect. Parts were successively sprayed and weighed through 2, 3 and 4 passes to evaluate the weight gain after each pass. Several points are evident:

- Inconsistency in weight gain per pass was evident particularly on the fourth pass where four out of six parts showed insignificant gains.
- Day-to-Day variation (i.e., group-to-group) variation was significant as three out of six parts showed similar or greater weight gain with one pass as compared with the other groups weight gain at two passes.
- Combustion “C” plates generally showed greater weight gains than did Reformer “R” plates

A new braze house was contracted that employs a dispense method rather than spraying in response to these findings and other brazing concerns. Braze alloy dispensing is done using a hypodermic needle and braze alloy is applied only in certain fillet areas based on part geometry. This relies on the wicking action to distribute braze alloy evenly and does not require any part settling during the braze cycle. This has the potential to eliminate hang-up and may impact other braze failure modes, in particular clogging due to uncontrolled excess braze. At this point in the program, it was decided to focus the planar reformer efforts on resolving the manufacturing issues while in parallel producing a relatively straight forward tubular design for use in advancing our systems development efforts.

3.3.1.8.5.2 Performance Evaluation of H2 Hardware

Initial Testing

The initial test objective was to start the reformer and verify basic functions. This involved exercising and evaluating control loops and assessing thermal management capabilities. **Figure 3.3.1-35** shows the test setup employed.

Figure 3.3.1-35: H2 Reformer Test Setup

Testing proceeded as follows:

The Gas Phase Combustor was started first, rather than the reformer, in order to avoid any catalyst damage or soot formation during a cold start of the reformer. This was done via a bottled reformat (21% H₂, 24% CO, balance N₂) feed to the combustor. Rich fueling commenced and reforming began when reformer plate temperatures were approximately 550 °C.

The combustor showed stable temperature control throughout the test. Run phi was approximately 0.13, with 0.12% CO emissions, which was comparable with H1 data. Reformer response showed fast light-off on the front edge. Reformer out stream temperatures were comparable to those of H1 for the short duration of this test, indicating that temperature distribution in the reforming layer was at least as good as the H1 part.

Reformer was ramped to a 0.3 scale factor (0.19 g/s) and N₂ was needed in comparable amounts to that of H1 to control lead edge temperature.

Testing was terminated because the Air Control Valve (ACV) for reformer inlet air temperature control was not controlling T18 (air inlet temp to vaporizer) within range (target of 180 °C), and temperatures were getting too high and threatening gas phase combustion in the vaporizer.

Flakes of washcoat were found in the outlet of the reformer indicating that adhesion to the substrate was compromised. This was presumed to be the cause for performance degradation. Subsequent attempted starts of the reformer confirmed that catalyst performance due to washcoat loss was continuing to degrade performance.

The Air Control Valve control showed that more restriction through the reformer heat exchanger leg was necessary in order allow the Air Control Valve to force more cool air directly into the Vaporizer. By adding restrictive foams to the heat exchanger leg the Air Control Valve then had enough authority to regulate temperature through the flow range.

Start-Up Controls Testing

Several Vaporizer/Combustor starts were conducted with the H2 Serial Number B2 hardware to evaluate start time, emissions, temperatures, and formulate a start and run routine that was repeatable on each cold start. Data for the starts are listed in **Table 3.3.1-5**. Of particular importance is the 'time to reform' average value that for this data set was 103 seconds. A portion of these starts was specifically aimed at determining the effects of igniter placement and is summarized in **Table 3.3.1-6**. The revised igniter placement did have the desired effect of reducing 'time to ignite' from 12 to 8.5 seconds. Due to limitations in igniter

length, only a small change in location was possible and it was recognized that more work and more flexible hardware would be needed to properly optimize ignition.

Table 3.3.1-5: H2 Start Evaluation

Date	hardware	Start Emission Peaks (emission bench) during k_NCV_startflow fueling					Run Emissions (emission bench) during k_NCV_fuelflow fueling					time = 0 when injector turns on (DC >0%)					
		HC (ppm)	Nox (ppm)	CO2 (%)	O2 (%)	CO (%)	HC (ppm)	Nox (ppm)	CO2 (%)	O2 (%)	CO (%)	Peak TC temp @ T2 loc (C)	Peak RTD temp @ T2 loc (C)	time to ignite (sec) (rise)	time to reform (sec) (fr fuel on till T2 shows)	fuel flow change (sec) enable_reforming_temp	ref out temp (sec) when T11 cal face = enable_reforming_temp
7/31/2002 am	NCV2 H2 B2	10000	12	10.1	6.34	0.12	6737	6	5.54	10.33	0.10	884	216	8	81		
7/31/2002 pm	NCV2 H2 B2	17000	15	10.4	6.05	0.14	8130	6	5.65	10.33	0.11	901	230	11	77		
8/1/2002 pm	NCV2 H2 B2	17407	15	10.4	5.84	0.15	7677	6	6	10.33	0.13	925	273	12	75	13	36
8/2/2002 am	NCV2 H2 B2	15201	18	10.52	5.8	0.18	7755	8	6	10.41	0.15	920	265	10	78	13	36
8/2/2002 am	NCV2 H2 B2	14470	20	10.98	5.17	0.18						978	na	19	na		
8/19/2002 am	NCV2 H2 B2	11151	15	10.68	5.87	0.23	10420	6	4.17	10.33	0.11	847	138	6	129	9	41
8/20/2002 pm	NCV2 H2 B2	11325	21	11.57	4.44	0.21	9600	6	4.48	10.31	0.13	na	na	na	na		
8/21/2002 am	NCV2 H2 B2	15175	18	11.81	4.4	0.19	10177	1	4.42	10.25	0.11	883	138	11	119	14	37
8/21/2002 pm	NCV2 H2 B2											1017	166	4	51		
8/21/2002 pm	NCV2 H2 B2	6625	17	11.94	3.61	0.19	4364	6	9.46	8.83	0.18	1029	669	4	51		
8/22/2002 am	NCV2 H2 B2	20469	55	13.29	2.24	0.36	na	na	na	na	na	1107	222	38	na		
8/22/2002 am	NCV2 H2 B2	11094	17	11.35	4.55	0.22	3713	13	8.84	8.75	0.20	1014	183	7	58		
10/23/2002 pm	NCV2 H2 A8	na	na	na	na	na	na	na	na	na	na	857	475	4	313		
	NCV2 H2 AVG	13628.8	20	11.2	4.9	0.20	7619	6	6.1	10.0	0.14	947	270	11	103	12	38

Table 3.3.1-6: H2 Starts – Effect of Igniter Location

Date	hardware	inj S/N	notes	time = 0 when injector turns on (DC >0%)					
				Peak TC temp @ T2 loc (C)	Peak RTD temp @ T2 loc (C)	time to ignite (sec) (rise)	time to reform (sec) (fr fuel on till T2 shows)	fuel flow change (sec) enable_reforming_temp	ref out temp (sec) when T11 cal face = enable_reforming_temp
7/31/2002 am	NCV2 H2 B2		ignitor is located on edge near NCV2 wall	884	216	8	81		
7/31/2002 pm	NCV2 H2 B2		ignitor is located on edge near NCV2 wall	901	230	11	77		
8/1/2002 pm	NCV2 H2 B2		ignitor is located on edge near NCV2 wall	925	273	12	75	13	36
8/2/2002 am	NCV2 H2 B2		ignitor is located on edge near NCV2 wall	920	265	10	78	13	36
8/2/2002 am	NCV2 H2 B2		ignitor is located on edge near NCV2 wall	978	na	19	na		
				922	246	12.0	78	13	36
8/19/2002 am	NCV2 H2 B2		ignitor angle is increased by about 5 degrees (correct design)	847	138	6	129	9	41
8/20/2002 pm	NCV2 H2 B2		ignitor angle is increased by about 5 degrees (correct design)	na	na	na	na		
8/21/2002 am	NCV2 H2 B2		ignitor angle is increased by about 5 degrees (correct design)	883	138	11	119	14	37
				865	138	8.5	124	12	39

Gas Phase Combustor Highflow Evaluation

Testing turned to evaluation of the Gas Phase Combustor behavior given that the reformer function was lost on this sample. The primary objective was to run with bottled reformat (nominally 21% H₂, 24% CO, balance N₂) at high flow rates to simulate actual system start-up conditions and evaluate Gas Phase Combustor temperature management. See **Figure 3.3.1-36**.

Figure 3.3.1-36: H2 B2 Gas Phase Combustor Temps/Flows 8/21/02 Testing

Conclusions from this test included:

During the test, air was commanded to 11.4 gm/sec (Total_comb_flow) and bottled reformat at 1.4 gm/sec (Combustor_Reformat gm/sec) yielding phi between 0.086 and 0.096. Temperature (T14_Gas Phase Combustor_Comb_Zone) remained in control at ~950 °C to this point.

Airflow rate for the Auxiliary Power Unit system was approximately 15 gm/sec for start-up but during this test was limited to 11.4 gm/sec due to supply pressure limitations to the air mass flow controller.

Pressure drop across the combustion chamber, represented by P3_Comb_dP ran very high at 6.7 kPa.

Emissions were low considering exhaust catalyst condition was probably poor at this point (loss of washcoat adhesion similar to reformer side). **See Figure 3.3.1-37.**

CO 0.15% (on the Mass Spectrometer)
 CO 0.0 % (on emissions bench)
 NO_x 0-1 ppm
 HC's None expected due to bottled reformate.

Figure 3.3.1-37: H2 Serial Number B2 Gas Phase Combustor Emissions 8/21/02 Testing

Systems Testing of H2 (Gas Phase Combustor function only)

The several samples of H₂ produced were used in systems tests to provide the Gas Phase Combustor function after their reforming catalysts had degraded. This allowed system startup testing to proceed. This testing led to observations of severe distortion inside the Gas Phase Combustor cavity (see **Figure 3.3.1-38**). Specifically the entrance to the combustor plate appeared distorted with evidence of globules of either molten metal or molten brazes.

Figure 3.3.1-38: H2 Serial Number B2 Gas Phase Combustor

3.3.1.9 Develop Catalytic Partial Oxidation Reformer – Gen1 Tubular

Due to the difficulties in producing the H2 planar hardware and the success of previous (as well as parallel) programs using tubular reformers, Delphi decided to adapt a tubular design that could be fit within the current Auxiliary Power Unit packaging and allow the continuation of systems level development (**Figure 3.3.1-39**). Development, with respect to fabrication and performance, was rather rapid but resulted in very favorable performance. The first test effort once initial hardware was available was to develop start calibrations specific to this new geometry.

Figure 3.3.1-39: Tubular Reformer Assembly (side view)

A consequence of this simple construction was the deletion of the gas phase combustor function. The initial configuration utilized ceramic mixing foam to separate combustion and mixing zones. Using a small quartz tube inserted in this area allowed for rough determination of start calibrations and visualization of the start combustor process. Subsequent to this, the quartz tube was removed and final start calibrations were evaluated. Several configuration variants involving the use of different elements to separate mix and combustion zones were evaluated.

During this effort an oscillation in the control of inlet air temperature (T12) was observed. A modification to the vaporizer air manifold air routing was made that involved bringing pre-heated air from the reformer pre-heat loop together with un-heated air prior to their entering into the donut shaped manifold supplying air to the director. T12 senses air from this donut manifold and were too closely coupled (via proximity) to the pre-heat air feed.

Table 3.3.1-7 shows the results of preliminary evaluation of start-up. Notice that “time to reform” is 9 seconds as compared to 103 seconds for the H2 Planar reformer. Given relatively stable start up behavior, reformers were released to the Systems group for inclusion into the Auxiliary Power Unit system test plans. While the degree of integration varied relative to which sub-systems were present and functional, in all cases the reformer was mounted to an Integrated Component Manifold that had been modified to provide the Gas Phase Combustor function now absent from the reformer.

Table 3.3.1-7: Gen 1 Tubular Start Evaluation

Date	hardware				time = 0 when injector turns on (DC >0%)						
					Peak TC temp @ T2 loc (C)	Peak RTD temp @ T2 loc (C)	time to ignite (sec) (rise)	time to reform (sec) (fr fuel on till T2 shows)	fuel flow change (sec) _ ref _ temp)		
11/16/2002	Tubular Reformer sn1				613	n/a	19	10	3		
11/16/2002	Tubular Reformer sn1				391	n/a	3	12	7		
11/18/2002	Tubular Reformer sn1: Start and Run on video				333	n/a	2	9	6		
11/19/2002am	Tubular Reformer sn1				410	n/a	6	9	none		
11/19/2002am	Tubular Reformer sn1				484	n/a	3	6	5		
11/19/2002pm	Tubular Reformer sn1				501	n/a	2	6	5		
11/21/2002	Tubular Reformer sn1				420	n/a	2	9	5		
	TUBULAR GEN1 AVG				450		5	9	5		

During several of the system level runs in which both reformer and Gas Phase Combustor were functioning, increases in system pressure readings indicated an increased reformer pressure drop and subsequent teardowns revealed varying degrees of inlet and/or catalyst coking. After ruling out any lab / control based differences, tests were conducted that isolated the use of the Gas Phase Combustor (as integrated into the Integrated Component Manifold passages) as the primary cause for the inlet / catalyst coking. The use of this combustor is thought to both radiate and conduct heat to the reformer (the combustor is located within the area of the Integrated Component Manifold directly beneath the reformer rear tube section).

The current reformer lab test fixture was then replumbed so that a Gas Phase Combustor function would be possible. While not identical to the physical modifications made to the Integrated Component Manifold, it did prove adequate in helping to recreate the carbon forming conditions. Once the thermal conditions experienced in the systems lab were recreated and verified through the witnessing of catalyst and inlet coking we proceeded to alter inlet and catalyst configurations to control key temperatures.

Table 3.3.1-8 provides a listing of inlet / catalyst configurations tested. Data from December 2002, represents a condition where the reformer coked. Analysis of the gas temperature grade line through the inlet and into the catalyst suggested that if temperatures were kept below critical values (less than 600°C near the center of the combustor and less than 450°C at the exit of the mixing element separating the mixing and combustion zones), pre-combustion could be avoided. Each configuration that was tested did a good job of limiting these two temperatures. Past experience with 1" tubular reactors suggested that a steep rise in temperature as reactants enter the catalyst was more desirable. This goal competed with the need to have rapid vaporization in the mix zone, which was greatly assisted by radiation from the catalyst face.

Table 3.3.1-8: Catalyst/Inlet Configurations vs. Carbon/Filter Results

Col#	1	3	4	5	6	7	8	9
Temps are from:	SS before pre-comb event	SS	SS	SS	SS	not as SS as other runs	SS	SS
Internal Inserts	None	rad shield	mix foam	monolith	rad shield	rad shield w/ spikes	rad shield w/ spikes	rad shield w/ spikes
Catalyst Position (Flush, recess, beyond)	flush	flush	beyond	beyond	recessed	recessed	recessed	recessed
Catalyst Size	1.75"	1.75"	1"	1"	1"	1"	1"	1"
GPC or No GPC	GPC	GPC	GPC	GPC	GPC	GPC	GPC	No GPC
O/C	1.04	1.10 / 1.04	1.04	1.04	1.04	1.04	1.04	1.04
Day of Week	Fri	Tues	Wed	Thur	Thur	Fri	Tues	Wed
Date & Time of Run	12/13/02	12/17/02	12/18/02	12/19/02	1/2/03	1/3/03	1/7/03	1/8/03
Catalyst delP change during test?	Yes	No	No	No	No	No	No	No
Reformer Out Filter Status	very black	clean	very black	some carbon	some carbon	Black	very black	some carbon

Additional developments were made to the air pre-heat heat exchanger. The initial design used a single loop of tubing. This was awkward to fabricate and did not provide sufficient heat exchange. The subsequent design utilized stainless steel bellows to form a U-shaped loop. This design, while superior to the full loop tube, still could not provide

rapid heat for vaporization during start-up. To provide this a 42V coiled rod heater was added to the reformer pre-heat return tube. This provided rapid and clean start up heat.

Data in **Figures 3.3.1-40** and **3.3.1-41** show mass spectrometer and temperature data respectively for a typical tubular reformer. Six reactors were built and all underwent performance validation testing before being offered for Auxiliary Power Unit testing. Reformate quality was very good and remarkably consistent.

Figure 3.3.1-40: Tubular Data: Mass Spec

Note: The “CORR” suffix refers to a water knockout correction only

Figure 3.3.1-41: Tubular Data: Temperature Data

Gas Chromatograph data (**Table 3.3.1-9**) confirmed what had been observed via Mass Spectrometer data, that reformate quality was very good and met preliminary

requirements ($\Sigma\text{HC's} \geq \text{C}_2 < 0.1$ mole%, $\text{CH}_4 < 1$ mole % and $\text{H}_2\text{O}/\text{CH}_4$ ratio ≥ 3) with the exception of brief periods during start up.

Table 3.3.1-9: GC Data

GC Data	Average
% H ₂	0.0000
% CO	21.5589
% Methane CH ₄	0.0000
% Methane CH ₄ (Mass Spec)	0.6665
% Ethane C ₂ H ₆	0.0158
% Ethylene C ₂ H ₄	0.0405
% Propane C ₃ H ₈	0.0008
% Propylene C ₃ H ₆	0.0212
% Butane C ₄ H ₁₀	0.0002
% Iso-Butane C ₄ H ₁₀	0.0006
% Butene C ₄ H ₈	0.0033
% N ₂	48.8873
% CO ₂	1.4267
Sum of All C ₂ (%)	0.0563
Sum of All C ₃ (%)	0.0220
Sum of All C ₄ (%)	0.0040
Sum of C ₂ and Greater (%)	0.0822
Sum of C ₃ and Greater (%)	0.0260

NOTE: % H₂ is shown as 0 due to initial setup problem with this GC

3.3.2 Develop Catalysts

3.3.2.1 Catalyst Formulation and Characterization

3.3.2.1.1 Alumina-based Washcoats

The catalyst consists of a shaped substrate carrying a washcoat containing active metals. Earlier testing had revealed that zirconia-toughened alumina to be amongst the best choice of substrates, and rhodium to be a good choice of active metal. While having good activity, the earliest generation of catalysts exhibited limited durability, thought to be due to instability of the washcoat. Exposed to high temperatures for long time intervals, the Al₂O₃ principal component of the washcoat is known to undergo phase transition, to the more stable α form, and also undergo sintering; both transformations contributing to encapsulation or loss of active metal, and loss in catalyst performance.

A series of different alumina oxides were obtained from suppliers, and tested in the as-received and thermally treated forms. Thermal treatment results in greater physical stability in that the alumina resists further sintering and loss of surface area. These

aluminas were selected based on availability in commercial quantities and on properties thought to be important to reforming.

All of the catalysts exhibited good initial activity; however, only the most stable washcoat formulation, Al_2O_3 -TG, had good durability over the duration of testing, having nearly the same activity after over 50 hours of testing as for the fresh catalyst. This can be attributed to the stability of $\alpha\text{-Al}_2\text{O}_3$ and the reasonable stabilized surface area of the washcoat material, likely resulting in good Rh dispersion.

While the catalyst exhibited differing degrees of deactivation for H_2 production, nearly the same amount of CO was produced by all of the catalysts over most testing intervals. Delphi found that only when significant loss in H_2 production occurs, being less than 17% in the product gas, does diminishment of CO production occur, indicative of severe loss in catalyst performance. This decoupling of H_2 and CO selectivity's is an indication of differing reaction pathways for the formation of the two primary products. The sensitivity of H_2 selectivity to washcoat properties, and so presumably to Rh availability on the washcoat, can be an indication of the H_2 formation pathway involving surface-phase chemistry, while the CO formation pathway may have significant gas-phase contributions.

Another interesting feature of the data was the extremely low Rh dispersion, as measured by CO chemisorptions. For example, Rh supported on the NC washcoat was almost completely lost, yet the tested catalyst still retains over 80% of the fresh H_2 production. Similar behavior was observed on the CNC washcoat material. This result implied that little Rh is required for the reaction to proceed, perhaps indicating that active surface sites have extremely high turn-over frequencies.

3.3.2.1.2 Zirconia-based Washcoats

A parallel development effort to test zirconium based washcoats was undertaken in 2002. Zirconium oxide was selected based on the material's well known stability at very high temperatures. Materials were obtained from MEI, Flemington, NJ, and washcoats were prepared with the same active metal and substrate and testing procedure employed with the alumina-based washcoats.

In general, the zirconium oxide based washcoat materials had equivalent CO production activity, and while having less H_2 production activity, and exhibited the same stability over 50 hours of testing as compared to alumina-TG. Characterization of the Zirconia-based washcoats was not completed due to the immediate focus on the better performing Alumina-based washcoats.

3.3.2.2 Operational Development

3.3.2.2.1 Thermodynamic Considerations

Of concern to reformer design was the amount of heat generated by the partial oxidation reaction and how selectivity to the desired products, CO and H₂, and undesired products, such as carbon, change as a function of processing parameters, including O/C molar ratio and reaction temperature. A simple model was developed using ASPEN process simulation software which indicated that situations of poor mixing could lead to either poor yields and excessive heat generation in cases of higher O/C, or carbon formation in cases of lowered O/C. Additionally, operating at 900 °C, provided sufficient residence time is provided to reach equilibrium, was sufficient to approach maximum H₂ and CO production, while minimizing hydrocarbon production. Operating at above 950°C, while helpful in preventing carbon deposition when O/C is close to unity, provides no additional benefits and may be detrimental due to increased catalyst and material degradation.

3.3.2.2.2 Operating Regime Definition

Preliminary recommendations and constraints on reformer operations were proposed based on knowledge obtained from catalyst testing and the thermodynamic considerations. These results were based on cylindrical catalyst testing experience, using both flow-rate and temperature-based criteria, and the amounts of washcoats that can be added to planar substrates.

Results of equilibrium modeling, predicted energy produced by the reaction as a function of O/C and product H₂ concentration, using multi-component gasoline composition simulation are shown in **Figure 3.3.2-1**.

Figure 3.3.2-1: Equilibrium Modeling Results – Carbon Formation

Figure 3.3.2-2: Equilibrium Modeling Results Product Compositions

3.3.2.3 Testing Protocol Development

The ability to discriminate between catalyst formulations via testing was paramount to identifying the best formulation. Experience testing gasoline partial oxidation catalysts at the recommended temperatures of from 900°C to 950°C resulted in nearly identical levels of H₂ and CO product for all but the least appropriate compositions. Consequently, processing parameters and reactor wall temperatures were adjusted so that average catalyst center temperatures were 1050-1100°C. In this way, the catalysts were exposed to thermal stress and exhibited rapid aging, and so permitting elimination of all but the best catalyst formulations within a reasonably short period of time, usually after 20 to 50 hours of testing.

3.3.2.4 Improvements to Catalyst Durability

Catalyst formulations were developed using highly consistent, controllable, and well instrumented test stands. These test stands held a 1" diameter tubular reactor, operated in a downflow mode, and configured with a fuel vaporizer, a mixing and heat retaining reticulated foam in front of the catalyst, separated from the catalyst by a flame arrester, 1" length of catalyst, and then a post-catalyst heat retainer. The goal of the testing was to eliminate or minimize all variables except for catalyst composition.

Catalysts consisted of active metal bearing washcoats held on ceramic substrates. Typical compositions were rhodium on alumina over zirconia-toughened alumina (ZTA) reticulated foam substrates. The major assumption of the catalyst testing was that catalyst rankings and performances determined from these development test stands were directly transferable to differing hardware configurations.

Determination of optimum catalyst compositions relied on testing the performance of these catalysts using an aggressive testing protocol. Testing was conducted by establishing total space velocities and air-fuel ratios such that catalyst center temperatures exceeded 1050°C. Under these conditions only the best catalysts maintained good performance during the relatively short duration of the tests. Good performance was observed in at least 20 mole % hydrogen of the total product gas over the duration of the testing. Testing typically proceeded for 50 to 70 hours.

3.3.2.5 Durability Test Stands

Greenlight Power Technologies, of British Columbia, Canada, was contracted to provide modular durability test equipment. These units featured a control module capable of independently operating up to six test modules and were designed for continuous unattended operation. The control module was equipped with data collection, continuous process monitoring, and process control features, and contains process gas analysis, waste-gas combustion, and primary gas and liquid feed sources. The test modules were configured for up-flow tubular reactors, and contained all controllers and instrumentation for each reactor. Each test module could be independently configured with a variety of fuels, including gasoline, diesel fuel, or natural gas, as well as air and water.

3.3.2.6 Understanding of Deactivation and Aging Mechanisms

Work in this area focused on the effects of fuel impurities on catalyst performance. Exposing the catalyst to SO₂ during reforming resulted in a product containing significantly lowered concentrations of H₂, and elevated levels of H₂O and CH₄; CO and CO₂ followed similar trends but to a much lesser extent. A different behavior was observed from different classes of organic components contained in fuel. Reforming with a single component, such as iso-octane, resulted in repeatable light-off behavior. However, exposing the catalyst to gasoline, such as CARB Phase II, produced a delay in H₂ light-off, which was not restored upon switching back to iso-octane.

3.3.2.7 Rapid Aging Test Development

An oxidative aging method was demonstrated, taking advantage of the observation that heating catalyst samples in hydrogen had little to no effect on performance, while heating in air had a significant impact. Under reducing conditions, a high degree of metal dispersion is obtained, overcoming any effects of washcoat morphology changes

due to the temperatures of heat treating. In an oxidative environment, metal particles are assumed to exhibit significant sintering.

Various catalysts were exposed to air at 1200°C for six hours. These were then tested for gasoline partial oxidation, according to the usual procedures, and the performances compared to tests of similar catalysts not pre-aged in air. The washcoat formulation used, generation 1, referred to as alumina-NC, exhibited deactivation after about 2000-3000 minutes of testing. Use of the oxidative aging test reproduced this same behavior after only 300 minutes of testing, although the test was extended to 1000 minutes for behavior confirmation.

Selectivity to H₂ and CO was found to respond to aging differently. For example, frequently the amount of hydrogen a catalyst could produce deteriorated much more rapidly than the amount of carbon monoxide produced. This behavior was mirrored in the aged catalysts. Aging was able to reproduce the hydrogen (and water) performance that a fresh catalyst exhibited after 1000 minutes of testing, CH₄ and C₂'s performance after 2000 minutes, and minimal changes in CO and CO₂ performance. These results suggested that catalyst properties responsible for H₂ formation were most sensitive to thermal degradation mechanisms, while those responsible for CO formation were relatively stable, aligning with the results from the SO₂ deactivation studies.

Evaluation of this oxidative aging method was repeated on a more advanced washcoat, designated alumina-TG, and the results of testing aged and fresh catalysts indicated no difference could be observed between the aged and fresh catalysts. The aged catalysts, tested for 300 minutes, had the same performance as the fresh catalysts after a test of 3500 minutes. Compared to the findings with the NC washcoat, this suggested that alumina stability played a key role in determining catalyst performance during the first 60 hours of testing.

3.3.2.8 Improved Catalyst Formulations

The rapid aging test was used to evaluate a series of modified Rh/alumina-TG catalyst compositions. Simultaneously, a different Rh addition method was tested. Adding Rh by chemisorption instead of equilibrium adsorption resulted in a catalyst with lower initial activity and very poor stability. However, preparing a catalyst with modifier and by rhodium chemisorption resulted in very stable performance, even after aging, equivalent to or better than the standard equilibrium adsorption method.

3.3.3 Develop Reformer and System—General

3.3.3.1 Lab Test System Development

Two Gas Chromatographs were added to Delphi's lab equipment in 2002. One for reformer development and the other for the Catalyst durability stands.

4 2003 TECHNICAL PROGRESS AND ACHIEVEMENTS

4.1 Task 1: System Development

4.1.1 Define System Requirements

Definition of product design level generally follows SOFC stack design level, with a suffix letter defining an intermediate System (Auxiliary Power Unit, APU) design level. For example, the APU hardware with Generation 2 (Gen 2) SOFC Stack technology is identified as Gen 2B. This represents an evolution of APU design over the Gen 2A design. The high-level design targets are given in **Table 4.1.1-1**. The Phase 1 SECA targets are shown in the figure for reference.

Table 4.1.1-1: SOFC APU System High-Level Targets

Target Metric	System Design / Mechanization Level Targets						Automotive SOP ¹
	Gen 2 B	Gen 3 A	Gen 3 B	SECA Ph 1	Gen 4	Gen 5	
Target Implementation	07 / 03	12 / 03	6 / 04	1 / 05	6 / 06	7 / 07	
System Type:	Mobile APU	Mobile APU	Mobile APU	Demo Sys "A"	Mobile APU	Mobile APU	
Fuel	Gasoline	Gasoline	Gasoline	Nat Gas	Gasoline	Gasoline	
Net Full Power (kW)	0.1	1.25	2.2	> 3	4	5	
Fuel to Electric Efficiency @ Full Power	1%	12%	26%	35%	36%	39%	
System Cost (\$/kW)	N/A	1000	1000	800	800	600	
Life (hours)	50	1000	2000	1500*	4000	10000	
Cycle Durability (cycles)	<5	150	250	10*	1000	7000	
System Mass (kg)	74.9	60.0	63.9	N/A	50	50	
(kg/kW)	749.0	48.0	29.1		12.5	10.0	
System Volume (liters)	60.5	49.2	49.2	N/A	49.2	49.2	
(l/kW)	605.0	39.4	22.4		12.3	9.8	
¹ SOP: Start Of Production *Test Procedure: Steady State 1000 hours Transient 10 cycles Steady State 500 hours Degradation < 2% / 500 hours Degradation < 1% after 10 cycles (Dates in brackets are when each target metric will be met internally)							

The high-level design targets included metrics for net power, fuel to electric efficiency, cost, life, and durability. The targets shown for the Gen 2B design level were based upon anticipated performance. Note that for Gen 2B, just over break even net power was expected. Rapid progression of Life and Durability targets are shown in **Figure 4.1.1-1**. Current system performances in these areas were below Phase 1 targets, and special attention must be paid to the progress in these areas to targets.

A feature roadmap covering Gen 2B to commercial design levels is shown in **Table 4.1.1-2**. Each major design level change was an opportunity to deploy new SOFC stack

technology. For example, the major difference between Gen 2 and Gen 3 design levels was the specific design and technology deployed for the SOFC stacks. More detailed specifications and targets for each design level are defined in the allocations that are to follow.

Table 4.1.1-2: SOFC APU Feature Roadmap

System Features:	System Design / Mechanization Level Targets					
	Gen 2 B	Gen 3 A	Gen 3 B	SECA Ph 1	Gen 4	Commercial SOP ¹
STACK Stack and Cell Combination Flow arrangement Gross output power (kW) Power density (0.7 V/cell, full power)	GEN 2.x 2 x 15 cell ISM Cross-flow 6.5 (294 mW/sq.cm)	GEN 3 2 x 30 cell ISM Co-flow 2 (322 mW/sq.cm)	GEN 3.x 2 x 30 cell ISM Co-flow 3.2 (500 mW/sq.cm)	GEN 3.x 2 x 30 cell ISM Co-flow 4 (590 mW/sq.cm)	GEN 4 2 x 30 cell ISM TBD-flow 5 (701 mW/sq.cm)	GEN 4.x 3 x 30 cell ISM TBD-flow 6.1 (852 mW/sq.cm)
REFORMER Reforming Modes Gross efficiency Output power, LHV _{gas} (kW)	GEN 1.1 TUBE POX ONLY 77% 7.2	GEN 1.2 TUBE POX ONLY 77% 7.3	GEN 3 REFORMER POX + RECYCLE 120% 10.2	GEN 3.x REFORMER POX + RECYCLE 125% 13.9	GEN 4 REFORMER POX + RECYCLE 125% 13.9	GEN 4.x REFORMER POX + RECYCLE 130% 16.8
POWER ELECTRONICS Type Conversion efficiency (full power)	GEN 2 3 kW, 42 VDC 87%	GEN 3 4 kW, 42 VDC 91%	GEN 3.x 4 kW, 42 VDC 91%	GEN 3.x 4 kW, 120 VAC 91%	GEN 4 5 kW, 42 VDC 92%	GEN 4.x 6 kW, 42 VDC 92%
Design Goals:	Automatic APU Function Finish Gen 2 Stack	Achieve Target APU Size Gen 3 Stack Implementation Improve: Reliability Durability Power Efficiency	Deploy Anode Tail Gas Recycle (TGR) Deploy high-eff reformer Improve: Reliability Durability Power Efficiency	Demonstrate Natural Gas Stationary System	Gen 4 Stack Implementation High volume capable: Tooling capacity Pilot plant Achieve cost targets Application validation target	High volume capable: Tooling capacity Production Plant Achieve cost targets

The metrics defined in **Table 4.1.1-1** as well as additional high-level system targets are presented graphically in **Figure 4.1.1-1**. Commercial application targets are shown in the outer ring of the diagram. Planned performance levels of the Gen 2B design are shown as the innermost curve. This diagram emphasizes the gaps between Gen 2B and required performance for the commercial application. From the figure, the largest gaps appear to be with the system function, specifically power, efficiency, life and durability.

Figure 4.1.1-1: SOFC APU System Targets

Graphical depictions of SOFC stack and fuel reformer targets are shown in **Figure 4.1.1-2** and **Figure 4.1.1-3** respectively. Like the chart for the System, the charts covering SOFC stack and fuel reformer show the commercial application targets in the outer ring, and Gen 2B performance in the inner-most ring. Significant gaps existed between Gen 2B performance and application requirements.

Figure 4.1.1-2: SOFC APU Stack Targets

Figure 4.1.1-3: SOFC APU Reformer Targets

A table summary of the information presented graphically in **Figure 4.1.1-1**, **Figure 4.1.1-2** **Figure 4.1.1-3** is given in **Table 4.1.1-3**. These targets are specific to the mobile APU application.

Table 4.1.1-3: Requirements Summary Table

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APU System / Subsystem		System Design / Mechanization Level				
		Gen 2 B	Gen 3 A	Gen 3 B	Gen 4	Commercial (SOP) ¹
		08 / 03	12 / 03	6 / 04	6 / 06	06 / 07
System	Units	RP204408				
Net Power	kW	0.1	1.25	2.2	4	5
Electrical Efficiency	%	1.1%	12.2%	25.9%	36.1%	38.6%
Mass	kg	74.9	60	63.9	50	50
Volume	liters	60.5	49.2	49.2	49.2	49.2
Life	hours	50	1000	2000	4000	10000
Cycle Durability	cycles	<10	150	250	1000	7000
Audible Noise	dB(A)	69	65	67	55	50
Start-Time (25 C to Full Power)	min	60	48	45	30	10

SOFC Stack		2x15 Gen 2.1	2x30 Gen 3.0	2x30 Gen 3.x	2x30 Gen 4.x	2x30 Gen X
Flow Arrangement		Crossflow Thick Cassette	Co-flow Thin Cassette	Co-flow Thin-Cassette	TBD	TBD
Gross Electric Output Power (Full Power)	kW	0.9	2.0	3.2	5.0	6.1
Overall Efficiency ($P_{elec}/P_{fuel,in}$) Full Power	%	13%	26%	31%	36%	36%
Mass	kg	22.7	15.9	15.9	11.4	11.4
Volume	liters	6.8	6.8	6.8	6	6
Life	hours	>10	3000	6000	8000	10000
Cycle Durability	cycles	>5	500	1000	3000	7000

Gasoline Reformer + Fuel-Air Prep		Gen 1.1 Tube	Gen 2.0 Tube	Gen X RefWER (Tube or Other)	Gen X RefWER (Tube or Other)	Gen X RefWER (Tube or Other)
Reforming modes		POX Only	POX Only	POX + Recycle	POX + Recycle	POX + Recycle
Output Power, LHV _{H2, CO} (System run, full power)	kW	7.2	7.9	10.2	13.9	16.8
Output Power, LHV _{reformer} PoX (System Start-up)	kW	18	18	18	18	18
Conversion Efficiency ($\dot{m}_{dot,out} \times LHV_{H2, CO}/LHV_{fuel,in}$)	%	77%	77%	120%	125%	130%
Mass	kg	6.5	4.6	4.6	3.3	3.3
Volume	liters	2.75	2.4	2.4	2.4	2.4
Reformer Life (Full Power, 18kW @ Quality)	hours	50	400	600	800	1000
Reformer Life (Steady State, 5kWnet sys @ Quality)	hours	500	3000	6000	8000	10000
Cycle Durability	cycles	250	500	2000	5000	7000

¹ SOP: Start Of Production

System and subsystem efficiency allocations were made to support the product development plan. The efficiency allocation for the mobile Auxiliary Power Unit (APU) is shown in **Table 4.1.1-4**. This allocation included targets (limits) for parasitic system loads caused by heaters, pumps and blowers, actuators, and electronics. The parasitic loads reduce the gross output of the power plant. A parasitic loss factor is shown in the figure for reference to show the effect of the parasitic loads if they were treated like a forward power conversion efficiency. Power electronics conversion is not treated as a parasitic load, but a forward energy conversion efficiency. Anode tail gas recycle (TGR)

improves the effective fuel utilization of the SOFC stack (based on gasoline input to the reformer) and may contribute to improved reformer efficiency due to the water content of the anode tail gas when the stacks are under load. For purposes of the efficiency allocation table, fuel utilization in the stack is true utilization based upon fuel input to the stack, and all anode tail gas recycle (TGR) benefit is applied to reformer efficiency only. Reformer efficiencies over 100% are then possible when looking at produced reformat Lower Heating Value (LHV) to fuel input (Gasoline LHV).

Table 4.1.1-4: System Efficiency Allocation

Revision 05.13.03

APU Efficiency Allocation		System Design Level				
		Gen 2 B	Gen 3 A	Gen 3 B	Gen 4	Commercial (SOP) ¹
Steady State	Units	POX	POX	POX + Recycle	POX + Recycle	POX + Recycle
Reformer Efficiency	%	77%	77%	120%	125%	130%
Fuel Utilization	%	25%	50%	60%	70%	70%
Stack Conversion Efficiency (0.7 V/cell)	%	52%	52%	52%	52%	52%
SOFC Stack Conv Efficiency	%	13%	26%	31%	36%	36%
Gross Stack Output Power	kW	0.9	2.0	3.2	5.0	6.1
Reference Power Density	W/cm ²	0.294	0.322	0.500	0.701	0.852
Power Conditioner Efficiency	%	87%	91%	91%	92%	92%
Gross Conversion Efficiency	%	8.7%	18.2%	34.1%	41.9%	43.5%
Parasitic Loss Factor	%	12%	67%	76%	86%	89%
Net System Efficiency @Net Power	%	1.1%	12.2%	25.9%	36.1%	38.6%
Net Elec Power	kW	0.1	1.3	2.2	4.0	5.0
Fuel Power	kW	9.3	10.2	8.5	11.1	13.0
Gasoline Flow	g/sec	0.21	0.23	0.19	0.25	0.29
Fuel Consumption	gal/hour	0.27	0.29	0.24	0.32	0.37
Allowable Electrical Parasitic Load	W	712	612	692	642	642
APU Parasitic Load Allocation						
Full Time Loads:						
Blower/Motor/Driver	W	650	550	550	500	500
Recycle Pump	W	0	0	80	80	80
Product Controller	W	27	27	27	27	27
Sensors:						
Reformer Out (S1)	W	5	5	5	5	5
Combustible Gas (S4)	W	15	15	15	15	15
Air Control Valves (5)	W	15	15	15	15	15
Total	W	712	612	692	642	642
Transient Loads:						
Reformer Air Heater	W	300	300	300	300	300
Igniter 1	W	25	25	25	25	25
Igniter 2	W	25	25	25	25	25

¹ SOP: Start Of Production

The efficiency allocation shown in **Table 4.1.1-4** applied to the full power output operating point. Off-peak power efficiency benefits could be realized due to reduced parasitic load levels, improved power conditioner efficiencies, and higher operating voltage of the SOFC stack that yields higher Stack conversion efficiencies. An estimate of the off-peak power efficiency is shown in **Figure 4.1.1-4**. From the figure, the benefit of anode tail gas recycle (TGR) was clear.

Figure 4.1.1-4: SOFC APU System Efficiency

The mass allocation of the system is shown in **Table 4.1.1-5**. Gen 2B figures represent the measured mass of the subsystem components. This design had approximately 60% of its mass in the Hot Zone Module (HZM). The Hot Zone Module was mostly comprised of Nickel-based super alloy and ceramic materials that must be heated to operating temperature. Balance of Plant components represent approximately 40% of the system mass. Much of this mass consisted of electronic modules, electric motors, insulation material, and sensors and actuators. These components represented relatively mature technology where mass reduction potential was less significant.

Table 4.1.1-5: SOFC APU Mass Allocation

Gasoline SOFC APU System Mass Allocation (kg)													
		Gen 2 B			Gen 3 A			Gen 3 B			Gen 4		
	Module	APU		Module	APU		Module	APU		Module	APU		
	%	%		%	%		%	%		%	%		
ISM 1	22.7	50%	30%	15.9	50%	26%	15.9	50%	25%	11.4	50%	23%	
ICM 2	11.4	25%	15%	8.0	25%	13%	8.0	25%	12%	5.7	25%	11%	
Reformer	6.5	14%	9%	4.6	14%	8%	4.6	14%	7%	3.3	14%	7%	
CHEX (2) 3	5.1	11%	7%	3.6	11%	6%	3.6	11%	6%	2.6	11%	5%	
Total Hot Zone Module	45.7	100%	61%	32	100%	53%	32	100%	50%	23	100%	46%	
	100%			70%			70%			50%			
Thermal Insulation	9.1	31%	12%	9.5	34%	16%	9.5	30%	15%	9.2	34%	18%	
Product Enclosure	6.4	22%	9%	5.6	20%	9%	6.6	21%	10%	5.4	20%	11%	
Space Frame	2.4	8%	3%	2.0	7%	3%	2.0	6%	3%	1.9	7%	4%	
Subtotal	17.9	61%	24%	17.1	61%	28%	18.1	57%	28%	16.5	61%	33%	
Process Air Module (PAM)	5.1	17%	7%	4.9	17%	8%	4.9	15%	8%	4.7	17%	9%	
Hoses and couplings	0.6	2%	1%	0.6	2%	1%	0.6	2%	1%	0.6	2%	1%	
Subtotal	5.7	20%	8%	5.5	20%	9%	5.5	17%	9%	5.3	20%	11%	
Power Conditioner	3.6	12%	5%	3.5	12%	6%	3.5	11%	5%	3.3	12%	7%	
Product Controller	0.9	3%	1%	0.9	3%	1%	0.9	3%	1%	0.9	3%	2%	
Wiring Harness, Relays, Sensors	1.1	4%	1%	1.1	4%	2%	1.1	3%	2%	1.0	4%	2%	
Subtotal	5.6	19%	7%	5.4	19%	9%	5.4	17%	8%	5.2	19%	10%	
Recycle Pump Subsystem							3.0	9%	5%	3.0			
Total Balance of Plant	29.2	100%	39%	28	100%	47%	31.9	100%	59%	27	100%	54%	
Total APU	74.9		100%	60		100%	63.9		100%	50		100%	
	100%			80%			85%			67%			

¹ ISM: Integrated Stack Module

² ICM: Integrated Component Module

³ CHEX: Cathode Air Heat Exchanger

The package volume allocation representing a Gen 3 system is given in **Figure 4.1.1-5**. This allocation is organized into three main modules, Hot Zone Module (HZM), Plant Support Module (PSM), and Application Interface Module. The Application Interface Module (AIM) was designed to be the configurable application-specific interface to the rest of the APU plant that may be mostly common application to application. About 62% of the APU is allocated to the Hot Zone Module that comprised the core of the SOFC plant including Fuel Reformer Reactor, High Temperature Heat Exchangers (Energy Recovery), Tail Gas Burner, SOFC Stacks, High Temperature Gas Manifolding, High Temperature Sensors, and Thermal Insulation. About 28% of the total volume was dedicated to low temperature Balance-of-Plant components and electronic components like blowers and pumps, low temperature sensors and actuators, controllers, power electronics, and wiring. About 10% of the total APU, is dedicated to configurable application interfaces. The package outline of the Gen 2B APU is the same as that shown in **Figure 4.1.1-5**, but with a 275 mm package height, instead of 200 mm as shown.

Figure 4.1.1-5: SOFC APU Volume Allocation

A system cost allocation was created to give targets to subsystems consistent with the SECA targets of \$800/kW, \$600/kW, and \$400/kW (**Table 4.1.1-6**). This allocation begins with a Gen 3 design level. This allocation emphasized the challenge in achieving targeted cost levels. It was anticipated that initial cost distribution would be 60% Hot Zone Module and 40% Balance of Plant at the onset of Gen 3 (\$1000/kW). In this allocation, cost reductions of 70% in the Hot Zone Module and 45% in Balance of Plant would be required to meet final cost objectives of \$400/kW. The final cost distribution was targeted to be about 47% Hot Zone Module, and 53% Balance of Plant.

Table 4.1.1-6: SOFC APU Cost Allocation

Gasoline SOFC APU System Factory Cost Allocation (\$)																									
100 k Units / Year																									
		Module		APU		Module		APU		Module		APU		Module		APU		Module		APU					
*Costs Include fasteners & gaskets		Gen 3 B		%		%		Gen 4		%		%		APP SOP ⁴		%		%		SOP CI ⁵		%		%	
ISM*	\$	1,800.00		78%	48%	\$	1,496.62		78%	50%	\$	1,023.38		78%	46%	\$	550.13		78%	37%					
ICM	\$	180.00		8%	5%	\$	149.66		8%	5%	\$	102.34		8%	5%	\$	55.01		8%	4%					
Reformer	\$	220.00		10%	6%	\$	182.92		10%	6%	\$	125.08		10%	6%	\$	67.24		10%	4%					
CHEX (2)*	\$	100.00		4%	3%	\$	83.15		4%	3%	\$	56.85		4%	3%	\$	30.56		4%	2%					
Total Hot Zone Module		\$	2,300.00	100%	61%	\$	1,912.35	100%	64%	\$	1,307.65	100%	58%	\$	702.95	100%	47%								
		100%				83%				57%				31%											
Thermal Insulation*	\$	300.00		21%	8%	\$	225.00		21%	8%	\$	195.00		21%	9%	\$	165.00		21%	11%					
Product Enclosure*	\$	75.00		5%	2%	\$	56.25		5%	2%	\$	48.75		5%	2%	\$	41.25		5%	3%					
Space Frame*	\$	50.00		3%	1%	\$	37.50		3%	1%	\$	32.50		3%	1%	\$	27.50		3%	2%					
Subtotal	\$	425.00		29%	11%	\$	318.75		29%	11%	\$	276.25		29%	12%	\$	233.75		29%	16%					
Process Air Module (PAM)*	\$	250.00		17%	7%	\$	187.50		17%	6%	\$	162.50		17%	7%	\$	137.50		17%	9%					
Hoses and couplings*	\$	40.00		3%	1%	\$	30.00		3%	1%	\$	26.00		3%	1%	\$	22.00		3%	1%					
Subtotal	\$	290.00		20%	8%	\$	217.50		20%	7%	\$	188.50		20%	8%	\$	159.50		20%	11%					
Power Conditioner*	\$	150.00		10%	4%	\$	112.50		10%	4%	\$	97.50		10%	4%	\$	82.50		10%	6%					
Product Controller*	\$	173.00		12%	5%	\$	129.75		12%	4%	\$	112.45		12%	5%	\$	95.15		12%	6%					
Wiring Harness, Relays, Sensors*	\$	284.00		20%	8%	\$	213.00		20%	7%	\$	184.60		20%	8%	\$	156.20		20%	10%					
Subtotal	\$	607.00		42%	16%	\$	455.25		42%	15%	\$	394.55		42%	18%	\$	333.85		42%	22%					
Recycle Pump Subsystem*	\$	125.00		9%	3%	\$	93.75		9%	3%	\$	81.25		9%	3%	\$	68.75		9%	3%					
(includes recycle cooler, sensor, valves)																									
Total Balance of Plant		\$	1,447.00	100%	39%	\$	1,085.25	100%	36%	\$	940.55	100%	42%	\$	795.85	100%	53%								
		100%				75%				65%				55%											
Total APU Material		\$	3,747.00	100%		\$	2,997.60	100%		\$	2,248.20	100%		\$	1,498.80	100%									
		100%				80%				60%				40%											
Burden Rate		16%				16%				16%				16%											
Assembly Labor	\$	450.00		36%	9%	\$	300.00		32%	8%	\$	300.00		37%	10%	\$	200.00		37%	10%					
Capital Investment	\$	200.00		16%	4%	\$	150.00		16%	4%	\$	150.00		19%	5%	\$	100.00		19%	5%					
Burden / Overhead	\$	599.52		48%	12%	\$	479.62		52%	12%	\$	359.71		44%	12%	\$	239.81		44%	12%					
Total APU Assembly	\$	1,249.52		100%	25%	\$	929.62		100%	24%	\$	809.71		100%	26%	\$	539.81		100%	26%					
		100%				74%				65%				43%											
Total APU Material	\$	3,747.00			75%	\$	2,997.60			76%	\$	2,248.20			74%	\$	1,498.80			74%					
APU Factory Cost	\$	4,996.52		100%		\$	3,927.22		100%		\$	3,057.91		100%		\$	2,038.61		100%						
		100%				79%				61%				41%											
Cost/kW, 5kW net	\$	999.30				\$	785.44				\$	611.58				\$	407.72								

¹ ISM: Integrated Stack Module

² ICM: Integrated Component Module

³ CHEX: Cathode Air Heat Exchanger

⁴ APP SOP: Application Start of Production

⁵ SOP CI: Start of Production/Continuous Improvement

4.1.1.1 Transportation Auxiliary Power Unit System Requirements

The system requirements for the Generation 3B system are outlined in **Figure 4.1.1-6**, with estimates of capability in the Generation 2B/2C Auxiliary Power Unit shown for reference. There were significant capability gaps between Generation 2B and Generation 2C system capability and Generation 3B design level targets.

Figure 4.1.1-6 Transportation SOFC APU—Generation 3B System Targets

To support the efficiency target of 21% fuel-to-net electrical output (regulated, 42 VDC), the Generation 3B reformer had to support an endothermic (waste heat recovering) mode of operation facilitated by anode tail gas recycle. The recycling of anode tail gas from the stack to the reformer allowed for a first order benefit of recycling a percentage of the un-utilized H_2 and CO from the first pass of the reformat through the stack back to the reformat stream, and ultimately back to the stack for potential conversion to electrical energy. The second order benefit was the reforming (endothermic) of a fraction of the H_2O and CO_2 contained in the anode tail gas back to H_2 and CO for potential conversion to electrical energy in the stack. Due to these two effects, the output power of the reformer in terms of Lower-Heating-Value and reformat mass-flow rate could exceed the fuel power, similarly derived, supplied to the reformer. In this way, the effective reformer efficiency, expressed as the ratio of output power to input power, may certainly exceed Catalytic Partial Oxidation levels (80%) and even exceed

100%. This boost of reformer efficiency allowed for effective increases in fuel-to-gross electrical output system efficiency without requiring very high fuel utilization in the stack.

However, this boost of efficiency was not without limit, and it came with the price of having to effectively extract waste heat in the form of combusted stack tail gasses to support the reforming endothermic reaction. The interplay of the anode tail gas recycle strategy and stack fuel utilization (single-pass) and its effect on system efficiency is shown in **Figure 4.1.1-7**. The figure was generated for the Generation 3B target of 3.2 kW gross electric output power from the SOFC stack. For the 5 kW net system, gross stack output power approaches 6.0 kW and will scale resultant system mass-flows and reactor duties, but it does not affect the relationships shown in **Figure 4.1.1-7**.

Figure 4.1.1-7 Transportation SOFC Auxiliary Power Unit - SOFC Auxiliary Power Unit Efficiency Map

From **Figure 4.1.1-7**, reformer efficiency is primarily a function of anode tail gas recycle fraction. Gross system efficiency (neglecting power electronics and parasitic load losses) depends on both anode tail gas recycle fraction and stack fuel utilization (single-pass). The red region in the upper-right corner of the efficiency map represents the area where heat release at the burner is less than the required endothermic heat of reaction in the fuel reformer. The boundary of this field may be thought of as a line of constant reformer temperature. Higher reformer temperatures progress towards the lower-left of the map and lower reformer temperatures progress further into the red region. The blue region in the upper-right corner represents the region where reformer feed air is zero and reformer feed-stream O:C ratio is no longer constant and on target.

The lines representing constant reformer temperature are parallel with lines of constant gross-system efficiency. These lines are also parallel with constant reformer fuel mass-flow rates (**Figure 4.1.1-7**). Higher the required reformer operating temperatures, the lower the overall system efficiency ceiling. For a given reformer operating temperature requirement driven by reformer size and reaction kinetics, there are a multitude of choices between stack fuel utilization and anode tail gas recycle fraction that will yield the same target system efficiency.

Targets allowed for a progression towards higher system efficiencies by increasing both fuel utilization in the stack and anode tail gas recycle fraction. This path is along a line roughly perpendicular to lines of constant system efficiency that results in steepest ascent of system efficiency. This path also resulted in the steepest drop in reformer temperature. Unfortunately, for target reformer operating temperatures of 900 °C or higher, reformer temperatures could not be maintained at the high utilization and recycle rates required to reach high system efficiencies.

An alternative path is shown in **Figure 4.1.1-7**, where instead of increasing both fuel utilization and anode tail gas recycle fraction, higher system efficiencies are achieved by increasing anode tail gas recycle fraction only. The map of reformat quality for H₂ and CO and H₂O species is shown in **Figure 4.1.1-8**. From **Figure 4.1.1-8** it can be seen that the best way to increase reformat quality is to increase the rate of anode tail gas recycle. Since high power density in an SOFC stack favors lower fuel utilizations and high concentrations of H₂ and CO, the strategy of high anode recycle at moderate fuel utilizations is a good strategy to improve power capability in the system for a given maximum practical system efficiency.

For the Generation 3B target and proposed operating points, **Figure 4.1.1-9** shows a characteristic map of burner power and reformer endothermic heat of reaction. **Figure 4.1.1-10** and **Figure 4.1.1-11** show reformer air and fuel mass-flow and anode tail gas recycle and reformat mass-flow respectively.

Figure 4.1.1-8 Transportation SOFC Auxiliary Power Unit – Reformate Quality

Figure 4.1.1-9 Transportation SOFC Auxiliary Power Unit – Reformer and Burner Power

Figure 4.1.1-10 Transportation SOFC Auxiliary Power Unit – Reformer Fuel and Air Mass-Flow

Figure 4.1.1-11 Transportation SOFC Auxiliary Power Unit – Reformate and Anode Tail Gas Recycle Mass-Flow

The target operating point for the Generation 3B system and proposed operating points for the Generation 4 and Commercial 5 kW net auxiliary power are shown in **Table 4.1.1-7**

The topic of fuel utilization and anode tail gas recycle fraction and resultant system efficiency was limited to the maximum output power operating point. For off-peak load points, stack fuel utilization and anode tail gas recycle targets were defined as control targets. Generally, high system efficiency is desirable across the power output band of the fuel cell power plant. However, at lower loads, turn-down issues come into play with respect to fuel and air metering systems, as well as reformat and air distributions in the fuel cell stack. At low loads, low fuel utilization in the stack helps to keep reformat mass-flows at higher levels to avoid starving cells of reformat in the stack. In addition, low fuel utilization improves transient handling at the onset of application loads.

Off peak load, the target fuel utilization and anode tail gas recycle may be adjusted on a load schedule to optimize desirable characteristics in the plant. One interesting off-peak operating line is along a line of constant gross system efficiency, with lower loads driving a reduction in fuel utilization, but with an increase in anode recycle fraction. The consequence of this is near constant reformer temperature over the power band that is desirable. With subsequent reductions of fuel utilization with reduced load, the ability of the powerplant to respond to load onset transients without starving the fuel cell is improved. For high turn-down conditions, like powerplant, idle where mass-flows are near minimum values, high recycle rates help to displace air mass flow in the front-end of the reformer. Since the anode tail gas is devoid of diatomic oxygen, the high proportion of recycle in the mix will help to reduce the propensity of the air/fuel/recycle mix to pre-ignite at low mass-flow rates (burn-back).

A conceptual schedule for stack fuel utilization and recycle fraction for Generation 3B off-peak loads is shown in **Table 4.1.1-8**. The resulting projected efficiency curve and resultant fuel consumption utilizing this strategy is shown in **Figure 4.1.1-12**. From the figure, it can be seen that this strategy resulted in a fairly linear fuel consumption rate as a function of load in the 40 – 100% power band, with peak efficiencies between 40 and 60% load.

**Table 4.1.1-7 Transportation SOFC Auxiliary Power Unit - Generation 3B
Conceptual Design**

APU Efficiency Allocation		System Design Level					
		Gen 2 B	Gen 2 C	Gen 3 A	Gen 3 B	Gen 4	Commercial (SOP)
		11 / 03	12 / 03	04 / 04	6 / 04	06 / 06	06 / 08
Steady State Units		POX	POX	POX	POX + Recycle	POX + Recycle	POX + Recycle
Reformer Efficiency	%	78%	78%	78%	120%	130%	140%
Anode Tail Gas Recycle Fraction	%	0%	0%	0%	35%	40%	44%
Fuel Utilization	%	25%	25%	50%	50%	50%	50%
Stack Conversion Efficiency (0.7 V/cell)	%	52%	52%	52%	52%	52%	52%
SOFC Stack Conv Efficiency	%	13%	13%	26%	26%	26%	26%
Gross Stack Output Power	kW	0.759	2.0	2.3	3.2	4.9	6.0
Reference Power Density	W/cm ²	0.239	0.309	0.363	0.504	0.686	0.832
Power Conditioner Efficiency	%	87%	87%	87%	87%	95%	95%
Gross Conversion Efficiency	%	8.8%	8.8%	17.6%	27.1%	32.1%	34.6%
Parasitic Loss Factor	%	30%	73%	75%	79%	85%	88%
Net System Efficiency @Net Power	%	2.7%	6.4%	13.2%	21.4%	27.4%	30.4%
Net Elec Power	kW	0.200	1.25	1.5	2.2	4.0	5.0
Fuel Power	kW	7.5	19.4	11.4	10.3	14.6	16.5
Gasoline Flow	g/sec	0.17	0.44	0.26	0.23	0.33	0.37
Fuel Consumption	gal/hour	0.21	0.55	0.33	0.29	0.42	0.47
	hours/gal	4.7	1.8	3.1	3.4	2.4	2.1
Exhaust Gas Condensate (H ₂ O)	L/hour	0.68	1.76	1.03	0.93	1.32	1.49
	gal/hour	0.18	0.46	0.27	0.25	0.35	0.39
Exhaust Power	kW	6.82	17.67	9.38	7.49	9.92	10.76
Allowable Electrical Parasitic Load	W	460	460	510	590	690	690

Table 4.1.1-8 Transportation SOFC Auxiliary Power Unit –System Off-Peak Characteristics

APU Efficiency Estimate		System Design Level Gen 3B							
		Idle	Load	Load	Load	Load	Load	Load	Load
		0%	10%	20%	30%	40%	50%	60%	70%
Steady State	Units								
Reformer Efficiency	%	150%	150%	150%	150%	150%	150%	150%	142%
Anode Tail Gas Recycle Fraction	%	48%	48%	48%	48%	48%	48%	48%	45%
Fuel Utilization	%	5%	10%	20%	30%	40%	40%	40%	43%
Cell Operating Voltage	V	1.07	1.03	0.96	0.91	0.86	0.82	0.79	0.76
Stack Conversion Efficiency	%	80%	76%	72%	68%	64%	61%	59%	56%
SOFC Stack Conv Efficiency	%	4%	8%	14%	20%	26%	25%	24%	24%
Gross Stack Output Power	kW	0.126	0.321	0.641	0.962	1.28	1.60	1.92	2.24
Reference Power Density		0.017	0.045	0.089	0.134	0.178	0.223	0.267	0.312
Power Conditioner Efficiency	%	85%	85%	86%	87%	88%	89%	90%	89%
Gross Conversion Efficiency	%	5.1%	9.7%	18.4%	26.4%	33.9%	32.7%	31.7%	30.2%
Net Elec Power	kW	0.00	0.155	0.378	0.607	0.843	1.085	1.33	1.55
Net System Efficiency	%	0.0%	5.5%	12.6%	19.2%	25.3%	24.9%	24.4%	23.4%
Fuel Power	kW	2.1	2.8	3.0	3.2	3.3	4.4	5.5	6.6
Gasoline Flow	g/sec	0.05	0.06	0.07	0.07	0.08	0.10	0.12	0.15
Fuel Consumption	gal/hour	0.06	0.08	0.09	0.09	0.10	0.12	0.16	0.19
	hours/gal	16.6	12.5	11.7	11.0	10.5	8.0	6.4	5.3
Exhaust Gas Condensate (H ₂ O)	L/hour	0.19	0.25	0.27	0.29	0.30	0.40	0.49	0.60
	gal/hour	0.05	0.07	0.07	0.08	0.08	0.10	0.13	0.16
Exhaust Power	kW	2.00	2.53	2.44	2.33	2.20	2.93	3.73	4.62
Allowable Electrical Parasitic Load	W	107	118	174	230	286	342	398	449

4.1.1-12 Transportation SOFC Auxiliary Power Unit – System Off-Peak Characteristics

4.1.2 Update on Conceptual System Design

The Gen 2B conceptual system design progressed in 2003. New features in the design included:

- Configurable Application Interface Module (AIM)
- Modified open access space frame
- Improved Process Air Module (PAM)
- New Gen 1.1 Tube Pox Reformer
- Improved SOFC Stack Terminal Interface
- Improved Reformer Insulation Pass-Through Collar

The Gen 2B APU assembly with major integration modules is shown in **Figure 4.1.2-1**, and **Figure 4.1.2-2**. The general partitioning of function and subsystem content is shown in the figures. Many of the design updates from Gen 2A to Gen 2B design levels were driven by the need to improve the overall design for assembly of the APU. A reconfiguration of the assembly space frame and the removable Application Interface Module (AIM) panel at the end of the assembly were a direct result of the need for improved access and increased serviceability. The Application Interface Module effectively increased the interior space of the APU by about 5 liters. This space was used to package the Power Conditioner and Electronic Control Unit more effectively. The Process Air Module represents a more highly integrated design over what was used in the Gen 2A APU. Lastly, more convenient SOFC Stack terminal routing and design has been implemented in the Gen 2B APU. It was found that the previous design, with terminal routing between reformer and cathode air heat exchangers was

susceptible to terminal shorting to these components. This detail is best viewed in **Figure 4.1.2-3** that depicts the current Gen 2B Hot Zone Module Assembly.

Figure 4.1.2-1: SOFC APU Modular Assembly

Gen 2B APU Design

Figure 4.1.2-2: SOFC APU Assembly

Figure 4.1.2-3: SOFC APU Hot Zone Module

The Application Interface Module (AIM) is the integration site for most of the application specific electronics and external interfaces. Each potential application has specific requirements for their respective application powernet, communications bus, Air filtration, and fuel treatment. On the other hand, it is advantageous to commonize as much of the Balance of Plant and Hot Zone Module components as possible application to application. The following is a list of interface issues an APU system must address:

AUTOMOTIVE:

Electrical Power:	12Vdc
Communication:	J1850/CAN High/Low Speed
Process Air:	Standard Automotive Filtration
Fuel:	Gasoline (may require de-sulfurization)

STATIONARY:

Electrical Power:	120VAC/240VAC/480VAC 60/50Hz
Communication:	Cable modem/Ethernet/UL/RS-232/Other
Process Air:	Standard Furnace Filter
Fuel:	Natural Gas, Propane (will require de-sulfurization)

HEAVY DUTY TRUCK (Class 8):

Electrical Power:	28Vdc/12Vdc/120VAC 60/50Hz
Communication:	Computer Area Network High Speed
Process Air:	Heavy Duty Filtration

Fuel: Diesel (may require de-sulfurization)

AIRCRAFT:

Electrical Power: 120VAC 400Hz
Communication: SAE AS4074 (2.1.1) and AS4075 (2.1.2)
Process Air: High and Low elevation/Temperature
Fuel: Jet A (may require de-sulfurization)

The Application Interface Module (AIM) between the existing APU and the customer interconnect provides a gateway solution for Electrical, Mechanical, Air Handling, and Pre-Fuel Preparation. The conceptual design of the Application Interface Module (AIM) for the Gen 2B APU is shown in **Figure 4.1.2-4**.

Figure 4.1.2-4: SOFC APU Application Interface Module (AIM)

For larger capacity Stationary Power Systems (SPS), the Hot Zone Module comprised of SOFC Stack (Integrated Stack Module, ISM), High Temperature Manifold (Integrated Component Manifold, ICM), Fuel Reformer and Cathode Air Heat Exchangers (CHEX), may be viewed as a reusable module. A conceptual design for such a system is shown in **Figure 4.1.2-5**, and **Figure 4.1.2-6**. In this concept, multiple Hot Zone Modules (HZM) from the 3-5 kW Mobile APU may be placed in an insulated rack configuration to create a Stationary Power System with between 10 and 25 kW, depending on the multiple. Benefits of this conceptual design include:

1. Flexible Power/Voltage Output

60V Hot Zone Module Elements can be combined and/or connected to serve different application power levels and/or voltage requirements.

2. Start-Up Bootstrap

For system start-up, each Hot Zone Module can be started individually such that power generated by operating units can supplement the start-power during the starting period for subsequent units.

3. Increased Reliability

Reduced downtime / flexible maintenance schedule. Independent Hot Zone Modules may allow for maintenance of SOFC core plant components without necessarily having shutting down the whole Stationary Power System (SPS).

Figure 4.1.2-5: Stationary Power System Concept

Figure 4.1.2-6: Stationary Power System Concept Detail

The System Architecture for the Generation 3B Transportation Auxiliary Power Unit is shown in **Figure 4.1.2-7**. In the figure, the major system and subsystem modules are identified with associated component content. The general architecture was similar to Generation 2B and Generation 2C Auxiliary Power Unit designs, but the Generation 3B System Architecture included an anode tail gas pump, anode tail gas heat exchanger (cooler), and associated sensors to support their operation. In addition, the burner of Gas-Phase-Combustor function is partitioned to the reformer to support endothermic (high-efficiency) operation.

The Generation 3B Auxiliary Power Unit concept is shown in **Figure 4.1.2-8** with overall dimensions and intended application connections. The target for the application was 50 Liters. The hot system exhaust is connected at the opposite end of the product from the vehicle connections (not shown in the figure).

The conceptual design for the Generation 3B Auxiliary Power Unit is shown in **Figure 4.1.2-9**. Note the single cathode air heat exchanger the new position of the reformer, and the addition of the anode tail gas recycle pump. For comparison purposes, the conceptual design of the Generation 2B/2C Auxiliary Power Unit is included in **Figure 4.1.2-10**.

Figure 4.1.2-7: Transportation SOFC Auxiliary Power Unit - Generation 3B System Architecture

Figure 4.1.2-8: Transportation SOFC Auxiliary Power Unit - Generation 3B Conceptual Design

Figure 4.1.2-9: Transportation SOFC Auxiliary Power Unit - Generation 3B Conceptual Design

Figure 4.1.2-10: Transportation SOFC Auxiliary Power Unit – Generation 2B/2C Design

4.1.3 Develop System Mechanization (Schematic)

System Mechanizations were created to support the Gen 2 and Gen 3 APU applications. In addition, a Gen 3 Mechanization was developed to support a Natural Gas Stationary Power System (SPS). Details of these Mechanizations are presented in **Figure 4.1.3-1**, and **Figure 4.1.3-2** for the Gen 2B design level, **Figure 4.1.3-3**, and **Figure 4.1.3-4** for the Gen 3B design level, and **Figure 4.1.3-5**, and **Figure 4.1.3-6** for the Gen 3 Stationary Power System (SPS).

With reference to the figures, a summary of changes to the Gen 2B mechanization include:

- V2 Reformer Preheat Bypass Valve has now become a 3-Way proportional valve. This change was made to improve the temperature control authority (span) at T12.
- EH1, a Resistive Electric Heater element has been added to the reformer air preheat circuit to improve cold-reformer-start air preheat and fuel vaporization performance.
- Left and Right designations have been added to the following temperature sensor inputs to distinguish Left and Right locations downstream of flow bifurcations.
 - T4 – Cathode Air Feed to SOFC Stacks
 - T5 – Anode Tail Gas from SOFC Stacks
 - T6 – Burner Exhaust Temperature
- V1 Preheat Bypass Valve is now directly sourced from the source air manifold, and this circuit now has its own dedicated mass flow sensor S10. Additionally, a mass flow sensor, S9, was added to the main cathode air feed circuit, V8. This change was made to simplify the air hose routing and have a dedicated mass flow sensor on every air input to the Hot Zone Module.
- Previously, a mass flow meter (S6) was located on the inlet to the process air source blower and the cathode air feed mass-flow was computed as the difference between inlet air (S6), and the sum of Reformer air (S5) and Burner Cool Air (S8). This indirect flow measurement method could result in significant errors if air leakages were present in either the blower inlet system, or the exhaust system of the process air source blower.
- The Reformate Quality Sensor at the outlet of the reformer, S1, was changed to be a gas mass-spectrometer sample port. This was done because the requirements for a Reformer Quality Sensor are not clearly defined at this time, and sufficient characterization of the reformer has occurred such that the need for such a sensor is questionable at this time. For development purposes, a sample port for a gas mass-spectrometer is all that is required at this time.

Figure 4.1.3-1: Gen 2B Physical Plant Mechanization

Figure 4.1.3-2 Gen 2B: Electrical Mechanization

With reference to the Figures, a summary of changes to the Gen 3B (Tail Gas Recycle added) with respect to the Gen 2B mechanization:

- An Anode Tail Gas Recycle (TGR) pump, B3, was added to the system. This pump is required to pump approximately 1 – 1.5 g/sec of Anode Tail Gas at approximately 100-200 °C, requiring no more than 100W of parasitic electrical power. This pump discharges into the air mix plenum at the front of the reformer so that it may participate in air/fuel prep and temperature regulation. Heat in discharge stream of the pump will displace the need for recuperated heat from the Reformer Air Preheat heat exchanger, so V2 will be required to adjust the T12 (air mix) temperature so that T2 (air/fuel prep temperature) is at target. This pump must be sealed against leakage to the environment, and it required an in-line check valve so that short-circuiting of reformer air does not occur when the pump is not in operation.

- An elevated-temperature-capable Anode Tail Gas mass flow sensor, S11, is required to properly characterize the TGR mass flow. This sensor will be required to operate with manageable error with changes to Anode Tail Gas temperature and composition.
- An Anode Tail Gas Recycle (TGR) Cooler will be required to cool the Anode tail gas to under 200C for operation of the TGR pump (B3). The coolant will be the normally supplied cathode air supplied by V8 and V1 circuits. The inlet temperature to the TGR pump will be measured by T14.
- The Reformer Catalyst element is shown with a heat exchanger symbol with the burner exhaust gas providing the hot-side flow. This schematically represents a reformer that has the capability to run in an endothermic mode, with heat to the reaction provided by the burner exhaust gases. This type of function will be required when Tail Gas Recycle (TGR) is employed, and there is significant water vapor present in the Anode Tail Gas.
- The exhaust flow around the outside of the SOFC stacks, a characteristic of the Gen 2B Mechanization, has been eliminated from the Gen 3 Mechanization. Evaluation of the Gen 2 system, has shown that this feature provides no improvement, and in fact, increases the start-up time for the system. Additionally, this feature has proven to be a reliability risk due to poor sealing of the exhaust manifold around the stacks.

Figure 4.1.3-3: Gen 3B Physical Plant Mechanization

- A Natural Gas Supply Pump, B1, was required assuming a standard regulated Natural Gas Supply of 15 – 17 mbar. The feed pressure at the front of the reformer, V7, is approximately 10 times the regulated feed pressure. This supply pump was required to deliver Natural Gas at a pressure necessary to drive flow through the system.
- An electrically heated desulfurization unit, EH2, was required to remove H₂S and other harmful sulfur compounds from the Natural Gas feed stream.
- A water supply to the Stationary Power System is shown as optional. A water supply supplement allows for steam reforming modes during periods of low load

on the stack, and or start-up periods. Additionally, a water supply and metering injector allows for additional margin against carbon formation in the anode supply stream, post reformer.

- A 36V storage battery is employed (42V charge voltage) to provide fully, or supplement the start-up power requirements for the Stationary Power Plant. In addition, the storage battery will provide load onset buffering to the Stationary Power Plant (SPS).
- To provide the internal 14V powernet of the Stationary Power Plant, a small 42VDC/14VDC converter will be employed.
- A 2-way, single phase, 42VDC to 115VAC Inverter is employed for the Stationary Power System (SPS) to provide normal application power service (AC), and provide 36V battery charging and SPS plant internal power during the start period of the plant.
- Normally open Isolation Relays will be provided to physically break the power connections to the Stationary Power System (SPS) during periods of maintenance, fault, or overload.
- An optional 230 VAC output stage may be provided at the power conditioner to service higher voltage stationary electrical loads.

Figure 4.1.3-5: Stationary Power System Physical Plant Mechanization

Figure 4.1.3-6: Stationary Power System Electrical Mechanization

A simplified system mechanization showing the target operating point of the Generation 3B Auxiliary Power Unit with anode tail gas recycle is shown in **Figure 4.1.3-7**. Expected values of subsystem efficiencies and electrical power are shown on the figure.

The detailed physical plant mechanization to support the target operating point described in **Figure 4.1.3-7** is shown in **Figure 4.1.3-8**.

**Figure 4.1.3-7: Transportation SOFC Auxiliary Power Unit - Generation 3B
 Target Operating Point**

Some of the thermal management improvements in the Generation 3B Auxiliary Power Unit are illustrated in **Figure 4.1.4-1**. The surface temperature improvements of the Auxiliary Power Unit are shown in **Figure 4.1.4-2**. The insulation allocation allowed the Generation 3B Auxiliary Power Unit to meet interim targets, but improvements in insulation technology will need to be employed to meet the application target of +40 °C over ambient temperature for the skin of the Auxiliary Power Unit.

Figure 4.1.4-1 Transportation SOFC Auxiliary Power Unit - Generation 2B to Generation 3B Insulation Allocation

Figure 4.1.4-2 Transportation SOFC Auxiliary Power Unit - Target Surface Temperatures

4.1.5 System Control Development

Advances in system control development primarily focused on introduction and maturation of the code to make it compatible with the Electronics Control Unit controller, a production-like controller which replaces the dSPACE[®] micro-autobox development controller. Further advances in the control algorithm itself were made; however, the pace of changes decreased as the performance control algorithm was becoming more mature.

4.1.5.1 Control System Development Stage

Control Results:

The performance of the control system on an experimental test is depicted in **Figure 4.1.5-1**. This experimental run was performed on a Generation 3 Integrated Component Manifold, with a “mule” stack. The “mule” stack is just a physical pneumatic connection between the inlet and outlet of the stack on the Integrated Component Manifold and is electrically inert. It is not thermally representative. Warm up time is shorter than expected owing to the lower mass of the “mule” stack. On each of the curves, the darker line indicates desired temperature, and the lighter line indicates measured temperature.

4.1.5-1 Control Results

4.1.5.2 Executive

The Executive (Exec) sub-system continued as the coordinator of set-point requests throughout the system, and as the major system state “conductor”. The sub-systems communicate almost exclusively through the Exec when communicating completion of states, and desired set points for other sub-systems. For example, in “Initialization”, all sub-routines complete passive self-test and initialization, and communicate completion to the Exec – which then advances the system to the next logical state in the sequence. The Exec also “arbitrates” among set-point choices for “downstream” users of the set points. For example, during different major system states, each of the “Reformer” and “Stack” control sub-routines in turn decide upon the desired cathode flow. The Exec determines which sub-system will actually “have control” of this flow. In addition, the Safety and Diagnostics “action” routines (as opposed to “detection” routines) are “housed” in the Exec. This allows for the Safety and Diagnostic sub-system to request (and receive) override of system set points in cases of obvious or imminent system failure. Finally, the Exec receives set-point requests from the “Operator Interface” block.

4.1.6 System Analysis

4.1.6.1 Steady State Hysys[®] Model

A picture of the Hysys[®] flowsheet can be seen in **Figure 4.1.6-1**. The flowsheet reflects a superset of the currently intended mechanization to accommodate variations on the mechanization to be evaluated.

Figure 4.1.6-2 Hysys® System Results

The graph shows system efficiency and burner temperatures versus recycle for 50% (circle symbols) and 60% (square symbols) stack utilizations, CH₄ 200 °C stack delta, and 950 °C reformer. Color in the symbol has been utilized to indicate “design possible” (green) versus “not possible” (red) conditions. Notice that though it is thermodynamically possible to achieve system efficiencies above 28%, with the given assumptions of sub-system operating points (e.g. 950 °C reformer temperature), there is not enough temperature in the gas phase combustor to drive heat into the (endothermic) reformer at higher recycles. This issue is exacerbated by the fact that even when there is enough temperature post transfer of heat to the reformer, the adiabatic flame temperatures for the condition are higher than expected, implying materials design concerns at the combustor.

4.1.6.2 Operator Interface

The Operator Interface allows the system operator to “inject” set-point overrides on all of the controlled system signals, and to set actuator states differently from the “automatic control” intended states. Advancements in this area included the following:

4.1.6.2.1 Ldesmeasxxxx

In addition to “Ldesxxxx” values (which stand for “laboratory desired xxxx where xxxx is a signal set-point or an actuator state), the Operator Interface contained parameters called “Ldesmeasxxxx”. These parameters allow the system operator to override the currently measured values on each of the system sensors. This feature, along with Ldesxxxx had been invaluable in the development of the control system during “live” operation. For example, if a particular control loop is not operating properly during a critical development system run, the system operator can override the output of the control loop (so the system continues to operate properly), and then explore the reasons for the problem right at that time by changing the condition of the “Ldesmeasxxxx” signal being used by that particular control loop. This combination provides a powerful method to accomplish contemporaneous control system development and fully integrated system component test, thereby reducing development time.

4.1.6.3 Safety and Diagnostics

Major advancements were made in the Safety and Diagnostics sub-system. The Safety and Diagnostic system is near completion of the “Level I” Safety and Diagnostics. This level implies that all system sensors and all control loops are monitored for failure. In addition, “Level I” implies that the action taken on any failure is Emergency Stop. The result is that the system is safe, consistent with an early stage of development, but may be less reliable than a production system. The following tests were performed in the Safety and Diagnostics sub-system:

1. All system mechanization sensors are monitored for being within the range expected for that sensor in the system independent of system state.
2. All system mechanization sensors are monitored for rate of change of signal being within the range expected for that sensor in the system independent of system state.
3. All control loops are monitored for the controlled condition being within a range of the set-point with appropriate “hold-off” times to allow the system to get into control.
4. External monitoring of two discrete signals that can come from a system operator action, or from an external control source (like a combustible gas monitoring system).

4.1.6.4 Process Air

The Process air control sub-system is responsible for controlling blower speed to achieve target system pressure and air control valve positions to achieve desired system flows. Process air also controls warm space temperature to a maximum limit by running the blower and opening a purge valve if needed. Improvements in the process air control system since last report include:

1. **Process Air Module (PAM) Control:**
The system mechanization has changed in the area of process air in that there are now 4 mass air flow meters (S5 – reformer, S8 gas phase combustor, S9 heated cathode air, S10 bypass cathode air) rather than the three (S5 – reformer, S8 gas phase combustor, S6 blower) that used to exist. Accommodation of this change, which required modification in many areas, has been completed and is in operation.
2. **Cathode Flow Versus T5:**
The cathode flow set point during stack warm-up is now a function of T5 (Stack anode outlet). The non-monotonic nature of the current cathode air heat exchangers implies a need for more sophisticated / cooperative control between the T4, T5, and T6 control loops. In the interest of time, this problem has been solved with the simple approach of a pre-programmed cathode flow versus T5 temperature. The approach works well for the conditions tested (mostly start from fully cold). Future control in this area will likely need to be more sophisticated.
3. **Warm Space Temperature Control:**

An algorithm for control of the warm space temperature has been further developed to the point of correct operation on the bench. This algorithm has not yet been tested during a system test due to limited availability of the system test stand, and lack of availability of intended design solenoid valve.

4. **Normal Shut Down:**

A new algorithm has been added which resides primarily but not totally within process air control. This is the normal shutdown algorithm. Careful control of system flows during a shutdown is required to avoid two major system damage conditions: first, a lean condition associated with stopping the fuel without coincident stopping of the air may result in damage to the reformer catalyst due to lean or stoichiometric burning. Second, oxygen must be kept from the anode of the Solid Oxide Fuel Cell stack while it is at elevated temperature, or the anode may be damaged. These conditions are avoided by gradually lowering the flow on both the fuel and the air to a point and then shutting both simultaneously. This algorithm has been tested and is in use.

4.1.6.5 Control Loop Calibration

Many man-hours of calibration on the control loops have resulted in simultaneous / stable control of the following control loops:

1. Control of system air manifold pressure (P2) via blower command speed.
2. Control of reformer mixing zone temperature (T12) via reformer heater bypass air fraction (V2) and control of an electric heating element.
3. Control of stack cathode inlet flow temperature (T4) via cathode heater bypass mass flow (V1).
4. Control of stack anode outlet temperature (T5) via total cathode airflow (heated and unheated).
5. Control of measured reformer airflow to desired set point via reformer airflow valve (V7) steps.
6. Control of measured gas phase combustor airflow to desired set point via gas phase combustor cool air valve (V9) steps.
7. Control of measured cathode heated airflow to desired set point via cathode heated air valve (V8) steps.
8. Control of measured cathode unheated (bypass) airflow to desired set point via cathode heater air bypass valve (V1) steps.
9. Control of maximum warm space temperature via control of warm space purge solenoid valve (V10).

4.1.6.6 Power Management

The power management control sub-system receives power capacity requests from external command sources (e.g. grid control) and translates the need into gross stack power requirements comprehending the Auxiliary Power Unit's (APU) own internal need for power for internal devices. In addition, in certain systems (e.g. automotive), there may be need for distribution of power among both high voltage uses (e.g. 42v) and normal 12v load uses. The power management control routine makes these power allocation decisions as well. Since the last report, the power management system has

been designed and implemented. The system has been tested on the emulation bench. This “electrical emulation bench” uses the capability of the embedded plant model (see later section) to execute “virtual” runs. During this virtual run, the system plant model is exercised to create virtual temperature and system flow response as if in a real system. The power electronics parts of the system however are either real (as in the case of e.g. the power conditioner) or emulated (as in the case of the stack). The plant model includes a stack model (derived from the Pacific Northwest National Laboratory model) that drives a power supply to perform as a real stack would given the temperature and flow conditions.

4.1.6.6.1 Control Desk

The dSPACE® product “Control desk” is used for system control development. Shown in **Figure 4.1.6-3** is a picture of one of the approximately 10 interface panels with which the system operator interacts. The “lay” shows are the SOFC system “lay”.

Figure 4.1.6-3: Control Desk System Lay

4.1.6.7 SYSTEM CONTROL RESULTS

Shown below is the data from a recent cold start and stack warm-up to operating temperature. **Figure 4.1.6-4** shows various system temperatures plotted for the start. **Figure 4.1.6-5** shows corresponding system flows for the same period. Please refer to **Figure 4.1.6-4** (system temperatures) for the following comments.

Figure 4.1.6-4: Experimental System Temperatures

1. **Point A:** Point A indicates the range of temperatures seen within the gas phase combustor area. Note that they vary by perhaps 250 °C. One of the difficulties presented to the control system, is selecting the control point for the temperature measures. In the present case, the peak temperature of the same flow varies substantially over only a few centimeters. Before this was understood, a test was conducted which led to physical failure (melting) of cathode heat exchanger braze. Through experiment, an optimum placement of the T6 (gas phase combustor) temperature control point has been determined. There also exists (not shown) a substantial temperature imbalance between the left and right “halves” of the system. This is not fully understood. The result may be associated with the gas phase combustor flow design, and is still being evaluated.
2. **Point B:** Point B is associated with the reformer mix zone temperature (T12). This temperature is controlled to 150 °C by adjustment of the reformer pre-heater bypass flow (V2) and the reformer electric pre-heater. Note the excellent control performance during the warm up. Control of this temperature sets a mix temperature that allows for full vaporization of the fuel and air mixture, and therefore, improves reforming performance.
3. **Point C:** Point C titles an arrow depicting the total time to warm up the system of approximately 74 minutes.

4. **Point D:** Point D draws attention to control of the cathode air inlet temperature (T4). Note that this temperature is controlled to a set point that is 100 °C above the stack anode outlet temperature (T5). T5 is currently used as a surrogate for bulk average stack temperature. Further study is needed to confirm the validity of this assumption – as we have learned that the reformat might not be fully cooled upon exit from the stack.
5. **Point E:** Point E is just above the black anode outlet temperature (T5) line. Note the (overly) tight control of T5, and the associated oscillation of control efforts cathode heated air, unheated air, gpc cool air flow, and even in the reformat air flow. Further work is needed to “calm” this control loop, but it is instructive to note how highly coupled this system is. Changes in flow impact not only the controlled temperature, but also other temperature and flow control points through both thermal and source pressure control dynamics.
6. **Point F:** Point F labels a temperature sensor that is in the middle of the reforming catalyst. This peak temperature (over 1200 °C) is unusually high by approximately 100 °C for this condition. This high temperature is attributed to a higher than intended reformer air flow. It has been determined that the process air module air (PAM) air meter’s flow indication is (unfortunately) sensitive to air control valve step position to some extent. This causes inaccurate flow indication when the air control valve is at a different step position for a given flow than the one at which it was calibrated. The circumstances of this particular warm-up (which was run at .3 g/s fuel) resulted in an inability of the blower to maintain the target system pressure of 15kpa. The net result is that the air control valves had to open further to maintain target flow, resulting in air meter operation away from the calibration point, and inaccurate (and higher than intended) flow. The higher reformer airflow led to closer to stoichiometric combustion, and higher reformer temperatures. The impact on reforming performance will be discussed when the mass spectrometer curves are referenced later in this section.

Figure 4.1.6-5: System Flows

7. **Point H:** Note that at the point labeled H, the reformer airflow is reducing gradually during the warm-up. This is due to the fact that the target oxygen to carbon ratio is decreasing as the system warms up – allowing for richer reformer operation with lower likelihood of carbon formation throughout the system, especially in the stack.
8. **Point I:** Below the point labeled I on the flow curves are the left and right cathode heater bypass (V1) flows. Note that these flows are decreasing at this time, and that the heated flows (V8) are increasing. During the early part of the warm up, since the stack is cold, cathode air passing through the cathode pre-heaters is heated to a temperature higher than the target (100 °C) above the stack temperature. During this time, cathode flow bypasses the heaters to keep the cathode temperature (T4) in control. As the stack heats, this bypass flow (V1) is reduced, and the balance of the target cathode flow (which is a function of stack temperature T5) is achieved with heated cathode flow (V8 flow). Note also that the gpc cool air is also increasing during this time. The total of the three flows (heated and unheated cathode flow and gpc cool air) is delivered to the gpc as oxidant to combust stack anode tailgas. The gpc temperature (T6) is also controlled according to a schedule versus stack anode out (T5) (see the pink T6_gpc point near label A on the system temperatures plot). Gpc temperature is

controlled by controlling the “phi” (fuel to air ratio as a fraction of stoichiometric) of the combustor taking into account the possible consumption of reformat by the stack during electro-chemical combustion.

9. **Point J:** Note that at point J, the total cathode flow is reducing. Again, the cathode flow is pre-programmed versus stack anode temperature (T5.) When T5 approaches target temperature, target cathode flow is reduced due to the limited inlet temperature difference (ITD) available to the heat exchangers at this point. This allows higher temperature / lower flow cathode air to complete the final stack temperature increase. Note also the difference in flow from left to right side. Reasons for this are not fully understood.

Figure 4.1.6-6: Mass Spectrometer Signals

Now referring to **Figure 4.1.6-6**.

10. **Point Q:** The mass spectrometer outputs signals corresponding to various species of interest to the fuel cell system. Sample tubes are sequenced so that during different sections of time, different points in the system are presented to the mass spectrometer. During this test, only two points were sampled – “anode feed” and “anode tailgas”. The heavy blue signal called “Anode feed L” is a logic signal used to switch between these points. When this signal is at a “1”, the mass spectrometer is sampling the anode inlet to the stack. Likewise, when the “Anode feed L” signal is “0”, the mass spectrometer is sampling the anode tailgas. All signals below 15 % (on the left axis) are plotted versus the right hand Y axis (lower scale). Both axis are in units of mole percent. At point Q, note the

relatively poor quality of reformat. Reformat from this generation of reformer will typically be higher than 20%, and can hit 22% when the catalyst is fresh. As discussed in a previous section, this poor reformat can be attributed to the reformer running too lean due to inaccurate air meter flow indication.

11. **Point R:** At point R, the mass spectrometer is sampling the anode tailgas. Note that the reformat quality is lower still than the feed, and that the CO₂ in the stream has increased. This is an indication of a system leak – possibly in the stack, possibly across seal gaskets, and possibly within the Integrated Component Manifold itself (ICM). This is being investigated further. Note also that flow out of the anode has elevated levels of methane, and reduced levels of ethane. Apparently, higher hydrocarbons are being further oxidized as they move through the system.

4.1.7 System Analysis

Multiple system models were further developed and refined. The results of these models were very instructive on their own and when used in interpretation of experimental work. Advances on two of the more major of these models will now be discussed.

4.1.7.1 Integrated Dynamic Simulink® model for System Design

The Simulink® plant model represented dynamic system plant performance within the same environment as the actual control model. Results are representative of performance that would be expected in a real system with the control law operational. “Real” limitations of control are therefore embedded in the results predicting (for example) start time. The results of one of a set of 20 “batch” runs executed on the Simulink® system model are shown in **Figure 4.1.7-1**.

Figure 4.1.7-1: Modeled System Temperatures

There is general, but imperfect agreement between the model run and the actual experimental run. The start time is 83 minutes for the model versus 72 minutes for the experiment. There are still observable differences between the experimental run and the model run. First, there is a poorly understood temperature imbalance side to side in the experimental hardware. Temperature differences of up to 150 °C have been observed. Second, it will be noted that the gas phase combustor temperature (T6) oscillates near the end of the warm up on the simulation run. T6 control has been problematic even on the experimental hardware, however the gains developed on the experimental hardware are oscillatory in some circumstances on the model. Neither the blower mechanical nor pneumatic dynamics are currently included in the plant model – this is a likely explanation for the difference. Third, note that the trajectory of the stack cathode inlet temperature (T4) “flattens” in the real system hardware earlier than in the simulation run. This difference must be understood and corrected, however, would not be expected to improve the correlation on the start time between model and experiment. Further work on correlation between the system model and the experimental runs is needed.

4.1.7.2 Hysys® Plant for System Design

Figure 4.1.7-2 below is a Hysys® model run of the Auxiliary Power Unit. The elements are arranged to reflect the thermodynamic, species, and electrical performance of the

whole system. The operating point is 5kw net at 44% efficiency with 35% anode tailgas recycled to the reformer inlet. Fuel is CH_4 . Reformate composition is 59% H_2 , 29% CO . Internal electric parasitic are considered. Flows are controlled to set points consistent with the actual control of the system. Some of these key levels are circled in red on the flow sheet. Key observations:

1. The amount of heat that needs to be transferred from the gas phase combustor to the reformer during this high recycle condition is about 4kw.
2. Total cathode flow required for cooling with real / possible heat exchangers is about 19 g/s.
3. Total system flow is also about 19 g/s. Why is all the flow cathode flow? The answer is that this operating point is designed to be near the highest recycle possible as limited by zero reformer air. As the recycle level is increased, more and more oxygen from H_2O and CO_2 in the anode tailgas is available as an oxidant for the reformer (resulting in an endothermic reaction) and less and less air needs to be put in – zero in the limit. This limit though may be difficult to achieve due to control and sensing limitations.
4. The overall system efficiency can be 44%.
5. Conclusion: This model has been very effective to help us trade off different system configuration options, and to set sub-system design requirements with respect to function and e.g. flow levels.

Figure 4.1.7-2: Hysis® Flow Sheet

4.2 Task 2: Stack Development

4.2.1 Design Stack

Design work focused on developing the complete Generation 3 stack module with load frame, base plate and retaining plate. (Figures 4.2.1-1 and 4.2.1-2) The design is consistent with the design of the Integrated Stack Module in Generation 2 stack assembly.

Figure 4.2.1-1: Generation 3 Cassette (Exploded View) Showing Cell-Picture Frame and Separator Plate

(The two parts are laser welded together to form the complete cassette (repeating unit). The red stripes represent the anode contact mesh (Ni). The cathode contact mesh is welded to the bottom of the separator plate.)

Figure 4.2.1-2: Generation 3 Stack Module (Exploded View) Showing Repeating Cassettes with the Current Collectors, Load Frame and a Base Plate.

Multiple Generation 3 cassettes (repeating units for stack) were successfully fabricated and tested. The Generation 3 cassettes are 2.1 mm thick and weigh 155 grams (50% reduction compared to Generation 2). The cassettes are fabricated using high-volume manufacturing processes like stamping, brazing and laser welding.

The exploded view of a Generation 3 cassette is shown in **Figure 4.2.1-3**. The cell is brazed (silver copper braze) to the picture frame. Major process improvements have been incorporated to improve the consistency of the braze application. The cathode and the anode contact mesh are welded onto the separator plate. The two parts are then laser welded to make the complete cassette. **Figure 4.2.1-4** shows a picture of a completed cassette.

Figure 4.2.1-3: Exploded View of a Generation 3 Cassette

Figure 4.2.1-4: Generation 3 Cassette

4.2.2 Develop High-Performance Cathode

Cathode development efforts focused on testing of button cells to characterize and optimize the performance of several cathode materials. The cathode materials of primary interest were:

- Sr-doped lanthanum cobalt ferrite $[(\text{La},\text{Sr})(\text{Co},\text{Fe})\text{O}_3]$: LSCF],
- Sr-doped lanthanum ferrite $[(\text{La},\text{Sr})\text{FeO}_3]$: LSF] and
- Copper-doped LSF $[(\text{La},\text{Sr})(\text{Fe},\text{Cu})\text{O}_3]$: LSFCu].

Button cell tests were normally conducted at 0.7 V and 750 °C using 1:1 mixture of nitrogen and hydrogen as a fuel in order to simulate the reformat gas used in full scale testing. The standard test conditions are listed in **Table 4.2.2-1**.

Table 4.2.2-1: Normal Test Conditions

Active area	2.83 cm ²
Air flow rate (cathode)	250 sccm
Fuel flow rate (anode)	200 sccm
Fuel composition	50% N ₂ , 50% H ₂
Test temperature	750 °C
Test voltage	0.7V
Current collecting layer (Cathode)	Ag or Pt grid
Current collector (cathode)	Pt mesh
Current collecting layer (Cathode)	N/A
Current collector (anode)	NiO mesh
Cut-off voltage (current sweep)	0.3V
Interval (current sweep)	10 h
Sweep rate	1 mA/s

4.2.2.1 Sr-Doped Lanthanum Cobalt Ferrites (La,Sr)Co_{0.2}Fe_{0.8}O₃: (LSCF)

4.2.2.1.1 La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ (LSCF-6428)

Both commercial and in-house prepared LSCF-6428 powders were investigated. In all tests, a Sm-doped ceria (SDC) protective layer was used to prevent the reaction of cathode with the 8YSZ electrolyte. A silver grid was applied to the cathode to act as a current collector during operation.

Figure 4.2.2-1: Performance of LSCF-6428 Fired at 1050 °C for 1 Hour

Figure 4.2.2-1 shows the power density-time behavior of several button cells using a commercial LSCF-6428 powder (Praxair Specialty Ceramics). The maximum initial power density obtained in these tests was >700 mW/cm² under normal test conditions. The degradation of the power density with time in these cells was found to be

dependent upon current sweeps used to characterize the polarization behavior of cells. The sample SC0038d experienced a current sweep, from OCV to 0.3 V, every 10 hours and exhibited a rapid degradation (1.6%/hour up to 20 hours). On the other hand, cell JK0027c, which was only exposed to an initial current sweep was found to degrade initially and then stabilize after 20 hours of operation. Elimination of the initial current sweep (JK0027e) was further shown to give a relatively stable power density. These results indicate that either the low cell potential or the higher current densities influence the degradation rate of LSCF-6428 cathode in the button cell tests. It appears that the LSCF-6428 is stable at 0.7V, unless it is exposed to a low potential condition, which enables high current density through the cell and a steep oxygen concentration gradient through the cathode layer. The variation in initial power densities in these cells appears to be due to variations in SDC processing conditions, which is an ongoing investigation.

Figure 4.2.2-2 shows the performance difference observed in LSCF-6428 cathodes sintered at 975 °C and 1050 °C, with a ~25% improvement in power density achieved for the cathode sintered at 1050 °C.

Figure 4.2.2-2: Effect of Sintering Temperature on the Power Density of LSCF-6428

Sintering behavior of this LSCF6428 powder (new 6428 P4368) is shown in **Figure 4.2.2-3**.

Figure 4.2.2-3: Sintering Behavior of Various LSCF Powders

4.2.2.1.2 $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$: LSCF- 8228

Unlike LSCF-6428 compounds, LSF-20 cathodes did not show degradation at high current densities. In order to determine the effect of Co concentration or increased Sr content on the degradation mechanism, LSCF compounds were prepared with lower Sr content (20% vs. 40%). Performance of a 20% Sr-doped LSCF ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$: (LSCF8228-2AD) [here '2AD' stands for 2 mol% A-site deficiency] is shown in **Figure 4.2.2-4**. Overall, the initial specific power of LSCF8228-2AD was lower than that of LSCF6428. However, this cathode composition reveals two distinctive differences in comparison with LSCF-6428. First, this powder exhibits a “burn-in” phenomenon with time similar to LSF-20 compositions. Although the initial power of the sample sintered at 1050 °C for 1 hour (JK0030b) was low (350 mW/cm²), it “burned-in” to ~670 mW/cm² over 100 hour. The other difference is the stability of LSCF8228-2AD under the current sweep. As shown in **Figure 4.2.2-4**, the sample tested with current sweep every 10 hours (JK0030b) exhibits a similar “burn-in” rate compared to the sample tested without current sweep (JK0030a), although overall power density is different due to the different sintering temperature.

Figure 4.2.2-4: Performance of LSCF8228

Based on the above results, the stability and power (especially initial power) of LSCF was related to the doping level of Sr (or oxygen vacancy concentration), enabling the stability and power of Sr-doped lanthanum cobalt ferrite to be optimized by controlling Sr doping level.

4.2.2.1.3 Sr-doped lanthanum ferrite $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$, (LSF-20) and Cu-doped LSF-20 $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{Fe}_{0.98}\text{Cu}_{0.02}\text{O}_3$, (LSFCu2)

Figure 4.2.2-5 shows the performance of LSF-20 sintered at 950 °C for 1 hour. In these samples, a Pt paste was used to print a current collecting grid and then fired again at 950 °C for 1 hour.

Figure 4.2.2-5: Performance of LSF20 Sintered at 950 °C/1hour

Therefore, the cathode layer was exposed at 950°C for a total of 2 hours. LSF-20 sintered at 950 °C (SC0021c) had an initial power of ~300 mW/cm², which decreased until 50 hours before undergoing a “burn-in” to the maximum power (~800 mW/cm²) over 200 hours. To identify whether or not the “burn-in” phenomenon was thermally activated, the cells prepared using the same conditions were kept at 800 °C (SC0021e) and 900 °C (SC0021f) for 100 hours before testing started. The sample kept at 800 °C shows no improvement in terms of initial power. However, it reached the maximum power of >900 mW/cm² over a significantly reduced period of 50 hours. The fact that the initial power was not increased indicates that the burn-in effect is not just a thermally activated phenomenon. However, the change that occurred during the hold at high temperature (possibly further sintering or shrinkage) seems to help accelerate the

subsequent burn-in rate. The cell kept at 900 °C for 100 hours exhibited a low power density most likely due to undesirable reactions at the cathode/electrolyte interface.

To identify whether the “burn-in” phenomenon is reversed by thermal cycles, an LSF-20 cell were thermally cycled (cooled down to room temperature and heated up to 750 °C). As can be seen in **Figure 4.2.2-6**, the high power density achieved through the burn-in was maintained after the thermal cycle, indicating that the changes in the cell that occurred during the burn-in are irreversible. Furthermore, the power did not show significant degradation up to 500 hours.

Figure 4.2.2-6: Performance of LSF20 After Thermal Recycling

The SECA Core Technical Program (CTP) reported that the reaction of LSF and YSZ electrolyte could be minimized by lowering the sintering temperature to less than 1000 °C. Furthermore, the CTP reported that the addition of 2% Cu to LSF improved the performance since it lowered the sintering temperature and allowed the removal of the protective SDC layer. Performance of the CTP-developed Cu-doped LSF (LSFCu₂) cathode was investigated by this project, using commercially prepared powders (Praxair Specialty Ceramics) of LSF-20 and LSFCu₂, which were printed directly on top of YSZ electrolyte and sintered at temperature less than 1000 °C. Compared to the pure LSF-20 samples, the Cu-doped LSF exhibited a higher rate of burn-in. **Figure 4.2.2-7** shows the performance of an LSFCu₂ cathode cell (SC0034c) under both 50:50 mixture and pure hydrogen. When pure hydrogen was used as fuel, the power jumped up to over 1.3 W/cm², similar to power densities reported from the CTP. The current sweep behavior of this cell under pure hydrogen and 50:50 mixture is shown in **Figure 4.2.2-8**. While pure hydrogen shows no diffusion limit up to 7 A, the I-V curve of the cell operating on the 50:50 mixture revealed a diffusion limit around 5.7 A. This result

indicates that in the case of 50:50 mixture, hydrogen diffusion through the anode may be more limiting at high power compared to water vapor diffusion from the active layer of the anode.

The cell tested in **Figures 4.2.2-7 and 4.2.2-8** contained a Pt grid with Pt contact paste and Pt mesh.

Figure 4.2.2-7: Effect of Fuel Composition on the Performance of LSF Cu₂ (SC0034c)

Figure 4.2.2-8: Current Sweep Behavior of LSF Cu₂ (SC0034c) Under Pure Hydrogen and 50:50 Mixture

4.2.2.2 Cu-doped LSF-20 ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.98}\text{Cu}_{0.02}\text{O}_3$, LSFCu-2

Previous testing with both in-house and commercially prepared LSFCu-2 cathode materials demonstrated power densities exceeding 0.9 W/cm^2 under normal button cell test conditions. Further research has shown that the high-power densities are extremely sensitive to the cathode sintering temperature as well as the presence of Pt in the system. Additionally, the high power density appears to be negatively impacted by the presence of Cr-forming metals in the cathode atmosphere, as shown in **Figure 4.2.2-9**. When a Cr-forming alloy, such as Crofer 22 Auxiliary Power Unit, is added to the test configuration, these cathodes failed to exhibit the superior power densities and are limited to $\sim 0.1 \text{ W/cm}^2$ in this configuration. These results were validated on intermediate scale tests with and active area $\sim 33 \text{ mW/cm}^2$ and further study was eliminated.

Figure 4.2.2-9: LSFCu-2 Power Density with Crofer 22 Auxiliary Power Unit Mesh

4.2.3 Develop High-Performance Anode

The standard electrolyte tape cast formulation used in cell production was determined to lack the desired robustness necessary to produce consistent high quality. Slight variations in the solids loading, binder content or solvent lead to lower part yields through formation of pinholes in the YSZ electrolyte. Research efforts were directed at developing an improved electrolyte formulation providing an improved sintered density and a reduction in the number of pinhole defects in the sintered electrolyte. Other research efforts focused on optimizing the anode tape cast formulation.

The second goal of this work was defining the sensitivity of the various components within the optimal “K” composition to yield reproducible, high quality tapes. The optimal dispersant range was determined to be $1.2 \pm 0.2\%$. Above 1.5% the slip is less fluid and does not flow well, displaying a "foamy" appearance. Increasing the solvent content in the cast from 65.2 to 70.2% by volume showed no significant increase in pinholes or other defects in the sintered cells. Although an upper limit for the solvent addition was not determined, some upper limit probably does exist, above which skin formation and cracking of the electrolyte tape would occur. The final stage of this work, which is currently in progress, is optimizing the binder and plasticizer content in the “K” composition.

4.2.3.2 ANODE TAPE OPTIMIZATION

Efforts focused on determination of the optimal solids loading for the anode tape composition. The optimal solid loading was determined to be $\sim 26 \pm 2.0\%$ by volume. Increasing the solids loading to above 30-vol% resulted in a viscous slurry unsuitable for casting. At a solids loading of 28% by volume, the open porosity of the sintered bilayer was found to decrease by about 1.5%, resulting in a slightly increased density at the same (1375 °C/1.0 hour) sintering conditions. This density increase aids in control of the camber development in the anode-supported cells. Future work is focusing on sensitivity testing of dispersant level, binder/plasticizer ratio and solvent content.

The cell fabrication effort focused on improving the robustness of the cell manufacturing process through a variety of designed experiments. These efforts have successfully identified a wide processing window for the cell fabrication in which the final cell properties are insensitive to small variations in batch compositions.

The primary variables are the slurry solids loading, specifically, the ratio of binder and plasticizer to solids (B+P/S), the binder to plasticizer ratio (B/P) and the wt% dispersant. The batch compositions and variables for the L9 are shown in **Table 4.2.3-1**. Because factors were assigned to each of the four available columns in the L9 matrix, the experiment is essentially a “Resolution 1” or “Screening” experiment. The primary metrics for this study were slurry viscosity, cast thickness, lamination ability, fired shrinkage, and open porosity. A representative column effects plot is shown in **Figure 4.2.3-2**, along with the data in **Table 4.2.3-2**. Complete analysis of the L9 has shown the selected compositional range to be extremely robust, allowing for 1-2% variations in tape batching without significantly impacting the tape quality or properties. While the L9 is valuable in determining the robustness of a system, a higher resolution L8 designed experiment is required in order to investigate the interactions of the main effects. Analysis of L8 metrics, shown in **Table 4.2.3-3**, is currently underway along with the development of a definitive quality control specification for the bulk anode tapes.

Table 4.2.3-1: Batch Compositions for L9 Robustness Study

L9	Batch	Slurry Solids Loading (vol. %)	B+P / S	Binder/ Plasticizer	Wt% Dispersant (P S-236)
1	SiC/Ni-53	30.00%	0.53	1.30	1.10
2	SiC/Ni-54	30.00%	0.55	1.35	1.20
3	SiC/Ni-55	30.00%	0.57	1.40	1.30
4	SiC/Ni-56	31.00%	0.53	1.35	1.30
5	SiC/Ni-57	31.00%	0.55	1.40	1.10
6	SiC/Ni-58	31.00%	0.57	1.30	1.20
7	SiC/Ni-59	32.00%	0.53	1.40	1.20
8	SiC/Ni-60	32.00%	0.55	1.30	1.30

DOE#2	Batch	Solids Loading (vol. %)	B+P/S	Binder/ Plasticizer	Wt% Dispersant (PS-236)	Cast thickness- center of cast only (um)	SSD Cast thickness- center of cast only
1	SIC/Ni-53	30.00%	0.53	1.30	1.10	135.77	5.20
2	SIC/Ni-54	30.00%	0.55	1.35	1.20	129.45	4.57
3	SIC/Ni-55	30.00%	0.57	1.40	1.30	125.55	4.06
4	SIC/Ni-56	31.00%	0.53	1.35	1.30	137.22	2.77
5	SIC/Ni-57	31.00%	0.55	1.40	1.10	131.58	3.26
6	SIC/Ni-58	31.00%	0.57	1.30	1.20	137.29	3.15
7	SIC/Ni-59	32.00%	0.53	1.40	1.20	136.80	2.62
8	SIC/Ni-60	32.00%	0.55	1.30	1.30	137.36	3.93
9	SIC/Ni-61	32.00%	0.57	1.35	1.10	131.88	2.17

Figure 4.2.3-2: L9 Column Effects Plot for Cast Thickness

Table 4.2.3-2: L9 Average and Standard Deviation for Cast Thickness

L9	Batch	Solids Loading (vol. %)	B+P/S	Binder/ Plasticizer	Wt% Dispersant (PS-236)	Cast thickness - center of cast only (μm)	SSD Cast thickness- center of cast only
1	SiC/Ni-53	30.00%	0.53	1.30	1.10	135.77	5.20
2	SiC/Ni-54	30.00%	0.55	1.35	1.20	129.45	4.57
3	SiC/Ni-55	30.00%	0.57	1.40	1.30	125.55	4.06
4	SiC/Ni-56	31.00%	0.53	1.35	1.30	137.22	2.77
5	SiC/Ni-57	31.00%	0.55	1.40	1.10	131.58	3.26
6	SiC/Ni-58	31.00%	0.57	1.30	1.20	137.29	3.15
7	SiC/Ni-59	32.00%	0.53	1.40	1.20	136.80	2.62
8	SiC/Ni-60	32.00%	0.55	1.30	1.30	137.36	3.93
9	SiC/Ni-61	32.00%	0.57	1.35	1.10	131.88	2.17

Table 4.2.3-3: L8 Variables and Metrics

L8	Batch ID	SSL	(B+P) /S	B/P	W % Disp	Lam. Rating	Cast thickness s	Fired shrinkage	Fired Thickness (um)	Density (g/cc)	OP (%)	η (cP)
1	62	30	0.53	1.30	1.20	3	142.08	15.21	518.50	4.98	21.5	49.20
2	63	30	0.53	1.40	1.20	3	134.17	15.24	477.00	5.01	19.5	60.05
3	64	30	0.57	1.30	1.20	5	138.86	15.34	484.00	5.06	19.0	104.50
4	65	30	0.57	1.40	1.20	3	131.90	15.19	463.75	4.98	21.5	57.23
5	66	32	0.53	1.30	1.20	3	156.63	14.64	530.00	4.90	23.0	101.05
6	69	32	0.53	1.40	1.20	3	144.80	14.75	504.25	4.91	22.3	117.00
7	67	32	0.57	1.30	1.20	5	134.50	14.77%	477.50	4.95	22.0	145.00
8	68	32	0.57	1.40	1.20	5	134.90	14.98%	472.63	5.00	20.5	150.00

4.2.4 Develop Separator and Support Components

Ferritic stainless steel was the material of choice for separator development. For Generation 2 cross-flow cassette fabrication, 430 stainless steel continued to be aluminized by slurry coating and heat treatment at 1000 °C to improve glass seal strengths. The lower mass Gen 3 co-flow cassettes were manufactured using Crofer 22 APU, a modified 430 stainless steel composition with improved oxidation resistance achieved by elemental alloy additions.

An alternative interconnect design was developed which fundamentally changed the interconnect train and the role of the separator plate. It had been well established that the largest contributor to resistance in the interconnect train electrical pathway was the oxide scale formed on the mesh and the separator. A proposed method to eliminate the oxide layer from the pathway is the “via” concept, consisting of an isolated, non-

oxidizing electrical path through the separator plate. One-way to achieve this is to form a via using a silver alloy in a machined or stamped hole through the separator. The Ag-CuO braze alloy being evaluated for PEN and cassette sealing has excellent wetting properties which lends it nicely to forming vias by simple heat treatment of a separator plate.

Although the phenomenon is not yet well characterized, it is known that hydrogen and oxygen diffuse through silver, affecting the ability of the via-formed separator plate to remain hermetic for the operating lifetime of the stack. With this in mind, the alternative interconnect design incorporated an offset via which creates a longer diffusion pathway between gas streams. As shown in **Figure 4.2.4-1**, a via cap is brazed into place in a cavity above the actual via through-hole formed in the separator plate. The perimeter of the via cap forms the longer diffusion path for either oxygen or hydrogen species.

Figure 4.2.4-1: Schematic of the Offset Via Design Using Ag-CuO Braze Alloy to Form Vias in Fecralloy Separator Plate and Coupled with Anode and Cathode Compliant Meshes

In order to assess the long-term hermeticity of an offset via, a series of dual atmosphere tests were conducted wherein an offset via is exposed to air on one-side and hydrogen on the other side while at operating temperature (750 °C) over a range of times. Test samples were fabricated by using a high-temperature braze to seal a Fecralloy via disc to the end of a metal tube. A smaller offset disc was then Ag-CuO brazed into a circular recess to simulate a rectangular offset via of a square separator plate.

4.2.5 Develop Gas Distribution Meshes

The anode and cathode gas distribution meshes are two key components of the interconnect train. These components must provide a low-resistance electrical connection between the separator plate and the corresponding electrodes, allow access of air and fuel gas to the electrodes, and offer some measure of compliance during the

assembly and sealing processes. For the Generation 2 and 3 cassette designs, both electrode meshes employed a “feather” design fabricated from woven mesh of nickel (anode) and Crofer 22APU (cathode). Both sets of mesh feathers were individually spot-welded to the ferritic steel separator plate to complete the electrical interconnection. As part of sealing investigation, a study of Crofer 22 APU mesh welding parameters is underway to ensure that joining of the mesh to the separator is optimized for strength and also to ensure that the spot weld provides a minimum contribution to the total electrical resistance of the interconnect train.

4.2.6 Develop Mesh/Electrode Interface Materials

Previous modeling of the electrical pathway between the anode in one cell through the anode interconnect and the separator to the cathode interconnect and cathode in the adjacent cell revealed that the highest contribution to interconnect train resistance is attributed the oxide scale which forms on the cathode mesh, and the second highest contribution comes from the sheet resistance of the cathode. Two intermediate-scale single-cell stack tests were run to assess the impact of a silver current collecting grid applied directly to the cathode layer. Test I-46 was fabricated with a silver current collector grid, whereas I-45 did not have any current collecting grid. Both cells were identical with Crofer 22 APU mesh, silver contact paste and LSCF-6428 cathode. The contact paste was applied in a 6 x 6-dot pattern; therefore, the contact paste area was the same for both cells. As shown in **Figure 4.2.6-1**, (Cell I-46 contained a silver grid and cell I-45 did not.) cell I-46 resulted in a power density of 0.65 W/cm^2 at 0.7 V , whereas cell I-45 produced only 0.25 W/cm^2 at 0.7 V .

Figure 4.2.6-1: Intermediate-Scale Stack Test Results Showing the Impact of Employing a Silver Current Collector Grid on the Cathode

4.2.7 Develop Glass and Glass-Ceramic Seals

One of the inherent problems found with glass seals is the formation of an oxide scale at the interface between the glass and the metal structural component, in our case the window frame or separator plate. Initially this scale layer is well attached to the underlying metal substrate, but after long-term exposure to the high temperature operating conditions of the SOFC stack, the scale thickens and thereby weakens, eventually become the source of failure in the glass-to-metal sealing joints, particularly upon thermal cycling. One way to alleviate this problem is to roughen the surface of the metal substrate such that the glass seal is mechanically locked into place. However, we have found that simple sand blasting or grain boundary etching do not provide a sufficiently “roughened” surface. On the other hand, welding a thin screen mesh of the same material type as the substrate does form a surface through which the glass seal material can infiltrate and mechanically lock in place. A schematic of this glass-fiber-mesh (GFM) composite seal is shown in **Figure 4.2.7-1** (The Crofer mesh is welded to the Crofer substrate. The glass, containing YSZ fibers, is then infiltrated into the mesh during the sealing operation.).

Figure 4.2.7-1: Schematic of Glass-Fiber Mesh (GFM) Composite Seal

The SEM micrograph in **Figure 4.2.7-2** shows the microstructure of a GFM seal. (Note the infiltrate of the glass around the metal wires of the mesh, providing additional adhesion strength to the seal.). The YSZ fibers are included to avoid a problem that is introduced by the metal mesh: in sealing one metal cassette to the next, spurious electrical conduction can occur. This is due to the mesh from one sealing surface touching the mesh from the adjacent surface, thereby providing a pathway for electrical conduction. The seal is required to be electrically insulating to avoid shorting the fuel cell stack. To eliminate this problem we have introduced ~10% random dispersion of YSZ fibers to the initial glass paste. The YSZ increases the viscosity of the glass during melting, allows the glass to maintain a minimum thickness during the sealing step and avoids mesh-to-mesh contact.

Figure 4.2.7-2: SEM Micrograph of Glass-Fiber Mesh Composite Seal

Rupture strength testing using the “pop-gun” test rig shown in **Figure 4.2.7-3** indicated that the average strength of the glass-fiber-mesh seal is significantly stronger than comparable glass seals (see **Figure 4.2.7-4**) while providing the same level of hermeticity. A thermal cycle testing program was undertaken to determine the viability of these seals under the prototypical operating conditions expected in a transportation application. The seals were heated in an infrared quartz lamp furnace at a rate of 75 °C / min to 750 °C, held at temperature for 10 minutes and cooled to ~100 °C within 40 minutes. The rupture strength test results indicated that up to the maximum number of thermal cycles tested in this manner thus far, 20 cycles, the composite seals perform quite well. Thermal cycle testing of these seals will continue, accumulating more cycles on the seals prior to rupture testing. In addition, time at operating temperature will be incorporated as a factor in our testing (e.g. by holding the specimens for longer periods of time at 750 °C to measure any high-temperature age-induced effects on seal strength).

Figure 4.2.7-3: Far Left -- Components of Rupture Strength Test Specimen; From Bottom, Metal Washer, Glass Sealing Ring, and Bi-Layer Disk. Middle -- Assembled Test Specimen. Right -- Rupture Strength Test Schematic

Figure 4.2.7-4: Rupture Strength Results For Glass Seals

4.2.8 Develop Alternative Seals

A joining technique, referred to as reactive air brazing or RAB, was used to seal the metal and ceramic components in a solid oxide fuel cell. However, a second seal is required to connect these cells into an integrated stack that is the seal between adjacent cells or cassettes. As shown in **Figure 4.2.8-1**, Delphi investigated the fabrication of such a joint using the RAB technique by inserting a thin ceramic insulator between the two cassettes and joining each to the insulator. The insulator used is zirconia-toughened alumina (ZTA), chosen not only because it is an electrical and ionic insulator at operating temperature, but also because its coefficient of thermal expansion is sufficiently high to nearly match that of the metal substrates and because it offers good mechanical toughness and high thermal shock resistance.

Figure 4.2.8-1: The Insulated Brazed Cassette Sealing Concept

4.2.9 Fabricate Developmental Stacks

Fuel Utilization studies were conducted on full sized Generation 2 1-cell stacks to evaluate the effect of power density at high utilizations. **Figure 4.2.9-1** shows results from a fuel utilization test on a Generation 2 1-cell stack. The stack had a welded Ni-mesh feather as the anode to separator plate electrical interface that also provides the fuel distribution in the plane of the cell. The test was carried out by keeping the voltage constant at 0.7 Volts and lowering the flow of fuel (increasing the utilization) and measuring the corresponding decrease in power output. Fuel flow was not lowered below the point at which there was a sharp decrease in power from fuel starvation in the stack. The data shows a power density of 400 mW/cm² at 15% fuel utilization that decreases to 335 mW/cm² at 50% fuel utilization and further decreases to 290 mW/cm² at 70% fuel utilization. This indicates a 16% reduction in power density in going to 50% fuel utilization and a 27.5% reduction in power density in going to a 70% fuel utilization. Development is ongoing to understand the root cause of this decrease in power and to minimize it. Some of the key areas of development include optimizing the mixing and distribution of fuel in the anode of the cell by mechanically changing the design of the feathers or adding other features for flow distribution. It also involves increasing the pressure drop across the cell thus improving flow distribution. The inherent effect of the porosity of the anode is also being investigated.

Figure 4.2.9-1: Fuel Utilization Study on a Generation 2 Single-Cell Stack

A redox test was carried out on a full sized Gen-2 1-cell stack to understand the extent of degradation from redox cycling. **Figure 4.2.9-2** shows the I-V curves from the redox cycling test. The initial I-V curve (cycle 0) after the reduction of the cell showed a baseline power density of 157 mW/ cm² at 0.7 Volts with 50% H₂, 47% N₂, 3% H₂O.

The anode of the stack was then purged with nitrogen at temperature and then a 4.5% of air mixed with N₂ was introduced to the anode of the stack for 3 minutes. A flow of 2 liters per minute of this gas mixture was maintained for the 3 minutes. The stack was then re-purged with N₂ followed by reducing gas and then with the same fuel mixture of 50% H₂, 47 % N₂, 3% H₂O. An I-V curve was then recorded under identical conditions to the baseline. This was repeated multiple times and the I-V curves are shown in the **Figure 4.2.9-2** after each redox cycle. Cycle 0 is the baseline I-V curve while cycle 1-6 is I-V curve after each redox cycle. The stack power after the first introduction of the air-N₂ mix (cycle 1) dropped to 144 mW/cm² (8% degradation from initial power) at 0.7 Volts. Subsequently in the course of the next two cycles (cycle 2 and 3), the power density decrease was minimal (142 mW/cm² and 147 mW/cm²). Cycle 4-6 showed a slightly higher decrease in power to 130 mW/cm² (17% from initial power). These results were the first step towards understanding the extent of failure that can be expected from oxidation of the anode. The amount of air introduced was controlled and the time for the oxidation reaction was also controlled. A catastrophic failure was not observed but a gradual decrease in power density was seen from redox cycling under these conditions. Further evaluation with higher concentrations of air and larger reaction times needs to be evaluated. Also, these oxidation conditions needs to be correlated to the actual quantity of air leak observed in the APU system during soak or cool down.

Figure 4.2.9-2: Redox Cycling Test on a Generation 2 1-Cell Stack

A thermal cycling test was conducted on a Generation 3, 3-cell stack, after it had been operated continuously for 200 hours. The stack was heated up from room temperature to 750 °C in a furnace in ~90 minutes. The stack completed 30 thermal cycles as shown in **Figure 4.2.9-3**. There was a 6% drop in power after the first 20 cycles. The leak rates on the anode side were 1% or less of the total anode flow for the first 20 cycles. It subsequently increased to 6% of the total anode flow. The seal used in this stack was the common glass seal and not the reinforced glass seal. The thermal cycling results in a stack from a reinforced glass seal is expected to be even better based on the initial results discussed in the earlier section.

Figure 4.2.9-3: Thermal Cycling Test on a 3-Cell Stack

4.2.10 Evaluate Stack Performance

Efforts were focused on building and optimizing 15-cell, Generation 3 stacks. Multiple 15-cell stacks were built and demonstrated good sealing and power. The sealing observed in the Generation 3 design is an improvement over the Generation 2 stack design. **Figure 4.2.10-1** shows the performance of a 15-cell Generation 3 stack. It produced 482 Watts (305 mW/cm²) at 0.7V/cell at 750°C with simulated recycle reformat (35% H₂, 40% CO, 3% H₂O, rest N₂). The reformat flow was 50 liters per minute.

Figure 4.2.10-1: IV Curve From 15-Cell Generation-3 Stack Test

Task 3: Reformer Development

4.2.11 Develop Steam Reformer for Natural Gas

4.2.11.1 Steam Reformer Concept Study, Evaluation, and Analysis

Endothermic reformer concepts developed in 2003 are illustrated in **Figures 4.3.1-1 to 4.3.1-8**. A flat plate design, as shown in **Figure 4.3.1-1**, is capable of delivering adequate heat transfer two fold, by maximizing surface area for heat transfer and second by increasing the active heat transfer coefficient due to decreasing the flow channel height. Calculated Computational Fluid Dynamics temperature profiles for co-flow, counter-flow, and cross-flow conditions are shown in **Figure 4.3.1-9**. The essentially identical profiles for the temperatures of combustor and reformer flow, as well as metal intercept, indicate independence of heat transfer. In other words, the designs performance would become independent of heat transfer and the limiting factor would be the endothermic reforming kinetics. Various other conceptual ideas are presented in **Figures 4.3.1-2 to 4.3.1-8**, including a “Pleated” design in **Figure 4.3.1-2**, “Multi-Tube” arrangements in **Figures 4.3.1-3 to 4.3.1-4**, and various “Tubular” designs in **Figures 4.3.1-1 to 4.3.1-8**. Temperature profiles of a “Square Pleated” concept are shown in **Figures 4.3.1-10 and 4.3.1-11**. Large temperature variations resulting from preferential flow conditions are visible. A better flow distribution is necessary. **Figures 4.3.1-12 and 4.3.1-13** show examples of temperature profiles in a “Round Tube Bundle” and a “Square Tube Bundle” design. Large differences between the profiles of combustor, reformer, and metal temperatures are apparent which leads to the conclusion that the geometry’s investigated might be heat transfer limited with respect to the overall reforming performance if no heat transfer augmentation is added. Examples of analysis results of “Tubular” reformer structures are presented in **Figures 4.3.1-14 to 4.3.1-16**. Concepts such as illustrated in **Figures 4.3.1-5 and 4.3.1-6** and (7-Tube and 6-Tube) do not comprise an internal Gas Phase Combustor or combustor flow as do the concepts shown in **Figures 4.3.1-7 and 4.3.1-8**. Essentially the combustor heating flow in these models is split in an internal counter flow followed by and external co flow. The benefit of such additional internal combustor flow (**Figures 4.3.1-15 and 4.3.1-16**) versus no internal combustor flow (**Figure 4.3.1-14**) is evident. The effects of heat transfer augmentation have been investigated on the basis of a 5-Tube design with center GPC flow. Augmented heat transfer as shown in **Figure 4.3.1-16** is much superior to simple non-augmented tube configurations, as shown in **Figure 4.3.1-15**. A more comprehensive study is underway.

Figure 4.3.1-1: Flat Plate General

Figure 4.3.1-2: Pleated Square

Figure 4.3.1-3: Multi-Tube General

Figure 4.3.1-4: Square Multi-Tube

Figure 4.3.1-5: 7-Tube

Figure 4.3.1-6: 6-Tube

Figure 4.3.1-7: 5-Tube Center Gas Phase Combustor

Figure 4.3.1-8: 5-Channel Center Gas Phase Combustor

Figure 4.3.1-9: Calculated Computational Fluid Dynamics Temperature Profiles

Figure 4.3.1-10: Temperature Profiles Square Pleated

Figure 4.3.1-11: Temperature Profiles Flat Plate

Figure 4.3.1-12: Round Tube Bundle Results

Figure 4.3.1-13: Square Tube Bundle Results

Figure 4.3.1-14: Tube Configuration

Figure 4.3.1-15: 5-Tube Center Gas Phase Combustor

Figure 4.3.1-16: 5-Tube Center Gas Phase Combustor Augmented Heat Transfer

4.2.12 Reforming Catalyst Development

Catalyst development was broadly partitioned into several activity areas which reflect the organization of the catalyst engineering department: formulation, which considers material selection and synthesis; product development – the chemistry of building catalysts and determination of appropriate loading and concentrations; process development, mechanical requirements and chemistry for manufacturing of catalysts; testing, performance and durability evaluation; applications – uses of the catalyst; mechanisms, understanding of underlying properties responsible for performance; and management, planning of these catalyst development activities. While interrelated, each of these areas is discussed in turn.

4.2.12.1 Catalyst Formulation

The various components of reforming catalysts: substrate, washcoat, and active metal, as well as the rationale of the performance testing are listed below. Extensive development work was completed on washcoat formulations, focusing on improving catalyst stability, as measured by our 'aggressive testing protocol' or our oxidative aging method. This development is summarized in **Table 4.3.2-1**.

Major Components Of Catalyst:

- Substrate - typically 20-65 pores per inch (ppi) zirconia-toughened alumina (ZTA) reticulated foam
- Washcoat - a slurry of support material and active metal applied to substrate, followed by calcining step
 - Usually applied in one step to substrate via production-intent hardware
 - If multiple passes, each pass can be the same or differing compositions
- Support - typically a high surface area aluminum oxide with or without stability or performance modifiers, sometimes zirconium oxide or other materials are employed
- Active Metal - for partial oxidation, rhodium (Rh) is preferred with or without modifier
 - Concentration in washcoat is typically 2-10 wt. %
 - Loading on substrate is typically 30-100 g/ft³ of substrate volume
- Lab Scale - 1" dia x 1" or 7/8" dia x 1" substrates
 - Performance rankings independent of hardware
 - Up to 40-60 hours continuous
 - Use of accelerated aging methods can reduce this to 2-6 hours
 - Testing conditions selected to 'stress' catalysts, excessive catalyst center temperature, usually 1000-1125 °C, achieved through high space velocity

Table 4.3.2-1: Properties of Alumina Used in Washcoats and Corresponding Catalyst Identification

finished catalyst code	base alumina properties				comments
	generation	alumina	phase	surface area (m ² /g)	
RDRC A0-001:CB	"0"	AT	δ alumina	~165	BaSO ₄ stabilized alumina for use in exhaust catalyst production, very poor stability at high temperatures
RDRC A0-100:CB	1.0	NC	θ and α alumina	150	La ₂ O ₃ stabilized alumina for use in exhaust catalyst production, poor stability at high temperatures
RDRC A0-200:CB	2.0	RS	γ, minor δ alumina	150	BaSO ₄ stabilized meso-porous alumina, unstable at high temperatures
RDRC A0-250:CB	2.5	TG	α alumina	8	based on RS, heat treated for improved stability
RDRC A0-300:CY	3.0	TG	α alumina	144	based on TG gen. 2.5, Y stabilized, minor degradation with high temperatures
RDRC A0-320:CB	3.5	TS	δ, θ, minor α alumina	64	BaSO ₄ stabilized, with improved addition method, good stability at high temperatures
RDRC A2-400:CN	4.0	TS	δ, θ, minor α alumina	64	dual layer technology (Rh over Ni), improved reforming function, same alumina technology as gen. 3.5

A summary of the improved catalysts are listed in **Table 4.3.2-2**, comparing the performance of catalysts built with modified and unmodified alumina-based washcoats, tested fresh and after aging. These results are shown graphically in **Figure 4.3.2-1**, **Figure 4.3.2-2**, **Figure 4.3.2-3**, and **Figure 4.3.2-4**. In all cases, approximately the same washcoat rhodium concentration and part loadings were employed.

Table 4.3.2-2: Performance Comparison of Partial Oxidation Catalysts

washcoat generation	0	1	2	3	3.5	4	4	4	4
catalyst code	RDRC A0-001:CB	RDRC A0-100:CB	RDRC A0-150:CB	RDRC A0-300:CB	RDRC A0-320:CB	RDRC A0-300:CY	RDRC A0-300:D// RDRC A0-300:CY	RDRC A2-400:CN	RDRC A0-300:CB// TG (1:10) (aged)
catalyst / alumina nomenclature	Rh/ AT	Rh/ NC/ BaSO ₄	Rh/ CNC/ BaSO ₄	Rh/TG-Y	Rh/TS	Rh/ Y modified via imp./TS	1/8" Pt // 1"Rh dual brick TG/TG	Rh/Ni dual layer TS/TS	10% Rh 1:10 blend
<i>average performance during first 600 minutes testing</i>									
product H ₂ (vol. %) tested fresh	21.1	20.1	20.6	21.1	21.9	22.0	22.6	22.1	21.4
product H ₂ (vol. %) tested aged	20.3	17.5		18.7	21.1	20.5	21.3	21.4	21.5
% retained fresh vs. aged	96.2	87.1		88.6	96.3	93.2	94.2	96.8	100.5
product CO (vol. %) tested fresh	22.9	22.9	23.0	23.1	23.5	24.0	23.3	23.6	23.5
product CO (vol. %) tested aged	23.1	22.4		22.5	22.8	23.1	23.1	23.2	23.6
% retained fresh vs. aged	100.9	97.8		97.4	97.0	96.3	99.1	98.3	100.4

All formulations contain ~2 wt. % Rh in washcoat, loaded to ~30 g/ft³ onto substrate.
 Testing with CARB Phase II gasoline, ~45,000/hr GHSV, O/C ~ 1.05 (mol/mol), analysis by GC.
 Aged catalysts treated in air at 1200 °C, 6+ hours, prior to testing.

Figure 4.3.2-1: H₂ Selectivity Comparison of POx Catalysts

All formulations contain ~2 wt. % Rh in washcoat, loaded to ~30 g/ft³ onto substrate.
 Testing with CARB Phase II gasoline, ~45,000/hr GHSV, O/C ~ 1.05 (mol/mol), analysis by GC.
 Aged catalysts treated in air at 1200 °C, 6+ hours, prior to testing.

Figure 4.3.2-2: CO Selectivity Comparison of POx catalysts

All formulations contain ~2 wt. % Rh in washcoat, loaded to ~30 g/ft³ onto substrate.
 Testing with CARB Phase II gasoline, ~45,000/hr GHSV, O/C ~ 1.05 (mol/mol), analysis by GC.
 Aged catalysts treated in air at 1200 °C, 6+ hours, prior to testing.

Figure 4.3.2-3: CH₄ Selectivity Comparison of POx Catalysts

All formulations contain ~2 wt. % Rh in washcoat, loaded to ~30 g/ft³ onto substrate.
 Testing with CARB Phase II gasoline, ~45,000/hr GHSV, O/C ~ 1.05 (mol/mol), analysis by GC.
 Aged catalysts treated in air at 1200 °C, 6+ hours, prior to testing.

Figure 4.3.2-4: C₂ Hydrocarbon Selectivity Comparison of POx Catalysts

4.2.12.2 Catalyst Product Development

Product development focused on selecting the formulation that can best meet the goal of extended catalyst durability, here determined by how close the performance of an aged catalyst can meet that of a fresh, high activity, catalyst. **Figure 4.3.2-5, Figure 4.3.2-6, Figure 4.3.2-7, and Figure 4.3.2-8** shows the steady improvement in catalyst formulations to meet this goal, primarily through use of chemically modified washcoats. This work will necessarily be extended by evaluation through extensive durability testing, to confirm the performance of the leading catalyst products to give high selectivity over a wide range of processing conditions.

Besides using the most appropriate formulations, catalyst product development is also involved with determining the optimum rhodium and washcoat loadings on the substrate. We have begun some evaluations aimed at understanding the effects of loadings on catalyst performance.

One goal of catalyst development is to minimize the amount of rhodium used. Rhodium loading is expressed as the concentration in the washcoat, and the amount on the part; both can be varied independently. We have completed some tests examining the effects of rhodium on performance and durability.

Figure 4.3.2-9 and Figure 4.3.2-10 show that as rhodium loading is increased, at constant washcoat concentration, both selectivity and durability are improved. Note that these figures illustrate the performance on a highly unstable $\gamma\text{-Al}_2\text{O}_3$. Provided sufficient rhodium is used, the destabilizing influence of the alumina can be overcome to some extent. **Figure 4.3.2-11** shows the same behavior for a much more stable alumina; this time tested after thermal aging. For a washcoat with twice the rhodium concentration, 4 % vs. 2% previously, **Figure 4.3.2-12** again shows the same behavior. Likewise, for lower rhodium concentrations in the washcoat, 1.0% Rh, again **Figure 4.3.2-13** shows the same. Only when Rh concentration is decreased to 0.5 wt. % in the washcoat is a detrimental effect shown.

All formulations contain ~2 wt. % Rh in washcoat, loaded as indicated onto 20 ppi substrates, washcoat catalyst code: RDRCA0-001:CB.

Testing with CARB Phase II gasoline, ~45,000/hr GHSV, O/C ~ 1.05 (mol/mol), analysis by GC.

Figure 4.3.2-5: H₂ Selectivity of Fresh Catalysts with Varying Rh Loadings

All formulations contain ~2 wt. % Rh in washcoat, loaded as indicated onto 20 ppi substrates, washcoat catalyst code: RDRCA0-001:CB.

Testing with CARB Phase II gasoline, ~45,000/hr GHSV, O/C ~ 1.05 (mol/mol), analysis by GC.

Figure 4.3.2-6: CO Selectivity of Fresh Catalysts with Varying Rh Loadings

All formulations contain ~2 wt. % Rh in washcoat, loaded as indicated onto 20 ppi substrates, washcoat is yttrium modified and stabilized alumina RS, samples tested after aging in air at 1200 °C for six hours.

Testing with CARB Phase II gasoline, ~45,000/hr GHSV, O/C ~ 1.05 (mol/mol), analysis by GC.

Figure 4.3.2-7: H₂ Selectivity of Aged Catalysts with Varying Rh Loadings

All formulations contain ~4 wt. % Rh in washcoat, loaded as indicated onto 20 ppi substrates, washcoat is yttrium modified and stabilized alumina RS, samples tested after aging in air at 1200 °C for six hours.

Testing with CARB Phase II gasoline, ~45,000/hr GHSV, O/C ~ 1.05 (mol/mol), analysis by GC.

Figure 4.3.2-8: H₂ Selectivity of Aged Catalysts with Varying Rh Loadings, Higher Rh Washcoat Concentrations

All formulations loaded as indicated onto 20 ppi substrates, washcoat is yttrium modified and stabilized alumina RS , samples tested after aging in air at 1200 °C for six hours.
Testing with CARB Phase II gasoline, ~45,000/hr GHSV, O/C ~ 1.05 (mol/mol), analysis by GC.

Figure 4.3.2-9: H₂ Selectivity of Aged Catalysts with Varying Rh Loadings, Lower Rh Washcoat Concentrations

A close examination of **Figure 4.3.2-7**, **Figure 4.3.2-8**, and **Figure 4.3.2-9** show that regardless of Rh concentrations in the washcoat, similar washcoat loadings give similar H₂ selectivities. This is illustrated in **Figure 4.3.2-10**, where the amount of Rh on the part was held constant, but the concentration of Rh, and consequently, the amount of washcoat, was varied. These results indicate that a more disperse rhodium in a thicker washcoat has better stability and performance.

All formulations loaded as indicated onto 20 ppi substrates, washcoat is yttrium modified and stabilized alumina RS , samples tested after aging in air at 1200 °C for six hours.
Testing with CARB Phase II gasoline, ~45,000/hr GHSV, O/C ~ 1.05 (mol/mol), analysis by GC.

Figure 4.3.2-10: H₂ Selectivity of Aged Catalysts with Different Washcoat Loadings, and Similar Rh Loadings

This behavior is somewhat moderated by washcoat composition, as shown in **Figure 4.3.2-11**. Less stable washcoats, such as RDRCA0-503C, have poorer performance than a lower loaded stabilized washcoat, RDRCA0-494:CL, while the Y and La stabilized washcoats have similar performances at different Rh concentrations and washcoat thickness.

All formulations contain ~1 wt. % Rh in washcoat, loaded as indicated onto 20 ppi substrates, washcoat formulations as indicated, samples tested after aging in air at 1200 °C for six hours. Testing with CARB Phase II gasoline, ~45,000/hr GHSV, O/C ~ 1.05 (mol/mol), analysis by GC.

Figure 4.3.2-11: H₂ Selectivity of Aged Catalysts with Varying Rh Loadings and Washcoat Modifications

The same effects were seen for nickel concentrations and loadings for dual layer catalyst builds, **Figure 4.3.2-12** and **Figure 4.3.2-13**. The finding for these figures is that thicker loadings of nickel bearing and rhodium bearing washcoats give better reforming performance.

All formulations contain ~2 wt. % Rh and ~2 wt. % Ni in respective layers in washcoat, loaded as indicated onto 20 ppi substrates, samples tested after aging in air at 1200 °C for six hours. Testing with CARB Phase II gasoline, ~45,000/hr GHSV, O/C ~ 1.05 (mol/mol), analysis by GC.

Figure 4.3.2-12: H₂ Selectivity of Dual Layer Fresh Catalysts with Varying Ni Loadings

All formulations contain ~2 wt. % Rh and 2 % Ni in respective layers in washcoat, loaded as indicated onto 20 ppi substrates, samples tested after aging in air at 1200 °C for six hours.
Testing with CARB Phase II gasoline, ~45,000/hr GHSV, O/C ~ 1.05 (mol/mol), analysis by GC.

Figure 4.3.2-13: H₂ Selectivity of Dual Layer Catalysts with Varying Rh and Ni Loadings

4.2.12.3 Catalyst Process Development

Formulation work completed included further investigation of the effects of barium modification of the washcoat on catalyst performance. These results are summarized in **Table 4.3.2-3**. All of the catalysts were prepared using the same nominal Rh concentrations in the washcoat and loadings on the substrate, and using the same moderate surface area α -Al₂O₃, alumina RS, washcoat precursor material. Barium concentrations in the washcoat were varied from zero to fifteen percent. Catalysts were tested, after air aging at 1200 °C for 6 hours, by the standard testing procedure using California Air Resources Board Phase II gasoline partial oxidation. Also investigated, but found not to have an effect on performance was the variation of washcoat slurry pH, from values between -0.45 and 4.45.

Optimum performance was obtained for a barium concentration of around 5 wt. %. Below this amount, the alumina washcoat is not sufficiently stabilized and so impacts on the effectiveness and dispersion of the Rh active metal. Above this amount, there is a possibility that excess barium is present, leading to the formation of discrete Ba-containing phases, such as barium aluminates or barium carbonate, which may interfere with the function of the washcoat or the active metal. To support this supposition, small amounts of highly concentrated barium bearing regions were observed by Z-contrast high-resolution electron microscopy in the 5% Ba sample; confirmed through energy-dispersive analysis.

Table 4.3.2-3: Influence of Ba Loading, used for Washcoat Modification, on Catalyst Performance

catalyst	8637-71-2	8636-157-1	8636-158-1	8636-159-1
% Rh in washcoat	2	2%	2%	2%
Rh loading (g/ft ²)	31	33	28	26
washcoat	TG	TG	TG	TG
% Ba in washcoat	0	5	10	15
state	aged	aged	aged	aged
treatment	air, 1200 °C	air, 1200 °C	air, 1200 °C	air, 1200 °C
performance after 30 minutes testing				
% H ₂	19.5	21.3	20.6	19.8
% CO	22.6	23.0	23.0	22.7
% CH ₄	2.14	1.31	1.65	1.88
% C ₂ 's	0.27	0.098	0.11	0.16

4.2.12.4 Catalyst Testing

Figure 4.3.2-14 compares durability results from our durability test stand and of that of one of our cooperating partners, Total-Fina-Elf's Feluy, Belgium research facility. Both stands were operated at about ~25,000/hr space velocity, resulting in a catalyst center temperature of about 950 °C (as compared to a catalyst center temperature of ~1050 °C for the aggressive testing protocol). Good agreement is obtained between the two test stands, even though different catalyst formulations were tested. The slow decrease in performance may be a result of gradual changes to the dispersion of the active metal. We will be evaluating the catalysts from this and similar durability tests with the goal of determining deactivation mechanisms. However, catalysts maintained acceptable performance for over 300 hours of operation, with indications that 1000+ hours of acceptable operations will be readily obtainable.

All formulations contain ~2 wt. % Rh in washcoat in primary 1" brick, tested after aging at 1200 °C for six hours. Testing with CARB Phase II gasoline, ~45,000/hr GHSV, O/C ~ 1.05 (mol/mol), analysis by gas chromatography and mass balance.

Figure 4.3.2-14: Performance of Dual Brick Catalyst Systems

4.2.12.4.1 Accelerated Aging Test Method Development

Using the method described above, the effects of startup method and shutdown atmosphere on catalyst degradation rates were evaluated. Catalysts based on the RDRCA0-320:CB formulation were tested using California Air Resources Board Phase II gasoline. These results are presented in **Figures 4.3.2-15 and 4.3.2-16**. While a flame-based startup initially causes an increase in catalyst deactivation rate (**Figure 4.3.2-15**), perhaps due to carbon deposition, catalyst degradation rate does not appear to be a function of startup method, as evidenced by the equivalent slopes of the curves in the figure.

Figure 4.3.2-15: Effect of Start-up Method on Catalyst Degradation

Figure 4.3.2-16: Effect of Shutdown Atmosphere on Catalyst Degradation

Using a flame-initiated startup, and either nitrogen or air shutdown, resulted in significant performance differences, as shown in **Figure 4.3.2-16**. Almost no degradation occurs during a 'soft' shutdown in N₂, but this soft shutdown procedure may lead to carbon deposition, as some residual fuel may be present, and which has not oxidant to facilitate chemical removal from the catalyst. When a catalyst is shut down in air, a brief interval of lean operating conditions may exist, as air continues to flow while the fuel is cut, resulting in brief but intense temperature excursions. This problem may be enhanced by the presence of carbon deposits, which will burn in an excess air atmosphere. In either case, the potential for brief, but intense, heating of the catalyst is likely the cause for the observed significant decrease in selectivity to hydrogen.

Evidence for carbon deposition is presented in **Figure 4.3.2-17**. A flameless startup was used with shutdown in either N₂ or air. Shutdown in air resulted in increased degradation rate. In contrast to the flame-start results of **Figure 4.3.2-16**, some degradation was also seen in this case, for flameless start and N₂ shutdown. During a flameless start, fuel and air (at reforming ratio), is introduced onto a cool catalyst, close to light-off temperature. Some fuel may not fully react, and instead, form carbon deposits on the catalyst. To test this, after about 75 start-stop cycles, the catalyst undergoing N₂ shutdown was switched to air shutdown. The immediate result was an increase in H₂ selectivity, due to removal of carbon deposits. Continuing operation of the catalyst, but with air shutdown, resulted in accelerated rates of deactivation that is observed for air shutdowns in general. This result clearly indicates that sub-system process development needs to focus on startup and especially shutdown methods that preserve catalyst performance.

Figure 4.3.2-17: Effects of Shutdown Method on Catalyst Degradation

4.2.12.4.2 Durability Testing – Sulfur Impact

Three, five-hundred-hour, durability tests were completed on RDRCA0-250:CB catalysts, using three gasoline formulations containing from 7 to 147 wppm sulfur. Basic properties of the fuels used in this study are listed in **Table 4.3.2-4**. Catalyst RDRCA0-250:CB corresponds to 2 wt. % Rh on moderate surface area α -Al₂O₃, loading to 30 g/ft³ Rh on the ZTA substrate.

formulation	Carb Phase 2	Gasoline 2010	Gasoline 2010+S
Density @ 15 °C (g/cm ³)	0.7352	0.7354	0.7354
Molar mass (g/mol)	101	100	100
Chemical formula	C _{7.1} H _{13.7} O _{0.13}	C _{7.2} H _{13.4}	C _{7.2} H _{13.4}
S content (wt ppm)	34	7	147 ¹

¹sulfur obtained through addition of:
78.4 ppm from 2-ethylthiophene
61.6 ppm from 2,5-dimethylthiophene
7 from base fuel

Table 4.3.2-4: Properties of Gasoline Blends used in Durability Testing

Deactivation rates and methane product concentrations for these three tests are compared in **Figure 4.3.2-18**. Rates of deactivation for selectivity towards H₂ or CO are linearly related to sulfur content of the feed gasoline. Product CH₄ concentration is also linearly related to feed sulfur content. Although speculative, proposed reason is that differing amounts of equilibrium rhodium sulfide form on the catalyst. A combination of several mechanisms may come into play as surface rhodium sulfide levels increase. First is a reduction in reforming active sites, in that reactions of CO₂ and H₂O, which form H₂ and CO from C₁ fragments, are suppressed, leading to lesser selectivities to H₂ and CO, and increased selectivity to CH₄ and C₂H₄ generated from the unreacted hydrocarbon fragments. Also, rhodium sulfide is a known catalyst for CO hydrogenation to CH₄. Further work will be required to elucidate the interaction of the sulfur on the catalyst and the resultant changes in product selectivities.

Figure 4.3.2-18: Impact of Sulfur on Deactivation Rates for Gasoline Partial Oxidation

4.2.13 Sulfur Removal Studies

Delphi had been developing a process to oxidatively convert organically bound sulfur to SO_2 , selective oxy-desulfurization (SODS). This can be useful as one part of a desulfurization process, as some potential sulfur removal schemes are significantly more efficient for SO_2 removal over organic sulfur removal. The process uses an acidic oxidation catalyst, such as V_2O_5 supported on Al_2O_3 . C-S bonds in organic molecules are broken, and an O_2 is inserted, resulting in the oxygenated equivalent organic compound and release of SO_2 . For example, thiophene, $\text{C}_4\text{H}_4\text{S}$, reacts with 2O_2 to yield $\text{C}_4\text{H}_4\text{O}_2$ and SO_2 .

A perceived advantage of this process was that inorganic sulfur should be easier to remove from a system than organic sulfur. Since the process operates at around 300 °C, an integrated SODS and reforming processes can be developed in which heat released from the reforming catalyst is sufficient to provide the heat needs of the SODS catalyst. A possible layout of the process, and the experimental setup for evaluating SODS and integrated SODS / reforming is given in **Figure 4.3.3-1**.

Figure 4.3.3-1: Selective Oxydesulfurization Experimental Setup

A first series of tests were completed to demonstrate the effectiveness of the vanadia-alumina catalyst. Testing results are presented in **Table 4.3.3-1**. A mixture of fuel and air was passed over the SODS catalyst; the liquid fuel product was then condensed and analyzed for remaining sulfur content. Several sulfur bearing compounds were blended with CARB Phase II gasoline, including thiophene, benzothiophene, and dibenzothiophene, representative of the range of sulfur compounds found in gasoline and diesel fuels.

Table 4.3.3-1: Results of Selective Oxydesulfurization Testing

SODS cat - V205/Al2O3 - cordierite monolith.

410 wppm sulfur, added as thiophene, blended with CARB phase II gasoline.

LHSV	fuel (g/min)	sulfur conversion vs. temperature (°C)	
		200	300
3.18	0.50	46%	76%
6.42	1.01	26%	
12.91	2.03	15%	

Results of testing using different sulfur containing species added to CARB phase II gasoline.

SODS cat - V205/Al2O3 - cordierite monolith, tested at ~ 250 °C.

	feed (wppm)	GHSV		
		~9000	~20,000	~42,000
octanethiol	243	sulfur conversion vs. GHSV (1/hr)		
benzothiophene	610	80%	41%	61%
dibenzothiophene	344	80%	29%	45%

Depending on flow rate and temperature, significant amounts of sulfur were converted to SO₂. Errors may have been introduced into the measurements in that some of the feed gasoline was lost to evaporation, resulting in low mass balance. This loss was accounted for in determination of sulfur conversion. Undoubtedly improvements to the sulfur conversion catalyst and the process can increase the selectivity to SO₂ even higher.

A second series of tests were performed to determine if this process improves the performance of the reforming catalyst. One test used the vanadia-alumina SODS catalyst ahead of the reforming catalyst, the other a blank monolith. The feed consisted of an interval of gasoline, followed by an interval of gasoline containing 500 wppm sulfur, as benzothiophene, again followed by an interval of gasoline. The same reforming catalyst was used in both tests.

The results of this testing are given in **Figure 4.3.3-2** and presented normalized, to take into account catalyst deactivation, in **Figure 4.3.3-3**. These results show that this level of sulfur can influence reforming catalyst performance, as about a 10% loss in H₂ selectivity was found. While marginal, use of the SODS catalyst may have improved the performance of the reforming catalyst for selectivity towards hydrogen production. Further work on this process is on hold, pending evaluation of SO₂ removal strategies.

SODS catalyst // mix foam // RDRCAD-250:CB // heat retainer

CARB phase II

CARB Phase II w/ 500 ppm S as benzothiophene

Figure 4.3.3-2: Results of Selective Oxydesulfurization / Reforming Tests

SODS catalyst // mix foam // RDRCAD-250:CB // heat retainer

CARB phase II

CARB Phase II w/ 500 ppm S as benzothiophene

Figure 4.3.3-3: Results of Selective Oxydesulfurization / Reforming Tests

4.2.13.1 Methane Reforming

Several catalyst products were evaluated for methane partial oxidation, auto-thermal reforming, and steam reforming. This work was conducted to demonstrate that current catalysts are effective for this set of processes, that the gasoline reforming test stands are capable of methane reforming, and to provide guidance for upcoming system-level methane and natural gas reforming. These processes were evaluated in our laboratory on some of our catalysts, using the same test stands employed for gasoline partial oxidation testing. The test stands were modified to permit introduction of methane and water; locations of catalysts and thermocouples are indicated in **Figure 4.3.3-4**. Major parameters investigated include steam to carbon ratio (H_2O/C) and oxygen to carbon ratio (O/C). For simplicity, methane was used as a substitute for natural gas in the experiments.

Figure 4.3.3-4: Natural Gas Reforming - Reactor Setup and Main Thermocouple Location

Three current catalyst products were evaluated for methane partial oxidation. Our standard Rh-based formulation, a Pd-Rh mixed metal composition, and a catalyst stated to be optimized for methane reforming, containing a complex mixture of La, Ni, and Pt on mixed oxide on top of La and Ru on mixed oxide, purchased from BIC, were tested. A summary of flow rates is listed in **Table 4.3.3-1**.

Table 4.3.3-1: Methane Gas-Hourly Space Velocities Employed During Partial Oxidation Studies

CH ₄ Flow SLPM	LHV CH ₄ kW	O/C atom/atom	GHSV hr ⁻¹
2.0	1.10	0.90	29765
		1.00	32036
		1.20	36578
		1.30	38849
3.5	1.94	0.90	52088
		1.00	56063
		1.20	64012
		1.30	67986
4.5	2.51	0.90	66970
		1.00	72081
		1.20	82301
		1.30	87411

The results of the testing can be summarized as follows and are presented in **Figure 4.3.3-5**, **Figure 4.3.3-6**, **Figure 4.3.3-7**, **Figure 4.3.3-8**, and **Figure 4.3.3-9**. While the

catalysts exhibited differences in light-off temperature, no distinct differences in methane conversion were found on these three catalysts. For all of the catalysts, methane conversion increased with increasing O/C ratios. Nearly 100% conversion was achieved at $O/C \geq 1.20$ when $CH_4 = 2.0$ standard liters per minute (slpm, taken at 1 atm. and 0 °C), and at $O/C \geq 1.00$ when $CH_4 = 3.5$ and 4.5 slpm. The hydrogen selectivity was determined to be comparable among the three catalysts at low O/C ratios; due to its simpler formulation use of the Rh only composition is recommended for methane partial oxidation, pending evaluation of more advanced formulations.

$CH_4 = 2.0$ slpm, $O/C = 0.90$, GHSV = 29765 hr^{-1}

Rh: 2%Rh/ATG/ $BaSO_4$ /20 ppi ZTA;

BIC: 11.03 wt% mixed oxide, 4.1% La-Ni-Pt, 0.23% La-Ru, ZTA-2 support;

Pd-Rh: 2%Rh/2%Pd/ATG/ $BaSO_4$ / 20 ppi ZTA

Figure 4.3.3-5: Methane Light-Off Activities Comparison in Partial Oxidation Mode

Rh: 2%Rh/ATG/BaSO₄/20 ppi ZTA;
 BIC: 11.03 wt% mixed oxide, 4.1% La-Ni-Pt, 0.23% La-Ru, ZTA-2 support;
 Pd-Rh: 2%Rh/2%Pd/ATG/BaSO₄/ 20 ppi ZTA

Figure 4.3.3-6: Methane Partial Oxidation - Methane Conversion and Slip

Rh: 2%Rh/ATG/BaSO₄/20 ppi ZTA;
BIC: 11.03 wt% mixed oxide, 4.1% La-Ni-Pt, 0.23% La-Ru, ZTA-2 support;
Pd-Rh: 2%Rh/2%Pd/ATG/BaSO₄/ 20 ppi ZTA

Figure 4.3.3-7: Methane Partial Oxidation - Hydrogen Concentrations

Rh: 2%Rh/ATG/BaSO4/20 ppi ZTA;
 BIC: 11.03 wt% mixed oxide, 4.1% La-Ni-Pt, 0.23% La-Ru, ZTA-2 support;
 Pd-Rh: 2%Rh/2%Pd/ATG/BaSO4/ 20 ppi ZTA

Figure 4.3.3-8: Methane Partial Oxidation - Efficiency, Hydrogen + Carbon Monoxide Yields

Rh: 2%Rh/ATG/BaSO₄/20 ppi ZTA;
BIC: 11.03 wt% mixed oxide, 4.1% La-Ni-Pt, 0.23% La-Ru, ZTA-2 support;
Pd-Rh: 2%Rh/2%Pd/ATG/BaSO₄/ 20 ppi ZTA

Figure 4.3.3-9: Methane Partial Oxidation - Catalyst Center Temperatures

4.2.13.1.1 Processing with Diesel Fuel

Processing studies were conducted using standard test conditions, but employing Swedish City Diesel as the fuel. The results of this testing, using the standard catalyst, RDRCA0-320:CB, corresponding to 2 wt. % Rh on moderate surface area stabilized α -Al₂O₃, loading to 30 g/ft³ Rh on the substrate. The results of systematically varying space velocity and oxygen to carbon ratio are presented in **Figures 4.3.3-10 and 4.3.3-11**.

Selectivity to H₂ decreases slightly with increasing space velocity, while the corresponding selectivity to CH₄ increases slightly. These results are suggestive of a global reaction rate. This is mostly controlled by mass transfer limitations with only a minor kinetics component. There is a significant effect of changing oxygen

ratio on selectivities to H_2 and CH_4 . Maximum H_2 production occurs at an O/C ratio of about 1.10. Below this value, insufficient conversion of hydrocarbons occurs, above this value, excessive O_2 results in increasing amounts of H_2O formation. In contrast, the selectivity to CH_4 continually decreases with increasing O/C ratio. Increasing O/C increases the amounts of reactants available for hydrocarbon conversion and may also increase catalyst temperature due to increased amounts of heat-of-reaction generated, thus increasing conversion of hydrocarbons, reflected in decreasing selectivities to methane.

Figure 4.3.3-10: Space Velocity Sweeps at O/C 0.95, 1.05, 1.15 Swedish Diesel

Figure 4.3.3-11: O/C Sweep at 15,000-75,000/hour Space Velocities - Swedish Diesel

4.2.13.2 Mechanistic Characterization of Reforming Catalysts

Work in this area was focused on demonstrating that commonly used and advanced methods for catalyst research are applicable to fuel reforming catalysts. Additional extensive work was completed on the effects of different sulfur bearing compounds on the partial oxidation of a range of hydrocarbon species. This work will serve as the foundation for characterization aimed at understanding structure – property relationships in reforming catalysts, ultimately leading to an understanding of and the mitigation of catalyst degradation mechanisms.

Several state-of-the art analytical methods were applied to fresh, aged, tested and model rhodium-alumina based partial oxidation catalysts. As a result of these analyses, a picture of the active form of the catalyst is being developed. While preliminary and requiring confirmation, the catalyst appears to contain a bimodal distribution of rhodium. A highly disperse Rh phase, likely a mixture of Rh_2O_3 and rhodium suboxides, exists as 5-10 Å domains, co-existing with well-faceted metallic rhodium particles ranging in size from 5 to 500 Å, depending on the treatment of the catalyst. The metallic rhodium particles may in turn exhibit a bimodal distribution and may also be coated by a surface layer of rhodium oxide.

Evidence also suggests that the rhodium oxide phase is catalytically active and responsible for a significant portion of the observed chemistry. For some samples examined, no evidence for Rh metal could be found, yet the samples exhibited high selectivity towards H_2 formation. Work during the next reporting periods will focus on confirming and exploring this proposed physical nature of partial oxidation reforming catalysts.

4.2.13.3 X-ray Photoelectron Spectroscopy

A series of Rh-only gasoline partial oxidation catalysts were examined by X-ray photoelectron spectroscopy (XPS). This technique can give information about the surface and near-surface environment of the catalyst, within several nanometers of the surface, with a focus on the state of the active metal. Results of this screening are given in **Table 4.3.3-2**.

Table 4.3.3-2: Results of XPS Survey of Reforming Catalysts

No.	Sample Name	Relative concentration of Rh	BE of $\text{Rh}3d_{5/2}$ (eV)	Rh states
1	RDRCA0-250:CB, fresh	3.36	308.5	Rh_2O_3
2	RDRCA0-250:CB, aged	0	305.4, 309.2	Rh, Rh_2O_3
3	RDRCA0-250:CB, tested	2.48	306.5, 310.1	Rh, Rh_2O_3 or RhO_2
4	RDRCA0-300:CY, tested	1.22	307.0*	Rh

* The $\text{Y}_{3P1/2}$ peak may overlap with $\text{Rh}_{3d5/2}$ of Rh_2O_3

XPS can clearly detect rhodium and rhodium oxide species on the catalyst, and distinguish between different oxidation states. Relative concentrations, as a ratio to the alumina response, set to 100 (a value of 3.36 indicated 3.36 atoms observed for every 100 Al atoms), are an indication of the surface concentration of rhodium on the sample. While only limited conclusions can be had from this small set of tests, decreasing amounts of rhodium are observed on aged and tested catalysts, as compared to the fresh, untested, catalyst.

The observation of no observable rhodium on the aged catalyst may imply that the Rh is either lost from the surface or migrated to the bulk of the catalyst during aging; however, similar samples evaluated after aging still exhibit significant reforming performance. In addition, the observation of less observable rhodium in the more active of the two tested catalysts is also interesting. For the next reporting period, we are planning a systematic investigation of tested catalysts, using XPS to determine if this technique provides further information on catalyst behavior.

4.2.13.4 High-Resolution Transmission Electron Microscopy

A series of samples were studied by high-resolution transmission electron microscopy (HRTEM). As for the XPS work, the purpose of this HRTEM study was to determine the applicability of this technique to the analysis of fuel reforming catalysts. Representative micrographs and explanatory texts are given in **Figure 4.3.3-12**, **Figure 4.3.3-13**, **Figure 4.3.3-14**, **Figure 4.3.3-15**, **Figure 4.3.3-16**, and **Figure 4.3.3-17**.

Figure 4.3.3-12: Results of HRTEM Survey of Reforming Catalysts

RDRCA0-250:CB, 1200°C aged for 10 hours

- * As shown in Fig. 1-A, TG particles appear to be bigger in this sample than in sample **RDRCA0-250:CB, fresh**, suggesting TG sintered during the aging process.
- * No Rh particles appeared in either the TEM images or the STEM Z-contrast images, although in some areas weak Rh signals show up in the EDX spectra (Fig. 1-B). These results suggest that most of the Rh was lost during the aging process.

Figure 4.3.3-13: Results of HRTEM Survey of Reforming Catalysts

RDRCA0-250:CB, tested for reforming reaction, low H₂ (18-19%)

- * Fig. 1-A is a low-magnification image in which Rh particles are shown as small black particles (some of them are indicated by arrows) on the sponge. Rh particles appear crystalline and faceted. Particle size ranges from a few nanometer to about 40 nm.
- * High resolution images revealed that the surfaces of the Rh particles are coated. Some of the coatings show graphite (0002) fringes (with a spacing of 0.34 nm). This surface coating is probably the reason that no Rh was detected using a chemisorption method. A typical image is shown in Fig. 1-B where the graphite (0002) fringes are indicated by arrows. It can be seen that graphite also formed on the TG sponge.

Figure 4.3.3-14: Results of HRTEM Survey of Reforming Catalysts

RDRCA0-300:CL, 20-21% H₂

- * Fig. 1-A and B are low- and high-magnification images, respectively from this sample. Compared with sample RDRCA0-250:CB, tested for reforming reaction, low H₂ (18-19%), sponge particles in this sample are smaller, more crystalline and more faceted.
- * Rh particles have sizes less than 10 nm in diameter. However, Rh particle density is lower than sample RDRCA0-250:CB, tested for reforming reaction, low H₂ (18-19%). Some of the Rh particles are indicated by arrows in Fig. 1-A. These results suggest that La hinders the Rh and TG sintering process.

Figure 4.3.3-15: Results of HRTEM Survey of Reforming Catalysts

RDRCA0-320:CB, standard prep tested fresh

- * Fig. 1-A is a low-magnification STEM Z-contrast image where Rh appears as white particles. Some of them are indicated with arrows. It shows that Rh particles have a bimodal size distribution depending on their location. In most of the areas the Rh particles are less than 10 nm in diameter, but in some areas their size can range from 20 to 100 nm. A particle with 260 nm in diameter was observed. High-resolution images (Fig. 1-B) show that there is an amorphous layer formed on the Rh particles. Fig. 1-C shows a typical EDX spectrum confirming that the Pd is Rh. Cu is from the sample supporting grid.

Figure 4.3.3-16: Results of HRTEM Survey of Reforming Catalysts

RDRCA0-320:CB, standard prep tested aged

* Most of the Rh particles are less than 15 nm in diameter, but a particle with 21 nm in diameter was observed. Fig. 1-A is a STEM Z-contrast image in which Rh particles appear with white contrast. These metal particles are crystalline and faceted. However, in one area, STEM Z-contrast image (Fig. 1-B) showed Rh atomic clusters (less than 1 nm in size, some of them are indicated by arrows), it is not certain if this result is representative. Generally speaking, TG particles in this sample were bigger than in the sample RDRCA0-320:CB, standard prep tested fresh.

Figure 4.3.3-17: Results of HRTEM Survey of Reforming Catalysts

Depending on sample pretreatment and testing history, a range of rhodium particle morphologies was observed. This includes well-faceted crystallites ranging in size from 5 to 100+ nm. In addition, the crystalline state of the washcoat, and the presence of graphitic carbon were also observed. The results qualitatively confirm the XPS observations; similarly, we are planning to conduct a more systematic survey of reforming catalyst to determine the usefulness of HRTEM and related nano-analysis and Z-contrast imaging techniques. The ability to directly observe rhodium, and other crystallized or high contrast species, will most likely be invaluable in understanding these catalysts.

A summary of samples analyzed by bright-field and Z-contrast high-resolution transmission electron microscopy is listed in **Table 4.3.3-3**. All of the catalysts tested were formulated with washcoat RDRCA0-320:CB, corresponding to 2 wt. % Rh on moderate surface area stabilized α -Al₂O₃, loading to 30 g/ft³ Rh on the substrate. Catalysts were tested by the standard methods, using partial oxidation of California Air Resources Board Phase II gasoline. For those catalysts that were tested, samples for TEM were obtained by removing a small portion in the front-face, inlet, region of the catalyst. Also listed in **Table 4.3.3-3** is a summary of CO chemisorption results for the same set of catalysts. The combination of CO chemisorption data and direct observation of the catalyst samples by transmission electron microscopy help to confirm and extend the '*operando*' laser Raman results.

Table 4.3.3-3: Summary of HRTEM Imaging and Related Testing Observations

ID	state treatment		time (min)	H ₂ (%)	CO (%)	CH ₄ (%)	C ₂ s (%)	T (°C)	Rh dispersion (CO chemisorption)	TEM observations
8645-186-2	fresh	air, 570 °C							73.1%	no observable Rh by Z-contrast or bright field lattice imaging
8637-99-6	fresh	air, 570 °C	60	22.1	23.5	0.72	0.08	994	16.0%	many 5-10 nm particles
8645-187-7	fresh	air, 570 °C	600	22.0	23.5	0.77	0.08	1035	0.0%	very sparse 50-200 nm particles, evidence of highly disperse 10-20 nm patches by Z-contrast
8645-187-8	fresh	air, 570 °C	2650	19.2	22.5	2.26	0.14	1078	0.0%	very sparse 50 nm particles, evidence of highly disperse 1-10 nm patches by Z-contrast
8645-186-1	aged	air, 1200 °C							5.0%	no distinct Rh particles
8645-187-5	aged	air, 1200 °C	1017	20.1	22.9	1.65	0.31	1049	0.1%	small 1-5 nm particles and patches

4.2.13.5 Laser-Raman Spectroscopy

Laser-Raman spectroscopy (LRS) is a technique that permits detection of chemical species containing certain classes of atom-atom bonding. For example, most platinum group elements metal to oxygen bonds can be observed, as can surface species such as adsorbed CO, CO₂, H₂, and H₂O. Consequently, this technique can be applicable to characterizing reforming catalysts under ex-situ, in-situ, and operando conditions.

An example of results, obtained under ex-situ conditions, is given in **Figure 4.3.3-18**, **Figure 4.3.3-19**, and **Figure 4.3.3-20**. No interference, other than that arising from sample fluorescence, indicating by the rising background in **Figure 4.3.3-18**, was observed from LRS of the alumina support, as aluminum oxides are not Raman active. A signal arising from rhodium-oxygen bonding is clearly observable on two different catalyst products in **Figure 4.3.3-18** and **Figure 4.3.3-19**.

Ambient UV-Raman Spectroscopy of alumina-TS

- A. as received
- B. after 500 °C calcination

The UV-Raman spectra of the ATS alumina only gave rise to noise due to sample fluorescence. This is quite surprising since UV excitation should minimize this problem and is the first sample that we have encountered this situation.

Figure 4.3.3-18: Results of Laser Raman Spectroscopy Survey of Catalysts

The 2% Rh/RS gave rise to a strong UV-Raman band at $\sim 540 \text{ cm}^{-1}$, which shifted to $\sim 550 \text{ cm}^{-1}$ upon calcinations at 500 °C. The strong Raman bands at $540\text{-}550 \text{ cm}^{-1}$ are due to Rh-oxide on alumina. At the present time, these small shifts are not understood and will require *in situ* Raman studies to better understand their origins.

Figure 4.3.3-19: Results of Laser Raman Spectroscopy Survey of Catalysts

The 2% Rh/ATS UV-Raman spectrum gave rise to many vibrations between $300\text{-}1200 \text{ cm}^{-1}$, which indicates that the ATS alumina fluorescence is not present when Rh is deposited on ATS. After calcinations at 500 °C, The Rh-O main vibration at $\sim 510 \text{ cm}^{-1}$ became much stronger. This is the first time that the Raman spectrum of Rh-oxide on alumina has been obtained since none are reported in the literature.

Figure 4.3.3-20: Results of Laser Raman Spectroscopy Survey of Catalysts

4.2.13.6 Impact of Sulfur on Reforming Catalyst Performance

Of significant concern was the effects of fuel-borne sulfur on reforming catalyst performance, particularly for processing of heavy diesel fuel, which is perceived to contain highly refractory and consequently difficult to process sulfur containing molecular species. Delphi completed a series of experiments in which hydrocarbon feedstocks were blended with up to 100 ppm of either SO₂ or thiophene, and then processed for partial oxidation reforming using a rhodium-based alumina supported catalyst.

Figure 4.3.3-21 and Figure 4.3.3-22 illustrates the effects of thiophene on the reforming of iso-octane using two different rhodium based catalysts. Similar behavior was observed on both. Selectivity decreases with increasing levels of thiophene, with hydrogen bearing species, H₂, H₂O, and CH₄, exhibiting the largest impacts. In contrast, the selectivity to CO and CO₂ is not impacted nearly as much.

Catalyst code: RDRCA0-250:CB, tested as received

Testing with iso-octane, ~50,000/hr GHSV, O/C ~ 1.01 (mol/mol), analysis by mass spectroscopy.a

Figure 4.3.3-21: Influence of Thiophene on Iso-Octane Reforming Performance

Catalyst code: RDRCA0-300:CB, tested as received
Testing with iso-octane, ~50,000/hr GHSV, O/C ~ 1.01 (mol/mol), analysis by MS.

Figure 4.3.3-22: Influence of Thiophene on Iso-Octane Reforming, Improved Catalyst

4.3 Task 4: BOP Component Development

4.3.1 Air Delivery and Process Air Subsystem

The investigative test for studying the effects of the type and location of various flow straighteners on mass flow sensor noise was based on the test set-up in **Figure 4.4.1-1**. Also shown is the flow straightening devices in **Figures 4.4.1-2 through 4.4.1-4**.

Figure 4.4.1-1: Flow Conditioner Position in Relation to Pintle

Figure 4.4.1-2: Machined Straightener

Figure 4.4.1-3: Honeycell in Pintle Seat

Figure 4.4.1-4: Honeycell in Mass Air Flow Sensor

Figure 4.4.1-5 and Figure 4.4.1-6 show a side-by-side comparison of the Delphi impeller with the original impeller design. Notice the swept shape of the Delphi impeller, and the change in vane width over length. These improvements will lead to increased impeller efficiencies.

Figure 4.4.1-5: Original Process Air Impeller

Figure 4.4.1-6: Redesigned Impeller Swept and Splitter Vanes

4.3.1.1 Gaskets

For stack gaskets, newly ground fixtures with more precisely controlled sealing surfaces demonstrated significant improvement in gasket sealability. This improvement is directly applicable to any of the other gasketed components for a similar gain. Flourophlogopite mica gaskets in particular have reacted well to the new sealing conditions. Previously discounted due to excessive leakage in the system, the increased performance of mica due to improved sealing surface finish warrants it further evaluation. Though minimal potential exists for improving the mica gasket itself, gains can still be made by increasing the number of bolts as demonstrated with the heat exchanger and reformer gaskets.

Figure 4.4.1-7: Typical Raised Bead for Increased Seating Pressure

Figure 4.4.1-8: Typical Reformer Gasket Using the Raised Bead Approach

4.3.2 Integrated Component Module

Below are pictures of ICM 6 showing details of internal geometry. The complex machining required for gas routings, make this an important component in the system.

Figure 4.4.2-1: ICM as Viewed from Bottom with Bottom Plate Removed

Figure 4.4.2-2: ICM with Top Plate Removed

ICM 6 as viewed from top,
looking at top plate; with cut-
outs for Anode Oxidation
abatement approach

Cut-outs allowing for
access

Figure 4.4.2-3: Cut for Anode Oxidation Prevention

4.3.3 Anode Oxidation Abatement (Via Oxygen Getters)

The anode of the solid oxide fuel cell (SOFC) is composed of nickel oxide (NiO) and yttria stabilized zirconia (YSZ). During operation of the fuel cell, the NiO of the anode is reduced to nickel (Ni). When the SOFC is turned off and the stack is cooled from 800 °C to room temperature, the anode is susceptible to re-oxidation of the Ni to NiO, until the temperature of the fuel cell is below 450 °C. Ni is a face-centered cubic (FCC) crystalline structure with a unit cell volume of 43.76 Å³ while NiO has an FCC crystalline structure with a unit cell volume of 72.87 Å³. The volume change, associated with the phase change from Ni to NiO, creates stresses in the anode. These stresses can lead to cracking of the anode and failure of the fuel cell. One way to prevent anode re-oxidation is to keep the anode of the fuel cell from coming into contact with oxygen at high temperature. Delphi's approach for anode re-oxidation is to add nickel, metal foam, filters in the anode inlets and outlets of the SOFC stack. These filters act as getters to the oxygen in the air that is drawn into the system during cooling due to volume changes caused by the temperature decrease. The Ni metal will oxidize and bind the oxygen. When the system is restarted, fuel flowing through the anode channels will reduce the oxide layer on the nickel filter. Typical, oxygen getter, materials used in industry such as titanium, aluminum and zirconium will oxidize and remove the oxygen. However, these materials will not reduce back to metal during normal SOFC operation. These getter materials will be usable for only a short time. In addition, if some of the nickel, metal, foam spalls and the particles travel into the stack they will not poison the stack anode. For these reasons nickel was chosen. The metal foam was chosen to provide a large surface area. However, this Ni filter solution to the anode re-oxidation problem will not allow large amounts of air to be driven into the system. A catastrophic backpressure to the system at high temperature will destroy the oxygen getter filters and the SOFC stack.

Experimental Approach:

The nickel filters were tested to evaluate the viability of the solution to the system. A piece of reduced, fuel cell, anode was weighed and placed in a metal tube. Nitrogen (N₂) was flowed through the tube while it was heated from room temperature to 500 °C. The flowing N₂ was then changed to flowing N₂ with 10% hydrogen (H₂) and heated to 800 °C. At 800°C, the flowing N₂ + H₂ was changed to a calibration gas with a composition of 20.93% H₂, 22.96% carbon monoxide, 1.74% methane, 1.90% carbon dioxide, 0.700% argon and the balance N₂. The calibration gas was flowed for 30 minutes at 800 °C. The flowing gases were then shut-off and the tube was ramped down to room temperature using the following schedule.

- From 800 °C to 700 °C in 15 minutes
- From 700 °C to 600 °C in 2.75 hours
- From 600 °C to 500 °C in 4.75 hours

The fuel cell sample was weighed and examined under a microscope.

Results:

The sample lost weight due to the reduction of the cathode layer, which was also exposed to the low pO_2 atmospheres. No cracking of the anode was observed using a scanning electron microscope (SEM). This experiment was repeated. The second attempt was performed with a reduced anode/electrolyte bilayer. This anode showed no cracking and no weight change was detected. A control anode-bilayer test performed in which a reduced bilayer was placed in a heated metal tube without the oxygen getter filters. When the anode was examined using SEM, it exhibited the signs of cracking. However, the weight change was indeterminate. These tests indicated that the idea is worth testing further and more rigorously. Another test was planned in which the actual ICM hardware would be used. The oxygen getter filters would be exposed to a more rigorous testing procedure that will determine in which situations the filters act to protect the stack and in which situations the filters do not. This more rigorous experiment has not yet been carried out.

Figure 4.4.3-1 through 4.4.3-4 shows the multi step process for applying the thermal barrier coating , 8YSZ (Yttrium Stabilized Zirconium) .

Figure 4.4.3-1: Applied Ceramic Coating / ICM Number 6

Figure 4.4.3-2: Applied Ceramic Coating Internal / ICM Number 6

Figure 4.4.3-3: Thermal Barrier Coating; Top Plate

Figure 4.4.3-4: Applied Ceramic Coating to Top Plate / ICM Number 6

4.3.4 Cathode Heat Exchanges

Figure 4.4.4-1 shows the heat exchanger test results for the designs tested to date. The flat plate fin tall shows the best effectiveness; however moving towards a smaller package size (for example short fin) design is more desirable. Delphi Thermal Group formerly Harrison has joined the heat exchanger development activity, bringing their braze and thermal management expertise to the program. A second short fin heat exchanger design has since been manufactured by Delphi Thermal Group and is awaiting testing. **Figure 4.4.4-2** shows the flat fin design with fins turned to improve the turn down ratio.

	# pieces	Ratio to base CHX	air passes	Height (mm)	Effectiveness	Ratio to base CHX	Pressure drop -Exhaust (KPa)	Ratio to base CHX	Pressure drop -air (KPa)	Ratio to base CHX	Weight (kg)	Weight Ratio (kg)	Braze cycles
Description													
Typical Flat Plate CHE	104	100%	2/1	85	0.68	1.00	4.2	1	3	1	2.2	1	1
Typical Dimpled Plate CHE	104	100%	2/1	85	0.68	1.00	4.2	1	3	1	2.2	1	1
Tube/Shell	27	26%	4/1	80	0.72	1.06	4.4	1.05	4	1.33	1.5	0.68	2
Tube/Shell Thick Manifold	47	45%	2/1	110	0.57	0.84	8.6	2.05	3.7	1.23	1.5	0.68	2
Tube/Shell w/ turbulators	67	64%	2/1	110	0.55	0.81	4.8	1.14	4	1.33	1.5	0.68	2
Fin Plate - Tall	168	162%	2/1	106	0.73	1.07	4.4	1.05	3.5	1.17	2.4	1.09	1
Fin Plate - Short	88	85%	2/1	90	0.70	1.03	4.61	1.1	3.42	1.14	2	0.91	1

Figure 4.4.4-1: Cathode Heat Exchanger Test Summary

Figure 4.4.4-2: Flat Finned Heat Exchanger Close-Up with Fins Turned 180 Degrees

Figure 4.4.4-3 shows one of the restrictions added to exit flow to improve turn down ratio.

Figure 4.4.4-3: Exit Airflow Restriction

4.3.4.1 Igniters

Figure 4.4.4-4 shows the prototype igniters with design improvements for high temperature materials, higher braze material at connector interface, and closed end ceramic. These design improvements should significantly improve igniter reliability and will be tested going forward.

Figure 4.4.4-4: Higher Temperature Igniters with Closed End Design

4.3.5 Combustible Gas Sensor

Development activity on the gas sensor involved further characterization of the sensor's response to Hydrogen and investigating alternative sensor controller strategies. Additionally, packaging studies carried out at the system level, highlighted a need for not only reducing the overall size of the sensor itself, but more importantly, the controller box. The sensor was characterized using hydrogen from 0 to 45,000 ppm, as the test gas. Shop air was used to purge the test enclosure.

Figure 4.4.5-1 shows the relationship between hydrogen concentration and sensor output voltage.

Figure 4.4.5-1 Combustible Gas Sensor Calibration

Figure 4.4.5-2 shows an oscilloscope trace plot of the sensor output signal. At 2.78 volts, the noise in the sensor signal as indicated from the oscilloscope is ± 120 mV. Although the sensor detects concentrations of 0 to 45,000 ppm of hydrogen, the noise of ± 120 mV on the signal is greater than the entire operating range of the sensor, 2.700 to 2.8066 volts or 110 mV. This means that the sensor could falsely indicate due to noise and as currently calibrated does not have adequate sensitivity.

Figure 4.4.5-2 Gas Sensor Signal Trace

4.3.6 Develop Air Delivery and Process Air Sub-System

4.3.6.1 Process Air Blower Motor

The Delphi Process Air Module Blower Motor is a two-pole, three-phase AC Induction Motor capable of 94.1 N-mm at a maximum speed of 68,000 RPM. The motor in combination with the compressor is capable of providing 18g/s at 68,000 RPM with 45.0°C inlet air. The machine controller utilizes sinusoidal waveform reproduction, V/Hz controls (Open Loop). The system efficiency (motor and controller) is 82% at 65,000 RPM and 100% Auxiliary Power Unit power. **Figure 4.4.6-1** shows the Delphi designed Process Air Module motor.

Figure 4.4.6-1: Delphi Process Air Motor

Significant analysis was performed to determine the optimal machine and controller technology for this application. Variations of Permanent Magnet and Induction Machine technologies were evaluated to determine the best fit for the application. The following machine and control technologies were evaluated: Induction Machine Sine, Permanent Magnet Square Wave, Permanent Magnet Sine Wave, and Permanent Magnet Six Step. System efficiency was determined at various speeds, inlet air temperatures, and Auxiliary Power Unit power levels for each of the technologies mentioned, to be used for the technology down select. Analytical tools SPEED PC-BDC[®] software and ANSOFT[®] Software were used for permanent magnet technology evaluation. Custom Delphi software, which includes statistical machine optimization capability, was used for induction machine technology evaluation.

Thermal analysis was performed using ANSYS[®] on both the motor and controller to verify satisfactory operating temperatures. Analysis was performed using 30 cfm at 45 °C inlet air condition and 85 °C ambient.

Structural Finite Element Analysis was performed on several motor components using ANSYS[®] to verify structural and material design decisions. The following components were analyzed: Rotor Core and End Ring structural analysis, rotor shaft to core interference fit analysis, motor housing structural analysis, complete rotor dynamic analysis with critical speed identification, and various additional analyses on component interfaces.

Induction machine and permanent magnet six-step technologies were found to be the best selections for the current Auxiliary Power Unit application based on efficiency,

technical risk, fabrication, and projected cost. Induction machine technology was ultimately chosen due to high efficiency across the entire operating speed range, even though it is slightly less efficient than Permanent Magnet at higher speed. **Figure 4.4.6-2** shows machine speed vs. efficiency for the above mentioned machine technologies.

Figure 4.4.6-2: Machine Speed vs. Efficiency

Thermal analysis revealed that both motor and controller temperature profiles would be within the limits of component materials and sub-assembly operating capability. **Figure 4.4.6-3** shows results of motor thermal analysis and **Figure 4.4.6-4** shows results of controller thermal analysis.

Figure 4.4.6-3: Motor Thermal Analysis

Figure 4.4.6-4: Controller Thermal Analysis

Finite element analysis yielded satisfactory results in all areas. The components and interfaces that were analyzed included the rotor core and end-ring structural analysis, rotor shaft to core interference fit analysis, motor housing structural analysis, rotor dynamic analysis with critical speed identification, bearing sleeve to housing interface, and various additional analyses on component interfaces.

4.3.6.2 Process Air Manifold

The Delphi Process Air Module, shown in **Figure 4.4.6-5**, was redesigned to improve performance and reliability while enhancing manufacturability. A major objective of the design team was to develop an integrated package that readily mounts to the Auxiliary Power Unit assembly using a minimum number of electrical and mechanical connections. The Process Air Module utilizes ambient air and provides four variable, measured output airflows to supply the combustor, cathode, reformer, and cathode bypass and is comprised of four subassemblies; inlet shroud and filter, manifold, motor and impeller, and motor controller.

Figure 4.4.6-5 Delphi Process Air Module

The manifold assembly, shown in **Figure 4.4.6-6**, provides the inlet and outlet scroll air passages for the impeller and includes an air control valve and a mass airflow sensor for each of the four air outlets. The manifold assembly also provides the mounting structure for the motor, motor controller, and inlet air shroud. EFD[®] lab computational fluid dynamics software, supplied by Nika Fluid Solutions, is being used to assess the behavior of the manifold assembly. A test manifold (**Figure 4.4.6-7**) was fabricated from high strength, high temperature stable material using a stereo-lithography process so that the air control valves can be integrated and tested on a flow bench to determine their performance characteristics.

Figure 4.4.6-6 Manifold Assembly

Figure 4.4.6-7 Test Manifold

4.3.7 Hot Zone Components

4.3.7.1 Gasket

Delphi tested multiple variations of metal gaskets, including flat stock metal gaskets, chemically etched metal gaskets and water-jet flat stock metal gaskets. Mechanically processed flat stock tended to leave a jagged burr on the exit side. Attempts to remove this slight burr resulted in either machining scratches on the sealing area or in incomplete burr removal. Adding an over-plate to the gasket only enhanced the surface scratches or the burr. The metal gaskets also tended to leak along long edges of a joint due to the reduced compressive force in those areas. Increasing the number of bolts slightly increased the sealing of the gaskets, and required component design changes.

As previously reported, die cut F-mica gaskets generally advanced sealing capability. Die cut F-mica gaskets were designed, fabricated and tested as component interface seals between the Reformer, Stack and Cathode Heat Exchangers to the Integrated Component Manifold. Reviewing the manufacturing process of 1 mm thick mica gasket cut with a steel rule die showed that the material was de-laminating, and that some would break apart with handling. Process changes resulted in eliminating the de-lamination and part breakage and significantly advanced the sealing capability of F-mica gaskets.

A new component gasket was also developed during this reporting period. In the Integrated Component Manifold design configuration number 9 (refer to section 4.4.3.2 Integrated Component Manifold), a new insertable Gas Phase Combustor was introduced. An additional seal was required to seal the Gas Phase Combustor to the Integrated Component Manifold. Discussions with vendors lead to the selection of an internal pressure metal “C” –Ring gasket. The sealing concept of the metal “C”-Ring is based on elastic deformation of a metal “C” substrate that gives a contact point on each sealing surface. The base metal was plated with a deformable plating to increase the seal. The metal “C”-Ring was placed into a machined groove that restricted lateral movement of the ring when axial pressure was applied. The depth of the groove was maintained so as to not allow the Combustor base and mating surface to bottom out as the “C”-Ring was compressed. The “C” of the ring is open to the side of higher pressure so that the high pressure actually helps maintain the seal.

Figure 4.4.7-1 illustrates the “C”-Ring gasket design. Testing to date has shown adequate sealing of the Combustor to the Integrated Component Module with this gasket technology.

Figure 4.4.7-1: “C”- Ring Gasket

Figure 4.4.7-2 and **Figure 4.4.7-3** are examples of the die cut F-mica gaskets. Sometimes parts would break upon removal from the die. Others would break apart during handling. Gaskets that didn't break apart all had some amount of de-lamination on the edge.

Rib areas breaking off due to weakening from pinching by die cut operation

Figure 4.4.7-2 Die-Cut Gasket

"Wrinkled" part that has broke off during post stamping handling

Figure 4.4.7-3 Die-Cut Gasket, Close-up

4.3.8 Re-Cycle Pump

In order to increase overall net system efficiency of the Auxiliary Power Unit, a strategy that involved taking a portion of the anode tail gas from the stacks and re-cycling it back into the reformer was developed. A system mechanization for the approach has been developed. Analysis and optimization of re-cycle parameters is currently in process by the system team. Balance of Plant efforts on Re-cycle during this reporting period included writing component specifications, conducting a technology down-select and selecting the supplier. Prototype pumps were ordered and received. Initial testing confirmed significant pump capacity. Future issues to be addressed with the Re-cycle pump involve packaging studies and possible pump re-design for improved thermal robustness. **Figure 4.4.8-1** shows the prototype Re-cycle pump.

G_100 - 280 W

max. 180 mbar

max. 34 m³/h

48 VDC, 58 dB (A)

Figure 4.4.8-1 Re-cycle Pump

The pump evaluated during this period was a Nash-Elmo 280W regenerative side-channel compressor. The balance of plant process air lab is currently limited to testing components with air as the test gas only. A standard test with air allows for pump-to-pump comparisons and provides an indication of generalized performance characteristics. It is within the capability of the lab to supply the pump with heated and variable downstream resistance to flow. This permits fairly detailed mapping of the performance of the pump over a range of speeds, inlet temperature, differential pressures from inlet to inlet, and power consumption levels.

A full-range characterization of the pump is shown below in **Figure 4.4.8-2**, for an inlet of 23 °C air.

Figure 4.4.8-2 Re-Cycle Pump Performance

Higher temperature testing of the pump is currently in process. Thus far, the pump has demonstrated its ability to withstand temperature excursions in excess of 120 °C. Flow versus power decreases as is expected at higher temperatures; however, the pump remains more than capable of maintaining required flow. Alternative pumps are also being acquired for evaluation.

4.4 Task 5: Manufacturing Development (Privately Funded)

Results to date have indicated that functioning Solid Oxide Fuel Cell components could be built using prototype processes. The quantities required are small enough that volume throughput is rarely an issue. The welding processes for the reformer are successful as are the brazing processes. Stack component processes have been improved to where the yields are sufficient, but long-term costs are an issue. Glass dispensing has made much improvement in this area in the quality and throughput of the stack assembly process. The area still needing much work is stack component fabrication. The tape casting process through the flattening and noble metal deposition are areas where improvement is not only necessary but also very attractive. Because there are so many of these pieces used in every system, cost and throughput improvements multiply the effect.

The cost study of the system coupled with Crystal Ball[™] analysis software will point to areas to focus for improvement. Because the probability is part of the analysis, varying degrees of success can be examined and decisions can be made from that analysis.

Details for manufacturing development activities are reported on within subcomponents of the solid oxide fuel cell system.

4.5 Task 6: System Fabrication

During this reporting period, the system fabrication activities began with the final assembly for operation of the last Gen 2A systems. A review and assessment of that Gen 2A design followed to provide the system design and integration activities further feedback. Preparation of the Gen 2B based system modules for development and testing concluded the report period.

Figure 4.6-1: Design of Gen 2B SOFC APU Assembly

4.5.1 Generation 2A System Fabrication Assessment

An analysis of the system to date was completed. Assessment of assembly and fabrication issues of the modules was completed along with mass and volume measurements. These established some of the design goals of the future generations of system components and modules. This data and budget will be the basis for several significant Gen 3 design decisions in the second reporting period of 2003.

Figure 4.6.1-1: Gen 2B APU Modular Assembly

4.5.2 Hot Zone Module Fabrication and Assembly

The Hot Zone Module assembly approach maintained an increased level of measurement ports for additional data collection during system tests. As the core module of the product, a majority of the testing is done with this hardware. Fabrication and assembly of the insulation systems was compromised at times for this access. Better fitting and developed insulation solutions were accomplished in final product assembly efforts. Sample ports, repairs, and modifications were added during initial brazing and build. Additional work was done using a manual TIG welding process.

The Hot Zone Module assembly was built with new temperature sensors, a revised tubular reformer, revised stack electrodes, revised gas connection tubes (input side) and additional fasteners used to secure and seal the fuel cell stack module to the integrated component manifold within the base of the Hot Zone Module. The insulation package for the Hot Zone Module was unchanged except for altered access points in the front to allow for Plant Support Module connections and better insulation fitment around these penetrations.

4.5.3 Plant Support Module Fabrication and Assembly

The Plant Support Module assembly approach (including the system space frame) was to assemble and complete fabrication of the bracketry and wiring not completed in the basic solid modeling / CAD used to layout the components. Changes would be necessary for the application interface module and the functions that it would undertake for the product. When complete, this module would receive the Hot Zone Module for close-coupled testing. An additional test cart for the system for airflow delivery and control was developed and fabricated to allow simple reconfigurations of system flows. This approach allows more precise measurement and fast implementation of air metering concepts (both hardware and software driven).

The Plant Support Module assembly (including the system space frame) underwent a layout change to utilize a new process air delivery system. The space frame redesign allows for easier assembly and development access to hardware within the product assembly. The system module now has easier air connections and clamping surfaces. The system wiring harness has been improved to higher temperature insulations and a power and ground distribution bus. This module has also had the electronics moved out to a new third module called the application interface module.

4.5.4 Application Interface Module Fabrication and Assembly

The Application Interface Module (**Figure 4.6.4-1** and **Figure 4.6.4-2**) assembly approach focused on fabricating a compact interface that combined all the inputs and outputs to the system (except for system exhaust). The housing for this needs to be low in mass and volume. The air filter housing and the electronics hardware dominate the interface module fabrication. This approach will also allow concurrent development of

this module and ultimately allow the adaptation to new markets without large disruption to the other modules.

Figure 4.6.4-1: Application Interface Module

The Application Interface Module assembly brings several improvements to the preparation and adaptability of the fuel cell system. Assembly now allows the air filtration filter and sound attenuator, input/output signals and fluid connections, electric power conditioner and the system controller to be pre-built before inclusion to the product. This approach will also allow concurrent development of this module and allow adaptation to new markets without large disruption to the other modules.

Figure 4.6.4-2: Complete APU Assembly

4.5.5 Product Enclosure Fabrication and Assembly

The housing for the system had no change in approach in this period except for the new coordination of the application interface module. The main internal modules (Hot Zone Module and plant support module) are assembled and installed in a vertically oriented

manner. The outer enclosure fabrication did not address additional environmental and safety issues in this period

No major changes occurred to the overall system assembly process. The main internal modules (Hot Zone Module and plant support module) will be assembled and installed into an outer enclosure that provides a structurally safe and sealed housing for the product. The new application interface module is now fastened to form one of the outer walls of the product.

4.5.6 Transportation Auxiliary Power Unit System Fabrication

During the period covered by this technical report, the following systems were fabricated and tested:

- Generation 2B Close-Coupled System
- Generation 2B Auxiliary Power Unit
- Generation 2C Close-Coupled System

The fabrication of the Generation 2B Auxiliary Power Unit is shown in **Figure 4.6.6-1**. The design differences between the Generation 2B and Generation 2C system consist of the SOFC stack and associated Integrated Component Manifold. This hardware is located within the Hot Zone Module. Therefore, the system images presented in **Figure 4.6.6-1**, **Figure 4.6.6-2**, and **Figure 4.6.6-3** are representative and typical for system hardware fabricated during the period covered by this report.

**Figure 4.6.6-1: Transportation SOFC Auxiliary Power Unit –
Generation 2B System Hardware**

Figure 4.6.6-2: Transportation SOFC Auxiliary Power Unit - System Test Stand

Figure 4.6.6-3: Transportation SOFC Auxiliary Power Unit - System Test Stand 2

4.6 Task 7: System Testing

The development testing in 2003 focused on the following system issues:

Auxiliary Power Unit Thermal Issues:

High internal Auxiliary Power Unit temperatures:

- Large heat leakage from Hot Zone to Plant Support Zone (cool) due to the following:
 - Increased number of sensor pass-throughs and access vias
 - Reduced insulation thickness near front of Integrated Control Module in burner area
 - Large opening for reformer pass-through with lower-grade insulation
 - Potential exhaust gas leakage from Hot Zone resulting in high-energy transfer to Plant Support Zone
 - High internal controller temperatures Electronic Control Unit due to the above. Supplemental air-cooling (external) required

Reliability:

Thermal cycle durability:

- High-temperature interfaces have low-cycle durability (<5)
 - Cathode air heat exchanger durability limited due to high-burner temperature gradients / material compatibility
 - Generation 2 Stacks have very limited durability in System (1 cycle)

Small Turn-Down Ratio:

Left to right burner temperature imbalance and large temperature gradients in burner exhaust path limit ability to turn-down fuel flow rates.

- High reformer air/fuel mix zone temperatures result in propensity for air/fuel fixture to pre-ignite (burn-back) at lower fuel flows
 - Cathode air-heat exchangers experience degradation in effectiveness at lower mass-flows due to non-uniform vertical flow distribution (reduced utilized heat transfer area)

Electronic Controller Unit Deployment to System:

Replacement of commercial controller with product intent controller.

Integrate SOFC Stacks Into System Function:

Most of the development testing at the system level is performed with thermally representative, non-functioning stacks ("thermal stacks").

- When SOFC stacks are available, attempts are made to integrate them into the system and evaluate the resulting performance of the integrated system.

5 System Cycles with E/C Stack: Incomplete

Auxiliary Power Unit completed 3 contiguous cycles with E/C stack (Integrated Stack Module #25) from 9/30 – 10/2.

First Cycle: 660 W gross stack output, 186 W net (42 V loads only) During stack warm-up, reformer experienced air/fuel burn-back at low fueling rate. Test resumed and completed with supplemental cooling fans and without enclosure lid.

Second and Third Cycle: Completed test entirely within enclosure and with minor manual control adjustments to O:C to manage cat temp. Stack temperatures out-of-control due to combustion of reformat in the stack tail gas.

Second Cycle: 405 W gross stack output

Third Cycle: 237 W gross stack output

All tests had combustion of reformat evident in stack tail gas due to leaks. After the third thermal cycle, testing was halted, and the stack returned to the stack laboratory for analysis.

Deploy ECU / Auxiliary Power Unit08: Complete

Several weeks of Auxiliary Power Unit tests completed to date with Electronic Control Unit and Auxiliary Power Unit 08 software.

Build and Test a Generation 2C Auxiliary Power Unit: Incomplete

During December 2003, 7 tests were conducted on System Stand I with Generation 2C system hardware to debug new system hardware and calibrate the system for Generation 3 stacks.

A summary of the development effort during the tests shown in **Figure 4.7-1** is given in **Figure 4.7-2**. From the figure it can be seen that the main focus of Stand I activity during the period was work directed toward resolving system left-to-right burner temperature/system temperature imbalance. The second major topic of development effort was software development and calibration. Electro-chemical SOFC stack testing occupied a relatively small fraction of the effort (13% of the test time, but only 8% of the tests).

Figure 4.7-1: Transportation SOFC Auxiliary Power Unit – System Test Effort (July-Dec 2003)

Figure 4.7-2: Transportation SOFC Auxiliary Power Unit – System Development Effort (July-Dec 2003)

For Auxiliary Power Unit testing, the thermal management of the Plant Support Module, as well as reformer control development to resolve turn-down/thermal issues, occupied approximately half of the effort. Like the Stand I activity, electro-chemical SOFC stack testing occupied a relatively small amount of the development effort.

During the period covered by this technical report, 9 SOFC stacks (2 x 15 cell) were tested in the system laboratory in both close-coupled and Auxiliary Power Unit systems. A summary of the results is given in **Table 4.7-1**. While limited success was achieved with Generation 2 SOFC stacks in the system, very promising results were shown with the first and only test to date of Generation 3.0 stacks in the system laboratory.

Table 4.7-1: Transportation SOFC Auxiliary Power Unit –System Test Summary Electro-Chemical Stack

Stack Model	Stack Serial Number	Number of Series Cells	Test Date	Test Location	Test Duration	Status / Comments:
Gen 2	17	30	6/23/2003	Gen 2B System Stand 1	System start-up to shutdown was 50 min	Stack open-circuit voltage rose to 28.8 V @ 600°C, however an apparent internal leak forced a shutdown of the test prior to reaching stack operating temperature.
Gen 2	19	30	7/3/2003	Gen 2B System Stand 1		
Gen 2	20	30	7/31/2003	Gen 2B System Stand 1		
Gen 2	21	30	-----	Stack Test Lab		
Gen 2	22	30	9/16/2003	Gen 2B System Stand 1	System Start-up to Shutdown was 7-1/2 Hours	Stack open-circuit voltage achieved 28.9 V. Maximum output power of 255.5 W, and a total of 5 power curves were generated over the course of the test. Rapid degradation was observed and stack open-circuit voltage was 23.7 V immediately prior to test start.
Gen 2	23	30		On Reserve		
Gen 2	24	30		On Reserve		
Gen 2	25	30	9/30/2003	Gen 2B APU	Total test time 3 hrs - 45 min	Two test stoppages / re-starts during test: one due to reformer alarm in pre-ignition, and one due to overheating of the blower motor controller. Maximum output power 653 W (44A @ 14.84 V). With load removed, stack open circuit voltage recovered to
Gen 2	25	30	10/1/2003	Gen 2B APU	System Start-up to Shutdown was 1 hr -15 min	Good system control demonstrated during test. Achieved maximum output power of 405 W (27A @ 15 V). After load removal, open circuit voltage recovered to 30 V (2nd Cycle)
Gen 2	25	30	10/2/2003	Gen 2B APU	System Start-up to Shutdown was 1 hr -21 min	Good system control demonstrated during test. Large temperature difference observed between left and right stack (100°C). Maximum Power achieved 237W (16A @ 14.8 V). After load removal, open circuit voltage recovered to 29.5 V (3rd Cycle).
Gen 3	MG735C238 (L) & MG735C240 (R)	30	12/14/2003	Gen 2C System Stand 1	System Start-up to Shutdown was 1 hr -50 min	One test stoppage / re-start during test due to reformer alarm in pre-ignition. Maximum power achieved 766 W Gross, 276 W Net (APU @6.5A @ 21V). Load removal brought stack open circuit voltage back to 33.98 V.

On December 14, 2003, the first test of Generation 3, 2x15 cell stacks was made on the close-coupled Generation 2C system on System Stand 1. The most stack gross power and system net power produced by a Delphi system was achieved during the test. A summary of the results is given in **Figure 4.7-3**.

**Gen 3 2x15 Cell Stack Integrated
into Gen 2C APU Test Stand 1**

	Load
Stack Output Power, W	766.5
Terminal Voltage, V	21
Current, A	36.5
Output Power - 42V Regulated, W	660.8
Terminal Voltage, V	42.36
Current, A	15.6
Parasitics, W	384.6
42V Circuit Supply Voltage, V	42
42 V Load Current, A	8
12V Circuit Supply Voltage, V	12.8
12 V Load Current, A	3.8
Net Power, W	276.2

**Figure 4.7-3A: Transportation SOFC APU - Gen 2C System Test #1
Results**

5 2004 TECHNICAL PROGRESS AND ACHIEVEMENTS

5.1 Task 1: System Design and Integration Development

5.1.1 Define System Requirements

5.1.1.1 Transportation APU System Requirements

The Gen 3A and Gen 3B System Architecture (Partitioning) from 2004 is given in **Figures 5.1.1-1 and 5.1.1-2**, respectively. The Gen 3A and Gen 3B APUs followed a parallel structure throughout, with the notable exception being the change in reformer and burner Gas Phase Combustor (GPC) integration and the addition of Anode Tail Gas Recycle Pump to the Gen 3B Architecture. Key emphasis was made on the Fuel Cell Power Plant integration as separate from the Application Enclosure to allow core Fuel Cell Power Plant technology to serve flexible application power and packaging needs.

Figure 5.1.1-1: Transportation SOFC APU – Gen 3A Auxiliary Power Unit Architecture

**Figure 5.1.1-2: Transportation SOFC APU – Gen 3B
 Auxiliary Power Unit Architecture**

The Gen 3A and Gen 3B System Mechanizations (Process) are given in **Figure 5.1.1-3** and **5.1.1-4**, respectively. The Gen 3A APU has a simple CPOx reformer design and fairly straightforward system mechanization. With the deployment of Anode Tail Gas Recycle in the Gen 3B APU, a significant increase in system complexity was required. Significant changes in mechanization between Gen 3A and Gen 3B included an Endothermic Reformer (Reformer and Heat Exchanger integration), Anode Tail Gas Recycle Pump, Recycle Gas Cooler, and a fixed orifice burner air bypass path.

Figure 5.1.1-3: Transportation SOFC APU – Gen 3A APU System Mechanization

Figure 5.1.1-4: Transportation SOFC APU – Gen 3B APU System Mechanization

To support the generation of component requirements, the mechanization of each system was modeled using a Simulink[®] – based Steady-State System Model. The output format for the system models was standardized by stream reference point. The System model outputs for Gen 3A and Gen 3B system mechanizations are given in **Table 5.1.1-1 and 5.1.1-2**, respectively. Note that for each reference point in the corresponding system mechanization, stream mass flow, temperature, and composition results are given. In addition, a convenient summary of Heat Exchanger and Pump/Blower performance is given on the model output data sheet.

Table 5.1.1-1: Transportation SOFC APU – Gen 3A APU System Model Results

Model Operating Point: 5/5100		Input / Results									
State Assumptions:		State Results:									
Fuel	Gasoline	Reference Efficiency	77.8%								
Utilization	94%	Stack Elec Efficiency	62.3%								
Recycle	6%	Number of SOFC cells	80								
GPC Temp	1000°C	Stack Gross Power	3.215 MW								
O/C Ratio	1.18	Stack Power Density	0.406 W/cm²								
Stack Operating Temp	750°C	Stack Current	73.2 Amps								
Stack Cooling Gradient	100°C	Stack Voltage	0.72 V Per Cell								
Equation Temp		Power Conditioner Efficiency	87.8%								
Gradient	80°C	Parasitic Derating Factor	77.5%								
Power Conditioner Efficiency	87%	Total Parasitic Load									
C = Cathode Side		System Net Power	2100 W								
A = Anode Side		Net System Efficiency	13.7%								
E = Exhaust Post (PC)		Fuel Consumption:	0.301 g/sec								
			0.44 g/kWh								
Stream Characteristics:											
Mechanization Label	STREAM Description / Name	Mech Sensor Cross Reference	Temperature, °C	Flowrate, g/sec	N2	O2	H2	H2O	CO	CO2	CH4
A1	INLET		25.0	10.04	78%	21%	0	0	0	0	0
A2	BLIND INLET		42.1	10.04	78%	21%	0	0	0	0	0
A3	PURGE AIR INLET		9.8	9.88	8%	21%	0	0	0	0	0
A4	PURGE FAN OUTLET	T1	26.1	13.88	78%	21%	0	0	0	0	0
A5	PURGE FAN INLET		43.2	13.88	78%	21%	0	0	0	0	0
A6	POWER COND OUTLET		74.1	13.88	78%	21%	0	0	0	0	0
C1	MIXED CATH AIR	S8	63.3	7.38	78%	21%	0	0	0	0	0
C2	PURGE FAN COOLER		79.8	7.38	78%	21%	0	0	0	0	0
C3	COOL FAN		864.7	7.38	78%	21%	0	0	0	0	0
C4	PREHEAT INPASS	S10	63.8	6.74	78%	21%	0	0	0	0	0
C5	CATH AIR FEED POST HEAT EX		111.7	16.10	78%	21%	0	0	0	0	0
C6	CATH AIR FEED POST HEAT COOLER	T4L, T4R	600.8	16.10	78%	21%	0	0	0	0	0
C7	CATHODE TAIL GAS		750.0	15.74	78%	21%	0	0	0	0	0
C8	GPC AIR INPASS		750.0	0.88	78%	21%	0	0	0	0	0
C9	GPC COOL AIR	S6	63.3	0.88	78%	21%	0	0	0	0	0
C10	GPC NOT AIR FEED		750.0	15.86	78%	21%	0	0	0	0	0
A7	FUEL TAIL GAS INPASS	T6	25.0	0.30	0	0	0	0	0	0	0
A8	DISPERSED AIR PREHEAT INP	S5, T12	100.0	1.44	0	0	0	0	0	0	0
A9	DISPERSED FEED INPASS	T2	100.0	2.28	0	0	0	0	0	0	0
A10	DISPERSED OUT	S1, T3	1182.0	2.28	0	0	21.39%	2.27%	22.89%	1.62%	0.9928%
A11	EXHAUST FEED		712.0	2.28	0	0	21.39%	2.27%	22.89%	1.62%	0.9928%
A12	GPC FUEL	S2, T5L, T5R	750.0	2.83	0	0	16.29%	13.39%	11.84%	12.80%	0.9928%
A13	TAIL GAS RECYCLE FUEL		750.0	0.88	0	0	16.29%	13.39%	11.84%	12.80%	0.9928%
A14	RECYCLE PUMP INLET COOLER	T14	100.0	0.88	0	0	16.29%	13.39%	11.84%	12.80%	0.9928%
A15	RECYCLE PUMP OUTLET	S11	100.0	0.88	0	0	16.29%	13.39%	11.84%	12.80%	0.9928%
E1	GPC EXHAUST OUTLET	T6L, T6R	1001.3	18.31	78%	16.1%	0	3.8%	0	3.9%	0
E2	DISPERSED EXHAUST OUTLET		1001.3	18.31	78%	16.1%	0	3.8%	0	3.9%	0
E3	HEX NOT AIR FEED		1000.5	18.30	78%	16.1%	0	3.8%	0	3.9%	0
E4	GPC EXHAUST STREAM		991.3	18.30	78%	16.1%	0	3.8%	0	3.9%	0
Heat exchanger characteristics:											
		Arrangement	Gas 1	Gas 2	Effectiveness (%)	Heat Capacity Ratio	Cmin (kW/C)	NTU	Positive Q into stream		
H1	DISPERSED AIR PREHEAT HEX								Duty Q1 (kW)	Duty Q2 (kW)	Q (kW)
H2	CATHODE AIR HEX	Counterflow	EXHAUST, E3	AIR, C2	66.4%	0.30	0.04	4.60	-7200	7200	37.50
H3	DISPERSED COOLER HEX	Co-flow	AIR, C5	REFORMATE, A4	76.0%	0.19	3.33	1.90	1963	-1963	0.00
H4											
H5	EXHAUST COOLER HEX	Counterflow	EXHAUST, E1	REFORMATE, A3	121.1%	0.15	3.30	12.88	0	3444	42.04
H7	GPC STACK	Co-flow	REFORMATE, A5	AIR, C6	N/A	N/A	N/A	N/A	144.3	2632.7	N/A
Blower/Pump Characteristics:											
		Massflow (gpm)	Total Efficiency (%)	Motor Power (kW)	Heat Temp (°C)	Outlet Temp (°C)	Pressure Ratio				
B1	PURGE AIR BLOWER	13.0	24.0%	13.0	25.0	26.1	1.0000				
B2	DISPERSED AIR BLOWER	18.0	45.0%	318.0	42.1	43.2	1.10				
B3	EXHAUST COOLER PUMP	0.000	16.0%	0.0	100.0	100.0	1.1				

Input / Results

State Assumptions:

Fuel

Stack Gross Power

Utilization

Recycle

GPC Temp

O/C Ratio

Stack Operating Temp

Stack Cooling Gradient

Equalizer Temp

Gradient

Power Conditioner Efficiency

Gasoline

3,215 kW

58%

25%

1180 °C

1.18

730 °C

150 °C

65 °C

87%

State Results:

Reformer Efficiency

Stack Elec Efficiency

Number of SOFC cells

Stack Gross Power

Stack Power Density

Stack Current

Stack Voltage

Power Conditioner Efficiency

Parasitic Derating Factor

Net Possible Load

System Net Power

Net System Efficiency

Fuel Consumption:

119.2%

51.3%

60

3,215 kW

0.513 kW/m²

78 A/m²

0.758 V (Per Cell)

87.9%

78.2%

2136 kW

20.3%

0.242 g/kwh

9.36 gal/hour

C = Cathode Side

A = Anode Side

E = Exhaust (Post GPC)

Stream Characteristics:

Mechanization Label	STREAM Description / Name	Mech Sensor Cross Reference	Temperature, °C	Flowrate, g/sec	N2	O2	H2	H2O	CO	CO2	CH4
A1	INLET		25.0	17.63	79%	21%	0	0	0	0	0
A2	DOWNER INLET		42.1	17.63	79%	21%	0	0	0	0	0
PA1	PURGE AIR INLET		25.0	13.00	79%	21%	0	0	0	0	0
PA2	PURGE AIR OUTLET	T1	26.1	13.00	79%	21%	0	0	0	0	0
PA3	PUMP AIR COOL. INLET		43.3	13.00	79%	21%	0	0	0	0	0
PA4	POWER COND. OUTLET		75.1	13.00	79%	21%	0	0	0	0	0
C1	AIR (HEAT) CATH. AIR	39	63.5	12.27	79%	21%	0	0	0	0	0
C2	POST RECYCLE COOLER		116.6	12.27	79%	21%	0	0	0	0	0
C3	POST HEAT		886.7	12.27	79%	21%	0	0	0	0	0
C4	PREHEAT INPASS	S10	63.5	4.60	79%	21%	0	0	0	0	0
C5	CATH. AIR FEED (POST RECYCLE AIR)		537.5	18.86	79%	21%	0	0	0	0	0
C6	CATH. AIR FEED (POST RECY. COOLER)	T4L, T4R	666.2	18.86	79%	21%	0	0	0	0	0
C7	COOL AIR (T4L, T4R)		756.0	18.86	79%	21%	0	0	0	0	0
C8	GPC AIR INPASS		756.0	8.78	79%	21%	0	0	0	0	0
C9	GPC COOL. AIR	38	63.5	0.80	79%	21%	0	0	0	0	0
C10	GPC HOT AIR FEED		756.0	7.71	79%	21%	0	0	0	0	0
A1	FUEL (GASOLINE) FEED	P6	25.0	9.34	0	0	0	0	0	0	0
A2	REFORMER AIR (PREHEAT IN)	S5, T12	150.0	9.79	0	0	0	0	0	0	0
A3	REFORMER FEED (E-H)	T2	150.0	1.75	0	0	0	0	0	0	0
A4	REFORMER OUT	S1, T3	1185.7	1.75	0	0	27.39%	2.81%	26.18%	2.18%	0.0048%
A5	REFORMER FEED		886.6	1.75	0	0	27.39%	2.81%	26.18%	2.18%	0.0048%
A6	GPC FUEL	S2, T6L, T6R	756.0	1.38	0	0	13.25%	17.85%	15.82%	16.24%	0.0048%
A7	T4L GAS RECYCLE (FAR)		766.9	0.76	0	0	13.25%	17.85%	15.82%	16.24%	0.0048%
A8	RECYCLE PUMP INLET (COOLED)	T14	67.3	0.76	0	0	13.25%	17.85%	15.82%	16.24%	0.0048%
A9	RECYCLE PUMP OUTLET	S11	146.0	0.76	0	0	13.25%	17.85%	15.82%	16.24%	0.0048%
E1	GPC EXHAUST OUTLET	T8L, T8R	1100.0	9.06	74%	15.3%	0	5.3%	0	5.4%	0
E2	REFORMER EXHAUST OUTLET		881.6	9.06	74%	15.3%	0	5.3%	0	5.4%	0
E3	CHX HOT GAS FEED		816.4	17.87	74%	15.3%	0	5.3%	0	5.4%	0
E4	SYSTEM EXHAUST STREAM		436.0	17.87	74%	15.3%	0	5.3%	0	5.4%	0

Heat exchanger characteristics:

	Arrangement	Gas 1	Gas 2	Effectiveness (%)	Heat Capacity Ratio	Cmin (W/C)	NTU	Duty Q1 (kW)	Duty Q2 (kW)	NTU
H1	REFORMER AIR PREHEAT HX	EXHAUST, E3	AIR, C2	82.3%	0.88	13.13	2.82	-7918	7918	37.88
H2	CATHODE AIR HX	EXHAUST, E3	AIR, C2	77.4%	0.14	2.65	1.88	-1165	-1165	5.68
H3	REFORMER COOL HX	REFORMATE, A4	RECYCLE, A7	95.1%	0.88	1.60	3.18	864	-664	3.25
H4	REFORMER COOL HX	REFORMATE, A4	RECYCLE, A3	100.0%	0.34	2.70	15.78	-2477	2578	42.54
H5	REFORMER HX	REFORMATE, A3	AIR, C8	NA	NA	NA	NA	279.2	2775.1	NA

Blower/Pump Characteristics:

	Massflow (g/sec)	Total Efficiency (%)	Electric Power (W)	Inlet Temp (°C)	Outlet Temp (°C)	Pressure Ratio
B1	PURGE AIR BLOWER	13.0	20.0%	13.0	25.0	1.0025
B2	PROCESS AIR B. OVER	17.8	45.0%	207.1	42.1	1.15
B3	RECYCLE PUMP	0.745	18.0%	67.3	92.3	1.08

5.1.1.2 SPU System Requirements Activity Summary

The requirements for the SPU targeted for SECA Phase I Demo A were refined. The target fuel, the SECA Demo A test-cycle requirements, and system operating points definitions were addressed.

The SPU system was designed to handle either desulfurized natural gas or methane gas. Methane gas was proposed as the target fuel for the demonstration as a convenient and consistent surrogate. Desulfurization levels required for the natural gas have been defined and are consistent with a 0.1 ppm H₂S limit for the Solid Oxide Fuel Cell (SOFC) stack.

In discussions with National Energy Technology Laboratory (NETL) staff during June 2004, initial definitions of system operating points were proposed. These included:

- **Rated Power**
Rated Power is the initial maximum net output of the system sustainable for one-hour minimum. This power is measured as the gross electric power measured from all stacks minus all electric power required to run internal system loads (parasitic loads). This is the basis for contracted system cost target (\$800/kW), net power minimum target (3-10 kW), and power degradation target (-7%). Fuel rate is measured at initial rated power. At the end of the 1500-hour durability cycle, rated power of the system is measured at this original fuel rate. The difference in power achieved before and after the 1500-hour durability cycle defines the system power degradation.
- **Nominal Operation Condition (NOC)**
The NOC is the peak efficiency operating point of the system sustainable for one-hour. This is defined as the gross electric power measured from all of the stacks, minus all electric power required to support internal system loads (parasitic loads), divided by the Lower Heating Value (LHV) rate of the fuel. This is the basis for the contracted system efficiency target of 35%.
- **Minimum Power**
Minimum power is defined as the minimum net power allowable for 1500-hour durability. This proposed target is 1 kW. The system should also be capable of an idle, or zero net power output, operating mode.

Based upon these requirements, system targets for an SPU 1 (3 kW net) and SPU 2 (5 kW net) were generated.

5.1.1.3 SPU System Targets

A summary of performance targets for SPU 1 and SPU 2 are given in **Table 5.1.1-3**. Sulfur limits are given for the fuel feed stream to the system based upon an assumption of a 0.1 ppmv H₂S limit for the SOFC stacks.

Table 5.1.1-3: SPU Demonstration System A Targets

0 System			SPU 1	SPU 2
Nominal Fuel			Methane Gas or Desulfurized Natural Gas	Methane Gas or Desulfurized Natural Gas
Maximum Sulfur Content				
	Gravimetric analysis	ppmw	0.65	0.65
	Volumetric analysis	ppmv	0.32	0.32
Rated Power Output (Peak)		kW	3.0	5.0
Rated Electrical Efficiency (At Rated Power)		%	21	35
Output Power at Nominal Operating Condition (NOC)		kW	1.5	2.5
Peak Electrical Efficiency (NOC)		%	35%	40%
Availability		%	80	80
System Cost		Cost/kW	800	800
Maximum System Degradation over 1500 hrs		%	7%	7%
Thermal Cycles		cycles	5	5
Load Cycles		cycles	15	15

The proposed Demo A test cycle is shown in **Figure 5.1.1-5**. The figure illustrates that initial Rated Power and NOC were evaluated at the start of the test and followed by 1000 operating hours subject to 80% power availability at a load condition at Minimum Power of 1 kW net. After completing 1000 operating hours, one full thermal cycle of the system would occur. The thermal cycle included cooling the system down to an ambient temperature of at least 25 °C, followed by a full re-start and warm-up to normal system run conditions. The system would then be subjected to 9 complete load cycles between Minimum Power and NOC Power. The application rate and removal rate of this load (slew rate) could be adjusted to accommodate system transient capability. The remaining 500 hours of operating time occurs at, or above, the Minimum Power. This phase is measured against 80% power availability. The Rated Power of the system is evaluated at the end of the test at the initial Rated Power fueling rate. The difference in the Rated Power before and after the test defines the System Power Degradation. The degradation targeted is 7%, or less, of initial Rated Power.

During the test cycle, all system hardware, except SOFC stacks, may be maintained or replaced subject to the 80% power availability requirement. The replacements are not to be included in the system cost estimate at this time.

Figure 5.1.1-5: Proposed Demonstration System A Test Cycle

5.1.2 Develop Conceptual System Design

5.1.2.1 Transportation APU Conceptual Design

Significant design detail was added to the Gen 3 APU design. The Gen 3 APU package is opened in **Figure 5.1.2-1** to reveal the APU design consistent with the Gen 3A Architecture and Mechanization. In the Gen 3 APU design, improved integration and organization of subsystem modules and interfaces resulted in improved assembly process and component access. In addition, improved modularity allowed for straightforward subsystem validation before system integration. Thermal Insulation was added strategically to improve the thermal management of the closely coupled Plant Support Module. Perhaps the most significant difference between Gen 2 and Gen 3 APUs is the layout and organization of the SOFC Plant.

A summary of the major thermal insulation differences between Gen 2 and Gen 3 APUs is given in **Figure 5.1.2-2**.

**Figure 5.1.2-1: Transportation SOFC APU –Gen 3
 Auxiliary Power Unit System Design**

Figure 5.1.2-2: Transportation SOFC APU –Thermal Insulation Improvements

The Gen 3A APU Fuel Cell Power Plant is shown in **Figure 5.1.2-3**. The full APU assembly would be complete if the Application Interface Module (AIM) and APU cover are added to the Fuel Cell Power Plant. In the **Figure 5.1.2-3**, the Tail Gas Recycle Pump is shown for reference. This pump was not present in the Gen 3A APU but was packaged in the design to support future Gen 3B (Recycle) APU expansion.

Figure 5.1.2-3: Transportation SOFC APU –Gen 3 APU Fuel Cell Power Plant Fuel Cell Power Plant with Structural Housing

The insulated Gen 3 Hot Zone Module (HZM) is shown in **Figure 5.1.2-4**. This module is the high-temperature technology integration site for the APU, and contains the SOFC plant within the insulation, including: SOFC stacks, high-temperature manifolds, Reformer, Burner (GPC), heat exchangers, and sensors.

Figure 5.1.2-4: Transportation SOFC APU – Gen 3 APU Hot Zone Module

The SOFC Plant is shown in **Figure 5.1.2-5**. This module represents the largest departure from the Gen 2 APU design. Major changes include:

- Enhanced gasket seal geometry and gasket technology
- Increased loading of seal gaskets with improved fastener patterns
- Improved manifold flow distribution to SOFC stacks
- Flow optimized GPC (Burner) assembly
- Improved sensor locations
- Reduced anode and cathode flow branching to improve flow distribution
 - Single cathode air heat exchanger
 - Single burner exhaust path
- Single stack module - no left and right pairing required
- Single air feed paths into the SOFC plant
 - No more split-Y tubes
- Organized routing of thermo-couple leads

Figure 5.1.2-5: Transportation SOFC APU – Gen 3 APU SOFC Plant

5.1.2.2 SPU Conceptual Design

Table 5.1.2-1 compares the SPU 1 and SPU 2 systems. The SPU 1 system is built around the Gen 3 APU package and operates with methane fuel and the initial methane reformer. This is a compact system using two stacks and a partial oxidation reforming system. Efficiency and power output will be sufficient for final DOE SECA requirements.

Table 5.1.2-1: Stationary Power Unit – SPU System Efficiency Allocations

SPU Efficiency Allocation		Rated Output	Rated Output
Stationary Power Unit - Methane		SPU 1	SPU 2
Steady State- Rated Power (SS100)	Units	Sep-04	May-05
Fuel Power	kW	12.81	17.67
CH ₄ Massflow	g/sec	0.26	0.354
CH ₄ Fuel Consumption	SCFH	45.28	62.45
	M / hr	1.39	1.92
	L / min	23.25	32.06
Anode Tail Gas Recycle Fraction	%	0%	34%
Reformer Efficiency	%	86%	130%
Reformer Power Loss (-) or Gain (+)	kW	-1.793	5.300
Fuel Utilization	%	50%	50%
Stack Electrical Conversion Efficiency	%	52%	51%
SOFC Stack Conv Efficiency	%	26%	26%
Stack Power Loss (-)	kW	-8.16	-17.09
Cell Operating Voltage	V	0.70	0.70
Stack Output Power	kW	2.851	5.879
Reference Power Density	W/cm ²	0.448	0.462
Power Conditioner Efficiency	%	96%	96%
Power Conditioner Loss (-)	kW	-0.114	-0.235
Parasitic Load Efficiency	%	76.7%	84.2%
Electric Parasitic Load (-)	kW	-0.637	-0.894
Net System Efficiency @Net Power	%	16%	27%
Net Elec Power	kW	2.100	4.750
Peak Efficiency (Nominal Operating Condition-NOC)	%	N/A	40%
Power at Peak Efficiency (NOC)	kW	N/A	2.375

The design points of the system must also consider the effects of off-peak power output (below rated power point) for the purposes of system efficiency and durability. The SPU 2 system off-peak load points in the chart below (**Table 5.1.2-2**) are the most significant points that the system operated during the Phase 1 system life testing. The 0% load-point is the operation point the system “idles” during the load cycling of the system, and for some diagnostic tests for troubleshooting problems. The 20% load point is the operation point for long-term durability testing and is a balance of operating conditions that maintain adequate gas distribution within the system and a reasonable output of 1000 watts. The 50% load-point is the operation point for peak system efficiency (also called the Nominal Operating Condition or NOC point). The 100% load-point is the peak-rated power point for the system. The two points shown on the table, at 100% rated output power and 100% degraded condition power, are being considered the start and final points of the system life testing.

Table 5.1.2-2: Stationary Power Unit 2 System Efficiency Off-Peak Allocations

SPU Efficiency Allocation		Minimum Output			Rated Output	Degraded Condition
		IDLE	LOAD	LOAD	LOAD	LOAD
Stationary Power Unit -Methane		0%	20%	50%	100%	100%
Percent of Rated						
Steady State	Units					
Fuel Power	kW	5.49	5.55	5.90	17.66	17.56
CH4 Massflow	g/sec	0.11	0.11	0.12	0.354	0.35
CH4 Fuel Consumption	SCFH	19.41	19.63	20.87	62.44	62.07
Anode Tail Gas Recycle Fraction	%	34%	34%	34%	34%	39%
Reformer Efficiency	%	130%	130%	130%	130%	140%
Reformer Power Loss (-) or Gain (+)	kW	1.65	1.67	1.77	5.30	7.02
Fuel Utilization	%	8.2%	27.0%	60%	50%	50%
Stack Conversion Efficiency	%	77%	71%	62%	51%	49%
SOFC Stack Conv Efficiency	%	6%	19%	37%	26%	24%
Stack Power Loss (-)	kW	-6.69	-5.84	-4.80	-17.08	-18.60
Cell Operating Voltage	V	1.05	0.96	0.85	0.70	0.66
Stack Output Power	kW	0.450	1.377	2.872	5.878	5.983
Reference Power Density	W/cm ²	0.035	0.108	0.226	0.462	0.470
Power Conditioner Efficiency	%	96%	96%	96%	96%	96%
Power Conditioner Loss (-)	kW	-0.018	-0.055	-0.115	-0.235	-0.239
Parasitic Load Efficiency	%	0%	72%	86%	84%	83%
Electric Parasitic Load (-)	kW	-0.432	-0.372	-0.382	-0.893	-0.994
Net System Efficiency @Net Power	%	0.0%	17.1%	40.2%	26.9%	27.1%
Net Elec Power	kW	0.0	1.0	2.4	4.8	4.8

The outcome of the design process generated a system architecture block diagram for the SPU 2 system. **Figure 5.1.2-6** shows the relationship that hardware had to the engineering organization of the Delphi product. The diagram also outlines the document layers that are the basis for the final product requirements document.

The conceptual physical layout of the SPU 2 design was completed to assist engineering and management during intermediate design reviews and strategy discussions for our Phase 1 SPU system. This layout, completed for a basic visual check of the relationship of the hardware and overall sizing, is the next step towards SPU 2 subsystem requirements documentation and the 3D solid modeling design work.

The SPU 2 design included several features that are different from the APU design work in the Generation 2 and 3 products. The arrangement is a vertical cabinet layout that positions the high temperature insulated volume for the stacks to the top of the product. The space allows for up to six of the Gen 3 stack modules. The intermediate layer is planned to house a second insulated zone for the reformer, cathode heat exchanger and system combustor (GPC) hardware, room for the smaller system pumps and the power electronics (positioned close to the stack for minimal DC power loss). The base layer of the layout allows for the process air module and air handling systems as well as

a space for energy storage (such as batteries) for system start and load transient assistance. (See **Figure 5.1.2-7.**)

Figure 5.1.2-7: Stationary Power Unit 2- Physical Layout Design

The SPU 1 system design is a reformer technology substitution on a Gen 3 APU system platform. The modular organization of the SPU 1 system is shown in **Figure 5.1.2-8**. The figure shows the familiar arrangement of Hot Zone Module (HZM), Plant Support Module (PSM), and Application Interface Module (AIM). The PAM and the anode Tail Gas Recycle (TGR) pump are also shown in **Figure 5.1.2-8**. The general features of the SPU 1 system includes:

- Improved gasket technology (C-ring gaskets) between ICM and high-temperature components. This has been demonstrated to greatly improve the integrity of the high-temperature interfaces.
- Increased integration and smaller packaging of the HZM. This allowed for a reduction in overall package height from 275 mm to 250 mm and has allowed for increased thermal insulation between the HZM and PSM.
- Flow optimization in the HZM. Computational Fluid Dynamics (CFD) analysis tools were employed in the design of all ducts, manifolds, and heat exchangers to improve flow distribution and reduce pressure drop. This has resulted in reduced pressure losses in the system.
- Redesigned an insertable GPC nozzle for improved mixing, burner control, temperature distribution, and reduced emissions.
- Single counter flow CHEX for improved temperature effectiveness, left-to-right system temperature balance, and improved performance at lower flow rates.

- Highly integrated, high-performance PAM to support increased system flow capacity, pressure requirements, and improve efficiency.
- Highly integrated AIM featuring integrated power electronics, system cooling air circuit, inlet air filtration, and Bussed Electrical Center (BEC) interface.

5.1.3 Develop System Mechanization

5.1.3.1 Develop Transportation APU System Mechanization

5.1.3.1.1 Transportation APU Electrical and Electronics System

Electrical Harness Design

In order to simplify the verification and integration of each subsystem, a new partitioned harness design was implemented (see **Figure 5.1.3-1**). This design incorporated individual harnesses for each subsystem. This allowed each subsystem design team to verify and checkout their subsystem prior to system integration. A partitioned harness makes assembly of the system easier and leaves less opportunity for error. As part of this redesign, a number of new connectors were added and/or substituted to make the interconnections between the subsystem harnesses and the main Fuel Cell Power Plant harness. The harness was partitioned into the following 5 main pieces: 1) Fuel Cell Power Plant harness, 2) Reformer harness, 3) Process Air Module harness, 4) Recycle harness, and 5) Instrumentation harness.

The Bussed Electrical Center contains the combustible gas sensor, the warm space Thermistor, 14 and 42 Volt fuses, relays, 14 and 42 Volt power busses, a single point ground plane, and connectors that were previously in various places throughout the Application Interface Module (AIM) and the warm space (see **Figure 5.1.3-2**). The Bussed Electrical Center is intended to clean up the AIM and the warm space by organizing power and ground planes as well as containing sensors that previously did not have a designated position or mounting point. This also neatly organizes and routes signals and power into and out of the system to the user. The Bussed Electrical Center has been designed and laid out and is currently being built (see **Figure 5.1.3-3**). A mock-up was created to verify fit and to demonstrate the concept (see **Figure 5.1.3-4**).

Figure 5.1.3-2: Bussed Electrical Center Schematic

Figure 5.1.3-3: Bussed Electrical Center Board Layout

Figure 5.1.3-4: Bussed Electrical Center Mock-Up

5.1.3.1.2 Power Conditioner for Transportation APU

The power conditioner was tested across its operating temperature range. This test verified the functionality of the unit's over temperature protection and allowed for documentation of the converter's behavior at high temperature. The converter over temperature protection functions properly. Above 100 °C, the converter opens its contacts and stops producing a regulated 42 Volt output. This is expected, but the future solution shall be capable of operating at temperatures greater than or equal to 125 °C. Data was collected across the power conditioner's full power range, 0-3kW, at 25 °C, 50 °C, 85 °C and 100 °C. The results show less than 4% efficiency degradation across the operational temperature range (see **Figure 5.1.3-5**). This confirms that this power conditioner performs better at lower temperatures, but that degradation across the temperature range is minimal.

Figure 5.1.3-5: Solectria 3kW Power Conditioner Efficiency versus Power Across Temperature 40V Input

The Solectria power conditioner was also characterized across input and output voltage ranges. Tests were completed to determine the optimal operating conditions with respect to input and output voltages. All tests were completed at 25 °C, with input and output voltages spanning the operation limits of the unit. Data was collected for 36 Volts, 46 Volts and 56 Volts in with the output varying from 30 volts to 50 volts in all cases (see **Figures 5.1.3-6 through 5.1.3-8**). In all tests, average efficiency was highest at 50 Volts. The data shows an approximate 4% efficiency gain across the output voltage range. This data supports increasing the power conditioner's output voltage to 50Volts to increase efficiency. Since the ISO standard for *Road Vehicles – Electrical and Electronic Equipment for a 42-Volt Network – Electrical Loads (N103 ISO/DIS 21848.5)* requires that 42-Volt bus voltage never exceed 50-Volts, the APU system will be tested with the power conditioner output at 50-Volts to verify system

efficiency gains. Further testing is underway, which will result in well-documented requirements for the future transportation APU power electronics solution.

Figure 5.1.3-6: Efficiency versus Power at Vin=36V and Vout=30-50V

Figure 5.1.3-7: Efficiency versus Power at Vin=46V and Vout=30-50V

Figure 5.1.3-8: Efficiency versus Power at Vin=56V and Vout=30-50V

5.1.3.2 Develop Stationary SPU System Mechanization

Detailed system mechanizations were generated for the SPU 1 and SPU 2 systems and these were analyzed with Excel®, MATLAB®/Simulink®, and HYSYS® system analysis tools. These mechanizations were targeted toward desulfurized natural gas as the target fuel, and feature optional DC/AC conversion for their output. Both designs utilize an anode TGR and moderate system fuel utilization to achieve high efficiency operation without need for a source of external water.

As an alternative to Endothermic (Plate) reforming, system mechanization work was initiated using Light Internal Reforming (LIR) concepts as an alternative fuel-processing scheme for natural gas. This mechanization concept allows for use of a simple tubular CPOx reformer with anode TGR to achieve high-fuel processing efficiency. This concept has the additional benefit of reduced stack cooling loads and increased system air utilization.

The organization of both SPU 1 and SPU 2 systems are the same with respect to partitioning and modular content. This structure is reviewed in **Figure 5.1.3-9**. The figure shows the high-level partition of the system between a fuel-to-DC conversion FCPP and an application-specific Application Enclosure (AE). The AE features are flexible in content, function, and value. The technology required in the AE is mature and commercially available; with the exception of very high efficiency, low cost, DC/AC

inverters. The design emphasis was placed on the FCPP. This is where most of the content is highly adapted, newer technology. The rated power, system efficiency, and system cost are based primarily on the FCPP.

Figure 5.1.3-9: SPU System Architecture

The main difference between SPU 1 and SPU 2 is the stack flow arrangement. SPU 1 uses 2x30 cell stacks arranged in a parallel-flow, series-current architecture. This requires that cathode and anode feed streams be split evenly between the two stacks in the manifold. This allows for an electrical architecture based upon 60 cells in electrical series. The electrical architecture for both Gen 3 APU and SPU 1 are designed based a 60-cell series SOFC stack power source. Challenges in the 2x30-cell parallel flow arrangement include left-to-right flow temperature balance, system fuel utilization and air utilization. System cathode airflow is driven by the sum of the individual cooling needs of each stack in the parallel arrangement. To achieve a moderate system fuel utilization of 60%, each individual stack in the parallel arrangement must operate at a fuel utilization of 60%.

When additional stacks are added to a system with a parallel-flow arrangement, fuel and air distribution among the stacks may become more complex. System cathode airflow capacity requirements go up proportionally with each additional stack. For example, at rated power, if each 30-cell SOFC stack requires 6 g/sec of air for cooling,

then a 2-stack system requires 12 g/sec, and a 4-stack system requires 24 g/sec. This will require a large capacity process air system. At lower system power output (<50% of rated power), and at moderate system efficiencies, anode feed stream mass flows can become quite low. Vertical fuel distribution issues in the stack may arise. During high-efficiency operation where system fuel utilization is moderate (>50%) and anode TGR is high (35% to 50%), if a large quantity of cathode airflow is required for stack cooling, it is difficult to maintain an adequate burner temperature. Under this condition, it may be impossible to maintain system operation temperature to target and burner blowout may become an issue. For this reason, high efficiency system concepts with anode TGR and Endothermic (Plate) reforming have required an additional burner air bypass valve. This valve directs a fraction of cathode tail gas around the burner to keep burner equivalence ratios (ϕ) within the desired range. This valve is an externally actuated high-temperature valve in the system and would require significant development for sealing, thermal isolation, and reliability. It is not desirable to have this type of valve required in the system mechanization.

One mechanization alternative employed in the 4x30-cell stack SPU 2 system is series - flow architecture. In this concept, pairs of 30-cell stacks are arranged in flow and electrical series. A 4-stack system would be comprised of 2 branches of paired-series-flow stacks. The two arrangements are compared in **Figure 5.1.3-10**.

Figure 5.1.3-10: Stack Flow Architectures

5.1.4 System Control Development

5.1.4.1 Control Development Environment

A unique approach to the several applications to which this control system is applied has been developed with respect to calibration and sub-system configuration election. It is now possible to elect which of several target applications this control / plant model will be used for, and with a single action, initialize all calibrations and select among all configurable sub-systems within the model. For example, the reformer lab, which is now running on this code, can elect an initialization option that sets all performance and configuration calibrations appropriate for the lab's hardware and test purpose. In addition, the initialization action causes a specific set of configurable sub-systems to be elected. For example, an advanced control algorithm for reformer control can be easily substituted for the base algorithm, while the rest of the control still employs "released" code.

A renaming tool was developed and applied which allows for a global find and replace of variable names throughout all levels of the model and in all configurations of the sub-systems. This tool has allowed improvement in variable and calibration naming in order to make a more understandable model.

5.1.4.2 Controller Hardware Development

There was a significant effort to advance the system controller towards a more production-intent unit in 2004. The second generation Engineering Development Unit (EDU) was built and tested (**Figure 5.1.4-1**). A number of hand modifications made during development were implemented in the EDU 2 controller layout. Additional features and protection circuits were also added. The communication hardware was upgraded and made configurable by hardware pin selection. The controllers had a selectable speed dual Controller Area Network (CAN) bus. The user selects either 100 kilobaud per second low speed fault-tolerant CAN, or 500 kilobaud per second high speed CAN. A number of additional features and protection circuits were added including: Additional fault detection circuitry, 60 Volt I/O protection on required circuits, added nonvolatile Random Access Memory (RAM), lower quiescent current draw (< 2 milliAmps with CAN Wake-Up), increased temperature protection (125 °C), and added input captures.

Figure 5.1.4-1: SOFC System Controller Engineering Development Unit 2

5.1.4.3 Controller Software Development

Many software developments were conducted that enhanced the APU system. Developments were made in the following areas: reformer control updates, plant model updates, and safety and diagnostics updates.

Reformer Control Updates

Individual state monitors for “lit” conditions of the reformer and the Gas Phase Combustor (GPC) have been added and are incorporated in the safety and diagnostics area. Added GPC metal temperature predictor used for minimum allowable GPC combustion equivalence ration (ϕ).

Plant Model Updates

Several plant model updates have been accomplished including the introduction of metal-to-metal heat transfer in plant model on several modules, a 40x improvement in plant model speed, and the addition of GPC internal bypass to simulate incomplete mixing that allows better model-to-experiment correlation. Other additions include temperature dependent specific heat calculations in the masses of the plant model, addition of influence of close proximity hot metal to temperature sensor (T5) signal in plant model, and computation of GPC exhaust composition to the GPC model.

Safety and Diagnostics updates

In the safety and diagnostics area, we added control-loop monitors on the few control loops that did not have them already. All closed loops now have safety and diagnostics monitors that are fully implemented through variable window allowable error, including fixed minimum allowable error at steady state.

Control Results

Figure 5.1.4-2 shows the results of post-processing of a control loop diagnostic during warm-up. The control loop monitor tolerates a varying amount of error based on how

quickly the desired set point is changing. Note that near the 5000-second point, the temperature sensor (T6) GPC temperature control fails and the signal become oscillatory. The safety and diagnostics monitor “caught” this as indicated by the “controlled fault” signal going high shortly after the oscillations exceeded the allowable threshold.

Figure 5.1.4-2: Demonstration of Diagnostics in Action

5.1.5 Perform Design Optimization

5.1.5.1 Transportation APU System Design Optimization

5.1.5.2 SPU System Design Optimization

Design optimization was limited to modeling analyses and configuration evaluations. The following charts are the highlights from the rated peak-power analysis completed to assess the SPU 2 configuration and the intended operating points being considered from the concept design and final design approval processes. Please note that the charts have a legend keyed to the specific points on the DOE System Life test schedule proposed.

These characteristic maps were generated with a Simulink® model that is presently configured for the demands of the SPU. The set-up parameters used for these maps are noted at the top of each graphic. A review of these values are:

- Reformer: Fuel -> Methane (CH₄)
 - Oxygen to Carbon ratio (O/C) feed to reformer: 1.30 (assuming recycle)
- Stack Arrangement: 4 stack modules (total of 120 cells)
 - Operating at 0.70 volts / cell and 1440 watts per stack (0.450 w/cm²)
 - Stacks using an effective cathode air temperature gradient of 300 °C
- System Combustor: 1025 °C operating temp

Within the following charts, points A and B represent the rated power test points at the initial and final tests. Point A is the initial point that “peak” rated power will be met at. Point B is the final point the reformer and fuel cell power plant will run using a boost in anode tail gas recycle % to compensate for stack degradation. The strategy is planned to allow for a 10% degradation of the stack power with little to no degradation at the system output.

The map for system efficiency of the SPU 2 system (see **Figure 5.1.5-1**) shows the relationship of the rated peak-power operating points planned for the system. The reformer efficiency can be seen as a constant function of recycle percentage. The system efficiency can be seen as a function of both recycle (and therefore reformer efficiency) and stack fuel utilization. Maximum recycle fractions for the higher power points are nearly 80% of the maximum recycle the system can tolerate.

**Figure 5.1.5-1: Stationary Power Unit - System Characteristic Map:
System Efficiency**

The map for reformer flow rates shown in **Figure 5.1.5-2** of the SPU 2 system shows the relationship of the operating points planned for the system. The rated peak power points at 50% fuel utilization correlate to the increased reformer efficiency projected from point A to point B.

**Figure 5.1.5-2: Stationary Power Unit - System Characteristic Map:
Reformer Flow Rates**

The map shown in **Figure 5.1.5-3** system burner operation of the SPU 2 system shows the relationship of the operating points planned for the system. The burner operation at the rated peak-power points is critical due to use of excess air needed to cool the combustor and the impacts on process air system sizing. This operating point selection does not require a significant amount of additional air over that being supplied by the cathode air.

Figure 5.1.5-3: Stationary Power Unit - System Characteristic Map: Burner Operation

The map for reformer output composition of the SPU 2 system shown in **Figure 5.1.5-4** shows the relationship of the operating points planned for the system. The projected composition at these operating points is 43 to 47% H₂, 22 to 24% CO, and more significantly 5% to 6% water. The water content is a critical value due to our reliance on water content above 3-4% for carbon formation control. Development and work to increase the water composition to the 6 to 10% range with reformer and stack operation and recycle ratios will be investigated in the future.

Figure 5.1.5-4: Stationary Power Unit - System Characteristic Map: Reformer Output

The map for process air flows of the SPU 2 system shown in **Figure 5.1.5-5** shows the relationship of the operating points planned for the system. Process airflow rates shown support the burner and cathode air flow values for sizing and operation.

Figure 5.1.5-5: Stationary Power Unit - System Characteristic Map: Process Air Flows

The map for parasitic power losses of the SPU 2 system (see **Figure 5.1.5-6**) shows the relationship of the operating points planned for the system.

Figure 5.1.5-6: Stationary Power Unit - System Characteristic Map: Parasitic Power Losses

5.1.6 System Design and Integration Conclusions

Delphi's first methane-fueled (or desulfurized natural gas) SPU 1 derived from transportation APU designs represents the progress made through design optimization and development over several Transportation APU design generations. This system will be the first stable platform with which to evaluate system durability and reliability, and will be the first target for high-performance stack integration to the system. High stack power density and successful deployment of high-efficiency fuel-processing solutions, including anode tail gas recycle, are required for SPU 1 to meet SECA Phase I power and efficiency targets.

To better suit stationary power applications and specifically address needs of the SECA Phase I Demo A, the conceptual design and mechanization have been defined for SPU 2. SPU 2 features more capability towards meeting SECA phase I targets including Rated Power, efficiency, and cost \$/kW, while retaining a very high degree of subsystem and component reuse from SPU 1 systems.

5.2 Task 2: Stack Development

5.2.1 Design Stack

Multiple 15- to 30-cell Gen 3.0 stack sub-systems (called Integrated Stack Modules) were successfully fabricated and tested. These stack builds demonstrated that the low

cost, more manufacturable Gen 3.0 design can be successfully fabricated with lower mass and volume.

From the experience gained with the Gen 3.0 cassette design, further improvements were made to the design, designated as Gen 3.1. Detail changes were made to simplify laser welding, improve the dimensional repeatability of the cassette, improve electrical interconnection and optimize the anode and cathode flow cavities. Improvements were also made to improve sealing to the system manifold, and further reduce the mass and volume of the Integrated Stack Module.

The cassette flange was reconfigured for Gen 3.1 so that the entire perimeter of the cassette could be welded in one pass, without changing fixtures, resulting in significant savings in weld time. The detail changes are shown in **Figure 5.2.1-1**.

Figure 5.2.1-1: Cassette Design for Gen 3.1 Stack Showing Improved Laser Welding Path in the Perimeter of the Cassette

This flange configuration also prevents dimensional change of the cassette thickness during weld resulting in a more uniform, easier to seal part. Subtle design features were also added to the cell frame to improve the consistency of the braze application. The cathode and the anode contact meshes were redesigned to improve uniformity of the spacing between the cell and separator plate, which form the anode and cathode flow cavities. The Gen 3.0 contact meshes had a feather configuration that allowed the cell and separator plate to distort during operation. The Gen 3.1 design utilizes meshes that are sized to fit tightly between the cell and separator plate which forces a uniform spacing between the parts throughout the stack (see **Figure 5.2.1-2**).

Figure 5.2.1-2: Cassette Design for Gen 3.1 Stack Showing Improved Inter-Connection Scheme

The Integrated Stack Module was re-designed for Gen 3.1 to incorporate the gas distribution manifold into the base plate of the module (see **Figure 5.2.1-3**). This configuration then provides a single flange for communicating and sealing cathode and anode supply and return flows to the system that can be configured for a robust seal. The loading mechanism used to keep the cassette-to-cassette seals in slight compression was simplified and reduced in size and mass (see **Figure 5.2.1-4**).

Figure 5.2.1-3: Integrated Manifold in Gen 3.1 Stack Showing Improved Sealing Flange for Interface to the System

Figure 5.2.1-4: Load Mechanism for Gen 3.1 Stack

5.2.2 Model Stack Under Steady-State Conditions

The Delphi-Battelle Team used an electrochemical model with actual stack data to evaluate losses within the stack. The area specific resistance (ASR) is determined from a point on a current-voltage (I-V) curve. **Figure 5.2.2-1** shows the I-V curve for the 5-cell stack. The ASR calculated for the point at 0.75 volts (0.881 A/cm^2) is determined as the difference of the open circuit voltage, V_{oc} and the voltage at the point on the I-V curve (V_{load}), divided by the current density at said point (i_{load}):

$$ASR = \frac{V_{oc} - V_{load}}{i_{load}} = \frac{1.036 \text{ volts} - 0.750 \text{ volts}}{0.881 \text{ amps/cm}^2} = 0.32 \text{ ohm} \cdot \text{cm}^2$$

The line on **Figure 5.2.2-1** was fitted to the Delphi stack using the PNNL spreadsheet model. Certain stack performance parameters (overpotentials) can be inferred from the fit of the model, but it must be understood that these are merely rough estimates of the overpotentials, not direct measurements. The estimates for ohmic and contact resistance, anode kinetics, cathode kinetics and concentration polarization are shown in **Table 4.3.2-1** for the point on the I-V curve that was used to calculate ASR.

Figure 5.2.2-1: IV Curve from 5 cell Stack Fitted with Electrochemical Model

The exchange current density and the charge transfer coefficient can only be inferred from half-cell measurements, which are not part of the scope of Delphi's stack development work. Regarding Delphi's efforts to decrease losses, decreasing the cathode kinetics overpotential is the key to higher power densities in general and decreasing the concentration polarization is part of obtaining higher power densities at high fuel utilizations. These efforts are central to Delphi's current development priorities.

Overpotential	% of ASR
Ohmic and Contact Resistance	15.3%
Anode Kinetics	24.5%
Cathode Kinetics	54.0%
Concentration Polarization	6.1%

Table 5.2.2-2: Overpotential Estimated percentages of ASR

5.2.3 Develop High Performance Cathode

Previous cathode development efforts demonstrated that Cr-containing environments have a dramatic impact on both the performance and durability of the (La,Sr)FeO₃ (LSF)-based, and (La,Sr)(Co,Fe)O₃ (LSCF) cathodes. LSF-based cathodes, which exhibited power densities exceeding 0.9 W/cm² after burn in Cr-free environments, were found to be limited to 0.1 W/cm² when Cr-forming alloys, such as Crofer 22, were added to the test configuration as a vapor source. Further investigations showed that La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ (LSCF-6428) cathodes operating in Cr-environments had a ~ 25% decrease in the initial power and a ~ 3-fold increase in the degradation rate when compared to the baseline cathodes in a Cr-free environments. 2.8 mW/cm²/hr vs. 1.1 mW/cm²/hr baseline, (see **Figure 5.2.3-1**) SEM analysis on selected Cr- environment test samples revealed a constant Cr content, ~5 at%, in the bulk of the cathode in the form of a Sr-Cr-O. Based on this information, our efforts have focused on cathodes with a reduced Sr content in order to improve the Cr susceptibility of the cathode materials. In addition, our recent efforts have focused on optimization of the LSCF-6428 cathode for use in Cr-free stack testing with the goal of understanding the primary variables responsible for high power and degradation in this system.

Figure 5.2.3-1 LSCF Cathode with Various Cr Sources

5.2.3.1 Lanthanum Nickel Cobalt Ferrites (La),(Co,Fe,Ni)O₃ (LNCF)

Lanthanum Nickel Iron perovskites have conductivities greater than 100 S/cm at 800 °C, making them a viable candidate for SOFC cathodes, and may inherently have an improved Cr tolerance due to the lack of Sr acceptor dopant. Based on previous work

with LSF compounds, Co was added to the composition in an effort to improve the initial power density and reduce the burn-in cycle. Both commercial and in-house powders were prepared with various Co, Ni, and Fe concentrations. The primary compositions investigated were $\text{La}_{0.98}(\text{Ni}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.4})\text{O}_3$ (LNCF-424) and $\text{La}_{0.98}(\text{Ni}_{0.2}\text{Co}_{0.4}\text{Fe}_{0.4})\text{O}_3$ (LNCF-244). Both powders were found to exhibit a burn-in behavior similar to those previously reported for LSF-type compounds and were found to achieve power levels greater than 0.6 W/cm^2 under standard button cell test conditions (0.7 V, 750°C with 1:1 nitrogen and hydrogen fuel mixture). A plot of the burn in behavior and power density stability of LNCF-244 is shown in **Figure 5.2.3-2**. Incorporating a LNCF/SDC (samarium doped ceria) composite functional cathode resulted in a significant increase in the initial power density and showed excellent stability over the 250 hours tested (see **Figure 5.2.3-3**).

Figure 5.2.3-2: Electrochemical Performance of Two Samples of $\text{La}_{0.98}\text{Ni}_{0.2}\text{Co}_{0.4}\text{Fe}_{0.4}\text{O}_{3-x}$ (LNCF244-2AD) Cathode

Figure 5.2.3-3: Electrochemical Performance of $\text{La}_{0.90}\text{Ni}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.4}\text{O}_{3-x}$ (LNCF424-10AD) Cathodes

5.2.3.2 Reduced Sr content $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) Cathodes

Another series of tests was conducted in order to examine the impact of Sr content on LSCF power density and degradation rate. Samples were prepared with the general composition $\text{La}_{0.98-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ where $x = 0.4$ (LSCF-6428), 0.35 (LSCF-6.53.528), 0.3 (LSCF-7328) and 0.2 (LSCF-8228). As shown in **Figure 5.2.3-4** and **Table 5.2.3-1**, both the initial power and degradation rate appears to be directly proportional to the Sr content. However, for this series of materials the native degradation rate does not appear to be improved significantly until the Sr content is reduced to $x = 0.20$ in which the material undergoes a burn-in phenomena in a Cr-free environment. Further optimization of the processing parameters is necessary since the reduced Sr content can significantly alter the sintering characteristics of the cathode materials that, in turn, can impact the power density and degradation. In addition, Cr tolerance testing will also be conducted.

Figure 5.2.3-4: Power Density- Sr Content Relationship for $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.20}\text{Fe}_{0.8}\text{O}_{3-x}$ Cathodes

Sr content (mol%)	Initial Power (mW/cm ²)	Fade (%/h, 10 ~ 100h)
20	341	Burn in
30	598 (581~614)	0.1055 (0.105~0.106)
35	752 (759~745)	0.136 (0.133~0.139)
40	782 (778~786)	0.178 (0.175~0.181)

h= hours

Table 5.2.3-1: Power Density- Sr content Relationship for $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.20}\text{Fe}_{0.8}\text{O}_{3-x}$ Cathodes

5.2.3.3 Sr-doped lanthanum cobalt ferrite, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF-6428) Optimization

In parallel with the efforts to develop more Cr-tolerant cathodes, Delphi investigated the current LSCF-6428 cathodes in an effort to determine the primary factors controlling both the degradation rate and power density. This is important in terms of forming a better understanding of the system and may enable a higher power density cathode to be used in a Cr-free SOFC stack.

A screening experiment was set up in which the control variables were the functional cathode sintering temperature, thickness (number of prints), and porosity (%Carbon

added); bulk cathode sintering temperature, thickness, porosity (both %Carbon and Carbon size), and Ag/Pd content. The variable levels and results for the power density analysis are shown in **Table 5.2.3-2**. With the inherent low resolution of the full variable L8 screening test, we could only eliminate those variables that did not contribute to increased power density. Within the ranges of this study, the number of functional cathode prints (functional cathode thickness), vol% carbon in the functional cathode, the Ag-Pd content in the bulk cathode and the sintering temperature of the bulk cathode (1000 – 1050 °C) did not have a significant impact on the initial power density.

While the functional cathode sintering temperature, number of bulk cathode prints, and carbon black particle size in the bulk cathode all appear to contribute to the maximum power density, the low resolution of the screening study does not enable separation of variable impact from the confounding interaction of the variables.

None of the seven factors analyzed appeared to have a significant impact on the degradation rate, indicating that the primary control variable was not in the study or inherent to the material itself (i.e. not a process parameter). A plot of the degradation rate (mW/cm²/hr) of these cells vs. power density (mW/cm²) (see **Figure 5.2.3-5**) shows the general trend that increasing the current density results in an increased degradation rate for these particular cathode compositions and indicates that the degradation is primarily controlled by the material.

Table 5.2.3-2: L8 Screening Study (La_{0.6}Sr_{0.4})_{0.95}Co_{0.20}Fe_{0.8}O_{3-x} Cathodes

Factor/Int.	Funt. Cathode Prints	Funt. Cath. Sintering Temp (oC)	Vol% Carbon in Funt. Cath.	Bulk Cathode Prints	Ag-Pd content	CB Particle Size	BC Sintering Temp			
Level 1	1	1050	0	2	0	0.3	1000	Power Density (mW/cm^2)		
Level 2	3	1100	40	4	40	8	1050	<Data>	Value 1	Value 2
Trial # 1	1	1050	0	2	0	0.3	1000	858	878	838
2	1	1050	0	4	40	8	1050	903.5	861	946
3	1	1100	40	2	0	8	1050	408	307	509
4	1	1100	40	4	40	0.3	1000	852	849	855
5	3	1050	40	2	40	0.3	1050	783.5	811	756
6	3	1050	40	4	0	8	1000	851.5	846	857
7	3	1100	0	2	40	8	1000	573.5	686	461
8	3	1100	0	4	0	0.3	1050	797	833	761
Avg. Lvl. 1	755.4	849.1	783.0	655.8	728.6	822.6	783.8			
Avg. Lvl. 2	751.4	857.6	723.8	851.0	778.1	684.1	723.0			
Difference	4.0	191.5	59.3	195.3	49.5	138.5	60.8	753

Figure 5.2.3-5: Power Density vs. Degradation Rate From L8 Screening Study on $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.95}\text{Co}_{0.20}\text{Fe}_{0.8}\text{O}_{3-x}$ Cathodes

5.2.4 Develop Cell Fabrication Techniques

5.2.4.1 Contact Paste Improvement

Development of improved anode contact paste involved SEM analysis of the current paste material compared to a number of proposed changes. New formulations of contact paste included changes in the particle size/surface area of the nickel oxide powder and the addition of a pore former (fugitive) phase. After screening several materials with pore forming capabilities, particulate carbon was selected for further study. The type of particulate carbon was held constant while the solids loading was varied. **Figure 5.2.4-1** includes micrographs comparing the baseline contact material with sample materials with increased porosity. Paste samples 2-6 reveal the nature of the pore structure based on the size of the nickel oxide and the level of particulate carbon added. Based on these initial results, a recommendation was made to introduce 30-40 volume percent of the pore former to the fine grained nickel oxide paste. **Figure 5.2.4-2** shows SEM micrographs that compare the previous contact paste to the improved contact paste at 120X as applied to the bond between the interconnect mesh and the anode surface. Higher magnification (1000X) micrographs (see **Figure 5.2.4-3**) provide a better picture of the actual paste structure comparing the two paste materials. It can clearly be seen that the porosity has been improved.

A similar improvement was made to the cathode contact paste. Increased porosity in the sintered state was achieved with the addition of a fugitive phase into the paste formulation that is burned out during stack assembly. The paste had improved permeability permitting the oxygen on the air-side of the cell to reach the cathode of the cell in the interconnect locations.

Pf = pore former

Figure 5.2.4-1: Micrographs Comparing the Baseline Contact Material with Sample Materials with Increased Porosity

Figure 5.2.4-2: Micrographs that Compare the Previous Contact Paste to the Improved Contact Paste at 120X as Applied to the Bond Between the Interconnect Mesh and the Anode Surface

Figure 5.2.4-3: Micrographs that Compare the Previous Contact Paste to the Improved Contact Paste at 1000X as Applied to the Bond Between the Interconnect Mesh and the Anode Surface

5.2.4.2 Improved Adhesion of Anode Interconnect Component

Multiple methods were developed to increase the adhesive strength of the interconnect mesh to the anode cell surface. A qualitative method was used that compared the existing level of adhesion of the interconnect feather to samples made with alternative means. A rating system was developed based on a 1-5 scale that demonstrated the level of improvement observed compared to the existing baseline measurement.

Figure 5.2.4-4 is an SEM micrograph at 500X showing the previous (Gen 3.0) anode surface. Attached to the anode surface is a nickel oxide grid material fired on at 1200 °C creating a smooth outer surface with increased electrical conductivity compared to the anode cermet. The thickness of the fired grid is approximately 21-24 microns.

The first method to achieve improved adhesion of the interconnect mesh to the anode surface was a change in sintering parameters that leads to a stronger bond between the screen printed nickel oxide grid layer and the anode surface. A higher sintering temperature improved the bond strength and led to better adhesion results. A cross-section of a cell interconnect interface is shown in **Figure 5.2.4-5**. In this micrograph, the porous anode layer can be seen at the bottom. Above that, the nickel oxide grid bonded well and shows a slightly higher level of porosity. Finally, the contact paste material is seen above with good connection to the grid layer while allowing plenty of penetration of the fuel gas through the porous microstructure.

A second method to improve adhesion of the components was to apply the nickel oxide grid paste to the unfired bi-layer laminate and co-sinter at the sintering temperature of the anode/electrolyte bi-layer. This also produced a stronger bond but is more difficult from a process perspective, taking into account complex tooling and time considerations.

A third method included changing the texture of the anode surface by eliminating the screen-printed grid layer and implementing a porous tape as a backing layer, allowing for better mechanical contact with the anode surface. After sintering the bi-layer with this tape cast component added, a porous, rough surface results (see **Figure 5.2.4-6**). The modified anode surface has a highly conductive outer layer that is on the order of 14-18 microns thick. **Figure 5.2.4-7** illustrates the changes to the anode surface of the Gen 3.1 cell with the surface modification compared to the standard cell anode surface. Finally, **Table 5.2.4-1** contains the adhesion results comparing test samples made with the different proposed anode contact paste materials. Adhesive strength of the mesh material to the anode cell surface was maximized using a contact paste with fine nickel oxide particles and 40 volume percent pore-former. This result was combined with the process for creating a modified anode surface to create a system with improved permeability and adhesion. These improvements should contribute to cell power performance, cycling performance, and durability.

Delphi Cell @ 500X
NiO paste fired on at 1200°C

Figure 5.2.4-4: Micrograph at 500X showing the Gen 3.0 Anode Surface

Results:

Standard NiO grid paste, printed on dense bi-layer, fired on at 1400C
Fine NiO+40pf Interconnect Paste
Very good adhesion

Figure 5.2.4-5: A Cross-Section of a Cell Interconnect Interface is Shown with Improved Porosity and Adhesion

Delphi Cell 4929
Tape Cast Anode Layer
NiO + 40% Flake Graphite

Figure 5.2.4-6: Micrograph of a Cell with Improved Porosity and Adhesion

Delphi Std. Cell

**Delphi Cell 4932
Tape Cast Anode Layer
NiO + 40 % Flake Graphite**

Delphi improved Cell

Figure 5.2.4-7: Micrograph of a Cell with Improved Porosity and Adhesion

Grids printed to green bi-layer: fired @ 1400 C

adhesion scale: 1 (worst) - 5 (best) porosity scale: 1(lowest) -5 (highest)

Cell	Grid Paste	Grid / Green Anode	Grid Adhesion	Interconnect Paste	Reduced Paste Porosity	Feather Adhesion	Bedrolyte Quality
NDEC	N/A	N/A		Fine NiO / 0%pf	1	5	N/A
				Fine NiO / 40%pf	4	4	N/A
				Coarse NiO / 0%pf	5	1	N/A
				Coarse NiO / 40%pf	5	1	N/A
Gen 3	fine NiO/0pf	X	5	Fine NiO / 40%pf	4	5	Distinct pattern
				Coarse NiO / 0%pf	5	1	Distinct pattern
				Coarse NiO / 40%pf	5	1	Distinct pattern
Gen 3	fine NiO/40pf	X	5	Fine NiO / 40%pf	4	5	No Effect
				Coarse NiO / 0%pf	5	1	No Effect
				Coarse NiO / 40%pf	5	1	No Effect
Gen 3	coarse NiO/0pf	X	5	Fine NiO / 40%pf	4	3	No Effect
				Coarse NiO / 0%pf	5	1	No Effect
				Coarse NiO / 40%pf	5	1	No Effect
Gen 3	coarse NiO/40pf	X	4	Fine NiO / 40%pf	4	3	Subtle pattern
				Coarse NiO / 0%pf	5	1	Subtle pattern
				Coarse NiO / 40%pf	5	1	Subtle pattern

Table 5.2.4-1: Anode Paste Adhesion Results

5.2.5 Develop Separator and Support Components

Several perovskite coatings were evaluated and demonstrated to eliminate or reduce this interaction with encouraging durability for greater than 1000. Button cell testing demonstrated the use of alumina forming alloys to replace the chromia formers could mitigate this problem. Pre-oxidized Haynes[®] 214 and Kanthal (FeCr alloy) exhibited little or no impact on the degradation and power density of LSCF-6428 cathodes. The two primary concerns with using alumina-scale forming alloys in the current collection path (i.e., the separator plates and current collectors), were the formation of a resistive scale and potential mismatch stresses arising from the higher thermal expansion coefficient displayed by the alumina formers.

Delphi developed an interconnect via concept that, in conjunction with the use of silver coated FeCr alloy meshes as a current collector, could overcome the problem of using alumina former in the interconnect path. Shown in **Figure 5.2.5-1** is a schematic of this concept. A separator would be fabricated from two thin (~8 millimeter) FeCr alloy plates, each containing an array of holes spaced such that the holes in one plate fit directly in between the holes of the second plate when the two plates are aligned (known as the off-set via concept). The two plates would then be joined with a conductive, non-scale forming material to form an electrically conductive path from the filled holes of one plate to the filled holes of the second. In this way, the as-fabricated separator would be hermetic, form a predominantly alumina covered surface except in places (i.e., the holes) where the conductive filler material would be exposed. Conductive mesh would then be joined to the filled via holes on either side of the separator using a suitably conductive paste, likely the same material used to join each of the two plates, forming the anode and cathode current collectors.

FeCr alloys presented an additional problem in that their higher thermal expansion mismatch with other cell components (14.7 ppm/°C to 900 °C vs. 12.5 ppm/°C for the anode supported cell) can lead to significant deformations in the planar stack configuration. To minimize the amount of Al in the alloy, and hence reduce the thermal expansion coefficient (TEC) of the bulk alloy, different methods of applying thin Al layers to the surface of chromia-forming alloys were investigated.

Figure 5.2.5-1: The Off-Set Via Separator Plate Concept

Degradation of LSCF-based cathodes operating in Cr-environments showed a ~ 25% decrease in the initial power density and a ~ 3-fold increase in the degradation rate when compared to the baseline cathode configuration in a Cr-free environment. Conductive coatings for the ferritic stainless steel separator (three perovskite coatings ($\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (LSC), $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) and $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ (LNF)) as well as the CTP MnCo_2O_4 spinel coating) were investigated in terms of Cr-retention ability and ASR. Cr-retention studies were conducted in 8-button cell test stands in which coated Crofer disks were placed in proximity to the cathode but are not in the current path. This configuration is shown in **Figure 5.2.5-2** and allows the degradation due to Cr-volatility to be independently determined.

Figure 5.2.5-2: Configuration of Button Cell Testing of Cr-Retention Coatings Along with Magnification of one of the Coated Surfaces

While the baseline Cr-free cathode exhibited a degradation rate of 0.12%/hr in a Cr-free environment, newer cathode configurations developed showed no degradation over the course of 2000 hours of operation. The power density vs. time curves (**Figure 5.2.5-3**) show that all coatings tested improved the degradation rate over a typical uncoated Crofer sample (0.55%/hr). The LNF-coated sample (0.10%/hr) showed almost the same degradation rate as the Cr-free baseline indicating no Cr penetrated the coating during the run. Degradation rates were increased over the baseline Cr-free test for both the LSC (0.30%/hr) and the MnCo_2O_4 slurry coated sample (0.23%/hr). Due to coating irregularities discovered after testing, the LSM coated samples were removed from this study until they can be re-evaluated.

Figure 5.2.5-3: Selected Power Density vs. Time curves for Various Coated Crofer Samples

ASR measurements were conducted independently at a constant current density of 1 A/cm² and 750 °C on 430SS. As seen in **Figure 5.2.5-4**, all coatings exhibited an increasing ASR with time under these conditions with LSC having the lowest initial ASR. Recent discussions with the CTP regarding the high ASR of the slurry coated MnCo₂O₄ have indicated that the ASR is significantly higher on 430 SS than on Crofer, indicating that further testing might be required in order to determine a more appropriate ASR for this composition.

Figure 5.2.5-4: ASR of Selected Coating on 430SS

5.2.6 Develop Glass and Glass-Ceramic Seals

A two-cassette “dummy stack” with seals, made from a glass-fiber-mesh was assembled and thermally cycled 50 times while remaining hermetically sealed. After the initial 50 thermal cycles, the cassette stack was held at 750 °C for 500 hours, cooled to room temperature and then leak checked. The cassette stack remained hermetically sealed, and no further testing was done on the cassette stack. Additionally, a series of pop-gun samples were taken through the complete Phase I SECA durability goals, 1000 hour soak at 750 °C, 10 rapid thermal cycles, followed by a 500 hour soak at 750 °C. All samples survived with no leak. During pop-gun testing, all samples started leaking above 90 psi, but none were found to have completely broken. Pop-gun samples were prepared of the aluminum coatings developed for Cr-retention of the chromia forming alloys. The Al coating was deposited and treated as described in Section 4.3.7. The seven samples were tested with average breaking strengths of 52 PSI (34.4 min, 69.4 max). By comparison, bare Crofer yields around 20-25 psi and Hitemco[®] aluminized 430 yields around 55-65 psi.

5.2.7 Fabrication Developmental Stacks

The effect on cathode performance of chromium volatility from chrome oxide scale-forming stainless steel components was the focus of much of the intermediate scale testing. Initial tests to confirm the effect of chrome on the cathode were done with Pt contacts on the cathode side. A new set of tests were performed to evaluate alternate material sets on the cathode side that would still prevent chrome volatility but be more cost effective. A long-term test of one of these material sets was conducted in test number I-73. The interconnect plate was Crofer 22 but was coated with a $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (LSCo-20) layer on the cathode side. Contact from the interconnect to the cathode was made by a layer of Kanthol[®] mesh that had been electroplated with Ag. The Kanthol mesh is an alumina-forming stainless steel that has been shown to have minimal impact on the cathode.

The test ran for a little over 1200 hours, and then was cut short due to a power failure at the lab. The results are shown in the **Figure 5.2.7-1**. The cell degraded faster over the first 100 hours then slowed down to a rate of .007% per hour. The cell is currently being analyzed to determine the degradation mechanisms. The material set used on I-73 was repeated on F-19, a Gen 3 full-size cell. The initial power was the same as the chrome free button cell test of the cathode; however, the degradation rate was higher than expected at 0.2 % per hour. This is the first time Delphi achieved button cell power on a Gen 3 part. Some chrome was detected in the cathode during analysis of the cell and may have been the cause of the higher than expected degradation rate. The source of the chrome is currently being investigated. The fuel utilization of both the Gen 3 and intermediate cells was improved by increasing the flow uniformity in the anode channel. The flow was improved by changing the anode contact from feathers to a solid sheet of mesh. This eliminated areas of minimal or no flow obstruction that resulted in bypass regions. Most of the fuel flowed in these regions, starving the other areas of the cell. This resulted in steeper than expected utilization curves. The fuel utilization curves for both I-73 and F-19 are shown in **Figure 5.2.7-2**. The curves are linear from the low utilization range to around 70% fuel utilization. After that, the curve starts to roll over in what is most likely the result of diffusion limitations in the bulk anode.

Figure 5.2.7-1: Intermediate Stack Test Results for I-73

Figure 5.2.7-2: Fuel Utilization Comparison of I-73 and F-19

5.2.8 Evaluate Stack Performance

Delphi built and tested its Gen 3.0, 30-cell SOFC stack. The Gen 3.0 design consists of cassettes as repeating units for the stack, which are fabricated by high-volume manufacturing processes used in the transportation industry such as stamping, brazing and laser welding. These cassettes (including cell and interconnect) allow for the fabrication of a low mass, low volume stack. The Gen 3.0 design provided a 50% improvement in lowering mass and overall height of the stack. This is a key development because it demonstrates that a compact 30-cell stack can be fabricated from thin metallic cassettes with good sealing. This is an improvement over other designs in planar SOFC stacks with metallic interconnects which generally consists of thick separator plates (key to sealing) and interconnects that adds to volume, mass and most importantly, cost.

Further improvements were made in the Gen 3.1 design and multiple Gen 3.1 cassettes were successfully fabricated. Improved features in interconnection in the Gen 3.1 design allowed for improvements in power density and durability. The design changes also allowed for faster throughput for cassette production. Major progress in process development of stamping, brazing and laser welding is ongoing for the fabrication of Gen 3.1 cassettes for stack build and test. A 30-cell Gen 3.1 stack produced power density of 485 mW/cm² at 750 °C (0.7 Volts, 35% fuel utilization) with 48.5% H₂, 48.5% N₂, 3% H₂O compositions. An improvement in performance was observed in going from Gen 3.0 to Gen 3.1 stacks. Further evaluation and optimization of the Gen 3.1 design is in progress.

Initial testing of Generation 3.1 single cell stacks showed performance as high as 655 mW/cm² at 0.7 volts and 750 °C with a fuel composition of 48.5% H₂, 48.5% N₂ and 3% H₂O. **Figure 5.2.8-1** shows power density versus fuel utilization of a Gen 3.1 single cell; the power density remained relatively high up to almost 70% utilization. Multiple 30-cell Generation 3.1 stack modules were built and valuable lessons learned in the testing of these stacks. A 30-cell Gen 3.1 stack produced power density of 485 mW/cm² at 750 °C (0.7 Volts, 35% fuel utilization) with 48.5% H₂, 48.5% N₂, 3% H₂O compositions and 575 mW/cm² with simulated “recycle” reformat (35% H₂, 40% CO, 3% H₂O, rest N₂) (**Figure 5.2.8-2**).

Figure 5.2.8-1: Utilization Curve of a Gen 3.1 Single Cell on 48.5% H₂, 48.5% N₂, and 3% H₂O

Figure 5.2.8-2: Gen 3.1 Stack 30-Cell Stack on 48.5% H₂, 48.5% N₂, and 3% H₂O

Further optimization of interconnects, cells and the assembly process for Generation 3.1 stacks led to further improvements in power density and performance. A 10-cell stack produced power density of 580 mW/cm² at 750 °C (0.7 Volts, 39% fuel utilization) with 48.5% H₂, 48.5% N₂, 3% H₂O fuel composition, and 750 mW/cm² with simulated “recycle” reformat (35% H₂, 40% CO, 3% H₂O, rest N₂) (**Figure 5.2.8-3**).

Figure 5.2.8-3: Latest Gen 3.1 10-Cell Stack on 48.5% H₂, 48.5% N₂, and 3% H₂O

5.2.9 SOFC Stack Development Conclusions

Significant progress was made in stack development to reach the goals stated by SECA for the completion of Phase 1 targets. Full sized 30-cell stacks of the new and improved Gen 3.1 design were successfully built and demonstrated initial power densities that potentially meet stated targets. Durability testing on intermediate-sized stacks, with improved Gen 3.1 interconnect features demonstrated very encouraging results. Fundamental testing on the new glass fiber mesh (GFM) seal also demonstrated its capability for thermal cycling to meet the SECA targets.

5.3 Task 3: Reformer Development

Delphi divided its reformer efforts into two general categories based on the type of reforming to be done, either CPOx or Endothermic. The term “endothermic” is used to mean reformer configurations that have heat exchange features that allow for net endothermic reactions to proceed. This allows the energy recovered from anode tail gas to be put to practical use and as such represents integration of Reformer and Waste Energy Recovery function mentioned in earlier reports.

At present, the terms CPOx and Endothermic also correspond to Tubular and Planar Reformer configurations respectively.

Systems requiring CPOx-only reforming are serviced with tubular reformers while systems that will employ recycle-based reforming (which at higher recycle levels is endothermic) are serviced with planar reformers.

Table 5.3-1 shows the design progression for each reformer configuration and the system in which it is applied. Generation numbers are sequential in each family and are followed by the letter designation for reformer type (T= tubular, P=planar).

SOFC REFORMERS	
Tubular	Planar
Gen 0T (POC)	Single Planar (R&D Fixture)
Gen 1T (Gasoline Gen 2, 2A APU)	Gen 1P
Gen 1.1T (Gasoline – Gen 2C APU)	Gen 2P
Gen 2T	Gen 3P (Gasoline – Gen 3B APU)
Gen 3T (Gasoline Gen 3A APU)	Gen 4P (NG – Gen 3B / SPU 2)
Gen 4T (NG- Gen 3A / SPU 1)	Gen XP (NG – SPU 2 Demc Unit)

Same reactor
For 2nd iteration
of
design

Table 5.3-1: Reformer Generations

5.3.1 Develop Endothermic Reformer

5.3.1.1 Gen 2P Planar Reformer (referred to in previous reports as the ‘H2’ reformer) – Durability

Run time was accumulated on the Gen 2P Reformer to evaluate basic durability performance and washcoat adhesion. Eleven hours of testing were conducted at a low fueling rate (0.1 to 0.15 g/s). Cold starts were avoided by preheating the reforming layers with the Gas Phase Combustor (GPC) prior to reforming.

Initial CPOx performance was reasonable at approximately 0.7% Methane and 0.1% Ethylene. By the conclusion of 11 hours, which included some recycle operating points, performance had degraded to 1.3% Methane and 0.45% Ethylene. This rate of degradation is much higher than that seen on ceramic substrates previously tested. Washcoat adhesion had visibly failed at the front face of the reformer (see **Figure 5.3.1-1**), as well as on the back wall reformer-out chimney (both are surfaces that are perpendicular to the flow stream). Carbon formation was seen at the outlet ports of the reformer.

- Bare metallic substrate appears green
- Washcoated metallic substrate appears gray

Figure 5.3.1-1: Gen 2 Planar Washcoat Loss at Leading Edge

5.3.1.2 Gen 3P Planar Reactor - Combustor Evaluation

A phi slightly richer than typical steady state operation produced the most reliable starts (~0.4). (Phi is defined as the ratio of actual air/fuel ratio to stoichiometric air/fuel ratio.) Once lit, the flame was quite stable over a wide range of air/fuel mixtures and fueling rates. There were no visible hot spots on the simulated braze joints; the airflow pattern appeared to protect the sidewalls from the hottest part of the flame. The measured pressure drop on the air-side at the expected maximum flow rate was less than 0.5 kPa.

Two igniter locations were tested; one in an overhead position with respect to the burner similar to the Gen 2P reformer, and the second with the igniter slightly below the flame holder. The second position is the most attractive from a reliability and packaging perspective, as it locates the igniter upstream of the flame in a relatively cool zone, to

extend the life of the igniters. Though reliable ignition was possible, low flow rates were required to reduce the convective cooling of the igniter. Limitations of the design of the prototype caused some conductive cooling of the igniter, and the low wattage of the igniter used further exacerbated the problem. These limitations can be overcome in the final design. The key result was that ignition was demonstrated with an igniter upstream of the flame holder.

5.3.1.3 Gen 2P Planar Reformer with Pre-catalyst with Recycle

After resolving the manufacturing issues with the Gen 2P planar reformer design, operational characterization of the reformer showed several deficiencies. Although most of the issues were related to low surface area and high mass, solutions to the following problems were needed:

1. High hydrocarbons in the reformat, particularly ethylene
2. Relatively poor CPOx performance compared with the tubular reformers
3. High leading edge temperature on the reforming plates in CPOx mode

A concept that addresses these limitations was developed that uses a ceramic supported pre-catalyst ahead of the metallic reformer reactor. The concept was tested using a ½ inch thick, zirconia toughened alumina (ZTA) foam catalyst placed just upstream of the Gen 2P reactor. A CPOx catalyst formulation was employed on both the foam and metallic supports. Thermocouples were placed on the rear face of the ceramic supported catalyst, just ahead of the metal reforming layers. A gas sampling port was inserted in this same space.

Some key results of laboratory tests with and without a pre-catalyst are shown in **Table 5.3.1-1**. The Gen 2P reactor alone, without a pre-catalyst, demonstrated an efficiency of only 66% in CPOx mode, or about 10% lower than a typical tubular reformer with a foam-supported catalyst. With the short length of pre-catalyst in place, however, efficiency was restored to that of a tubular reformer. The greater gains in gross efficiency were observed when operated in endothermic mode, going from 88% without a pre-catalyst to 114% with the pre-catalyst. ("Gross" efficiency is the ratio of the lower heating values (LHV) of combined H₂ and CO output to the LHV of "new" fuel energy into the reformer, neglecting recycled energy content entering the reformer inlet. Recycled energy content contributes to the output without being calculated in the input, possibly resulting in a figure of merit greater than 100%) Methane content is included in the efficiency (gross) as its concentration is within the internal specification. Higher hydrocarbon conversion (ethylene) is greatly improved (order of magnitude), and is at least as good as the tubular reformer. Although the leading edge temperature has shown only modest reductions, we have not seen the washcoat degradation that was observed earlier without the pre-catalyst. In addition, the foam catalyst (pre-catalyst) temperatures appear to be lower than those observed with the tubular reformers under similar conditions, which has the potential for extending catalyst life.

These preliminary results are very encouraging, and this concept needs further investigation and optimization.

Table 5.3.1-1: Results of Testing Gen 2P Planar Reformer Effect of Pre-Catalyst

Reformer Configuration			Gen2P	Gen 2P w/ Pre-Cat
Reforming Efficiency @ 0.1 gps fuel		mole		
	POx Mode	%	66%	76%
	Endo Mode - Gross w/ methane	%	88%	114%
	Endo Mode - Net w/ methane	%	80%	89%
Reformate Composition-Endo mode		mole		
	Methane	%	0.7-0.8	0.6-0.7
	Ethylene	%	0.4-0.5	0.05-0.07
Leading Edge Temperature-Ref. Plate				
	POx mode @ 0.15 gps	°C	980	960
	Endo mode @ 0.10 gps	°C	890-910	860-910

5.3.1.4 Gen 3/4P Planar Reactor Design

5.3.1.4.1 Process Studies

Early Planar reformers were fabricated from Inconel; however, various brazing and operating problems were encountered. Having now developed braze methods for Haynes® 214, Delphi was successful in demonstrating improved operating durability. For ease of design execution, chemical etching was selected as the “machining” process for the reformer plates.

5.3.1.4.2 Square-to-Round Transition

The Feedstream Delivery Unit (FDU) was operated on previous tubular reformers for non-contact vaporizer, since this design was well characterized and developed. As this non-contact vaporizer has a round cross-section, and the reformer entrance is approximately square, a transition piece was needed. The goals of this transition piece are to: a) create small / negligible pressure drop, and b) provide good “filling” of each of the flow channels of the reformer. These characteristics were investigated using Computational Fluid Dynamics (CFD) modeling. Several inlet configurations were tested, and analysis showed that mass flow distribution within the reformer was more a function of the exit manifold configuration than entrance effects. The variation in flow distribution was acceptable and a large round tube to square transition was selected for the design. A flow profile is shown in **Figure 5.3.1-2**.

Figure 5.3.1-2:1A Results of CFD Analysis of Inlet Conditions on Mass Flow Distribution

5.3.2 Develop CPOx Reformer

5.3.2.1 Gen 3T Tubular Reformer Design (Gasoline CPOx)

The general intent of the Gen 3T reformer design was to continue along a line of continued improvement and refinement of a CPOx reformer that would enable systems level work to proceed without the added risk and complexity of a recycle based endothermic reformer system.

Steady-state mass flow inputs to the reformer were targeted at 2.5 g/s air and 0.45 g/s fuel. This is substantially higher than the 1.0 g/s air and 0.20 g/s fuel nominal flows that were frequently run with the Gen 1.1 Reformer and Gen 2C APU. The features employed to meet this requirement and the other stated objectives are listed below.

Testing on the Gen 3.0T Reformer design took place at both the subsystem and APU system levels. The initial design worked well with the exceptions of issues involving the design intent 12V start combustor igniter and the temperature capability of the reformer air pre-heat loop. The igniter issue was resolved using an alternate 42V igniter with similar geometry. Igniter development utilizing 12V input is continuing.

The reformer air pre-heat issue was one of concern over the adequacy of the temperature capability of the pre-heat loop. While initial performance of the reformer was good, it required use of the electrical air pre-heat coil to meet desired air inlet temperatures. This coil would normally be on only during a cold start and would be turned off after the reformer achieved steady state run mode.

5.3.2.1.1 Physical Features Incorporated in Gen 3 T Reformer -- Annular Air Pre-Heat at Reformer Inlet

Figure 5.3.2-1 shows the annular air pre-heat path employed in the Gen 3T reformer. This approach addresses several design objectives. By removing heat from the reformer inlet stream instead of the reformer outlet stream (as in previous designs), it is expected that all three thermal management issues will be improved. Reduced inlet temperatures will improve: a) pre-combustion tendencies, b) injector tip temperatures and, c) general heat flow thru the reformer to the Plant Support Module (PSM).

Additionally, the cylindrical shape achieved by making the air passages in an annulus allows accurate, gap-free mating of the insulation collar to further prevent unwanted heat leaks from the Hot Zone Module (HZM) (via reformer pass thru) to the PSM.

Figure 5.3.2-1: Gen 3.0 Tubular Reformer - Top Cross Section View

5.3.2.1.1.1 Modular Feedstream Delivery Unit Construction

Figure 5.3.2-2 shows a Feedstream Delivery Unit (FDU) assembly. This assembly integrates all the non-reactor based functions into a single assembly that can be loaded and serviced from the PSM without disturbing either the reformer insulation collar or any component within the HZM.

Figure 5.3.2-2: Gen 3.0 Tubular Reformer - Modular FDU Side View

This approach was possible because the Feedstream Delivery Unit has no components that pass radially through the reactor walls. The temperature sensors, igniter, and screen assembly are all loaded as a module axially from the PSM. This assembly approach is made possible by the annular air pre-heat configuration and the fact that the annulus can extend thru the insulation zone for a sealing interface fully within the PSM zone. Both a low profile screen support and low profile igniter were incorporated to remove potential flow and mixing obstructions.

5.3.2.1.1.2 Filtered Air Path Routing thru Injector Jacket

Figure 5.3.2-3 shows a cross section of the Injector Air Jacket as mounted to the Feedstream Delivery Unit housing. This jacket creates a path for cooling air from the PSM to remove heat from the injector body and tip. Air for this purpose is drawn thru the air jacket via the slight vacuum created at the PSM filter inlet.

Figure 5.3.2-3: Gen 3.0 Tubular Reformer - Top Cross Section View

5.3.2.1.1.3 Serviceable Air Pre-heat Heater Coil

Figure 5.3.2-4 shows the air pre-heat path and the location of the air pre-heat heater coil. This configuration allows for servicing of the pre-heat coil from the PSM.

Figure 5.3.2-4: Gen 3.0 Tubular Reformer - Air Pre-heat Path

5.3.2.2 Gen 3T Design

Testing on this design took place at both the subsystem and APU system levels. The initial design worked well with the exceptions of issues involving the design intent 12V start combustor igniter and the temperature capability of the reformer air pre-heat loop. The igniter issue was resolved using an alternate 42V igniter with similar geometry. Igniter development utilizing 12V input is continuing.

The reformer air pre-heat issue was one of concern over the adequacy of the temperature capability of the pre-heat loop. While initial performance of the reformer was good, it required use of the electrical air pre-heat coil to meet desired air inlet temperatures. This coil would normally be on only during a cold start and would be turned off after the reformer achieved steady state run mode.

5.3.2.3 Gen 3T Performance Testing

Baseline evaluation consisted of collecting reformate compositions over the required reformate power range. Throughout this range, reformate composition is evaluated against specifications. **Figure 5.3.2-5** shows four key reformate qualities plotted on common axis. Current CPOx system requirements have specifications for reforming efficiency, CH₄ slip, HC slip (for HC's >C₂), and for the CH₄ / H₂O ratio.

Figure 5.3.2-5: Gen 3T Tubular CPOx Reformer Results

5.3.2.4 Gen 4 Tubular Reformer Design (Natural Gas CPOx)

Gen 4T Tubular Reformer design was based on natural gas reformation. The catalytic reactor has a two-inch ceramic foam substrate coated with CPOx catalyst for natural gas reforming. The fluid mixer / start-up combustor was created by a swirl stabilized vortex breakdown. A quartz tube is used for initial tests of start-up, mixing, and reforming. **Figure 5.3.2-6** also shows a quartz tube for initial tests of start-up, mixing, and reforming.

Figure 5.3.2-6: Gen 4 Tubular Reformer / Isometric View

The general swirl generator assembly is shown in **Figure 5.3.2-7**. A conical device has, in this case, 2 tangential air inlet slots. The arrangement generates a highly swirling flow within the cone and represents an easy way to achieve such a flow field at lowest pressure loss expense. The strongly swirling flow breaks down and recirculates due to an upstream static pressure gradient, as illustrated in **Figure 5.3.2-8**.

Figure 5.3.2-7: Gen 4 Tubular Reformer / Swirl Generator

Figure 5.3.2-8: Gen 4 Tubular Reformer / Flow Field

5.3.2.5 Feedstream Development Unit Tubular Reformer

5.3.2.5.1 Swirl Testing Development

Testing was conducted to study the impact of swirl (angular momentum flux) on reformer performance and operating stability. To vary swirl, the number of director plate air inlet holes were reduced from 12 to 3. Refer to **Figure 5.3.2-9** for a representation of the inlet geometry modifications.

Figure 5.3.2-9: Geometry Modifications used in Experimental and Analytical Analysis

Experimental results showed increased temperature stability, as well as reduced hydrocarbon breakthrough and CO₂ content with fewer inlet holes. To validate the test results, modeling was conducted to look at the geometry's impact on air/fuel ratio distribution within the mix zone, the combustion zone, and at the catalyst face.

A Computational Fluid Dynamics (CFD) model was created to better understand the impacts of swirl and its correlation to experimental results. The model geometry, conditions, and assumptions are shown in **Figure 5.3.2-10**. Referring to **Figure 5.3.2-11**, two perpendicular planes were selected in the CFD model to calculate the angular momentum flux (swirl) through each plane in the mixing chamber using similar flow conditions as the experimental runs.

Model Description:

- Fuel Reformer with multi-species (C_7H_{16} as evaporating specie)
- Turbulent s-ke, coupled discrete phase model.
- Density as ideal gas
- inlet air at 150C
- n-heptane (liquid) in solid cone shape (angle = 73 deg)
 27C (32 micron diameter) with velocity = 16.75 m/s
- total fuel flow rate = 0.45 g/s
- Reformer wall temperatures as shown in the figure above.

Figure 5.3.2-10: CFD Analysis Conditions – Steady State

Figure 5.3.2-11: Planes/Surfaces for Angular Momentum Flux

The model used the Gen3T reformer geometry, similar to the Gen1.1 geometry tested. The angular momentum flux (amf) through a surface is a quantity that determines the strength of the swirl. It is defined as:

$$\text{amf} = \int r * V_t * \text{density} * V \, dA$$

Where r is the radial distance to the center of rotation, V is velocity vector, V_t is the tangential velocity at element dA.

Results of the CFD model are tabularized in **Table 5.3.2-2**. Angular momentum flux through the z-plane for 12 inlets was calculated to be 1.52e-4 N-m, where angular momentum flux for 3 inlets was calculated to be 6.55e-4 N-m, so the swirl generated using the 3-inlet geometry is 4.3 times greater than the 12-inlet geometry. Angular momentum flux through the y-plane for 12 inlets was found to be 5.68e-5 N-m, where the angular momentum flux for 3 inlets was 3.67e-4 N-m, so the swirl generated using the 3-inlet geometry is 6.5 times greater than the 12-inlet geometry. Increased swirl translates to longer particle residence time within the mixing chamber, which can aid with vaporization and distribution. The average fuel particle residence time was shown to increase substantially with the 3-inlet configuration versus the 12-inlet configuration.

Table 5.3.2-2: CFD Model Results Summary

	<i>CFD Model Results Summary</i>				
	Angular Momentum Flux (N-m)		Total Pressure Drop (kPa)	Fuel Particle Residence Time (s)	Max Mass Fraction n-Heptane Delta Across Catalyst Face
	Y-plane	Z-Plane			
12 inlets	1.52E-04	5.68E-05	1.73	Shorter	0.119
3 inlets	6.55E-04	3.67E-04	22.1	Longer	0.008

5.3.2.5.2 Short Combustor Testing

Testing was conducted to investigate the impact of a shortened Gen1.0 NCV mix zone on start and run stability, performance, and turndown capacity. The catalyst face was moved up towards the inlet by approximately 1.4 inches, thereby shortening both the combustion and mix zones within the reformer. The test was conducted to explore the possibility of shortening the reactor front-end to better accommodate other reformer designs within system packaging constraints. Test results are found within the body of the report.

5.3.2.6 Carbon Formation Study - Continuation

Examples of carbon found on the cold finger are shown in **Figures 5.3.2-12 and 5.3.2-13**. For a CPOx startup with gasoline, carbon deposition can be avoided during the warm-up phase if the O/C ratio is maintained at about 1.27; likewise, for steady state

operation at an O/C of 1.16. While these conditions are good for avoiding carbon formation in the SOFC stack, they are quite harsh in terms of catalyst durability. During steady state operation, catalyst center temperatures can reach 1100 °C to 1200 °C at expected fueling rates, which greatly diminishes catalyst longevity.

Figure 5.3.2-12: Cold Finger Showing Evidence of Carbon Formation Post-Reformer

Figure 5.3.2-13: Cold Finger Showing Evidence of Carbon Formation Post-Reformer: Close up

5.3.2.7 Effect of Humidity on Reforming

The results of cold finger testing with humidified air (2.5%w/w) in a tubular reformer with ceramic catalyst showed that the warm-up O/C could be reduced to 1.16 from 1.27 without carbon formation, however the steady state O/C could not be reduced. The results operating at this lower limit of O/C were somewhat confounded however, as fuel-puddling was observed in the mix zone of the vaporizer section (see **Figure 5.3.2-14**). The cause of the fuel puddling could not be determined and continues to be investigated. Spurious results have been observed on the cold finger when fuel puddling is present in the vaporizer.

Figure 5.3.2-14: Fuel Puddling in Mixing Zone

Despite being unable to reduce the steady state O/C ratio, substituting a small amount of moisture for oxygen in air resulted in reducing catalyst temperatures by about 25 °C across the rear face (see **Figure 5.3.2-15**). Though significant, this temperature reduction is considerably less than predicted if equilibrium conversion of all of the water is assumed. Only partial conversion of the water was confirmed by analysis of the reformat.

Figure 5.3.2-15: Moisture for Oxygen in Air Results

5.3.2.8 Reformer Design

Generation 4 tubular fuel reformer (Gen 4T) was developed to serve as a fuel reformer for gaseous fuels such as methane and natural gas. The reformer comprises the functions of gas mixing (fuel, air, recycle, steam, etc), start-up combustion, and fuel reforming in a single compact unit (**Figure 5.3.2-16** shows the Gen 4.1T Reformer as tested).

Figure 5.3.2-16: Gen 4.1T Tubular Reformer

5.3.2.9 Performance Testing (over turndown range)

The Gen 4.1 T reformer was tested under extended system SPU 1 turndown conditions. SPU 1 system requires the delivery of quality reformat between 38% and 115% of Rated Power condition. Testing was conducted on Gen 4.1T between 10% and 200% of Rated Power conditions.

Figure 5.3.2-17 shows reformat power vs. inlet fuel power plotted alongside the calculated equilibrium reformat power. The deviation that occurs between actual Reformat Power during testing is quite small at low rated power fractions and increases somewhat as higher power output is required of the reformer. The maximum reformat power required from the reformer, based on system operating modes, would be at 140% of rated power. The Gen 4.1T reformer did not show appreciable decreases in performance until well past reformat powers and space velocities associated equal to 200% rated reformat power. **Figure 5.3.2-18** shows the reforming efficiency vs. O/C for each of the relevant APU Power Modes.

Figure 5.3.2-17: Gen 4.1 Tubular Reformer / Turndown

Figure 5.3.2-18 : Efficiency vs. O/C vs Mode

5.3.2.9.1 Durability Testing

The Gen 4.1 T reformer was tested for durability of performance on the reformer test stand for 40 hours and on a reformer and stack stand (i.e., closely coupled to a SOFC stack) for 310 hours of continuous operation. During the reformer and stack test, three shutdown cycles occurred over a period of three weeks. No visible degradation was encountered during and after the tests. Durability test performance is summarized below.

- 310 hours accumulated with methane Gen 4.1T adiabatic reformer and 5 cell stack close coupled subsystem
- Reformer ran at an operating condition of 0.2gps fuel and 1.30 O/C with 83% reforming efficiency
- 3 start/shutdown cycles on reformer over 3 weeks of testing
- Initial mass spec readings: $H_2 = 33.2\%$, $CO = 14.4\%$, $CH_4 = 0.45\%$, $H_2O = 3.52\%$, $CO_2 = 2.54\%$
- Final mass spec readings: $H_2 = 33.2\%$, $CO = 14.2\%$, $CH_4 = 0.49\%$, $H_2O = 3.40\%$, $CO_2 = 2.55\%$
- Reformer outlet sample showed little to no degradation over 300 hours

The reformer temperature and hydrogen and carbon monoxide outputs remained stable for the entire test.

5.3.2.10 Gen 4.1T Design & Development

5.3.2.10.1 Reformer Design

Figure 5.3.2-19 shows a schematic of Gen 4.1 T reformer as instrumented for testing. Pictures of the test hardware are presented in **Figures 5.3.2-20 and 5.3.2-21**.

Figure 5.3.2-19: Gen 4 Tubular Reformer

Figure 5.3.2-20 highlights the conical mixing unit and **Figure 5.3.2-21** demonstrates the whole unit setup in the reformer test laboratory.

Figure 5.3.2-20 Conical FDU

Figure 5.3.2-21: Tubular Reformer

Design and functionality of the reformer have been reported in detail. The focus of this report is to evaluate and contrast experimental test results and development.

5.3.2.10.2 Start-Up Igniter Development

Initial tests with the Norton hot surface igniter proved unsuccessful. The Norton hot surface igniter was replaced with a Bosch spark igniter. The Bosch spark igniter performed ignition every time and without delay. Systems mechanization expects a 12V hot surface igniter and a study was engaged to refine position and strategy of ignition with the Norton igniter.

5.3.2.10.3 Pressure Loss Test

Pressure loss tests were conducted to ensure performance of Gen 4.1T with SOFC system requirements. **Figure 5.3.2-22** illustrates the air/recycle path of the conical FDU. All flow passages and hardware sections were tested separately to gain detailed knowledge of their performance. The projected pressure losses of the reformer sub-system (**Figure 5.3.2-23**) were well within the margin of system requirements.

Figure 5.3.2-22: Gen 4.1 Tubular Reformer / Pressure Loss

Figure 5.3.2-23: Gen 4.1 Tubular Reformer / Pressure Loss

5.3.2.10.4 NOC Performance vs O/C

Reforming performance tests were conducted with interest in quantifying the effects of O/C. Of particular interest, is the performance effect at NOC (Normal Operating Condition), as the system will spend a predominant time at these conditions.

Comparisons between equilibrium efficiency calculations and test data are demonstrated at load conditions of idle, 50%, rated power, and maximum power (**Figure 5.3.2-24**). At low power conditions (idle to 50% load), Gen 4.1 T reformer achieved almost 100% of the maximum possible performance while at high power the tests show a drop in efficiency of 1.5%. This is due to the increase in space velocity from 20,000 to 60,000 hr^{-1} .

Figure 5.3.2-25: Gen 4.1 Tubular Reformer / Efficiency vs O/C – NOC

5.3.2.10.5 Equilibrium vs Test Data Agreement & Repeatability

Figure 5.3.2-26 and Figure 5.3.2-27 show comparisons of calculated equilibrium compositions and temperatures alongside the average compositions and temperatures experienced during testing. The difference between test data and equilibrium are very small.

Figure 5.3.2-26: Equilibrium vs. Test: Species Averages

Figure 5.3.2-27: Equilibrium vs. Test: Temp and H₂O/CH₄ Average

The reformer has produced very near equilibrium compositions and temperatures. **Figure 5.3.2-28** is a demonstration of the repeatability of H₂ output of the reformer over

these 10 tests taken over 5-week period (with various catalysts). During catalyst “warm-up”, methane appears somewhat higher with hydrogen and carbon monoxide lower than at steady state operation. **Figure 5.3.2-28** includes warm-up tests as well as data from fully heated up steady state tests. Even including the warm-up cases the variation between measured hydrogen mole fractions only amounts to +/- 1.7%. Gen 4.1T has demonstrated performance and consistency well within systems specifications

Figure 5.3.2-28: Gen 4.1Tubular Reformer / Repeatability – Rated Power

5.3.2.10.6 Space Velocity

The effects of space velocity on fuel reforming performance are explained in **Figure 5.3.2-29**. At idle and NOC operating conditions, space velocity is nominally $\sim 20\text{K hr}^{-1}$ and at Rated Power and Max Power conditions space velocity is in the vicinity of 60K hr^{-1} . The 60K hr^{-1} space velocity was used as a design parameter in sizing the Gen 4.1T catalyst and reactor. Operating at space velocity of 20K hr^{-1} the loss of performance as compared to equilibrium calculated efficiency of typically less than 0.5%. Space velocity of 60K hr^{-1} results in typical loss in performance of around 2% to 2.5%. These results can be used to tune and minimize the reformer size for given system’s requirements.

Figure 5.3.2-29: Effects of Space Velocity on Fuel Reforming Performance

5.3.2.10.7 Durability Testing

5.3.2.10.7.1 Set-Up

A test was conducted with a Gen 4.1T reformer running on methane and a 5-cell stack close coupled to test their interaction and durability. The two subsystems ran on their own control systems to eliminate controls variability from the test. A valve between the two subsystems allowed them to be separated and run independently if required. The valve position was used to regulate the reformate flow to the stack.

Carbon formation was found within the plumbing in the furnace where the simulated reformate and reformer reformate paths came together and entered the stack manifold (**Figure 5.3.2-30 and Figure 5.3.2-31**).

Figure 5.3.2-31: Carbon Formation

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junction outside the furnace, a check valve could be used to reduce the amount of stagnant area that would allow carbon deposition.

5.3.2.10.7.2 Results

The durability test ran for a total of 310-hours over three weeks. An average of 100 hours of continuous steady state run time was accumulated during each week of testing. Methane CPOx reformat showed no discernible degradation with $H_2 = 33.2\%$, $CO = 14.4\%$, $CH_4 = 0.45\%$, $H_2O = 3.52\%$, $CO_2 = 2.54\%$. The SOFC stack showed about 9.5% degradation in power density at a steady rate over the span of the test.

Despite the flow path revision, carbon deposition was found in the tee fitting after the conclusion of the test (**Figure 5.3.2-32**). Further testing is being conducted to understand the carbon formation mechanisms.

Figure 5.3.2-32: Carbon Formation

Figure 5.3.2-33 and **Figure 5.3.2-34** shows the reformer hardware after 40 hours development stand testing and 310 hours steady state durability testing on the REFORMER and stack stand respectively. No visible degradation was observed during and after the tests. The highest material temperatures encountered were approximately $800^{\circ}C$, which would allow use of less expensive materials in future designs.

Figure 5.3.2-33: Carbon Formation

Figure 5.3.2-34: Durability: Condition @ 40h Operation

5.3.2.11 Carbon Formation

5.3.2.11.1 Reformer Carbon Testing using Coldfinger

Carbon deposition was found within the pipe connections between Gen 4.1T reformer and the SOFC stack after a 310-hour durability test. Tests at the same reformer operating conditions, with different hardware setup, revealed no deposition. A detailed investigation was initiated to determine the mechanisms and circumstances of carbon formation and deposition with the goal to understand and prevent carbon formation in systems applications. Tests were undertaken with Gen 4.1T reformer in combination with the “coldfinger” apparatus.

A schematic of the coldfinger is shown in **Figure 5.3.2-35**. The coldfinger is a carbon trap device where hot reforming gases from the reformer enter the coldfinger and pass over an internally cooled pipe (literally the coldfinger), which creates a decreasing temperature gradient on the pipe walls as well as within the gas flow. The temperature at which carbon first deposits is measured with thermocouples. The apparatus enables investigating the carbon formation behavior on different materials.

Figure 5.3.2-35: Cold Finger Geometry

Carbon deposition in the O/C=1.30 test started at 650 °C. Calculation prior to the test indicated a deposition temperature of 660 °C. Subsequent testing at O/C of 1.45 resulted in no carbon formation. The next steps in the investigation of carbon formation include detailed CFD and kinetics analysis of the test, further coldfinger tests with O/C's <1.3 using other materials.

5.3.2.11.2 Methane Carbon Formation Analysis

Equilibrium chemistry analysis was conducted as a first step in understanding the carbon formation issues encountered during various hardware tests. The simulations are conducted on a gas stream with Gen 4.1T reformer outlet temperature and gas composition. The cooling of the gas stream is simulated from reformer outlet temperature to room temperature. The carbon formation characteristics are calculated over the entire temperature range and the relative importance of various carbon forming and reducing mechanisms are compared. The following reactions and their reverse counterpart have been investigated in detail: Methane Cracking, Boudouard, and CO Reduction. The results are presented in **Figures 5.3.2-36** and **5.3.2-37** (solid carbon (graphite) mole fractions **Figure 5.3.2-36**).

Figure 5.3.2-36: Carbon Formation / O/C=1.30 Carbon

Figure 5.3.2-37: Carbon Formation / O/C=1.30 Species

The propensity of thermodynamically stable solid carbon is predicted below 670 °C with the reformer outlet temperature being 770 °C. Carbon was experimentally not observed (coldfinger test described above) until a temperature of approximately 650 °C. Above 670 °C, the reverse CO reduction and methanation reaction rates are larger than that of the Boudouard reaction, which prevents thermodynamically stable solid carbon. Below 920 °C, Methanation consumes solid carbon if formed by other reactions. The Boudouard reaction should precipitate solid carbon as soon as the temperature falls below 800 °C for the given reformer outlet composition. It is the reverse CO reduction reaction which is stronger in the temperature range of 900 °C to approximately 720 °C that consumes all the solid carbon formed by the Boudouard reaction. The reverse methane cracking, reverse CO reduction, and some N₂ dilution effects, together are finally responsible of reducing the carbon onset temperature to 670 °C with methane fuel at an O/C of 1.30.

5.3.2.11.3 Tubular Reformer w/ Recycle Concepts & Development

5.3.2.11.3.1 Fuel Reforming Concepts Study

A study was conducted to develop a fuel reformer concept that would fit the system SPU 1A design envelope. The success of Gen 4.1 tubular reformer together with its simplicity and durability initiated the question if Gen 4.1T reformer output could be boosted to meet system 1B performance requirements. Preliminary test results of some conceptual ideas are presented in the following section.

The general fuel reforming process is characterized in **Figure 5.3.2-38**. Fuel is synthesized to H_2 and CO in the presence of thermal energy and reforming agents, H_2O and CO_2 . The heat can be supplied by exothermic chemical reactions of molecular oxygen with fuel and/or hydrogen, as sensible heat, or by heat transfer in a heat exchanger. Reforming agents can be injected through steam or recycle, or as byproducts of the exothermic reaction of O_2 with fuel and/or H_2 . In any high efficiency system environment, most of the energy must come from the leftover energy of the fuel cell such as heat or unreacted chemical energy in the anode exhaust gas as illustrated in **Figure 5.3.2-39**.

Figure 5.3.2-38: Fuel Reforming Concepts / General Definition

Figure 5.3.2-39: Fuel Reforming Concepts / Reformer Sub-System Definition

5.3.2.11.3.2 Adiabatic Reformer with Recycle Test

Test results for several tests aimed at understanding the effects of ingested recycle are tabulated in **Table 5.3.2-3** and captures conditions investigated to meet several test objectives.

Table 5.3.2-3 Table of Results

EWO	Test Pt	Input Variables							Results			Predicted	
		Reactant Pre-heat (nom)	mdot Air	mdot Fuel	mdot Recycle	O/C	Utilization	Recycle Fraction	Gross Reforming Efficiency w/ CH4	CH4	Gross Reforming Efficiency x Utilization	Gross Reforming Efficiency w/ CH4 Predicted	CH4 Predicted
		[deg C]	[g/s]	[g/s]	[g/s]	[-]	[-]	[-]	[-]	mol%	[-]	[%]	mol%
MG733C-153	1	150	1.150	0.200	0.400	1.397	0.19	0.211	1.00	0.42	0.19	1.011	0.3%
MG733C-153	2	150	1.250	0.200	0.400	1.480	0.15	0.206	0.975	0.140	0.15	0.982	0.0%
MG733C-153	3	150	1.200	0.200	0.400	1.438	0.17	0.209	0.992	0.218	0.17	0.997	0.1%
MG733C-153	4	150	1.150	0.200	0.400	1.397	0.19	0.211	1.005	0.421	0.19	1.011	0.3%
MG733C-153	5	150	1.140	0.200	0.400	1.388	0.21	0.214	1.008	0.428	0.21	1.014	0.3%
MG733C-153	6	150	1.100	0.200	0.400	1.355	0.23	0.216	1.017	0.662	0.23	1.022	0.6%
MG733C-153	7	150	1.050	0.200	0.400	1.314	0.25	0.219	1.026	1.069	0.26	1.031	1.2%
MG733C-153	8	150	1.000	0.200	0.400	1.272	0.27	0.223	1.031	1.600	0.28	1.038	1.8%
MG733C-153	9	150	0.950	0.200	0.400	1.230	0.29	0.227	1.035	2.210	0.30	1.045	2.5%
MG733C-153	10	150	0.900	0.200	0.400	1.189	0.30	0.230	1.038	2.944	0.32	1.051	3.4%
MG733C-153	11	150	0.850	0.200	0.400	1.147	0.32	0.234	1.040	3.754	0.34	1.057	4.3%
MG733C-153	12	150	0.800	0.200	0.400	1.106	0.34	0.238	1.042	4.657	0.35	1.062	5.3%
MG733C-167	13	150	0.560	0.100	0.400	1.407	0.20	0.351	1.12	1.78	0.22	1.165	1.0%
MG733C-167	14	150	0.475	0.100	0.200	1.230	0.23	0.290	1.011	2.94	0.23	1.034	2.5%
MG733C-167	15	150	0.510	0.100	0.300	1.319	0.21	0.320	1.076	2.29	0.23	1.102	1.8%
MG733C-167	16	150	0.560	0.100	0.400	1.407	0.20	0.351	1.141	1.59	0.23	1.165	1.0%
MG733C-167	17	150	0.580	0.100	0.500	1.442	0.17	0.400	1.209	1.62	0.21	1.236	0.9%
MG733C-167	18	150	0.600	0.100	0.600	1.461	0.16	0.435	1.280	1.63	0.20	1.310	1.0%
MG733C-167	19	150	0.600	0.100	0.700	1.476	0.14	0.470	1.360	1.92	0.19	1.385	1.0%
MG733C-167	20	150	0.404	0.066	0.530	1.489	0.13	0.506	1.449	1.86	0.19	1.460	1.1%
MG733C-167	21	150	0.379	0.062	0.559	1.492	0.12	0.535	1.532	1.98	0.18	1.537	1.3%
MG733C-167	22	150	0.357	0.058	0.585	1.494	0.10	0.563	1.617	2.07	0.16	1.608	1.4%
MG733C-167-2	23	400	0.470	0.100	0.000	1.098	na	0.000				0.912	0.7%
MG733C-167-2	24	400	0.450	0.100	0.075	1.097	0.47	0.096	0.960	1.71	0.45	0.968	1.2%
MG733C-167-2	25	400	0.450	0.100	0.225	1.178	0.47	0.237	1.072	2.03	0.50	1.050	1.2%
MG733C-167-2	26	400	0.450	0.100	0.300	1.214	0.47	0.291	1.124	2.40	0.53	1.087	1.2%
MG733C-167-2	27	400	0.450	0.100	0.450	1.278	0.47	0.378				1.151	1.3%
MG733C-167-2	28	400	0.460	0.100	0.600	1.347	0.47	0.442				1.192	1.1%
MG733C-167-2	29	400	0.470	0.100	0.750	1.405	0.47	0.492				1.224	0.9%
MG733C-167-2	30	400	0.490	0.100	1.200	1.530	0.47	0.598				1.301	0.7%
MG733C-167-2	31	400	0.320	0.100	0.750	1.240	0.47	0.519				1.460	4.9%
MG733C-169	32	350	0.318	0.091	0.591	1.240	0.60	0.560	1.293	5.36	0.78	1.317	4.7%
MG733C-169	33	350	0.318	0.076	0.606	1.378	0.60	0.563	1.232	3.60	0.74	1.252	2.8%
MG733C-169	34	350	0.307	0.073	0.620	1.399	0.60	0.569	1.221	3.55	0.73	1.253	2.2%
MG733C-169	35	350	0.296	0.070	0.634	1.418	0.60	0.575				1.253	1.7%
MG733C-169	36	350	0.237	0.056	0.706	1.488	0.60	0.671	1.349	3.49	0.81	1.368	2.6%
MG733C-169	37	350	0.225	0.053	0.722	1.513	0.60	0.679	1.314	3.55	0.79	1.363	2.1%
MG733C-169	38	350	0.231	0.070	0.699	1.333	0.60	0.680	1.459	5.59	0.88	1.480	4.7%
MG733C-169	39	350	0.213	0.051	0.736	1.539	0.60	0.684	1.270	3.50	0.76	1.354	1.5%
MG733C-170	40	20	1.790	0.320	0.000	1.300		0.00	0.81	1.11		0.826	0.4%
MG733C-170	41	150	1.790	0.320	0.000	1.300		0.00	0.82	0.51		0.832	0.1%
MG733C-170	42	300	1.790	0.320	0.000	1.300	na	0.00	0.83	0.14		0.834	0.0%
MG733C-170	43	300	0.720	0.170	0.760	1.750	0.60	0.380	1.068	3.35	0.64	1.075	2.7%
MG733C-170	44	300	0.360	0.090	0.390	1.750	0.60	0.380	1.077	4.06	0.65	1.058	3.3%

5.3.3 Develop Catalysts

Catalyst formulations were identified for processing of both low-sulfur Swedish diesel fuel and the same fuel with 50 ppmw sulfur added. This work was done in conjunction with optimizing process conditions, space velocity and oxygen to carbon mole ratio, and substrate parameters. Proper selection of catalyst and processes results in a durable means of conducting diesel fuel partial oxidation.

Factors relevant to washcoat-metal substrate adhesion were investigated. This includes: Washcoat thickness, washcoat slurry pH, particle size, solids content, and pretreatment of the metal substrate. After washcoating of test coupons and exposing the coupons to different rapid aging tests, washcoat adhesion was evaluated by a controlled scratch test. Coupled with analytical characterization, the influence of each factor on adhesion could be assessed.

Several washcoat formulations are being tested at steady-state conditions for partial oxidation of California Air Resources Board (CARB) Phase II gasoline. One test reached the 2000-hour mark. After 2300 hours, selectivity to H_2 contained in the reformat was within quality specifications, while total non-methane hydrocarbons remained below the maximum level permitted.

The single planar test stand was used to determine the applicability of the current catalyst formulations to process a combination of methane, air, and simulated anode-gas recycle to meet system level reformat quality requirements for five different processing modes: Start-up, minimum power, normal operating, rated power, and maximum power. For each operating mode, H_2 and CO in the reformat were within 95% of thermodynamic equilibrium predictions, while methane and water concentrations were also within requirements. Gross reforming efficiencies were close to or greater than target values. Minimum catalyst degradation was observed during these tests.

5.3.3.1 Kinetics Model Development

5.3.3.1.1 Ethylene Formation During Gasoline Partial Oxidation

The kinetic model was combined with the CHEMKIN fluid-flow model PLUG for predicting spatial variation in gas-phase species composition along the reactor. PLUG simulates the behavior of a plug-flow chemical reactor and is designed to model the non-dispersive, one-dimensional flow of a chemically reacting, ideal-gas mixture in a conduit of essentially arbitrary geometry. The simulation conditions are shown in **Table 5.3.3-1**.

Table 5.3.3-1: PLUG Simulation Conditions

Fuel	Iso-octane (C ₈ H ₁₈)
GHSV Gas Hourly Space Velocity	45,000 hr ⁻¹
Reactor	1" D, 1" L
Feed	160.88 cm ³ /s
O/C ratio	1.05
Initial reactor temperature	1000°C, adiabatic

The molar concentrations of products during the partial oxidation of iso-octane are illustrated in **Figure 5.3.3-1**, indicating approach to equilibrium and **Figure 5.3.3-2**, illustrating the rapidly changing behavior at the light-off point show. The inlet temperature is 1000 °C, the oxygen to carbon ratio is 1.05, and the pressure is 1 atm. As a starting point, only gas phase homogeneous kinetics are taken into consideration.

Figure 5.3.3-1: Simulation Results Obtained For Partial Oxidation of Iso-Octane at O/C=1.05 And 1000 °C (Adiabatic Reactor)

Figure 5.3.3-2: Simulation Results Obtained for Partial Oxidation of Iso-Octane at O/C=1.05 And 1000 °C (Adiabatic Reactor)

5.3.3.2 Catalyst Formulation

Bimetallic catalysts with and without Rh were tested. The testing results of these 1200 °C aged catalysts are shown in **Figure 5.3.3-3**. For comparison purposes, Rh-only catalyst using the same catalyst support was also tested. The combination of Pt-Rh shows the highest hydrogen concentration. Pd-Ni and Pd-Rh show a hydrogen selectivity as good as Rh-only catalyst. However, Pt-Pd is a poor catalyst for partial oxidation, delivering a hydrogen concentration is as low as 18%. Pt-Pd may be a good combustion catalyst, since a significant amount of hydrogen is completely oxidized to water.

Figure 5.3.3-3: Bi-metallic Catalysts Supported on Alumina-NC

In the partial oxidation process, catalysts are typically held at 900 to 1100 °C. Delphi's previous catalysts have an excellent stability and hydrogen selectivity. Durability testing showed that the catalyst is stable during 1000 hours continuous operation at normal operation conditions.

5.3.3.2.1 Importance of Washcoat (Rh catalyst support)

The performance of the catalyst with Rh directly applied to the substrate (in the absence of washcoat), compared to Rh/alumina on the same substrate, showed poor performance **Table 5.3.3-2**. The hydrogen concentration was 23.2% for the Rh/alumina catalyst compared to 17.6% for the Rh without a support. The result indicates that a high surface area stable catalyst support is necessary for a high catalyst selectivity and stability.

Table 5.3.3-2 : Rh Catalyst support verses H₂ Concentration

Catalyst	H ₂ concentration (%)
Rh/alumina	17.6
Rh directly on substrate	23.2

The total Rh loading is the same for the two catalysts, 130 g Rh/ft³. The substrate was 200 cpsi mullite monolith using California PH II gasoline with Gas Hourly Space Velocity (GHSV) of ~ 48000h⁻¹ and O/C ratio of 1.05.

5.3.3.2 Diesel Fuel Reforming Catalyst Development

Five different formulations were tested for Swedish diesel partial oxidation. Prior to testing, the catalysts were air aged at 1200 °C for 6 hours. The test conditions were: GHSV ~ 50000 1/h, O/C ratio = 1.21. The testing results (**Table 5.3.3-3**) indicate that all of these catalysts are stable at steady state condition. Hydrogen concentration was about 22% for all these aged catalysts. All catalysts were supported on Zirconia Toughened Alumina (ZTA) substrate.

Table 5.3.3-3: Performance of Different Catalysts for Swedish Diesel Partial Oxidation Reforming

Catalyst	H ₂ concentration at 1 hr (%)	H ₂ concentration at 5 hrs (%)
RDRCA0-320:CB	21.7	21.7
RDRCA2-090:E//090:C	22.6	22.3
RDRCA0-360:CN	22.2	22.2
RDRCA0-360:CL	21.8	21.8
RDRCA0-360:C	22.3	22.2

5.3.3.3 Catalyst Product Development

The results in **Figure 5.3.3-4** demonstrate that the influence of washcoat loading on catalyst selectivity and stability is significant. The H₂ selectivity increased with the increased washcoat loading. **Figure 5.3.3-4** also shows that the hydrogen concentration increased from 21.5 % to 23.0 % when the washcoat loading was increased from 30 g Rh/ft³ to 63 g Rh/ft³. Increasing the amount of washcoat over 60 g Rh/ft³ did not produce much improvement for hydrogen selectivity. Similar phenomenon was also observed for a variety of monolith and foam substrates.

Figure 5.3.3-4: Influence of Washcoat Loading on H₂ Concentration on CD₄ Monolith Substrate

5.3.3.4 Catalyst Product Development

An L56 Taguchi robust engineering study was performed to determine the washcoat adhesion to a metallic substrate. The study variables and levels are shown in **Figure 5.3.3-5**. The study was designed to determine the washcoat/metallic substrate couple that maintained contact under thermal cycling conditions within a 900 °C to 1100 °C temperature range. The tests were conducted in a 20% hydrogen-3% water-balance nitrogen atmosphere. Many factors were included in the study including substrate choice, washcoat composition, substrate surface treatment (prior to washcoating), binder dry-weight, particle size, pH, slurry aging time and cleaning method of the substrate prior to surface treatments.

Figure 5.3.3-5: L56 Taguchi Study Matrix

The study indicated that Haynes 230 and Haynes 214 with a $\text{CeO}_2\text{-ZrO}_2$ washcoat had the best results. The pre-oxidized surface treatment of the metal substrate, 0% binder dry-weight and slurry aging time contributed to the favorable results. However, the other factors (i.e. particle size, pH, cleaning method) were unimportant to these results. The study showed that the choice of substrate was the largest factor influencing the results with the composition of the washcoat as the second most important factor.

Improving washcoat adhesion to metallic substrates continues to be investigated. Metal studied in this reporting period was 2"x2" Haynes 214 coupons. Coupons were cleaned or pre-oxidized in the following procedures:

- Put coupons into furnace, run a program to the pre-oxidation temperature (usually takes 1.5 hours)
- Keep at the desired temperature for 1, 2 or 3 hours
- Turn off the power to the furnace
- Cool to at least 600 °C before taking out the coupons from the furnace

Slurry used to coat these coupons was 2%Rh/alpha-alumina, with a particle size of 5 μm , slurry pH of 3, and slurry solids at about 40 %. When coating the coupons with the slurry, a 150 μm slip cast was used. The wet weight target was kept at about 0.30-0.35 grams per coupon, coating one side only. The coated coupon was dried at 120 °C, or

calcined at 538 °C for 1 hour. Coupons were aged at 1150 °C for 2 hours in flowing air before the scratch test. Adhesion tests were carried out using an adhesion test rig. After scratching the coated metal coupons with three needles, which had three different degrees of sharpness, the coupons were air-knifed, with pressurized air and then observed by optical microscopy.

5.3.3.4.1 Substrate Development

Three types of metallic foam substrates were tested. Haynes 215 substrate failed after catalyst aging at 1200 °C, becoming so brittle that we could not load it into the reactor. Foams made with titanium and FeCrAlloy showed enough strength to be handled. For comparison with the currently employed ZTA foam, a 2 % Rh/ATS washcoat was applied to both the Ti and FeCrAlloy substrates; the testing results are given in **Figure 5.3.3-6**. It is seen that while the FeCrAlloy substrate has a stability as good as ZTA foam, the ZTA maintained a slight performance advantage in terms of product hydrogen concentration. The Ti substrate shows very bad hydrogen selectivity. With the same amount of washcoat catalyst, the hydrogen concentration in the reformat is only about 16% with Ti foam, compared to 21% for ZTA and FeCrAlloy substrates. The normal catalyst temperature is 1000-1100 °C when O/C ratio is kept at 1.05. At this temperature range, we did not see much difference between the ZTA and FeCrAlloy substrates. However, if we increase the catalyst temperature to 1300 °C, which may happen for start-up or shutdown, we did observed some oxidation of the front of the FeCrAlloy substrate. Further study is necessary to improve the thermal stability of FeCrAlloy substrate at temperatures higher than 1100 °C.

Figure 5.3.3-6: 2%Rh/TS on Metallic Foam Substrates

In **Table 5.3.3-4** the results of influence of substrate structure and composition on hydrogen concentration are given. For all these tests, the same washcoat RDRCA0-320:CB was used, and the washcoat loading was kept the same, only the catalyst substrate was varied. Catalyst performance was superior on the monolith substrate as compared to that over the ZTA foam substrate. The catalyst on ZTA foam only produced 21.5% H₂ at 5 hours of testing, while the hydrogen concentration was above 23% for most others when a monolith substrate was used, except alumina monolith. This means that the substrate structure is a crucial factor in catalyst selectivity. On alumina monolith, hydrogen concentration dropped with reaction. This may suggest that the monolith material also plays a minor role in hydrogen selectivity. Washcoat RDRCA0-320:CB was used in all tests.

Table 5.3.3-4: Influence of Substrate Structure and Composition

Substrate	H ₂ concentration at 1 hour (%)	H ₂ concentration at 5 hours (%)
Mullite Monolith	23.2	23.1
Zirconia Monolith	23.5	23.3
Alumina Monolith	22.7	22.3
CTI Monolith	23.2	23.0
CD4 Monolith	23.0	23.0
ZTA Foam	21.7	21.5

Table 5.3.3-5 gives the testing results for different washcoats on 400 cpsi alumina monolith substrate. No significant difference was observed for these washcoats tested. All of them started at a hydrogen concentration of 23%. After 5 hours of testing, H₂ concentration for RDRCA2-090:E//090:C, a dual layer Rh/gamma-Al₂O₃ over gamma-alumina formulation, dropped to 22.6%; those for RDRCA0-320:CB, a single layer Rh/alpha-Al₂O₃ formulation, and RDRCA0-360:CN, a single layer Rh and Ni modified alumina formulation, dropped to 22.2% and 22.4%.

Table 5.3.3-5: Different Washcoats on 400 cpsi Alumina Monolith Substrate

Washcoat	H ₂ concentration at 1 hr (%)	H ₂ concentration at 5 hrs (%)
RDRCA0-320:CB	22.7	22.2
RDRCA2-090:E//090:C	23.1	22.6
RDRCA0-360:CN	22.6	22.4

Table 5.3.3-6 gives the testing results for different washcoats on 400 cpsi zirconia monolith. Significant differences were observed for these washcoats with this substrate.

RDRCA0-320:CB and RDRCA0-360:CN showed higher hydrogen selectivity and stability, and the hydrogen concentration over these two catalysts was almost constant at 23.5% during the 5 hours of testing. Dual layer RDRCA2-090:E//090:C catalyst showed a bad stability. Its hydrogen concentration dropped to 22.1% from 23.0% after 5 hours of testing.

Table 5.3.3-6 Different Washcoats on 400 cpsi Zirconia Monolith Substrate

Washcoat	H ₂ concentration at 1 hr (%)	H ₂ concentration at 5 hrs (%)
RDRCA0-320:CB	23.5	23.4
RDRCA2-090:E//090:C	23.0	22.1
RDRCA0-360:CN	23.5	23.4

Table 5.3.3-7 gives the testing results for different washcoats on 200-cpsi mullite monoliths. Differences were also observed for these three washcoats. RDRCA0-320:CB and RDRCA0-360:C were the best. The hydrogen concentration over these two catalysts was over 23% during the 5 hours of testing. A drop of hydrogen concentration was noticed for the dual layer RDRCA2-090:E//090:C and RDRCA0-360:CN catalysts.

Table 5.3.3-7: Different Washcoats on 200 cpsi Mullite Monolith Substrate

Washcoat	H ₂ concentration at 1 hr (%)	H ₂ concentration at 5 hrs (%)
RDRCA0-320:CB	23.2	23.2
RDRCA2-090:E//090:C	22.8	22.5
RDRCA0-360:CN	23.3	22.6
RDRCA0-360:CL	23.4	22.8
RDRCA0-360:C	23.5	23.3

5.3.3.5 Catalyst Process Development

In order to compare the difference between gasoline partial oxidation and diesel partial oxidation, an O/C ratio study was carried out. It is seen from the results (**Figure 5.3.3-7**) that the O/C ratio of 1.05, appropriate for gasoline partial oxidation, was not suitable for diesel partial oxidation. An O/C ratio of 1.1-1.2 is preferred. At a low O/C of 1.05, H₂ concentration in the reformat was low and methane concentration was high. This is because the reaction temperature was low. Some of hydrocarbons were not converted

or oxidized at O/C ratio of 1.05. On the other side, when O/C ratio was over 1.21, H₂ concentration was also low because of the excess oxidation.

Figure 5.3.3-7: Influence of O/C Molar Ratio on Swedish Diesel Partial Oxidation

Because the sulfur level in the Swedish diesel is low (only 5 ppm), Swedish diesel with an extra amount of sulfur was tested. The total sulfur in the diesel was increased to 50 ppm via addition of benzothiophene. New test conditions with the sulfur added diesel were: GHSV ~ 48000 1/h, O/C ratio = 1.11. The catalysts degraded within the 5 hours of testing. The high sensitivity of sulfur to the catalyst performance probably may be a result of the low aromatics concentration in the Swedish diesel. The results in **Figure 5.3.3-8** demonstrate that the effect of sulfur is alleviated by the aromatics in the fuel. When there was only 5 ppm sulfur in the diesel fuel, the hydrogen concentration in the reformat was almost constant, at about 22% for the aged catalyst. When additional sulfur was added to this Swedish diesel, the hydrogen concentration dropped from 22% to below 20% after 5 hour of reaction. When gasoline with 33-ppm sulfur was tested over the same catalyst, the hydrogen concentration was kept at 22% during the 5 hours of testing. This is about 33% aromatic in the gasoline fuel as compared to 3% in the Swedish diesel.

Figure 5.3.3-8: Impact on Fuel Aromatic Content of Catalyst Deactivation Caused by Sulfur Content

5.3.3.6 Catalyst Testing

Catalyst durability to over 14,000 warm-starts was demonstrated using Swedish low sulfur diesel fuel, containing 5 ppm sulfur. A reformer was operated by allowing air to flow continuously, while the fuel was cycled on for 10 seconds, off for 45 seconds, over a period of about 200 hours of testing. During this test interval, about 45 cold-starts also occurred. These results can be compared to continuous testing of the same washcoat formulation, in this case RDRCA0-320:CB (as described previously, an alpha-alumina support containing 2 wt. % Rh, on ZTA foam, loaded to about 30 g. Rh per cubic foot of support). Both processes were operated at an O/C of 1.03.

Continuous testing was performed on CARB Phase II gasoline. As previously shown catalytic partial oxidation processing of both Phase II gasoline and low-sulfur diesel resulted in similar performance. A comparison of cyclic and continuous processing is given in **Figure 5.3.3-9**. For both processing scenarios, similar rates of deactivation occur, indicating that cyclic operation does not additionally deactivate the catalyst, provided certain processing restrictions are met, as described below.

Figure 5.3.3-9: Comparison of Continuous and Cyclic Testing For the Same Catalyst Formulation

5.3.3.6.1 Durability Testing

Significant durability milestones were met. A catalyst washcoat with a generation 3.5 formulation, RDRCA0-320:CB, 2 % Rh on alpha-alumina, was supported on a ceramic monolithic support, having 400 cells per square inch, and a zirconia-mullite composition. This catalyst was tested for CARB Phase II gasoline partial oxidation at an O/C molar ratio of about 1.12 and a total space velocity of about 40,000/hr. Except for occasional, unintended shutdowns, the test operated continuously for over 2300 hours. The results are presented in **Figure 5.3.3-10**. Product H₂ concentration was maintained at over 20 % for the duration of the test, while non-methane hydrocarbons were below about 0.2 %, both matching design targets for the APU system. While CH₄ was above the 1 % target at the end of the test, this level can be reduced by operating at a different space velocity, changing the catalyst temperature, or by using a more active generation 4 or 4.5 washcoat formulation.

Figure 5.3.3-10: Durability Testing of Rh/Alpha-Al₂O₃ Washcoat on Monolithic Substrate – Gasoline Partial Oxidation

5.3.3.6.2 Single Planar Reactor R&D Build and Test

A study to determine reformat composition, at a variety of system-specified processing conditions was performed using methane fuel, simulated anode gas recycle, and air, using the single planar reactor assembly. Processing modes examined include: System-start up (SSU), minimum power (MIN), normal-operating condition (NOC), rated power mode (RATED), and maximum power mode (MAX). These modes are differentiated, for the purpose of this test by operating at differing total flow rates and amount of simulated recycle added. For these experiments a feed temperature of 300 °C and a furnace temperature of 850 °C were selected.

Temperature profiles for these tests are given in **Figure 5.3.3-11**. All of the operating modes operated nearly isothermally, except at the entrance and exit to the reactor, indicating some impact of high thermal losses at the ends.

Figure 5.3.3-11: Temperature Profiles Measured at Different Power Levels for Methane Reforming

5.3.3.7 Catalyst Application Development

5.3.3.7.1 Process Understanding

The durability of reformer catalysts using the accelerated aging test stand was evaluated as a function of the method used for shutting down the reforming reaction. The effect of starting up and shutting down the reformer catalyst was investigated with respect to their effect on catalyst durability. It was found that the shutdown step was the single largest contributor to catalyst degradation. Preliminary work also suggested that shutdowns performed in a lean environment were especially damaging. To better understand this aspect, the protocol for testing catalyst durability was changed to focus specifically on the effects of shutdown. The rapid, flame-initiated light-off described in the previous report was replaced with the slower and gentler technique of introducing the air/fuel mix (at syngas ratio) to the catalyst at 400-500 °C and waiting for the reforming reaction to initiate at its own speed. This limited the amount of degradation that would occur during catalyst light-off.

A second reactor system was also modified for reforming diesel fuel. The higher vaporization temperature of diesel fuel, along with its tendency to pre-ignite before the catalyst, required adjustments of the reactor system (both temperature regimes and fuel introduction systems). High efficiencies (>98% for H₂) were obtained; indicating that subsequent work on catalyst durability using diesel fuel is feasible.

Accelerated Aging Test Results

Catalysts based on the RDRCAO-320:CB formulation, were tested using CARB Phase II gasoline. **Figure 5.3.3-12** demonstrates the deleterious effect of the presence of oxygen during shutdown.

Shutting the catalyst down in air (essentially by stopping the fuel flow) is a standard method of halting the reforming reaction, in part because this allows any carbonaceous material (which can deposit on the catalyst during reforming) to be burned off. However, the resulting combustion heating, in a lean environment, apparently degrades the catalyst – especially noticeable after a series of shutdowns. Shutting down in flowing nitrogen resulted in much better catalyst durability. Another, more feasible method of shutting down in the absence of oxygen would be to shutdown in reformat itself. As shown in **Figure 5.3.3-13**, shutting the catalyst down either in flowing reformat (supplied by another reactor) or by stopping all flow of air and fuel (meaning the catalyst is left to cool in its own, still reformat) also prolongs the life of the catalyst.

Figure 5.3.3-12: Effect of Oxygen During Catalyst Shutdown

Figure 5.3.3-13: Effect of Reformat on Catalyst Shutdown

Shutting down in the absence of oxygen does raise the issue of carbonaceous buildup on the catalyst since it cannot be burned off during the shutdown. Under our test conditions, shutting down in nitrogen or reformat did not appear to lead to the deleterious buildup of carbon since the catalyst activity remained high, even after many shutdown cycles. However, this apparently only applies to catalysts that are still relatively fresh. Once the catalyst has been aged, carbonaceous buildup does become a problem, as shown in **Figure 5.3.3-14**.

Figure 5.3.3-14: Differences in Carbonaceous Buildup Between Fresh and Aged Catalysts when Shutting Down in the Absence of Air.

5.3.3.7.2 Operando Surface Analysis

Propane and methane partial oxidation, steam reforming, and autothermal reforming were investigated over a 5% Rh on alpha-alumina model catalyst system, using an operando UV-Raman cell capable of reaching 1000 °C. A methane O/C molar ratio of 1.0 and steam/carbon molar ratio of 2.3 were employed as the base conditions, while for propane O/C was 1.0 and steam/carbon was about 0.5. To accommodate the requirements of the test cell, the reactants were diluted with He.

Figure 5.3.3-15 and **Figure 5.3.3-16** present equilibrium modeling of the carbon forming regimes for both methane and propane, and they also indicate the experimental values of temperature and O/C molar ratios that were evaluated during these tests. Any operating point above the appropriate steam/carbon ratio line is in a carbon-free regime, from a bulk-phase equilibrium standpoint. Since these experiments can analyze the surface of the catalyst at operating conditions, there is a potential for the observation of non-equilibrium carbon existing as reaction intermediates.

Figure 5.3.3-15: Equilibrium Modeling of Carbon Forming Regimes for Methane Autothermal Reforming

Figure 5.3.3-16: Equilibrium Modeling of Carbon Forming Regimes for Propane Autothermal Reforming

5.3.3.7.3 Methane Reforming Modeling

5.3.3.7.3.1 Kinetics Predictions of Coking Propensity of Methane Partial Oxidation

Coke formation is problematic to the reforming process as reformer catalysts are susceptible to deactivation by coke. It is desirable to avoid operating the reformer at the coke formation regime. The coke formation regime is typically determined via thermodynamic equilibrium calculations. **Figure 5.3.3-17** shows the extent of equilibrium carbon formation at various temperatures and oxygen-to-carbon ratios. The free-energy minimization procedure is accomplished with the Equil[®] software, that uses a Chemkin 3.7 interface to STANJAN subroutine. Solid carbon is considered a bulk-phase species, and is specified in the surface kinetics input file.

Figure 5.3.3-17: Equilibrium Carbon Composition as a Function of Temperature at Various O/C Molar Ratios

Carbon formation depends, not only on the temperature and the local chemical composition of the stream, but also on the residence time. To give a better prediction of carbon formation propensity under reaction conditions, including both transient and steady-state, a detailed model is required. Delphi has developed a kinetic model for the prediction of coking propensity during the partial oxidation of methane. The model is capable of providing essential information about mechanisms and rates of the associated reactions. The present study determines the primary reaction pathways and intermediates that can potentially lead to carbon formation. Both homogeneous gas phase kinetics and surface kinetics are included in the CHEMKIN kinetic model. Gas phase chemistry contains 2498 reactions and 292 species; 131 are with five or more carbon atoms and cyclic or polycyclic structure and are considered to be indicators of propensity to form carbon deposits. The kinetic model is developed based on the

reaction mechanism and thermodynamic data from various sources. Additionally, surface chemistry for Rh catalyst is obtained from Delphi's research and is used with minor modification. The kinetic model is combined with the CHEMKIN fluid-flow model PLUG for predicting spatial variation in gas-phase species composition along the reactor. PLUG simulates the behavior of a plug-flow reactor and is designed to model the non-dispersive, one-dimensional flow of a chemically reacting, ideal-gas mixture in a conduit of essentially arbitrary geometry. The conditions studied are tabulated in **Table 5.3.3-8**.

Table 5.3.3-8: Evaluation Conditions for Kinetics Predictions of Coking Propensity of Methane Partial Oxidation

O/C	Tot Vol F SLPM	Fuel CH ₄ SLPM	Air N ₂ +O ₂ SLPM	LV cm/s	CT s	GHSV hr-1
1.05	5.25	1.50	3.75	17.27	0.15	24474.76
1.05	9.66	2.76	6.90	31.77	0.08	45033.57
1.05	14.00	4.00	10.00	46.05	0.06	65266.04
1.05	19.25	5.50	13.75	63.32	0.04	89740.80
1.05	30.63	8.75	21.88	100.73	0.03	142769.45

5.3.4 Fabricate Developmental Reformers

Two tubular CPOx reformers designs were fabricated and advancement of process development of the next generation planar reactor was conducted.

5.3.4.1 Gen 3T Tubular CPOx Gasoline Reformer

The Gen 3.0 T gasoline reformer assembly incorporates a tube-within-a-tube design. Several meetings were held to discuss the feasibility of the part design and braze requirements. The braze alloy used on this assembly was BNI-9. Due to the thickness variations of the part geometry, it was difficult to predict the braze results based on thermal mass and time at temperature for a successful braze. The first braze trial proved to be unsuccessful due to the braze alloy diffusing through the outer tube creating leaks that were not repairable. For the second trial, less alloy was used in specific areas of the assembly and the temperature profile of the braze process was adjusted to help reduce the amount of diffusion. This changes resulted in a successful leak-free braze and the reformer was delivered for testing.

5.3.4.2 Gen 4.1T Tubular CPOx Natural Gas Reformer

Gen 4.0 and its subsequent derivative Gen 4.1 represented an entirely new Feedstream Delivery Unit (FDU) design that consisted of several intricate parts. There were several meetings between the design and braze development teams to understand how this

reformer would be brazed. The meeting resulted in a multiple subassembly design. The reformer was separated into three subassemblies that were fixtured and brazed individually using BNi-9 braze alloy. The braze trials were successful on the first attempt and subsequently two reformer assemblies were delivered for testing.

5.3.4.3 Planar Reactor Braze Process Development

Gen 3P reactor is the next generation of planar reactor and involves etching as the primary material removal process. Etching eliminates thermal mass and reduces the number of parts needed to make up an assembly. The components are assembled utilizing a vacuum braze process being developed and performed at Delphi - Harrison Thermal Systems. The braze filler material being used for this development is BNi-5 and the reactor material is Haynes 214. The process involves spraying the braze alloy onto the perimeter of the plates and also coating alloy along the outside of the assembly. Improvements to the fixture have enabled the entire reactor assembly to be brazed in a single process without the need for secondary braze cycles.

There have been two braze trials of the new Gen 3P reactors at Delphi - Harrison Thermal Systems. The first assembly utilized Haynes 214 with BNi-9 braze alloy. The resulting reactor had several internal crossover leaks (leaks between reforming and combustion passages). Failure analysis determined the braze alloy was diffusing through the layers of the reformer and was the primary cause of the internal leaks. The decision was made to continue development with BNi-5 braze alloy. BNi-5 alloy is not as aggressive as BNi-9 and will not diffuse through the layers of the reformer as quickly as the BNi-9 alloy.

The second braze trial of the new Gen 3P reformer was performed using BNi-5. The resulting reformer had small internal crossover leaks. Failure analysis determined that the amount of braze alloy filled between some of the layers and the resulting forces separated the layers creating a leak path. The time and temperature of the braze run was acceptable but future runs will have less braze alloy applied. Future part orders will have additional strength ribs added to the combustion layers of the reformer. The development of this new Gen 3 reformer is ongoing.

5.3.5 Develop Endothermic Reformer

5.3.5.1 Gen 2P Gasoline Reformer

An improved reactor configuration was described that involved placing a foam-supported pre-catalyst ahead of the Gen 2P Planar (heat-exchange capable) section of the reformer reactor. The results of preliminary runs using this configuration showed interesting improvements in the following areas:

- Reducing higher hydrocarbons (ethylene) in the final reformat
- Improving CPOx performance
- Reducing lead edge temperatures of the planar reactor

These results were obtained at a fairly low reforming capacity (4.9 KW on an LHV basis). Testing with more aggressive O/Cs and higher combustor temperatures has yielded higher efficiencies with somewhat higher fueling rate (7.8 KW on an LHV basis). This result did not meet expectations. The most recent results are shown in **Figure 5.3.5-1**.

Figure 5.3.5 -1 Gen 2P Planar Reformer Results

The limitations of this design are being addressed in the Gen 3 Planar reactor design (higher catalytic surface area, higher heat transfer rates and reduced heat losses). Fabrication of the Gen 3P reactor is in process.

5.3.6 Reformer Developments – Conclusions

5.3.6.1 Reformer– Subsystem

Planar reformer development progressed with the demonstration of >120% gross reforming efficiency on gasoline. While this was a significant improvement, performance did not meet requirements over the operating range. Features to reduce thermal losses, lower thermal mass and increase reformer / combustor heat exchange effectiveness have been made in the subsequent Gen 3P reactor design. The build of this design is in process.

Tubular reformer development saw the successful launch of Gen 3T reformer design for gasoline as well as the Gen 4.1T Reformer for Natural gas. The latter design demonstrated good performance over wide operating range and was successfully durability tested to 310 hours. Carbon formation within the test rig spawned both analytical and empirical studies that have furthered Delphi's understanding of carbon formation behavior.

A major focus of development testing with Gen 4.1T was achieving higher gross reforming efficiencies through ingested recycle. A full range of test conditions were explored and evaluated based on specific system requirements. Several novel concepts employing tubular reformers and recycle ingestion were modeled and analyzed.

5.3.6.2 Reformer – Catalyst

Progress continued to be made in developing catalysts to meet system-level requirements from both a performance and durability perspective. Catalyst durability was demonstrated over 2000 hrs. Catalyst formulations and appropriate processing regimes were identified for processing of diesel fuel containing up to 50 wppm sulfur. Methane reforming at five different system-applicable power levels were found to operate within reformat quality and system efficiency requirements. Work continues in identifying both equilibrium and non-equilibrium carbon formation regimes during methane reforming. Development is still required to meet longer-term durability goals and improve washcoat formations with respect to adhesion on metallic substrates.

5.4 Task 4: BOP Component Development

5.4.1 Combustible Gas Sensor

Figures 5.4.1-1, 5.4.1-2, and 5.4.1-3 show the sensor response in Tests 1, 2 and 3, respectively. The sensor response time is approximately 1 second. As received, the prototype sensors are not uniform and show slight differences part to part. Sensor # 403-2 saturates at 4000 ppm while # 403-1 saturates at 8000 ppm. Upon further discussion with the vendor, it was learned that the saturation level could be manually adjusted such that each sensor would be the same. The sensor response time of approximately 1 second was acceptable for its intended application.

Figure 5.4.1-1: Sensor Test 1

Figure 5.4.1-2: Sensor Test 2

Figure 5.4.1-3: Sensor Test 3

5.4.2 Develop Air Delivery and Process Air Sub-System

5.4.2.1 Process Air Blower Motor

Axial and radial tolerance studies confirmed that at “extreme” tolerance conditions, appropriate fit is maintained between individual components and system sub-assemblies. Eight motors and controllers were fabricated and assembled.

Fabrication of the custom test Dyne was completed in February 2004; however, test development continued to evolve due to the complexity of measuring high speed / low torque characteristics. **Figure 5.4.2-1** shows the Test Dyne for the Process Air Motor.

Figure 5.4.2-1: Process Air Motor / Test Dynamometer

Spin/burst testing of two rotors resulted in failures at greater than 115,000 rpm, which is significantly greater than the maximum operating speed of the device. This helped to confirm an adequate margin of safety was met with the design. **Figure 5.4.2-2** shows a spin-tested rotor core. The picture illustrates a core, which due to the extreme centrifugal loads at high-speed, lost its interference fit with its mating shaft. The picture

also shows the resultant damage after dropping to the spin pit floor at these high speeds.

Figure 5.4.2-2: Rotor Spin Test

Dyne characterization of the PAM confirmed that the torque specification was met across varying ranges of speed, while compressor flow characterization indicated that system pressure and flow requirements were also met.

5.4.2.2 Process Air Manifold

The CFD analysis predictions of the manifold closely matched the airflow test results. **Figure 5.4.2-3** shows the CFD results of one of the manifold designs that were also tested. As seen from the output pressure plot of the manifold with one of the four flow passages fully open and the others closed, approximately 10.2 kPa pressure drop occurs through the flow transition elbow, approximately 0.7 kPa drop occurs through the straight passage of the manifold, and approximately 8.3 kPa drop occurs through the actuator valve and outlet nozzle.

Figure 5.4.2-3: Manifold CFD Results

The airflow test stand is shown in **Figure 5.4.2-4**. The manifold was tested at various conditions including the one analyzed using CFD.

Figure 5.4.2-4: Air Flow Test Bench

Figure 5.4.2-5 provides a comparison the measured DC electrical input power to the PAM controller, the calculated compressor air power, and the PAM manifold output air power verses mass airflow. The manifold is the largest source of power loss due to the design constraints caused by the tight packaging requirements of the APU application. Potential opportunities to reduce the power losses in the PAM will continue to be investigated.

Figure 5.4.2-5: PAM Air Flow Test Results

Two motor controller failures occurred during separate PAM performance tests. One of the failures involved a field effect transducer that was subjected to excessive thermal stress. The controller cover, which pushes the transducers against the heat sink, was left off during the test so that voltage measurements could be made. The decision was made that further testing will be done with the cover in place. The other failure involved broken lead wires from two capacitors in the controller. The supplier weakened the leads by flattening them, making the leads more susceptible to vibration failure. An adhesive, used in production automotive controllers, was applied to the two capacitors in each of the motor controllers so that they would better resist vibration. The supplier was asked to review the capacitor lead forming operation.

PAM compressor test results (**Figure 5.4.2-6**) indicated the compressor operating at 68,000 RPM is capable of approximately 21 grams-per-second mass airflow at an output static pressure of 26 kilopascals. The motor dynamometer test results (**Figure 5.4.2-7**) indicate the PAM motors generally exceeded the required torque specification, with exception of maximum speed. It was found that the motor dynamometer, in spite of a significant effort to improve the measurement capability, was incapable of acceptable accuracy and stability at the high speed / low torque levels at which the PAM operates. The measured torque values could not be used for precise shaft power or motor efficiency calculations.

Figure 5.2.4-6: Compressor Characterization

Figure 5.4.2-7: PAM Torque vs. Speed

5.4.3 Hot Zone Components

5.4.3.1 Gasket

Figure 5.4.3-1 shows the results of the new seal technology.

Figure 5.4.3-1: Gasket Testing

The initial leak recorded at room temperature measured 0.28 sccm of helium. That rate stayed relatively level until the gasket was brought to a temperature of approximately 500 °C. At that point, the leakage dropped off significantly to a level of 6.5×10^{-4} .

The first thermal cycle of the gasket peaked at 600 °C and was allowed to cool to room temperature from there. The leak rate remained steady throughout that time and into the next cycle until the temperature approached 900 °C. Here the leak rate once again began to drop and continued to drop for the remainder of the cycle. Upon completion of the two cycles, the fixture was removed and disassembled.

A second sealing concept, based on the same technology, was also evaluated. The advantage of this concept lies in having a gasket that seals very well and allows for rapid change-out of components. The latter capability lends itself to a lab setting where such flexibility is likely to be needed. The results for one thermal cycle are shown below in **Figure 5.4.3-2**.

Figure 5.4.3-2: Gasket Testing/ Second Test

The leak rate measured at room temperature before the cycle was 4.1×10^{-2} sccm. This is notably better than the first concept and may be attributed to a more uniform loading provided by a four-bolt configuration. Throughout most of the first half of the cycle, the leak rate remains relatively level. At 700 °C the leak increases a small amount but drops again just as quickly to 3.9×10^{-5} sccm. At this high temperature, it is likely that the gasket becomes compliant enough to conform more closely to irregularities on the surfaces of the sealing faces. Upon reaching room temperature again, the leak rate is comparable to the rate at which it began the cycle.

The results of the “race track” C-ring geometry are shown in **Figure 5.4.3-3**. The results are similar to the initial results achieved with the round geometry previously reported. Sealing improves when the temperature in the first thermal cycle reaches 500 °C to 600 °C. This is likely the point where the nickel coating becomes compliant enough to create a light bond and further fill in any leak paths that exist. Sealing continues to improve through subsequent cycles, though not at as drastic a rate as previously observed. The exception to this is the gasket in the “cathode out” position. This will be investigated in subsequent work. Excluding that case, the gaskets performed exceptionally well. Leak rates ranged from 4.8×10^{-8} sccm to a low of 4.7×10^{-10} sccm per gasket.

Figure 5.4.3-3: C-Ring Geometry Gasket Results

At the end of the seventh thermal cycle, room temperature leakage of “anode in” increased abruptly and continued to rise, though with less severity, with each successive cycle. The final reading at the end of the tenth cycle was 4.4×10^{-6} sccm. Measurements from the high-temperature portion of these cycles did not rise in a similarly fashion but did trend towards increasing leakage that ended with a leak rate of 1.6×10^{-9} sccm. At room temperature, where leak rates are typically higher, these levels are not significant. This fact, combined with the lack of physical evidence upon autopsy, does not suggest a terminal gasket failure. The same gradual trend appears to be present for the remaining gaskets. Although there is no basis to conclude that leakage would continue to increase or not with further cycling, it does illustrates the need for longer-term testing beyond ten thermal cycles.

The performance of the “cathode out” gasket requires separate analysis. There was improvement throughout the ten cycles, (never below a rate of 1.0×10^{-3} sccm). The gasket is identical to the one used for the cathode inlet. In the inlet position, the gasket performed extremely well, which would suggest the poor performance in the exhaust position as possibly anomalous. An autopsy of the fixture post-test revealed a small gap in the witness ring left by the gasket. The witness ring is the mark left where the gasket was in contact with the fixture. This gap was the source of the gross leak and explains the poor performance in relation to the other gaskets. The root cause of the gap is yet unknown. It may be due to either a contaminant on the sealing surfaces, or a flaw in the plating on the gasket. Evidence of either possibility was lost during the test or the autopsy. Subsequent testing will reveal the frequency of such a failure and possible resolutions. It is important to note that despite the failure, the leak rate was below that of any other gasket technology previously tested.

5.4.3.2 Integrated Component Manifold (ICM)

The manufacturing approach used for the Integrated Component Manifold was very similar to previous generations. Three thin plates and two thicker plates are cut using a water jet cutter. These five plates, and several minor components, are then brazed together to form a solid manifold. This five-piece design has been used successfully in previous Auxiliary Power Units (APU). Knowledge gained from previous builds has been incorporated into the current generation to further improve the robustness of the ICM. Alternative manufacturing methods are constantly being examined but it has been decided that for the current low-volume prototypes the five piece brazed assembly is the most effective manufacturing approach. Testing is planned for the next reporting period for the current ICM design. **Figure 5.4.3-4** shows the brazed Gen 3 ICM assembly prior to machining.

Figure 5.4.3-4: Brazed Gen 3 ICM Assembly

The manufacturing of the ICM continues to be a learning process, especially the brazing operation. An image of the braze fixture is shown in **Figure 5.4.3-5**.

Figure 5.4.3-5: Braze Fixture

Data was obtained on the high-temperature components' performance during system tests with thermal stacks and electrochemical stacks. The ICM performed well in the system tests. Some small changes have been implemented to improve the performance of the next ICM manifolds currently being fabricated.

Gases burned in the GPC are used to heat the cathode air entering the system. Consistent function of the GPC is critical for both start-up and steady state operation. Previous GPC designs did not mix the gases well enough to keep the stream of gas lit. The intent of this design effort was to develop a device that could mix the low flow anode tail gas into the high flow cathode exhaust while staying within an allocated pressure drop of 1kPa. An image of the current GPC is shown in **Figure 5.4.3-6**.

Figure 5.4.3-6: GPC Model

The GPC was also tested during the system runs. It ran throughout the tests without losing its flame. The GPC is the hottest area of the entire system so material fatigue is of concern. The GPC was inspected after the systems tests and showed no signs of material fatigue due to the high temperatures. An area of the ICM that surrounds the GPC did see a large displacement caused by a local extreme temperature gradient. This area is being analyzed to address the issue.

5.4.3.3 Cathode Heat Exchangers

A final CFD analysis was run on the new Cathode Heat Exchangers with the new base-plate design. The pressure drop concerns were mitigated. **Figures 5.4.3-7, 5.4.3-8, - 5.4.3-9, and 5.4.3-10** show the CFD results.

Fuel Cell CHEX – Air

Fuel Cell CHEX – Exhaust Gas

Figure 5.4.3-7: CFD Cathode Heat Exchangers Geometry

Pressure CHEX - Air

Pressure CHEX – Exhaust

Figure 5.4.3-8: CFD Results/ Cathode Heat Exchangers – Pressure

Figure 5.4.3-9: CFD Results/ Cathode Heat Exchangers - Velocity

Figure 5.4.3-10: CFD Results / Flow Distribution

With a mutually agreed upon Cathode Heat Exchanger's design in place, the Cathode Heat Exchanger's components were detailed and drawings were produced. Subsequent to design, the Cathode Heat Exchanger component parts were sourced from various local suppliers with the intention of assembling and brazing them at Delphi Thermal & Interior in Lockport, New York. This sourcing activity is underway with all component parts expected in July 2004. **Figure 5.4.3-11** shows the released Cathode Heat Exchanger design.

Figure 5.4.3-11: Cathode Heat Exchanger / Assembly

The initial CHEX braze run included two units that were setup identically. **Figure 5.4.3-12** shows a completed Gen 3.0 Heat Exchanger.

Figure 5.4.3-12: Gen 3.0 Heat Exchanger

The parts produced from the braze furnace were visually inspected and had good braze joint characteristics including braze fillet formation and part color. Both units exhibited

minor leaks after the first braze run. A subsequent braze run successfully produced two units for initial component and system testing.

5.4.4 Recycle System

5.4.4.1 Recycle Flow Sensor and Control

The mass sensor flow characterization test matrix included twelve recycle gas compositions which represented various system operating points, and at two temperatures, 90°C and 100°C. With each composition and temperature, the gas flow was adjusted up to 1.50 grams/s and back down with increments at 0.375 and 0.75 grams/s. This approach provided a detailed mapping of the sensor's response with varying compositions, temperatures and flows. **Figure 5.4.4-1** shows an abbreviated test matrix, with the sensor results reported as sensor output in volts.

Composition	Percent Composition							Temp (°C)	Flow (gps)	Coriolis Flow (gps)	Sensor Output (V)
	H ₂	H ₂ O	CO	CO ₂	CH ₄	O ₂	N ₂				
A	21.4	16.8	9.3	9.7	0.0	0.0	42.2	90	0.375	0.372	2.80
									0.75	0.739	3.46
									1.5	1.478	4.33
									0.75	0.739	3.47
									0.375	0.372	2.80
								100	0.375	0.369	2.79
									0.75	0.736	3.47
									1.5	1.477	4.32
									0.75	0.742	3.49
									0.375	0.371	2.77
B	22.5	17.8	9.8	10.4	0.0	0.0	39.0	90	0.375	0.373	2.86
									0.75	0.742	3.55
									1.5	1.493	4.39
									0.75	0.745	3.54
									0.375	0.373	2.84
								100	0.375	0.373	2.83
									0.75	0.744	3.53
									1.5	1.492	4.38
									0.75	0.746	3.54
									0.375	0.373	2.82

Figure 5.4.4-1: Recycle Test Matrix and Results

Figure 5.4.4-2 shows sensor response plotted for all the compositions at 100°C. This plot shows adequate sensor sensitivity over the projected operating window.

Figure 5.4.4-2: Recycle Mass Sensor Response

5.4.4.2 Recycle Cooler

Figure 5.4.4-3 shows the total pressure streamlines of the cathode air in the recycle cooler. Design efforts are still ongoing for completing the recycle cooler with an integral valve concept. The next steps include: System level integration/ layout, detail component drawings, and prototype part fabrication and test. The results of this activity will be reported in the next report.

Figure 5.4.4-3: CFD Optimization of Recycle Cooler

5.4.5 Desulfurization

The first important consideration for a desulfurizer is size. A comparison of volumes for each type of sorbent was made. The volume calculations were performed using actual bench test data. The data was adjusted for space velocity and the level of sulfur in the input effluent entering the system. Further, some of the technologies were tested at sulfur levels exceeding 400 times that in the present application. A correction factor was calculated to normalize the data. This approach is applicable as long as there is a one-to-one correspondence between the sulfur compound and the sulfur reaction site in the sorbent. This assumption fits the theoretical models for sulfur adsorption on gas phase sorbents and, therefore, is suitable for this comparison. The volume of sorbent calculated is for 1000 hours of operation at a given space velocity and for an inlet gas stream containing 50 ppmv H₂S. These values can be seen in **Figures 5.4.5-1, 5.4.5-2 and 5.4.5-3**.

A height-to-diameter ratio of the sorbent bed is an important parameter, as a change in that ratio will represent a significant change in pressure drop or retention time in the sorbent. Assuming a general cylindrical design, a calculation of the height and diameter of the cylinder can be made. This gives a relative geometry from which to design the desulfurization unit. Although this is only a single column, it must be noted that multiple columns (or filters) would be advantageous and may represent a more compact design and easier packaging scenario than a single unit.

Type Sorbents	IGT SS-325A ZnTi- Sorbent	IGT SS-354 ZnTi- Sorbent	UCI-4169 Zn-Ti Sorbent	ZnTi+Co+ Ni	Zinc Titanate	ZnTi + Co
CALCULATIONS						
Volume of sorbent for 1000 hours of operation (L) scaled for 50 ppmv input and space velocity	0.3	0.3	0.3	0.013	0.013	0.013
height for 1000 hours (cm)	10.2	10.2	10.2	2.2	2.2	2.2
diameter for 1000 hours (cm)	6.4	6.4	6.4	2.8	2.8	2.8
Pressure required for system (kPa)	ambient	ambient	ambient	ambient	ambient	ambient
BENCH TEST CONDITIONS						
Ratio of height to diameter (h/D)	2	2	2			
Level of ppmv input	20,000	20,000	20,000	15000	15000	15000
Level of ppmv output	1	1	1	<200	<200	<200
Operation Temperature (°C)	538	450	550	480	650	650
REGENERATION CONDITIONS						
Regeneration Time (hours)	2.00	3.00	1.67	1.17	1.17	1.17
Regeneration Temperature (°C)	593	593	625	580	800	800
Any other issues not covered in other categories				flowing nitrogen	flowing nitrogen	flowing nitrogen

Not applicable for Delphi requirement

Figures 5.4.5-1: Zinc Titanate Based Gas Phase Sorbents

Type Sorbents	Zn-oxides	Fe/Zn-oxides	Fe-oxides	IGTSS-057 Mn-based Sorbent	IGTSS-179 Cu-based Sorbent	Sn-oxides
CALCULATIONS						
Volume of sorbent for 1000 hours of operation (L) scaled for 50 ppmv input and space velocity	14	14	25	0.33	0.33	273
height for 1000 hours (cm)				10.2	10.2	
diameter for 1000 hours (cm)				6.4	6.4	
Pressure required for system (kPa)	122	122	122	ambient	ambient	122
BENCH TEST CONDITIONS						
Ratio of height to diameter (h/D)				2	2	
Level of ppmv input	5500	5500	5500	20,000	20,000	5500
Level of ppmv output	5	5	5	1	1	10
Operation Temperature (°C)	450 - 650	450 - 650	500	538	538	450 - 650
REGENERATION CONDITIONS						
Regeneration Time (hours)						
Regeneration Temperature (°C)				750	750	
Any other issues not covered in other categories			pyrophoric			

Figures 5.4.5-2: Metal Oxide Based Gas Phase Sorbents

Type Sorbents	Morphologically altered ZnO	Morphologically altered ZnO	Morphologically altered ZnO	Commercial ZnO	Zinc Ferrite
CALCULATIONS					
Volume of sorbent for 1000 hours of operation (L) scaled for space velocity	0.7	2.4	2.4	14	0.37
height for 1000 hours (cm)	61.6	91.7	91.7	167.1	
diameter for 1000 hours (cm)	19.2	28.6	28.6	52.2	
BENCH TEST CONDITIONS					
Pressure required for system (kPa)	ambient	ambient	ambient	ambient	980
Ratio of height to diameter (h/D)	3	3	3	3	
Level of ppmv input	8	8	8	8	80
Level of sulfur in fuel output (ppmv)	0.1	0.1	0.1	0.1	<1
Operation Temperature (°C)	400	300	300	400	450
REGENERATION CONDITIONS					
Regeneration Time (hours)					
Regeneration Temperature (°C)					
Any other issues not covered in other categories					

Figures 5.4.5-3: Gas Phase Sorbent Polishers

Figures 5.4.5-1, 5.4.5-2 and 5.4.5-3 show several Zn-based sorbent technologies. The Zn-based technologies are the oldest and most advanced desulfurization technologies. Zn has been in use as a desulfurizing sorbent for the last 50 years. The Zn oxides are attractive due to their low volumes (0.3 to 14.4 L) required to clean a vaporized fuel for 1000 hours of operation without regeneration.

5.4.6 Develop Balance of Plant Components Conclusions

5.4.6.1 Combustible Gas Sensor

The new Gen 3 combustible gas sensor appears to have adequate response time and sensitivity. Evaluation and integration into a system will proceed in the next reporting period.

5.4.6.2 Develop Air Delivery and Process Air Sub-System

In the development of the motor, controller, and compressor, extensive system and component level analyses created a strong foundation for a clear understanding of the system operation along with additional confidence that the final design would be robust. System fabrication and functional / safety testing have provided necessary hardware to confirm proper operation and structural safety. Dyne performance testing and compressor flow testing have quantified system performance in relation to the system requirements.

Through continued use of CFD analysis and correlation with airflow test data, a good understanding has been gained of the designs factors that contribute to pressure losses in the manifold airflow. Continuing design, analysis, and prototype testing will lead to a manifold that minimizes the overall APU system power loss.

Testing of the PAM at the component level and within the APU system continues to add to Delphi's understanding of the air delivery and process air subsystem. Performance testing and durability testing have identified areas for improving the PAM design. PAM motor and controller thermal testing at extreme operating conditions was used to map the operating limitations of the controller. This data will be incorporated in subsequent APU tests. Performance data from the airflow test stand provided insight to the sources of power loss within the PAM. This information will be used to increase system efficiency.

5.4.6.3 Develop Hot Zone Components

5.4.6.3.1 Gasket Development

Advancements in sealing techniques and testing were made with the introduction of a new sealing technology. The discovery of this technology has immediately improved upon previous sealing techniques used in the system. Thermal cycle and life cycle testing is currently beginning on the seals to determine if they are a viable option for sealing the SOFC into the future. Delphi's goal is to determine, with a level of certainty, that this new sealing technology can with stand the harsh thermal environment over time.

The performance of the metallic gaskets is extremely encouraging and will be the technology of choice for system operation. Future testing will explore different gasket geometries, alternate plating options, expanded cycling, and the introduction of additional environmental factors.

5.4.6.3.2 Integrated Component Manifold

The ICM is an ongoing design that is continuously updated to receive new integrated stack modules, reformers, Cathode Heat Exchangers, and other SOFC subsystems. The next generation of manifolds will receive a Planar Natural Gas Reformer with an internal GPC, simplifying the design of the manifold.

The Gen 3 ICM and GPC designs are working very well. The computational analysis benefited the manufacture, assembly, and performance of the ICM components. The ICM will be used for both natural gas and methane system testing; eliminating the need for additional designs. The next development focus for the ICM is to identify the failures modes that effect durability and develop accelerated aging test methods.

5.4.6.3.3 Cathode Heat Exchangers

The next steps regarding the development of the Gen 3 Cathode Heat Exchangers include continued development of the brazing profile needed to successfully braze the Cathode Heat Exchangers using the new material. Once braze profile development is complete, several prototype Cathode Heat Exchangers will be produced and performance tested (including heat transfer and pressure drop testing) to verify the actual performance back to the predicted performance. If design changes are required in order to meet the required performance, they will be made as appropriate. These activities are scheduled to begin in August 2004 and will progress through the Gen 3 SOFC System life cycle as required.

Development efforts on the CHEX resulted in the successful fabrication of the Gen 3 CHEX design. The next heat exchanger development will include testing the units for evaluation to the SOFC System requirements (heat transfer and pressure drop) to verify the actual performance. This validates and updates the heat exchanger modeling / sizing characteristic data for similar heat exchanger designs. The durability of the CHEX will also be determined during the next reporting period.

5.4.6.4 Recycle System Conclusions

Modifications made to the existing pump technology will allow demonstration of operating a system with re-cycled tail gas. Additionally, Technical Concept Reviews are currently taking place with several suppliers to identify the optimal long-term pump solution.

Advances were made on recycle sub-system components. Two recycle pump designs are now available for sub-system and system testing. Control algorithm development has begun, and a recycle cooler design has been developed. The next developments will include: Completing the control algorithm, integration of recycle & reformer subsystems, and system level testing.

5.4.6.5 Desulfurization Conclusions

Gas phase sorbent materials include Zn -, Mn-, Fe-, Ca, Sn, Co, Mg, Mo-, Cu and Ni-based oxides as well as zinc titanates. Each material type has a different operation temperature, sulfur absorption capacity, initiation temperature, operation pressure, and reaction time. Each material also has specific regeneration conditions including initiation temperature, initiation pressure and reaction time. The mechanical properties of these materials such as: Crush strength, sorbent spallation resistance, sorbent volatilization and attrition resistance are important to the success of gas phase sorbent technologies. Factors enhancing absorption in packed beds are: Depth of packing, staging of the reaction, and increasing the residence time. The best desulfurization system for natural gas appears to be one based on a combination of a “coarse” gas phase sorbent bed followed by a “polishing” gas phase sorbent base.

Delphi’s current requirement for a desulfurization system has been set at < 0.1 ppmv. To meet this requirement, the desulfurization system must effectively remove sulfur constituents to less than 0.1 parts per million (volume based).

One desulfurization system approach for this type of technology is a combination of a “coarse” gas phase sorbent of zinc titanate (modified with additives such as Co and Ni for attrition resistance) operating at 400 °C followed by a “polishing” sorbent of morphologically modified ZnO sorbent operating at 400 °C. The sorbent volume of such a system operating for 1000 hours without regeneration would be approximately 3.5 L. This calculation is only the volume of the sorbent and does not include the other mechanical parts of the system.

5.5 Task 6: System Fabrication

5.5.1 Transportation APU System Fabrication

Development testing continued on the Gen 2C APU. There was only one Gen 2C APU (Set 1) built and tested. A summary of this testing may be found in Section 9.0 “System Testing”.

5.5.2 Stationary SPU System Fabrication

The first system fabrication of an SPU 1A (CPOx reformer) HZM is shown in **Figure 5.5.2-1**. The figure shows the HZM with both thermal stacks and 2x16 SOFC stacks installed. Additional electrical insulators are required for the SOFC stacks to isolate the

stack terminals, as well as protect the stacks from short-circuits to the metallic insulation liner. The Gen 3.1 SOFC stacks shown in **Figure 5.5.2-1** demonstrate that there is no longer a “cathode up” and “cathode down” stack polarity in the SPU 1A system. The 30-cell stack modules may be used interchangeably in either position in the system. This is advantageous for streamlining stack production. There is only one stack assembly design required for all SPU systems. The Gen 3 APU and SPU 1A system designs feature more tightly organized pass-through locations and improved pass-through insulation collars. The new collars are of simpler geometry, contain fewer parts, and have superior insulating performance over the Gen 2C designs. Both the Gen 3T (gasoline) and Gen 4.1T (natural gas) fuel reformers have round pass-through geometry which help to simplify the design of the pass-through collars.

Figure 5.5.2-1: SPU 1A Hot Zone Module Fabrication

The HZM, PSM components, and AIM were combined in a close-coupled arrangement to complete the SPU 1A Set 0 system assembly. This system is shown installed into the system laboratory in **Figure 5.5.2-2**. To support initial system shakedown and development testing, auxiliary air mass flow meters have been installed into each of the four process air supply streams to the system. They are: Reformer air, cathode air

preheat, cathode air preheat bypass, and burner cool air. With the exception of the system enclosure, additional air meters and some additional temperature instrumentation, the Set 0 system shown in **Figure 5.5.2-2** has exactly the same content as the full Set 1 system.

Figure 5.5.2-2: SPU 1A Set 0 System Fabrication

Summary detail of the SPU 1A system at the Set 1 integration level is shown in **Figures 5.5.2-3, 5.5.2-4, and 5.5.2-5.**

Figure 5.5.2-3: SPU 1A Set 1 System Fabrication (Final Assembly)

Figure 5.5.2-4: SPU 1A Set 1 System Fabrication (Cover Removed)

Figure 5.5.2-5: SPU 1A Set 1 System Fabrication (Top Insulation Shell Removed)

5.6 Task 7: System Testing

5.6.1 Transportation APU System Testing

A detailed full-power analysis for the first Gen 2C APU test is given in **Table 5.6.1-1**. The targets for the Gen 2C APU design level are given in column A of the figure. The full-power results for the first and second thermal cycle on the Gen 2C APU are given in columns B and C of the figure respectively. The full-power operating point data in column B is summarized in the system schematic, **Figure 5.6.1-1**, similarly, the data from column C is summarized in the system schematic, **Figure 5.6.1-2**. The time history of power and temperature data for the March 5, 2004 test is given in **Figure 5.6.1-3** and **5.6.1-4** respectively. Data from the test on March 8, 2004 is given for comparison in **Figures 5.6.1-5** and **5.6.1-6**.

From **Table 5.6.1-1**, the initial performance of the Gen 2C APU system fell short of the targets in two main areas: Total Parasitic Electrical Load, and Power Conditioner Efficiency. For the second thermal cycle, due to enhanced cooling of the power conditioner and reduced temperature of blower inlet air, much of the power conditioner performance gap, with respect to target, was closed. However, the parasitic electrical load of the blower was still significantly above target. The elevated blower electrical load is due to lower-than-target blower subsystem efficiency, and elevated output head pressure required by the fuel-reformer and anode side of the system. In addition, significant power degradation in the SOFC stack was exhibited on the second thermal cycle (25%). This degradation rate is higher than is typical with the Gen 3.0 stack under

idealized test conditions. The cause of this specific degradation is unknown at this time, but it may be related to stack seal leakage that developed during the system tests. The cathode-inlet to anode-outlet temperature inversion noted in **Figure 5.6.1-6**, is characteristic of internal stack leakage, or leakage at the stack gasket interface. Appreciable leakage rates in the stacks, both internal to external, and anode to cathode, were measured following the second thermal cycle (>10 Standard Liters-Per-Minute [SLPM] at 2 kPa gauge pressure). This could be the primary cause for degradation of power in the second thermal cycle. With better temperature control in the system, and the implementation of new stack sealing technology, this type of severe degradation may be eliminated.

Table 5.6.1-1, column D offers a forecast of Gen 2C APU performance based upon forecasted stack performance improvements, and the power conditioner efficiency demonstrated on March 8, 2004 (due to improved APU cooling). Blower parasitic load estimates are based upon recent blower subsystem tests that confirm a large increase in blower efficiency with reduced inlet air temperature. The forecast indicates potential for more-than double net power output and system efficiency compared to the APU test conducted on March 5. The forecast also predicts satisfaction of the original net power and efficiency targets set for the Gen 2C gasoline APU.

Figure 5.6.1-7 illustrates the revisions made to the Gen 2C APU, specifically the air paths used for the system blower and the auxiliary cooling fans. The original design drew ambient air through the power electronics, which are in close proximity to the hot zone of the APU, and into the blower. An additional fan drew air through the warm space, over the remainder of the low temperature components, and exhausted it through the Application Interface Module (AIM). The revisions allow ambient air to be drawn directly from the air filter to the blower inlet, rather than air that has been heated by the power electronics. The auxiliary cooling path has also been modified. In addition to the fan used to cool the low temperature components, a second fan has been installed to draw ambient air in through the AIM, and pass it through the power electronics before being exhausted. **Figure 5.6.1-8** compares a revised Gen 2C APU test with the test of March 5. **Figure 5.6.1-8** illustrates the temperature reduction in the blower and power electronics environment, and the subsequent effect on parasitic loads.

Table 5.6.1-1: Gen 2C SOFC APU Test Analysis Study

Gen 2C Test Results		Gen 2C TARGET	Gen 2C APU	Gen 2C APU	Gen 2C APU Projection
Auxiliary Power Unit-Gasoline		12 / 03	03/05/04	03/06/04	05/04
Steady State- Full Power		CPOX	CPOX	CPOX	CPOX
Fuel Power	kW	17.02	12.87	12.08	13.98
Measured Gasoline Flow	g/sec	0.39	0.29	0.27	0.32
Fuel Consumption	gal/hour	0.49	0.37	0.35	0.40
	lbots/gal	2.1	2.7	2.9	2.5
Chemical Endotherm (- exo)	kW	-3.841	-2.903	-2.677	-3.087
Estimated Reformer Efficiency	%	78%	78%	79%	79%
Estimated Reformer Power Loss	kW	-3.83	-2.90	-2.54	-2.94
Estimated Fuel Utilization	%	25%	32%	27%	32%
Estimated Stack Electrical Efficiency	%	52%	50%	47%	50%
SOFC Stack Efficiency	%	13%	16%	13%	16%
Estimated Stack Power Loss	kW	-11.49	-8.36	-8.33	-9.27
Stack Number of Cells		60	60	60	60
Cell Active Area	cm ²	106	106	106	106
Cell Operating Voltage	V	0.70	0.71	0.66	0.71
Stack Electric Output Power	kW	1.700	1.617	1.215	1.780
Reference Power Density	W/cm ²	0.267	0.254	0.191	0.280
Power Electronics Efficiency	%	87%	77.9%	86.4%	86.4%
Power Electronics Loss	kW	-0.221	-0.358	-0.165	-0.242
Gross Conversion Efficiency	%	8.7%	9.6%	8.7%	11.0%
Parasitic Loss Factor	%	68%	33.9%	38%	65%
Measured Electric Parasitic Load (42V+14V)	kW	-0.479	-0.832	-0.647	-0.538
Net System Efficiency @ Net Power	%	5.9%	3.3%	3.3%	7.2%
Measured Net Elec Power	kW	1.000	0.427	0.403	1.000

Indicates Measured Value ■ Laboratory

Figure 5.6.1-1: Gen 2C SOFC APU 03.05.04 Test Process Flow

Figure 5.6.1-2: Gen 2C SOFC APU 03.08.04 Test Process Flow

Figure 5.6.1-3: Gen 2C SOFC APU Temperatures (First Thermal Cycle)

Figure 5.6.1-4: Gen 2C SOFC APU Power (First Thermal Cycle)

Figure 5.6.1-5: Gen 2C SOFC APU Temperatures (Second Thermal Cycle)

Figure 5.6.1-6: Gen 2C SOFC APU Power (Second Thermal Cycle)

Figure 5.6.1-7: Revised Air Paths Through Application Interface Module (AIM)

Figure 5.6.1-8: Gen 2C SOFC APU Parasitic Load and Temperature Comparison

5.6.2 SPU System Testing

A detailed full-power analysis for the first SPU 1, Design Level A test is given in **Table 5.6.2-1**. The targets for the SPU 1A level are defined in column A. The forecast for the tested system is given in column B. This forecast is based on a fully integrated system with 2x16 cell stacks (as opposed to 2x30 cell stacks). The actual net power output was 45% of the forecast level of 1kW. Root cause analysis was performed on the system to determine the reason for the degraded power level.

Table 5.6.2-1: SPU 1A Test Analysis Study

12/16/2004 23:18		A	B	C
Stationary Power Unit (SPU) Steady State Rated Power Analysis (SS100)		Rated Output	Rated Output	Rated Output
		SPU 1A	SPU 1A	SPU 1A
		2x30G 3.1	2x16G 3.1	2x16G 3.1
		TARGET	12/22/04 FORECAST	12/22/04 ACTUAL
REFORMER (Methane)				
Fuel Power	kW	11.2	12.4	13.3
Fuel Massflow	g/sec	0.224	0.248	0.267
Reformer O/C Ratio		1.3	1.3	1.3
Reference Reformate Power	kW	10	11	11
System Fuel Utilization	%	50%	30%	23%
Cell Operating Voltage	V	0.78	0.69	0.60
Stack Output Power	kW	2.84	1.66	1.20
Stack Current	A	60.5	75.1	62.3
PARASITIC LOSSES				
Stack to DC Bus Power Conditioner Efficiency	%	100%	87%	87%
Power Conditioner Loss (-)	kW	0.000	-0.216	-0.156
Fuel to Regulated DC Conversion Efficiency	%	25.4%	11.7%	7.8%
Electric Parasitic Load (-)	kW	-0.591	-0.447	-0.587
Reformer Type		TUBE CPOX	TUBE CPOX	TUBE CPOX
NET SYSTEM OUTPUT				
Net System Efficiency @Rated Power	%	20.1%	8.1%	3.40%
Rated Output Power	kW	2.25	1.00	0.454
STACK SPECIFICATIONS				
Number of cells per stack: N		30	16	16
System Total Number of Cells		60	32	32
Reference Stack Power Density (0.7 V/cell, 50% utilization)	W/cm ²	0.650	0.480	0.260
System Total Airflow	g/sec	12.9	12.6	15.1
Blower Power	W	447	362	530
42 V Subtotal:	W	447	362	530
14 V Subtotal:	W	85	85	57
Total Parasitic Load:	W	591	447	587

Table 5.6.2-1 shows that the performance of the SPU 1 Level A system fell short of the targets in three main areas: Stack power density, stack power and system efficiency. When compared against the targets, the primary cause for this shortfall is the stack

power density. While the degraded performance seen in the system test is not typical of stack tests under idealized conditions, the cause of this reduction in power density was not immediately evident and is being investigation. Stack power density is an important development goal of this program and is addressed as part of Section 4.0 Stack Development.

During root cause analysis, the stacks from the December 22, 2004 test were evaluated for leaks after the initial cycle. The first stack was found to have a substantial leak in its base manifold. The second stack was found to have a smaller leak. This explains the uncontrollable high temperature noted in **Figure 5.6.2-1**. It would also explain the reduction in stack efficiency, power density, and total power. With fuel being utilized, or burned at the site of the leak, a reduced amount of fuel was made available to the cell for conversion in to electrical current. This prevented the SOFC system from meeting the forecasts.

Figure 5.6.2-1: SPU 1A System Power

5.6.3 System Testing Conclusions

5.6.3.1 Gen 2C APU Confirmation

The initial evaluation of the Gen 2C APU system placed emphasis on the thermal management design and performance of the APU. The low initial net power output of the first Gen 2C test is directly related to excessive heat losses from the high temperature zone of the APU to the low-temperature zone of the APU. This is primarily a result of inadequate insulation design, excessive air-feed, sensor, and reformer pass-throughs in the thermal insulation, and an APU cooling design that is incapable of rejecting such a high heat load.

The Gen 2C APU testing was concluded. The thermal management issues associated with the PSM were addressed, providing data for the final stages of control algorithm development. The balance of testing focused on developing and calibrating the safety and diagnostics portion of the software. Reformer development was performed in the first half of 2004. The majority of the effort during this period was devoted to algorithm and software development.

Figure 5.6.3-1 is a timeline of activities that concludes with a transition to SPU activities. **Figure 5.6.3-2** details the testing activities in the form of test percentages.

Figure 5.6.3-1: Gen 2C SOFC APU Development Timeline

Figure 5.6.3-2: Gen 2C SOFC APU Testing Effort By Activity

The Gen 2C system served as the test bed for software and controller hardware development. The safety and diagnostic system and power management algorithms were debudded, revised, and calibrated. Gen 2C system was operated with electrochemical four times, (**Figure 5.6.3-3**) just two with 30-cell stacks.

Figure 5.6.3-3: Gen 2C SOFC APU Testing Effort By System Configuration

The next generation SPU 1A hardware will serve as the test platform for electrochemical systems. The knowledge and experience gained with the thermal behavior of the Gen 2C system will enable rapid integration of hardware, and calibration of control software, for the SPU.

5.6.3.2 SPU 1A Confirmation

The solutions to the thermal management issues in the Gen 2C APU were implemented in the SPU 1A system design and stabilized the efficiencies of the blower and the power conditioner. The net power output of the first SPU 1A test was lower than originally predicted. Better power output results are expected in upcoming tests, due to corrective actions taken, based on root cause analysis.

The typical system temperatures seen in the SPU 1A system are shown in **Figure 5.6.3-4**. The more capable heat exchanger used in the SPU 1A system allows a 200 °C delta to be held across the stack during warm-up, and provide a significant reduction in start time. The controlled startup of a Gen 2C APU is shown in **Figure 5.6.3-5**.

Figure 5.6.3-4: SPU 1A 200 °C Stack Delta Warm-up

Figure 5.6.3-5: Gen 2C Start-Up Test

The laboratory and facility are prepared for 24-hour, unattended testing, allowing the group to focus on long-term durability testing. System testing of application specific load profiles is also anticipated in the next reporting period.

6 2005 TECHNICAL PROGRESS AND ACHIEVEMENTS

6.1 Task 1: System Development

2005 focused on the performance testing and final system development to support Delphi's SECA Phase I Demonstration A Testing. To meet contracted performance targets Delphi tested two Stationary Power Unit 1B SOFC systems and combined their outputs. Each unit was able to produce at least 2.1 kW net electric power output at greater than 35% fuel-to-electric system efficiency. Both test units met the 1500 hour durability target including one full-thermal cycle at better than 99% operational availability. As an integrated unit with elimination of duplicate or redundant components, Delphi was also able to meet the \$800/kW cost target for Phase I. All of these deliverables were achieved with a highly integrated system design weighing in at 85 kg (39 kg/kW), and with a package volume of 65 liters (30 liters/kW).

Achieving these Phase I deliverables was the result of system design and integration efforts performed during Phase I. Most notably: 1) High efficiency fuel reforming strategy encompassing both internal reforming of methane gas in the SOFC stack and anode tail-gas recycle. This provided efficient thermal management of the SOFC stack, as well as effective fuel processing efficiencies of greater than 160% which resulted in high system efficiencies. 2) High reliability fuel reformer, SOFC stack, process air blower, electronic controller and electronic subsystems, sensors and actuators. Delphi's dedication to integration and leverage of reliable automotive technology allowed for excellent durability performance. 3) MATLAB/Simulink-based control software with rapid auto-code generation capability. A rapid software development process and the opportunity for many design iterations allowed for deployment and optimization of new technology in an efficient manner.

The SOFC System development effort during Phase I benefited from the experience and lessons-learned from several design generations of hardware, and two different fuels: gasoline and methane. These design generations are shown in **Figure 6.1-1**.

Figure 6.1-1: Delphi SECA Phase I Systems

The experience and technology development that occurred at each of these system design levels resulted in improved package appearance and performance. **Figure 6.1-2** shows the performance history across the system design levels for systems that produced power with stacks. The dramatic increase in power from negative net output to greater than 2 kW net output and efficiencies in excess of 35% is apparent. What is not so apparent is that the sum of all the power-producing operational time in 2002-2004 is less than the duration of a single test's rated (peak) power producing time in 2006.

Figure 6.1-2: Phase 1 Performance Summary

6.1.1 Define System Requirements

In the first quarter of 2005, system and subsystem requirements were adjusted to reflect the Stationary Power Unit 1B performance targets, and SECA Phase I exit demonstration requirements.

The system test profile requirement was refined jointly between National Energy Technology Laboratory (NETL) staff and Delphi. The resulting test profile is given in **Figure 6.1.1-1**. Significant changes include an increase in Normal Operating Condition (NOC) power from 1 kW to 1.5 kW, and a Normal Current and Normal Fuel Rate basis for the evaluation of power degradation. Measuring power at a standard current and fuel rate fixes system fuel utilization to a constant value. Power degradation is to be evaluated at 4 points: 0 hours, 1000 hours, 1000 hours + thermal cycle, and 1500 hours. Rated power and peak efficiency is only evaluated at the start of the test, for one-hour duration each.

Figure 6.1.1-1: SECA Phase I Test Profile

The SPU 1B system was designed around a flexible high-efficiency fuel reforming strategy called Light Internal Reforming (LIR). This strategy features the use of an anode tail-gas recycle pump, a dual path fuel supply, a CPOx fuel reformer, and internal reforming in the SOFC Stack. SECA Phase I performance targets of 3 kW net and 35% peak efficiency were forecasted to be able to be met with a stack power density of 650 mW/cm² and an LIR fueling strategy where 50% of the methane fuel would be reformed in the CPOx reformer, and 50% of the fuel would be internally reformed in the SOFC stack. Performance shortcomings in a few key areas required a major adjustment of operation strategy in order to meet performance targets. While this enabled system efficiency targets to be met, target power levels of 3 kW net were not able to be achieved with a single SPU 1B unit as originally planned.

SPU 1B Development Issues:

1) SOFC Stack and blower manifold pressure drop higher than forecasted.

These high restrictions required much higher blower plenum pressures to be used to source the required cathode airflow. This resulted in higher parasitic loads, less efficient blower operation, and reduced airflow capacity for stack cooling. This had an impact on both net output power and efficiency. The solution was to radically increase the amount of internal reforming in the system at high stack power output levels (0.75-0.70 V/cell). This resulted in increased cooling and high fuel processing efficiency due to the endothermic fuel reforming reactions in the stack, and a reduction of the required airflow for stack cooling. The blower still had to operate in an inefficient region of its characteristic curve, but the increase in effective fuel processing efficiency and reduced airflow more than compensated for this penalty. As a final result, at full Rated power, all of the methane fuel entering the system was internally reformed in the SOFC stack aided by the water in the recycled anode tail gas. This operating mode was at the extreme end of the LIR fueling strategy and was given a special description: High Internal Reforming (HIR).

The resulting air, fuel, recycle flow curve for the SPU 1B system including CPOx, LIR, and HIR modes is shown in **Figure 6.1.1-2**. The progression of the system reforming mode from CPOx to LIR to HIR is based upon the software schedule for target fuel utilization, % recycle, and oxygen to carbon ratio as a function of stack current normalized to its current capacity at 0.7 V/cell.

Figure 6.1.1-2: SPU 1B High Efficiency Fuel Reforming Strategy

2) Lower-than-projected SOFC Stack power density. To achieve 3 kW net output power, the SPU 1B system requires at least a 650 mW/cm² power density of the

SOFC stack. The actual power density of the SOFC stack at 0.7 V/cell when operated in the system is approximately 420 mW/cm². This is about two-thirds of the power of the same SOFC stack at the same average cell voltage when operated in a stack test furnace. A matrix of tests were conducted to determine which of the factors between the system test environment and the stack test environment was causing the difference in demonstrated power. It was discovered in the test that the difference in power is caused by differences in internal stack temperature driven by differences in thermal environment and test duration. In the system, the stack is generally tested at steady-state in a highly insulated enclosure and it is thermally managed with air and reformat flows controlled to a prescribed temperature gradient. In the stack laboratory, stacks are characterized in a transient test in an electric furnace. In this environment, a significant amount of heat is lost from the stack to the furnace walls. The difference in demonstrated stack power density is a direct result of differences in operational cell temperature driven in large part by differences in thermal environment. Many updates to the stack test lab have since been made to better simulate the actual system thermal environment.

3) Low efficiency at the Normal Operating Condition. The original forecast for the SPU 1B system was to have the peak efficiency point occur at the Normal Operating Condition (NOC). This was targeted to be at the 50% load point, or 1.5 kW load for a 3 kW net system. Due to the lower-than-expected stack power density, the system rated power was reduced to 2.1 kW and the NOC point was chosen to be about 850W. This load is about 28% of the original 3 kW level. High amounts of internal reforming cannot be supported at low electrical loads because of the difficulty in keeping the interior of the stack at temperature without sufficient electrochemical activity. At this new NOC point, the system software schedule had to be adjusted so that it would run in CPOx mode which is at a much lower efficiency, but resulted in good temperature balance for the system.

After the system operating strategy was adjusted, a new forecast of requirements was created for the SECA Phase I Demonstration A prototype units (SPU 1B): See **Figure 6.1.1-3**.

Stationary Power Unit (SPU) Steady State Power Analysis		FORECAST					
		SPU 1B SET 2		SPU 1B SET 3		COMBINED	
		RATED	NOC	RATED	NOC	RATED	NOC
REFORMER (Methane)							
Fuel Massflow	g/sec	0.113	0.113	0.113	0.113	0.225	0.227
	L/min	10.2	10.3	10.2	10.3	20.4	20.6
Anode Tail Gas Recycle Fraction	%	48%	0%	48%	0%	48%	0%
Reformer (Fuel Processing) Efficiency	%	168%	84%	168%	84%	168%	84%
Stack Fuel Utilization	%	50%	43%	50%	43%	50%	43%
Stack Electrical Conversion Efficiency	%	53%	63%	53%	63%	53%	63%
SOFC Stack Conv Efficiency	%	26%	27%	26%	27%	26%	27%
Stack Air Utilization	%	25%	6%	25%	6%	25%	6%
Cell Operating Voltage	V	0.70	0.84	0.70	0.84	0.70	0.84
Stack Output Power	kW	2.500	1.304	2.500	1.304	5.000	2.608
Stack Current	A	59.5	25.9	59.5	25.9	59.5	25.9
Reference Power Density	W/cm ²	0.393	0.205	0.393	0.205	0.393	0.205
Stack to DC Bus Power Conditioner Efficiency	%	100%	100%	100%	100%	100%	100%
Parasitic Load Efficiency	%	84%	65%	84%	65%	84%	65%
DC/AC Inverter Efficiency	%	100%	100%	100%	100%	100%	100%
NET SYSTEM OUTPUT							
Net System Efficiency @Rated Power	%	37.4%	15.0%	37.4%	15.0%	37.4%	15.0%
Rated Output Power	kW	2.10	0.85	2.10	0.85	4.20	1.70

Figure 6.1.1-3: Phase 1 System Requirements

6.1.2 Develop Conceptual System Design

The SPU 1B System Design Level was completed. Both an Anode TGR and Fuel Metering Manifold (FMM) subsystem were added to the stationary power unit. The final system assembly representing the SPU 1B Design Level is shown in **Figure 6.1.2-1**.

Figure 6.1.2-1: SPU 1B System Assembly

Detail of the Anode TGR subsystem is shown in **Figure 6.1.2-2**. The Recycle Cooler Heat Exchanger cools hot anode tail gas to between 80 °C and 125 °C with cool cathode airflow. A proportional control valve is included on the heat exchanger to block heat exchange surface at low flows and prevent over-cooling and subsequent condensation of the water vapor in the anode tail gas. After the anode tail gas has been cooled, secondary methane fuel gas from the fuel-metering manifold is injected. The cooled anode tail gas and methane mixture is ducted to the recycle pump, where it is mixed by the recycle pump, and then discharged through a massflow sensor to the rear of the reformer where it mixes with methane Catalytic Partial Oxidation (CPOx) reformat. The recycle subsystem adds 4.2 kg to the system mass.

Figure 6.1.2-2: SPU 1B Anode Tail Gas Recycle Subsystem

The FMM is responsible for metering and sensing the massflow of both primary and secondary fuel streams. The primary fuel stream is to the CPOx reformer, and the secondary fuel stream is to the recycle stream, and is internally reformed in the SOFC stacks. Detail of the FMM is shown in **Figure 6.1.2-3**. The FMM adds approximately 2 kg to the system mass.

Figure 6.1.2-3: Fuel Metering Manifold

At the end of the Phase I period, Delphi supported two system designs: SPU 1B and SPU 2. These systems are shown in **Figure 6.1.2-4**

Figure 6.1.2-4: Active SECA Phase I Systems

6.1.3 Develop System Mechanization

Delphi built and tested a basic system utilizing a CPOx fuel reformer and a SOFC stack. Fuel and air are fed to the CPOx reformer, and the fuel is partially oxidized. These CPOx reactions convert the hydrocarbon fuel to mostly H_2 and CO gases, which are fuel gases to an SOFC stack. The CPOx reactions also release heat that serves to maintain the temperature of the reformer. A CPOx reformer is a very simple and easily controlled device with good transient behavior and dynamic range. The disadvantage of the CPOx reformer is that it has a low fuel processing efficiency (70-90%) that leads to reduced overall system efficiency.

The basic CPOx reformer system mechanization is shown in **Figure 6.1.3-1**.

Figure 6.1.3-1: Basic CPOx SOFC System

Delphi's SOFC System for transportation and stationary applications will use Stack Anode TGR to improve stack power density and reduce carbon precipitation and deposition in the system. The Stack Anode Tail Gas has a large amount of water vapor and CO_2 , as well as unreacted H_2 and CO gases. When these gases are fed back to the reformer, endothermic "steam reforming" reactions occur in the fuel reformer. In Delphi, Stack Anode TGR has been coupled with a fuel reformer technology that can sustain its temperature in the presence of endothermic (steam reforming) reactions. These "endothermic reformers" typically consist of a heat exchanger construction whereby hot combustor effluent passes on one side of the heat exchanger (combustor side), and fuel, air, and recycle gas mix passes through the other side (reforming side). The reforming side is catalytically treated to allow for the preferred reactions to occur.

This mechanization yields high fuel processing efficiencies that yield high system efficiencies. The disadvantages to this approach are: The complexity and potential durability issues with the heat exchanger/reformer device; the system complexity required to channel the combustor gases through the reformer; and the potential for carbon precipitation in the produced reformat which has low water vapor content by volume.

Where natural gas fuel is used, steam reforming with added water (no recycle) is a very common approach. The natural gas fuel is pre-reformed to break down higher hydrocarbons (above methane) and this high-methane mix is fed directly to an SOFC stack. H_2O is typically added to the reformat to allow steam reforming reactions to occur in the SOFC stack. This is called "Internal Reforming". In this approach, the heat to supply the endothermic reactions is supplied by the electrochemical heat release in the SOFC stack and not a heat exchange with the combustor gases. This approach is appealing for its high fuel processing efficiencies, but it requires a supply of external water injection to the system.

It is desirable to have a system that requires no external source of water but still achieves high fuel-processing efficiency and also maintains a simple construction and operation of the fuel reformer.

For SECA Phase I, Delphi has developed a hybrid system mechanization that combines the best of the simple CPOx reforming approach and the high-efficiency recycle and endothermic reforming approach without the resulting system complexity. This approach involves employing both a CPOx (primary) fuel reformer and Anode TGR to the system. The endothermic reactions occur in the SOFC stack, instead of being relegated to the heat exchanger/reformer subsystem.

The reformat supplied to the stack is a mixture of CPOx reformat, Anode TGR, and a secondary fuel input to the recycle just after the SOFC stack. The injection point of the secondary fuel at the stack anode exit point, and before the recycle pump, offers several advantages.

The anode tail gas has the highest Oxygen-to-Carbon (O/C) ratio anywhere in the entire system, with a very high concentration of H_2O and CO_2 . There are fewer tendencies to have carbon precipitation with the injection of secondary fuel.

The anode tail gas is hot. It is nominally at stack operation temperature of 750-800 °C. This allows for the mixture of anode tail gas and secondary fuel to be mixed and reacted in a clean-up catalyst to react higher hydrocarbons in the presence of water vapor and CO_2 . There is no O_2 oxidant present in the mix.

The resulting mixture of gases is rapidly cooled and fed to a recycle pump. This allows for an extra degree of good mixing of the anode tail gas and secondary fuel without further reactions occurring towards equilibrium.

The primary fuel reformer, which is a simple and robust CPOx technology reformer, supplies between 0% and 100% of the reformat to the SOFC stack, with typical values between 30% and 70%. At 100%, there is no secondary fuel injection to the recycle stream, and there is no internal reforming in the stack (0% internal reforming). At 0%, there is no CPOx reformat to the stack, and all of the fuel is internally reformed (100% internal reforming). Both 0% and 100% cases are known to industry, but Delphi is developing a strategy that employs a mixture of CPOx and stack internal reforming strategies (between 0% and 100% internal reforming). This blended strategy (or LIR) results in a reformat stream to the stack that has a high concentration of H_2 , and H_2O , as well as moderate amounts of CO and CO_2 , and a small amount (usually under 12%) of methane gas (CH_4). This allows for high fuel processing efficiencies, although not as high as 100% internal reforming strategies, without driving excessive concentrations of methane to the stack. This allows for a reduced internal reforming load on the stack, which may improve durability. The CPOx reformer primary fuel processing serves the needs of the system during the start-up phase when the stacks are warming-up, as well as under transient conditions where less internal reforming may be desirable.

Delphi's LIR scheme is shown in **Figure 6.1.3-2**.

Figure 6.1.3-2: Hybrid Light Internal Reforming (LIR) SOFC System

The benefits from LIR may be demonstrated numerically for a system with 60% fuel utilization, and η_1 of 1.25 in **Table 6.1.3-1**. The table gives system fuel processing efficiency (reforming efficiency) as a function of recycle, r , and η_2 . High recycle

fractions and lower Ω_2 values tend to improve reforming efficiency. Reforming efficiencies described in the table may be over 100% because it is calculated as the Lower Heating Value (LHV) of the reformat to the stacks divided by the LHV of the fuel input to the system; which is the LHV of the gas stream. Since the reformat to the stacks contains recycled gases, the reforming efficiency can exceed 100%.

Table 6.1.3-1: Fuel Processing (Reforming) Efficiencies for LIR

Estimated Effective Reforming Efficiency	Ω_2						
Recycle	1.5	1.55	1.6	1.65	1.7	1.75	1.8
0%	80%	78%	76%	75%	73%	72%	70%
10%	88%	87%	85%	83%	81%	80%	78%
15%	94%	92%	90%	88%	86%	84%	82%
20%	100%	98%	96%	94%	92%	90%	88%
25%	106%	104%	102%	100%	98%	96%	93%
30%	114%	112%	109%	107%	105%	102%	100%
35%	123%	120%	118%	115%	113%	110%	108%
40%	133%	130%	127%	125%	122%	119%	117%
45%	145%	142%	139%	136%	133%	130%	127%
50%	159%	156%	153%	150%	147%	143%	140%

Table 6.1.3-2 describes the values for Ω_1 and the limiting recycle cases for the reforming efficiencies tabulated in **Table 6.1.3-1**. Calculated values for Ω_1 that are above 1 or below 0 are outside the limit recycle fractions. Under these conditions, the system is either operating in full internal reforming domain ($\Omega_1 \leq 0$, or zero internal reforming domain ($\Omega_1 \geq 1$) and Ω_2 is not held to the target in the table (violates equations). Under most cases of practical interest to the system, the targeted values for Ω_1 are between 0.3 and 0.7. For Delphi's SECA Phase I demo system, a nominal target of 45% recycle reformat and 1.75 Ω_2 , has been chosen for the system NOC. It features approximately a 50%/50% fueling split between CPOx reformer and SOFC stack, and greater than 130% fuel processing efficiency.

Table 6.1.3-2: Primary Fuel Ratio, Y1 and Limiting Recycle Fractions

		Ω_1	1.25					
		Utilization	60%					
Ψ_1	Ω_2							
Recycle		1.5	1.55	1.6	1.65	1.7	1.75	1.8
0%		1.20	1.24	1.28	1.32	1.36	1.40	1.44
10%		1.07	1.11	1.15	1.19	1.24	1.28	1.32
15%		0.99	1.03	1.08	1.12	1.17	1.21	1.25
20%		0.90	0.95	0.99	1.04	1.08	1.13	1.18
25%		0.80	0.85	0.90	0.94	0.99	1.04	1.09
30%		0.69	0.74	0.79	0.84	0.89	0.94	0.99
35%		0.55	0.61	0.66	0.71	0.77	0.82	0.87
40%		0.40	0.46	0.51	0.57	0.62	0.68	0.74
45%		0.22	0.28	0.34	0.40	0.46	0.516	0.58
50%		0.00	0.06	0.13	0.19	0.26	0.32	0.38

Formula for min

$\Psi_1 \leq 1$	Ω_2							
		1.5	1.55	1.6	1.65	1.7	1.75	1.8
		14%	17%	20%	22%	25%	27%	29%

Formula for max

Formula for min

$\Psi_1 \geq 0$	Ω_2							
		1.5	1.55	1.6	1.65	1.7	1.75	1.8
		50%	51%	53%	54%	55%	56%	58%

In addition to using an enhanced fuel processing approach for the SPU 1B System, general improvements were made to the system mechanizations. For both SPU 1A (CPOx Reforming), and SPU 1B (Internal Reforming), the fuel supply system has been redesigned and re-mechanized. During early system development, methane fuel was metered to the system with Brooks® Massflow controllers. These controllers provide accurate and reliable fuel supply, but they are not practical and cost-effective for a commercially viable system. In earlier testing, adapted automotive fuel injectors were used to meter methane fuel, but the dry operation precluded critical lubrication and resulted in durability and accuracy issues. The system mechanization has been changed to reflect a combination of solenoid proportional valve and gaseous massflow meter to provide reliable and accurate fuel supply to the system under variations of temperature, supply pressure, and system backpressure. An integrated fuel-metering module has been designed and is currently being fabricated for use in the system.

An additional vent was added to the system to allow for the small amount of leakage at hot component interfaces to harmlessly merge with the exhaust stream instead of migrate to the cooler zones and sensitive electronics of the system. In the event of reformat leakage, CO and H₂ gas which would normally leave the system enclosure through the electronics cooling air stream, will now be collected and ducted towards the system exhaust. This vent is implemented as a separate and parallel exhaust path so

that a blockage in the exhaust pipe will not force hot system exhaust back into the system enclosure. This vent has been implemented and tested with very good results.

The discrete logical inputs and outputs required by the NETL test lab were added to the system mechanization and implemented in the system hardware.

The final system mechanizations for SPU 1A and SPU 1B (SECA Phase 1 Exit Target) are shown in **Figures 6.1.3-3 and 6.1.3-4**, respectively. The fuel metering valves and massflow sensors are denoted as V121 & S121 for primary fuel and V122 & S122 for secondary fuel source (internal reforming).

Figure 6.1.3-3: SPU 1A System Mechanization

Figure 6.1.3-4: SPU 1B System Mechanization

Operating point analysis was performed for the SPU 1B system with LIR fuel processing to ensure consistency with SECA Phase I performance targets. The operating point analyses references the stream nodes depicted in the SPU 1B system mechanization.

The rated power operating point (Steady State 100% Power, SS100) is shown in **Table 6.1.3-3**.

Table 6.1.3-3: SPU 1B Rated Power Operating Point Analysis

The NOC operating analysis has been performed (**Table 6.1.3-4**).

Table 6.1.3-4: SPU 1B NOC Operating Point Analysis

SOFC System Operating Analysis - SIMULINK										FOR REFERENCE ONLY									
21-Mar-05										MECH: SPU1B Rev02 Release									
System Operating Point: SS										Analyst: S.M. Kelly - SOFC SYSTEMS									
Recycle Fraction 1 (Ref Feed): 0%										System Rated Power: 3000 W									
Recycle Fraction 2 (Post Ref): 45%																			
Fuel Utilization: 60%																			
O ₂ Ratio 1: 1.25																			
O ₂ Ratio 2: 1.75																			
Reformer Efficiency: 131%																			
Stack Elec Efficiency: 38.1%																			
Power Conditioner Efficiency: 100.0%																			
Gross System Efficiency: 49.8%																			
Parasitic Load Efficiency: 80.0%																			
Net System Efficiency: 39.9%																			
Fuel Power: 1942 W																			
Reformer Power: 1683 W																			
Stack Gross Power: 1873 W																			
Cell Current: 37.0 Amps																			
Parasitic Load: 37.4 W																			
Net System Power: 1489 W																			
Blower Power: 1085 W																			
Blower Air Bypass Fraction: 0%																			
Blower Temperature: 315 °C																			
Total Parasitic Airflow: 5.6 g/sec																			
Primary Fuel Mass Flow: 0.039 g/sec																			
Secondary Fuel Mass Flow: 0.036 g/sec																			
Fuel Split Fraction (PSI): 0.516																			
Stack A: 1873 W										Stack B: 0 W									
Heat Dissipation: 1068 W										Electric Power: 1873 W									
Power Density: 295 W/cm ²										Cell Voltage: 0.844 V									
Stack Voltage: 25.3 V										Cell Efficiency: 63.7%									
Fuel Utilization: 59.8%										Fuel Conversion: 0.0%									
Mass O ₂ Transport: 0.184 g/sec										Anode Flow: 0.66 g/sec									
Anode Flow: 0.66 g/sec										Cathode Flow: 5.4 g/sec									
Cathode Flow: 5.4 g/sec																			
FUEL PROPERTIES																			
LHV: 50.03 MJ/kg																			
MW: 16.01 g/mole																			
G: 1.00 mole/mole H ₂																			
H: 1.00 mole/mole H ₂																			
O: 0 mole/mole H ₂																			
FLOW/LEG ANALYSIS																			
A per leg: 534 W										B per leg: 0 W									
A per leg: 537 W										B per leg: 0 W									
A per leg: 0.032 g/sec										B per leg: 0.000 g/sec									
A per leg: 0.33 g/sec										B per leg: 0.42 g/sec									
A per leg: 2.7 g/sec										B per leg: 2.6 g/sec									
Parasitic Load Summary																			
Blower: 211 W										Rec Pump: 32 W									
Fuel: 80 W										Purge Fan: 14 W									
Heater: 0 W										Rec Heater: 0 W									
Total 429 W										Total 149 W									
Total 337 W																			
Stream Characteristics:																			
Reference Label	BTDA Air Description / Name	Mass Flow, Grams / Sec	Temperature, °C	Pressure, Pa	H ₂	O ₂	N ₂	HD	CO	CO ₂	CH ₄	FUEL	Mass Flow, g/sec	Species					
A1	PROCESS AIR BLOWER INLET	25	5.64	79.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	1.17	1007						
A2	PROCESS AIR BLOWER OUTLET	36	5.64	79.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	1.13	1007						
PA1	PURGE AIR INLET	25	13.00	79.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	1.17	1007						
PA2	PURGE AIR OUTLET	26	13.00	79.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	1.17	1007						
PA3	PSM PURGE OUTLET	43	13.00	79.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	1.11	1008						
PA4	POWER COND OUTLET	43	13.00	79.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	1.11	1008						
G1	METERED GATH AIR	S18	62	5.00	79.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	1.01	1009						
G2	POST RECYCLE COOLER	114	5.00	79.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.81	1010						
C3	POST CHEK	856	5.00	79.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.31	1164						
C4	PREHEAT BYPASS	S20	62	0.43	79.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	1.04	1008						
C5	GATH AIR FEED POST BYPASS MIX	100	5.43	79.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.33	1154						
C6	GATH AIR FEED POST REFCOOL	T14	133	5.43	79.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.35	1152						
C68	GATH AIR POST STACK A	800	5.25	79.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.33	1154						
C6C	GATH AIR POST INTERCOOLING	T48	788	5.25	79.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.33	1152						
G7	GATH DE TAIL GAS	188	5.25	79.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.33	1152						
C8	GPC AIR BYPASS	188	0.00	79.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.33	1152						
G9	GPC COOL AIR	S19	62	0.00	79.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	1.04	1008						
C10	GPC HOT AIR FEED	788	5.25	79.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.33	1152						
A3	FUEL FEED	P6	25	0.01	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	100.0%							
A2	REFORMER AIR	S11, T12	50	0.21	19.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%								
A3	REFORMER FEED	T2	30	0.25	59.00%	15.70%	0.00%	0.00%	0.00%	0.00%	0.00%	25.2%							
A4	REFORMER OUT (POST MIX)	S1, T3	369	0.66	33.16%	0.00%	21.08%	18.40%	10.12%	9.63%	7.62%		0.40	16.41					
A5	ANODE FEED	133	0.86	33.16%	0.00%	21.08%	18.40%	10.12%	9.63%	7.62%			0.26	18.28					
A5B	ANODE TAIL GAS STACK A	T5A	800	0.85	26.31%	0.00%	14.51%	32.96%	7.00%	16.75%	0.00%		0.27	16.69					
A5C	ANODE TAIL POST INTERCOOL	788	0.85	28.71%	0.00%	14.51%	32.96%	7.00%	16.75%	0.00%			0.27	16.65					
A6	GPC FUEL	T5B	788	0.47	28.71%	0.00%	14.51%	32.96%	7.00%	16.75%	0.00%		0.27	16.65					
A7	TAIL GAS RECYCLE	800	0.38	26.31%	0.00%	14.51%	32.96%	7.00%	16.75%	0.00%			0.27	16.69					
A8	RECYCLE PUMP INLET	T11	91	0.38	26.31%	0.00%	14.51%	32.96%	7.00%	16.75%	0.00%		0.79	13.86					
A9	RECYCLE PUMP OUTLET	S11	125	0.38	28.71%	0.00%	14.51%	32.96%	7.00%	16.75%	0.00%		0.72	14.00					
E1	GPC EXHAUST OUTLET	T61, T6R	915	5.82	15.06%	18.00%	0.00%	4.63%	0.00%	2.31%	0.00%		0.29	12.33					
E2	REFORMER EXHAUST OUTLET	T11	5.82	15.06%	18.00%	0.00%	4.63%	0.00%	2.31%	0.00%	0.00%		0.29	12.33					
E3	CHEK HOT-SIDE FEED	914	5.82	75.06%	18.00%	0.00%	4.63%	0.00%	2.31%	0.00%	0.00%		0.29	12.22					
E4	SYSTEM EXHAUST STREAM	315	5.82	75.06%	18.00%	0.00%	4.63%	0.00%	2.31%	0.00%	0.00%		0.59	10.85					
I21	INTERCOOLER INLET AIR	25	0.00	19.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		1.17	1007					
I22	INTERCOOLER AIR TO HEX	19	0.00	19.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		1.09	1009					
I23	INTERCOOLER AIR POST HEX	0.00	0.10	19.00%	21.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%		0.33	1154					

The survey results are compiled and shown in **Table 6.1.3-5**. The survey includes results for a European target fuel North Sea Natural Gas (NG), as well as the analysis from the NETL test lab and the local Rochester New York utility company. An analysis was performed on the worst-case fuel (North Sea NG) as it contained the least amount of methane gas by volume, and was the closest fuel to the NETL test lab analysis. The resulting performance analysis of the SPU 1B system at its NOC operating point is given in **Table 6.1.3-6**.

Table 6.1.3-5: Natural Gas Fuel Analysis

	Desulfurized Natural Gas Fuel Sources			
	NORTH SEA NG	NETL Supply NG	ROCHESTER GAS& ELECTRIC UTILITY NG	"Typical" US NG
	Fuel 1	Fuel 2	Fuel 3	Fuel 4
N ₂	0.00%	0.96%	1.37%	1.29%
O ₂	0.00%	0.00%	0.00%	0.00%
H ₂	0.00%	0.00%	0.00%	0.00%
H ₂ O	0.00%	0.00%	0.00%	0.00%
CO	0.00%	0.00%	0.00%	0.00%
CO ₂	1.30%	0.10%	0.72%	0.58%
CH ₄	88.10%	89.60%	95.65%	95.40%
C ₂ H ₆	6.40%	7.70%	1.99%	2.12%
C ₃ H ₈	2.80%	1.01%	0.22%	0.41%
C ₄ H ₁₀	0.00%	0.36%	0.04%	0.12%
C ₅ H ₁₂	1.00%	0.15%	0.01%	0.04%
C ₆ H ₁₄	0.18%	0.115%	0.01%	0.04%
NH ₃	0.30%	0.00%	0.00%	0.00%
	100%	100%	100%	100%

SOPC System Operating Analysis - HY STYS										FOR REFERENCE ONLY									
25-Mg H ₂ S										Analyst: J. Rilling - Ete gels									
MECH: SPU 18 Rev02 Re Issue										SYSTEM RATING POWER									
Sys Operating Point SS:										3000 MW									
Recycle Fraction:		45%		Stack Series Stages		1		FUEL PROPERTIES		LHV		47.66		MW		18.79		M _W q	
Fuel Utilization:		61%		Stack Parallel Legs		2		MW		Type		2		kg/kmole		Recycle Cell		1.000	
O:C Ratio1:		1.25		Cells Per Stack		30		Cells		V		A		1=ch4, 2=North Sea Natural Gas					
O:C Ratio2:		1.75		Total System Cells		60		Stack Bus Voltage		24.0		40.00							
Reformer Efficiency:		98%		Stack Bus Current		40.00													
Stack Eleo Efficiency:		37.5%																	
Power Conditioner Efficiency:		100.0%																	
Gross System Efficiency:		46.3%																	
Parasitic Load Efficiency:		77.9%																	
Internal Reforming Efficiency:		125%																	
Net System Efficiency:		36.1%																	
Fuel Power:		4147		W															
Reformat Power:		3547		W															
Stack Gross Power:		1920		W															

A number of advancements were made in the design and implementation of the electrical and electronic system. The system electrical harness was modified to include updates and additions to the system mechanization for recycle, Light Internal Reforming (LIR), user interface, and SECA interface I/O requirements. Advancements were also made to the power electronics subsystem. A development power architecture was designed and implemented using off-the-shelf Vicor™ power modules. The Magenetek AC inverter has been integrated and tested using a light bulb load bank to consume fuel cell generated energy. A user interface unit was developed and integrated into the system that has switched system inputs, digital system outputs, and a liquid crystal display for visual feedback from the control system. These enhancements have been made to support the system changes for SPU 1B as well as advancement of the system design.

The system power architecture for development had been designed and implemented using off-the-shelf Vicor[™] power modules. The Magenetek AC inverter has been integrated and tested using a light-bulb load bank. A user interface unit was developed and integrated into the system that has switched system inputs, digital system outputs, and a liquid crystal display for visual feedback from the control system. These enhancements have been made to support the system changes for SPU 1B as well as advancement of the system design.

6.1.3.1.1 System Electrical Harness

The system electrical harness was modified in several ways. Although the general form and size are the same, the harness had to change to support system additions for SPU 1B. The additions include controls for recycle hardware, primary and secondary fueling control for LIR, and user interface connectivity. There were also modifications to allow the harness to properly route and fit into the warm space with the additional recycle and LIR hardware (**Figure 6.1.3-5**). This has proven to be challenging thermally as well as spatially.

Figure 6.1.3-5: SPU 1B System Electrical Harness

The system electrical harness has been modified and updated in several ways. The additions include controls for recycle hardware, primary and secondary fueling control for LIR, and user interface connectivity. There are also modifications to allow the harness to properly route and fit into the warm and limited space with the additional recycle and LIR hardware. This has proven to be challenging thermally as well as from a routing standpoint.

Figure 6.1.3-6: SPU 1B System Electrical Harness

6.1.3.1.2 Power Electronics

The power electronics were enhanced to support multiple system architecture designs for development purposes. There is now a development architecture which supports both stationary and transportation applications. This architecture uses off-the-shelf DCDC converter modules from Vicor™ with some tuned filter circuitry designed at Delphi. The new architecture is flexible and inexpensive, and it will be used for system development purposes. Additionally, the Magnetek® AC inverter, discussed in previous technical reports, has been integrated into the system. The inverter has been verified and has supplied energy to a light bulb load bank at levels up to 1.5 kilowatts system test.

6.1.3.1.2.1 Development Electrical Architectures

Since power electronics for fuel cells are very application specific and since technologies are improving rapidly, Delphi used a slightly less efficient, but very flexible architecture design (**Figure 6.1.3-7**). The 500 Watt and 1500-Watt Vicor™ DCDC converters are the development solution for internal power supplies.

Figure 6.1.3-7: SPU 1 Current Development Electrical Architecture

6.1.3.1.2.2 Development Power Electronics

The power electronics implemented in the system were based on the flexible development power architecture referenced above. The DCDC converters for both 14 Volt and 42 Volt internal loads were built using 500 Watt Vicor™ brick modules for 36-75 Volt input and 14 Volt or 42 Volt output (**Figure 6.1.3-8**). The 14V output converter uses one brick and is a 500-Watt device. The 42 Volt output unit is capable of transforming 1500 Watts of energy. The 14 and 42 Volt output devices were assembled at Delphi and tuned with filter circuitry to meet output ripple and voltage level requirements for the internal parasitic loads required to run the fuel cell system. Both devices are housed within the Application Interface Module (AIM), and have been verified in the system (**Figure 6.1.3-9**). The efficiency of both the 14 and 42 Volt converters is approximately 86%. This is reasonable, but not as good as some emerging power conversion technologies. The possibility of increasing the power conversion efficiency is discussed below. The stack isolation relay also resides with the power electronics and is used to disconnect the stack from the user during system start up for safety. The Kepco 42 Volt power supply is used to provide parasitic energy during start up prior to the stack being able to supply power. Once the warm-up is complete, the power supply is shut off, which disconnects the system from grid power. At this point the stack isolation relay is closed to allow the user access to stack energy. Some research was completed to improve the power conversion and isolation interaction in the system.

Figure 6.1.3-8: 500 W Unidirectional Vicor™ DC-DC Converter Module

Figure 6.1.3-9: SPU 1B Power Electronics Integrated into Application Interface Module

A variety of off-the-shelf DCDC converter products were evaluated for development use. The future development architecture developed is very similar to the current architecture, but it has a different power conditioner for each application, transportation or stationary (**Figure 6.1.3-10**). Delphi will also use in house assembled power electronics based on Vicor™ Vichips®, which are very small and efficient devices (**Figure 6.1.3-11**). Each device is capable of 240 Watts and is greater than 92% efficient. Both 14 and 42 Volt output units are currently being tested.

Figure 6.1.3-10: SPU Future Development Electrical Architecture

Figure 6.1.3-11: Vicor™ ViChip® High Efficiency DC-DC Converters

6.1.3.1.2.3 AC Load Bank

The Magnetek® AC inverter was integrated and verified in the system (Figure 6.1.3-12). In order to fully test the capability and limits of the inverter an AC light bulb load bank was designed and built (Figure 6.1.3-13). The load bank is capable of consuming

3000 Watts, and is switchable in 100-Watt increments via toggle switches. The light bulbs are a great visual indicator of energy production by the fuel cell.

Figure 6.1.3-12: 2400 Volt-Ampere Magnetek® AC-DC Inverter

Figure 6.1.3-13: 3000 Watt AC Light Bulb Load Bank

6.1.3.1.3 Liquid Crystal Display and System User Interface

Another very useful advancement developed during this reporting period was the user interface and display (**Figure 6.1.3-14**). On the left are toggle switches used for switching the system on or off, and an emergency stop switch. When this switch is thrown, the system immediately shuts down assuming that the user has determined that there is a safety critical issue. On the right side of the interface box are light emitting diodes (LED) that are illuminated for various system functions. If an LED is red, it is lit when that function is disabled (or off). The indicators are: 1) 42V disable, which is lit when the external power supply is sourcing the parasitics; 2) the heartbeat flashes at the same frequency that the system software runs; 3) fuel command indicates that the fuel is enabled and flowing; 4) the emergency stop LED is lit when the system is running and is not in EStop mode; 5) the power available indicator is lit when the user requested

power is available and the system is ready to be loaded. The interface also has a Liquid Crystal Display (LCD) screen that relays useful system and control information to the user. The LCD displays 2 pages of data each with 4 lines. The information communicated is system state, stack temperature, parasitic efficiency, system efficiency, runtime, cumulative energy produced in kilowatt-hours, gross power, and net power. The interface provides enough information for the user to get a good understanding of how the system is operating.

Figure 6.1.3-14: SOFC System User Liquid Crystal Display

6.1.4 System Control Development Update

Delphi migrated to the new control unit, which was a more production intent version of the previously integrated system controller. In addition, the system control algorithm and software set has advanced substantially in terms of functionality, but also with respect to safety and reliability. There has also been significant planning and design work to ensure that the control system continues to improve as the system moves towards a production ready solution.

The final months of Phase I focused mainly on testing the reliability and durability of the control system. With three 1500 hour durability tests initiated during the final months, resulting in over 5000 hours of operation at NOC, the control system proved to be functional throughout an extensive test period comprised of warm ups, cold and hot starts, thermal cycles, peak performance stability, load profiling, and other demanding tasks. Overall software development has slowly come to a close for the final version of SPU1B, providing a functional, reliable, and durable control system for all future tests and demonstrations. All verification and validation techniques used for Phase I

development and implementation, will be building blocks for new and improved techniques entering Phase II development.

6.1.4.1 Controller Hardware Development

The second generation Engineering Development Unit (EDU) was built integrated into the system and verified (**Figure 6.1.4-1**). A number of hand modifications made during development are implemented in the EDU 2 controller layout, and additional features and protection circuits are also added. The communication hardware is upgraded and made configurable by hardware pin selection. The controllers now have a selectable speed dual Controller Area Network (CAN) bus. The user can select either 100-kilo baud per second low speed fault-tolerant CAN, or 500-kilo baud per second high speed CAN. A number of additional features and protection circuits are added including: additional fault detection circuitry, 60 Volt I/O protection on required circuits, added nonvolatile RAM, lower quiescent current draw (< 2 milliAmps with CAN Wake-Up), increased temperature protection (125 °C), and added input captures. These upgrades are progress towards a more production ready controller. Although this EDU is based on production Engine Control Units (ECU), it has a lot of extra and unused input/output (I/O) circuitry for development flexibility. Most of which will be removed and replaced with protection and diagnostic circuitry required in a production grade controller.

Figure 6.1.4-1: SOFC System Controller Engineering Development Unit 2 (EDU2)

Four simple system breakout simulators, similar to the one shown in **Figure 6.1.4-2**, were manufactured internally to help in Phase II development. These systems had the following intended functionalities:

- Diagnosis of hardware failure using the EDU.
- Quick and easy command of hardware
- Simple sensor calibration
- Simplify current system component lab testing that requires frequent experimental setup
- Practical means of implementing lab tests with EDU

- Ensure proper functionality of EDU with individual hardware components as necessary
- Quick and easy view of controller response
- Perform simple I/O and communication checkouts at remote sites

Figure 6.1.4-2: Simple system break out box with EDU and LCD connected

6.1.4.2 Control Software Development

A large effort was dedicated to enhancing the system control algorithms and software. The purpose of this work was to optimize and stabilize the control system algorithms and add new functionality for anode tail gas recycle, light internal reforming, user interface, power management and safety and diagnostics. Up to this point in development, the system hardware and control software was changing frequently. As a result, an engineer was required to be present during all system tests to ensure that the system was operating safely and correctly. If problems occurred a hand calibration change or control override was often required. This is undesirable; hands free start-up and operation are required. The system control algorithms have been tuned and optimized to automatically start and operate the system. The system is now validated to run unattended indefinitely. In order to allow unattended operation, the system safety and diagnostic system was thoroughly calibrated and validated using an automated hardware-in-the-loop (HIL) simulator and system test runs.

6.1.4.2.1 Anode Tail Gas Recycle Control

Several additions were made to the system control algorithm to accommodate recycle. First, a method was developed to measure mass flow using a standard hotwire anemometer sensor by compensating for variable anode tail gas flow compositions using a scale factor based on percent recycle, percent utilization and oxygen to carbon ratio in the recycle stream. This allows for closed loop control of the recycle pump based on flow. Control of the pump was added as a proportional-integral control loop based on speed error. Second, a cooling control loop has been added to cool the

anode tail gas using process air. The recycle cooling control loop is a proportional-integral system based on recycle temperature error. The cooling loop system is a heat exchanger with an air control valve and a thermistor. The valve opens to cool the recycle more, and closes to allow warmer recycle to pass through the pump. This algorithm has been implemented in the model and is currently undergoing testing in the SPU 1B system test stand set 00.

Two control loops involving recycle feedback have been successfully implemented in the final Phase I testing. First, measurement of the mass flow using a standard hotwire anemometer sensor is used to compensate for a desired mass flow based on recycle, percent utilization and oxygen to carbon ratio in the recycle stream, using a proportional-integral closed loop control on the recycle pump speed. The second successful implementation for recycle feedback control was an anode tail gas cooling loop. This was accomplished using a control valve and a thermistor. Closed loop proportional-integral control was based on the temperature inlet to the recycle pump. Both control loops were implemented successfully in to the control algorithm, increasing system efficiency and helping to complete Phase I.

6.1.4.2.2 Primary and Secondary Fueling Control

In order to implement light internal reforming, primary and secondary fueling is required. Primary fueling refers to main fuel metering into the fuel reformer. Secondary fueling is mixed with anode tail gas and fed directly into the fuel cell stack for internal reforming. This method was developed internally to increase system efficiency. To accomplish this, the addition of fuel flow sensors and gaseous fuel injectors was required. The injectors are then controlled via proportional-integral control on flow error. A target flow is set and the controller regulates the injector to meter the desired amount of fuel mass flow into the system. The flow measurement is accomplished with a standard hotwire anemometer. This algorithm has been implemented into the software and is currently being tested and tuned on the test bench.

6.1.4.2.3 Optimized Pressure Control

System tests revealed that the parasitic losses derived from blower operation could be reduced, in certain operating states, by varying the desired inlet air pressure according to the actual required flow. The blower control function receives a constant target value of inlet air pressure. This target pressure is used to calculate the desired blower speed. In some operating conditions, the resulting inlet air pressure far exceeds what is necessary to meet the flow demand, and the blower is operating in a condition where it is delivering much greater output than what is actually required.

The purpose of the modifications is to allow the system to dynamically modify the inlet air pressure target delivered to the blower control algorithm in order to most efficiently reduce parasitic losses deriving from the operation of the blower. This dynamic control will only be functional in certain operating states. The control will be activated/de-activated based on valve step positions, and the control will act on the target airflow pressure used by the blower speed control sub-function (**Figure 6.1.4-3**). This

algorithm will reduce the dependence on mass airflow sensors for control, and is a step towards removing content from the system.

Figure 6.1.4-3: Optimized Pressure Control Strategy for Reducing Parasitic Loads

6.1.4.2.4 Power Management

For purposes of diagnostics, data logging and performance monitoring a number of calculations and measurement signals were added to the power management algorithm. These included: 1) net power, 2) gross power, 3) system efficiency, 4) parasitic efficiency, and 5) accumulated energy in kilowatt-hours. These values are very useful as monitors of system performance during and after a test. They are required metrics for evaluating system operation.

6.1.4.2.5 Safety and Diagnostics

The safety and diagnostics system underwent several advancements and extensive calibration throughout 2005. The system works well and is supporting unattended system testing. Significant work was accomplished to lead the system into its next generation, where it is more capable and closer in form and function to a production intent safety and diagnostic system.

This is depicted in **Figure 6.1.4-4**. This version of the safety and diagnostics, known as S&D Level I, proved to be effective for the then current level of hardware design and implementation. There still remains, however, extensive development necessary before Delphi SOFC systems enters into production development.

Figure 6.1.4-4: System and Diagnostics Level I

6.1.4.3 Hardware-in-the-Loop Simulator

The OPAL-RT[®] system is a dynamic Hardware-In-the-Loop (HIL) simulation package. It consists of a control PC and electronic hardware that emulates the physical components connected to the EDU. The OPAL-RT[®] system emulates the fuel cell system and therefore allows for rigorous, automated testing of all conditions that might be observed by the controller in a real system.

6.1.4.3.1 Hardware

The HIL hardware was received and assembled at Delphi. A wiring harness was specified and constructed. OPAL-RT[®] provided a Simulink[®] base model that is used to represent the OPAL-RT[®] specific hardware present in the system (**Figure 6.1.4-5**). The Delphi SOFC plant model is then integrated with this model to represent the complete system (**Figure 6.1.4-6**). Hardware I/O was further specified in the RT-LAB model with the assistance of OPAL-RT[®] personnel (**Figure 6.1.4-7**).

Figure 6.1.4-5: OPAL-RT® TestDrive Hardware-in-the-Loop Simulator Simulink Model

Figure 6.1.4-6: OPAL-RT® TestDrive Hardware-in-the-Loop Simulator Controller Model

Figure 6.1.4-7: OPAL-RT® TestDrive Hardware-in-the-Loop Simulator Console Model

6.1.5 System Analysis

Several enhancements to the HYSYS® System Model were made. These included: Sulfur species tracing, carbon formation indicators, complex fuel system analysis, and complex reacting heat exchanger analysis. A typical Process Flow Diagram (PFD) of the HYSYS® System Model is shown in **Figure 6.1.5-1**

Figure 6.1.5-1: Steady State HYSYS® Model

6.1.5.1 Sulfur Tracing

The system model was enhanced to allow various, sulfur-contaminated fuels to be simulated. Sulfur content of several critical product streams is displayed in the process flow diagram. This provides a foundation for study of alternative sulfur reduction technologies that can be simulated at any point in the system.

6.1.5.2 Natural Gas Analysis

A special formulation of fuel was developed to represent North Sea NG. This surrogate fuel contains 88.1% methane, as well as ethane, propane, pentane, hexane, carbon dioxide, and traces of NH_2 , N_2 and H_2S . Using this more accurate composition in the system model, as opposed to pure methane, allowed better estimation of actual performance on the various compositions of natural gas that will be encountered.

6.1.5.3 Hot vs. Cold Recycle Study

A study was completed to determine the value of cooling the recycle stream before it enters the recycle pump, as is typical of the system operation today. By keeping the recycle hot, there is an ability to recycle slightly more stack tail gas, thereby increasing system efficiency. The model showed that there would be a 1% allowable increase in recycle fraction to 44% and the resulting system efficiency increased by 0.5%. While efficiency gain is always an acceptable effect, the practicality of a recycle pump that could handle the 750 °C tail gas was a concern in light of the modest gain.

This study showed negligible system efficiency differences between hot and cold recycle if the pumps were assumed to be 100% efficient. The hot recycle required roughly 4 times the power to pump as the cold recycle regardless of pump efficiency. Realistic pump technologies are 10-25% efficient for this application, and at these real efficiency levels, there is a significant parasitic power penalty for hot recycle. There is an advantage to having cold recycle from a system efficiency standpoint.

6.1.5.4 Integrated Reformer-Heat Exchanger

Previous versions of the HYSYS® system model simply separated the heat exchange process from the reaction processes that take place in the endothermic, waste energy recovery reformer system. This could lead to very different results for reformat composition and reformer temperature profile. Improved versions of the reformer simulation couples the heat exchange between reformat stream and combustor streams throughout the reforming process. The result is a more accurate emulation of this advanced reforming technology, providing better correlation with test data.

6.1.6 Perform Design Optimization

An initial System DFMEA analysis was performed to support safe and reliable operation of the SOFC system. The DFMEA analyzes subsystem and component functions, lists failure modes, and assigns relative severity, risk of occurrence, and risk of no detection levels. These levels are numbered 1-10 with 10 being the highest risk. The product of severity, occurrence and detection levels is the Risk Priority Number (RPN). RPN is a relative measure of failure risk and impact. Severity alone determines risk in the failures outcome.

To aid in the creation of the System DFMEA, system states of failure and associated severity levels were assigned. These are shown in **Figure 6.1.6-1**. The highest severity (10) is assigned to system operation with a safety issue. The next lesser severity (9) is assigned to a system that shuts down with a safety issue. Shut down states with and without damage are assigned the subsequent lesser levels of severity. Low levels of severity are reserved for an operating system with varying degrees of performance or service life loss. Additional detail on Severity level conventions and the adopted SOFC system convention is given in **Table 6.1.6-1**. The figure also references the AIAG standard convention for reference.

Figure 6.1.6-1: System FMEA Failure States

Table 6.1.6-1: System FMEA Severity Encoding

Rank	Severity Keywords	Impact on Product		SOFC Conversion	System Ultimate Impact	Rank
		AIAG	Delphi Guideline (A) Appearance (F) Function			
10	Hazardous - without warning	Hazardous-without warning: Very high severity, causing a risk to the vehicle mode affects safe vehicle operation and/or breaks a compliance with government or regulatory without warning.	Hazardous-without warning: (F) May involve safety, and/or noncompliance with regulatory issues.	Hazardous-without warning: (F) May involve safety, and/or noncompliance with regulatory issues.	System operate with safety issue	10
9	Hazardous - With Warning	Hazardous-with warning: Very high severity, causing a risk to the vehicle mode affects safe vehicle operation and/or breaks a compliance with government or regulatory with warning.	Hazardous-with warning: (F) May involve safety, and/or noncompliance with regulatory issues.	Hazardous-with warning: (F) May involve safety, and/or noncompliance with regulatory issues.	System shutdown with safety issue	9
8	Very High	Very High: the system is operable, with loss of primary function.	Extremely High: System function lost (F) Can't use the system, but is safe for noncompliance with regulatory issues. Customer aware of issue.	Extremely High: System function lost (F) Can't use the system, but is safe for noncompliance with regulatory issues. Permanent damage.	System shutdown w/o damage	8
7	High	High: Vehicle is operable, but at reduced level of performance. Customer discomfort.	Significant High: Customer Discomfort (A&F) The driver causes a high degree of customer discomfort on the part used.	Significant High: Customer Discomfort (A&F) Loss of system function without permanent damage.	System shutdown w/o damage	7
6	Moderate	Moderate: the system operable, but some performance issues. Item (A) Inoperable. Customer experience of system fault.	Moderate: (F) Partial system function is lost, but is safe for use. It is not safety critical.	Moderate: (F) Partial system function is lost, but is safe for use. It is not safety critical. Some, but not noticeably reduced performance.	System operate with loss of power/efficiency	6
5	Low	Low: Vehicle is operable, but comfort/performance issues. Customer experience some discomfort.	Moderately Significant: Customer Discomfort (A&F) The user will notice a negative impact on drive occur, i.e. difficult to apply, difficult to steer, discomfort, etc.	Moderately Significant: Customer Discomfort (A&F) The user will notice a negative impact on drive occur. Moderate loss of performance.	System operate with loss of power/efficiency	5
4	Very Low	Very Low: Fit & finish, squeak & rattle item does not interfere. Defect solved by design or tolerance.	Very Low: (F) Parts of the system operable, at reduced performance, as other gradual performance degradation.	Very Low: (F) Parts of the system operable at slightly reduced performance, as other gradual performance degradation.	System operate with reduced service life	4
3	Minor	Minor: Fit & finish, squeak & rattle item does not interfere. Defect solved by design or tolerance.	Minor: Inconvenient, noticeable (F) Noticeable but likely negligible.	Minor: (F) Inconvenient but likely negligible. Loss of non-critical diagnostics.	Loss of non-critical diagnostics	3
2	Minor	Minor: Fit & finish, squeak & rattle item does not interfere. Defect solved by design or tolerance.	Minor: (A) The user will probably notice only a minor negative impact on the product.	Minor: (A) Fit and Finish / Customer Perception	Fit and Finish / Customer Perception	2
1	None	None: No effect.	Imperceptible: not noticeable (F) The consequence will not have any perceptible impact on the performance of the product (A) The user will not notice the consequence.	Imperceptible: not noticeable (F) The consequence will not have any perceptible impact on the performance of the product (A) The user will not notice the consequence.	System normal operation	1

For occurrence and detection risks, the appropriate conventions are given in **Tables 6.1.6-2 and 6.1.6-3**. These conventions were applied to “production” design levels. At the prototype level there is generally a much higher occurrence rate.

Table 6.1.6-2: System FMEA Occurrence Encoding

Rank	Keyword	Probability of Failure Product)	Possible Failure Rates	Likely Failure Rates
10 ----- 9	Very High	Extreme: Almost inevitable	$\geq 100,000$ PPM 50,000 PPM	≥ 1 in 10 1 in 20
8 ----- 7	High	High: Situation frequently occurs	20,000 PPM 10,000 PPM	1 in 50 1 in 100
6 ----- 5 ----- 4	Moderate	Moderate: Situation occasionally occurs	5000 PPM 2000 PPM 500 PPM	1 in 200 1 in 500 1 in 2000
3 ----- 2	Low	Low: Situation relatively rare	100 PPM 10 PPM	1 in 10,000 1 in 100,000
1	Remote	Remote: Situation unlikely	≤ 1 PPM	< 1 in 1,000,000

Table 6.1.6-3: System FMEA Detection Encoding

Rank	Keyword	Delphi Guideline for DFMEA	AIAG Guideline for DFMEA
10	Almost Impossible	Undetectable until failure occurred after SOP	Design Control will not and/or can not detect a potential cause/mechanism and subsequent failure mode; or there is no Design Control.
9	Very Remote	Failure w/warning while the product is in operating mode in the field, but prior to a failure occurring; ie. warning light, abnormal noise; after SOP	Very remote chance the Design Control will detect a potential cause/mechanism and subsequent failure mode.
8	Remote	Can be detected and corrected within downstream customer's manufacturing facility prior to SOP	Remote chance the Design Control will detect a potential cause/mechanism and subsequent failure mode.
7	Very Low	Can be detected and corrected prior to shipping out the finished product; <i>i.e. manufacturing end of line testing or manufacturing process control after PPAP</i>	Very low chance the Design Control will detect a potential cause/mechanism and subsequent failure mode.
6	Low	Can be detected and corrected in / after validation testing prior to print release, but will require major design changes	Low chance the Design Control will detect a potential cause/mechanism and subsequent failure mode.
5	Moderate	Can be detected and corrected in / after validation testing prior to print release, but will require minor design changes	Moderate chance the Design Control will detect a potential cause/mechanism and subsequent failure mode.
4	Moderately High	Can be detected and corrected through verification testing prior to design release, but will require major design changes.	Moderately high chance the Design Control will detect a potential cause/mechanism and subsequent failure mode.
3	High	Can be detected and corrected through verification prior to design release, but will require minor design changes.	High chance the Design Control will detect a potential cause/mechanism and subsequent failure mode.
2	Very High	Can be detected and corrected prior to engineering prototype; <i>i.e. math calculation, stackup analysis, modeling and simulation</i>	Very high chance the Design Control will detect a potential cause/mechanism and subsequent failure mode.
1	Almost Certain	Is designed to eliminate possibility of product not meeting requirements.	Design Control will almost certainly detect a potential cause/mechanism and subsequent failure mode.

6.1.7 System Integration Status

The SPU 1A System (CPOx Reforming) was fully integrated and tested. With the addition of a leak ventilation tube, all convective thermal issues were resolved within the enclosure. A picture of the SPU 1A system (1500 W net capacity) is shown on the durability test stand in **Figure 6.1.7-1**. The SPU 1A unit is approximately 65 Liters, and has a mass of 75.1 kg.

Figure 6.1.7-1: SPU 1A System with Vent Tube

Assembly detail of the SPU 1B initial integration is shown in **Figure 6.1.7-2**. With SOFC Stacks removed from the assembly, the recycle pump subsystem can be seen. The recycle cooler heat exchanger has a white coating that is a thermal barrier coat. This is to reduce parasitic heating of the air coolant and prevent shorting of the stack power output terminals to the heat exchanger due to close proximity in the assembly. At the time of this picture, the fuel metering manifold was not available, but a rapid-prototype mock up was used for assembly validation. A recycle pump electronic driver is also shown in the image. The driver is required to operate the recycle pump motor. All the additional hardware for SPU 1B adds approximately 6.2 kg to the SPU 1A system.

Figure 6.1.7-2: SPU 1B System Integration

6.1.8 System Design and Integration Conclusion

The focus of the system activity was system integration and testing of the SPU 1A system, and the design, simulation, and fabrication of the SPU 1B system which had Anode TGR and internal reforming. Major functional issues encountered in SPU 1A drove design enhancements in both existing and new hardware designs.

To support SPU 1B system operation, Anode TGR with internal reforming of fuel was developed analytically and extensively simulated to assure performance alignment with SECA goals. Supporting fuel metering and recycle subsystems were designed and fabricated.

To continuously progress towards a safe and reliable system, an extensive system-level DFMEA was performed, and high-risk items were highlighted for further development.

Initial cost analysis was completed for both SPU 1A and SPU 1B systems, and critical cost gaps and actions identified. Significant improvements in material cost were made in the stack subsystem area.

6.2 Task 2: Stack Development

6.2.1 Design Stack

Gen 3.1 stack design was implemented and continued to be validated. Progress in performance was demonstrated with this design.

6.2.2 Model Stack Under Steady-State Conditions

Data was collected from a full-scale, single-cell, stack test to investigate the causes of limiting currents and enable the writing of an algorithm for the Pacific Northwest National Laboratory (PNNL) spreadsheet stack performance model that would predict limiting currents.

Data was collected for a fuel composed of humid hydrogen (3-5% water) diluted by nitrogen. Inlet hydrogen concentrations were 15%, 46% and 95%. For each inlet hydrogen concentration, fuel flow rates were varied over a range such that the hydrogen flow rate was from 200 to 1000 or 1200 standard cubic centimeters per minute (sccm). **Figures 6.2.2-1 through 6.2.2-3** show the current-voltage (I-V) curves for 15%, 46% and 95% inlet hydrogen, respectively. Limiting currents were determined for each condition by extrapolating the I-V curves to zero voltage. These limiting currents are listed in the third column of **Table 6.2.2-1**.

Figure 6.2.2-1: I-V curves for single cell test F-22 for a range of flow rates with 15% H₂ with 3% H₂O in nitrogen

Figure 6.2.2-2: I-V curves for single cell test F-22 for a range of flow rates with 46% H₂ with 3% H₂O in nitrogen

Figure 6.2.2-3: I-V curves for single cell test F-22 for a range of flow rates with 95% H₂ with 5% H₂O in nitrogen

Table 6.2.2-1: Data for limiting current conditions

<i>Inlet Conditions</i>		Limiting Current Density, A/cm ²	<i>Conditions at Limiting Current</i>			
H ₂ Concentration	H ₂ Flow Rate, sccm		H ₂ Intf c Outlet	H ₂ O Intf c Outlet	Fuel Util	H ₂ O in Exhaust
15 %	207	0.261	1%	19%	93%	18%
15 %	302	0.364	1%	19%	89%	17%
15 %	398	0.460	1%	18%	85%	16%
15 %	588	0.651	2%	19%	82%	16%
15 %	776	0.832	1%	20%	79%	15%
15 %	964	0.992	2%	21%	76%	14%
15 %	1153	1.149	1%	22%	74%	14%
44 %	207	0.278	1%	48%	99%	48%
46 %	398	0.517	1%	50%	96%	48%
46 %	588	0.732	3%	50%	92%	47%
46 %	776	0.959	2%	51%	91%	47%
47 %	964	1.133	4%	50%	87%	45%
95 %	207	0.220	20%	80%	78%	79%
95 %	397	0.468	12%	88%	87%	88%
95 %	587	0.678	13%	87%	85%	86%
95 %	775	0.890	13%	87%	85%	85%
95 %	964	1.105	12%	88%	85%	85%

A calibrated spreadsheet model was used to predict stack behavior at high fuel utilizations. The model predicts actual stack behavior, including the crossover of the

curves for 46% and 95% hydrogen, which occurs near 60% fuel utilization (**Figure 6.2.2-4**). For fuel utilizations above 60%, higher power density can be achieved by diluting the inlet hydrogen with nitrogen. This is because the water content near the cell outlet is prevented from nearing 80%, as it does for the concentrated hydrogen fuel.

Figure 6.2.2-4: Power density versus fuel utilization curves at 0.7 volts

6.2.3 Develop High Performance Cathode

The best durability was achieved using a 60 μ m thick $(\text{La}_{0.80}\text{Sr}_{0.20})_{0.95}\text{Co}_{0.20}\text{Fe}_{0.80}\text{O}_3$ (LSCF- 6428 A/B = 0.95) cathode with a fully covered Ag current collector print across the entire surface of the cathode. The basic configuration of the cell with long-term stability is shown in **Figure 6.2.3-1**. Effects of the following processing parameters were investigated to optimize the performance of cathodes; cathode thickness (**Figure 6.2.3-2**), sintering temperature (**Figure 6.2.3-3**), use of pore former (**Figure 6.2.3-4**) and firing steps (**Figure 6.2.3-5**). The thicker cathode, higher sintering temperature, no use of pore former, and two-step firing resulted in better stability, although initial power was slightly lower. While a detailed explanation as to how these factors impact the stability and/or burn-in of the cell performance is still under investigation, Delphi was able to optimize the performance of $(\text{La}_{0.80}\text{Sr}_{0.20})_{0.95}\text{Co}_{0.20}\text{Fe}_{0.80}\text{O}_3$ (LSCF- 6428 A/B = 0.95) cathode by controlling these factors.

Figure 6.2.3-1: Schematic of current collector design for long term durability

Figure 6.2.3-2: Effect of cathode thickness on the performance of the fully covered cathodes

Figure 6.2.3-3: Effect of cathode sintering temperature on the performance of the fully covered cathodes

Figure 6.2.3-4: Effect of pore former in the cathode layer on the performance of the fully covered cathodes

Figure 6.2.3-5: Effect of firing steps on the performance of the fully covered cathodes

6.2.4 Develop High-Performance Anode

The sulfur tolerance of Ni-YSZ anodes was investigated. In this study, H₂S was used as a sulfur source and introduced to the anode with fuel gas. The degradation, due to the sulfur poisoning, occurred in two steps: (1) Rapid initial degradation, and (2) subsequent gradual degradation (**Figure 6.2.4-1**). Even 0.1 ppm of H₂S caused a 40% loss in power over 600 hours, although sulfur-poisoning kinetics is slower compared to higher H₂S concentrations losing >50% of power over 1000 hours. Almost identical degradation behavior was observed at 1 ppm and 10 ppm H₂S. After H₂S was turned off, the cells exposed to 1 and 10 ppm of H₂S recovered ~40% of lost power over 700 hours, leaving ~33% permanent loss in output power. As seen in **Figure 6.2.4-2**, Energy Dispersion Spectrometry analysis conducted on the cell exposed to 10 ppm H₂S for 1000 h exhibited no indication of sulfur compounds or the existence of sulfur within the limits of detectability (about 1 wt% within any one micron square area).

Figure 6.2.4-1: Sulfur tolerance of Ni-YSZ anode - (Cells ran initial 100 hrs without H_2S to determine baseline stability of the cell at 100 hrs H_2S was introduced.)

Figure 6.2.4-2: EDS analysis on the Ni-YSZ anode exposed to 10 ppm of H_2S for 1000 hrs

6.2.5 Development Cell Fabrication Techniques

6.2.5.1 Fuel Cell Process Development – Cost Reduction

6.2.5.1.1 Ceramic Tape Processing

Delphi continued to collaborate with Ragan Technologies Inc. (RTI) to develop formulations and process parameters for HSC-forming that leads to high-quality; low-cost, ceramic sheets that are optimized for the application of anode supported fuel cells. Two preliminary trials were run successfully producing tape for Delphi fuel cells. HSC sheets from a third trial were fabricated at RTI and are currently being evaluated by Delphi. This trial entailed the use of low-cost raw materials, along with an optimized formulation that provides a suitable material set for flat, strong, and highly performing cells. HSC films are being characterized and validated by applying such methods of tape thickness measurement, tape green density, dynamic mechanical analysis (DMA), and lamination quality on unfired tape. Sintered part characterization of bi-layers (anode and electrolyte) includes anode porosity, pore size distribution, microstructure, bi-layer flatness, bi-layer strength, helium leakage and electrochemical testing of button-size test cells of 3.5 cm².

The raw materials for Trial 3 were specified by Delphi, and a lower-cost anode cermet (NiO-YSZ) was developed with the cooperation of a commercial supplier. The raw materials were defined in detail regarding chemical composition and physical properties making this a unique blend of constituents for the anode component of Delphi's high-power density cells. American Elements has contributed to this study in the area of sourcing and manufacturing raw materials, compositional control, and powder preparation methods that meet Delphi specifications.

6.2.5.1.2 Co-firing Processes

To improve the electrical connection between the bulk anode and the metallic interconnect, Delphi has previously chosen to screen print an outer layer of nickel oxide paste to the outer surface of the anode electrode. Once fired and reduced, the nickel oxide is converted to nickel metal in the application, enhancing the electrical path between the cell and metallic interconnect materials. Previously, a specific firing step was needed to sinter this nickel oxide thick film to ensure good adhesion to the anode surface. A recent process improvement has been the development of a nickel oxide outer layer that not only improves electrical conductivity and adhesion to the metallic interconnect, but allows co-firing of this outer layer along with the bulk anode, active anode, and electrolyte (bi-layer). A specific firing cycle has been developed for sintering all the aforementioned layers in a single step.

A second process improvement was developed and implemented on the cathode interconnect portion of the cell. Previously, a similar conductive layer was screen printed to the fired cathode to improve the connection to the metallic interconnect on the air-side of the cell. This layer is composed of a silver based alloy, and organic additives used as process aids. Process improvements have led to the ability to co-fire the screen-printed cathode electrode with the screen-printed conductive surface layer to

yield the necessary bonding and microstructure while minimizing interfacial losses. Both co-firing process have been implemented in the Delphi cell fabrication process, leading to improved efficiency and significant cost reduction.

Another improvement that was implemented on a larger scale is the reduction in the number of firing steps to produce flat bi-layers. Previously, a bi-layer was formed and fired, and it had to be place back into the kiln and “creep-flattened” at a high temperature to achieve the required flatness necessary for post processing (i.e., thick film printing and other operations). A new step has been introduced into the Delphi cell fabrication process that allows for bi-layer sintering and bi-layer flatness to be achieved in a single, high temperature-firing step. The sintering temperature is set based on the need to fully densify the solid-state zirconia electrolyte, while maintaining proper porosity in the anode structure. By carefully designing and selecting a porous, weight-bearing constraintment cover layer over the ceramic bi-layer, ceramic films can be fired flat while achieving fully dense electrolytes. Success in this area was brought on by great efforts in process optimization. Compatibility between material set, constraintment layer design, and firing profile had been achieved through extensive experimentation. Scaling up of this procedure is still underway to improve yields at larger batch (higher volume) levels. By fabricating flat anode/electrolyte bi-layers in a single firing step, efficiency has increased leading to process time and cost savings.

6.2.5.2 FUEL CELL PERFORMANCE IMPROVEMENTS

6.2.5.2.1 Anode Adhesion Improvement

A conductive layer is added to the fuel cell anode surface to improve the electrical contact between the bulk anode and the metallic interconnect. Implementation of an improved surface layer has led to improved cell performance and durability of the solid oxide fuel cell stack. The improved interconnect design currently consists of a tape cast outer layer that is iso-statically laminated to the bulk anode in the unfired state and then co-fired with the entire bi-layer. This outer layer has been developed based on a selection of nickel oxide powder with a specific particle size, screen print organic vehicle for processing, and pore-former that burns out during high-temperature sintering. This burn out creates the necessary pore structure for enhanced surface adhesion to the adjacent layer. The adjacent layer is a contact paste that gets applied later during the stack assembly process. The contact paste also composed primarily of nickel oxide has been developed along with the co-fired surface layer in order to provide adequate adhesion and microstructure. The contact paste may contain a fugitive phase that burns out during operation of the stack, leaving added porosity to ensure permeability of the reactant gas through the structure. Due to the improvements in anode outer layer and contact paste optimization, improved performance and durability have been obtained, while a high-temperature firing step has been eliminated.

6.2.5.2.2 Cathode Interconnect Improvements

Ongoing cathode development activities at Delphi, in conjunction with Battelle PNNL research efforts, led to an improvement in the cathode/interconnect assembly on the air-side of the repeating unit. A cathode surface layer composed of a highly conductive

and stable alloy of silver is used to enhance the electrical connection between the cathode electrode surface and the metallic interconnect materials. The surface layer, previously applied in a grid pattern, has been altered to cover the full active area of the cathode. The silver-based alloy, full-coverage design has affected cell electrochemical performance by reducing degradation rate of the cell, improving the long-term durability of the cells, and subsequently the fuel cell stack. Along with the change in the amount of active area covered, process improvements have led to firing cycle optimization, leading to a co-fired process for the cathode and cathode full coverage layers. Reduced process cost and process time along with performance improvements have made this a substantial improvement to the ceramic fuel cell component.

6.2.5.3 Characterization Methods

6.2.5.3.1 Helium Leak Detection

A standard process procedure in the fabrication of solid oxide fuel cells includes checking the integrity of the ceramic bi-layer after it is sintered and flattened. The flattened bi-layer (anode, active anode, and electrolyte) goes through a post-sintering sizing adjustment, and then the electrolyte is checked for leakage. A fully dense electrolyte layer is required to optimize electrochemical performance and durability of the cell. Helium leak detection is the method chosen to check the hermeticity of the bi-layer based on the permeation of helium gas through the electrolyte layer. Supplementary observations used in the development of this test were Scanning Electron Microscope (SEM) and open circuit voltage measurements. This helium leak test can be run nondestructively and only takes approximately 1 minute per part. The system is charged with the test gas, and the flow of helium through the electrolyte is detected by a mass spectrometer and reported in cc/sec.

Figures 6.2.5-1 and 6.2.5-2 show the results of measurements made over a 16-month period on approximately 3000 bi-layers. Results in **Figure 6.2.5-1** refer to the cell by specimen number. **Figure 6.2.5-2** displays the results as a function of process time period. Based on the results and feedback on fuel cell power performance and durability, a maximum helium detection limit has been determined. Well over 95% of parts fabricated with the standard process and material set pass the helium leakage detection check and proceed to the next step in the process which is thick film printing of cathode layers. A measurement system evaluation has been run on the apparatus and shows good test repeatability. **Figure 6.2.5-3** shows the results of the measurement system evaluation (MSE). The data shows the helium leakage results from parts that range from 1E-02 cc/sec to 1E-06 cc/sec and run by two operators. The plot shows that all data points lie very close to the 45-degree trend line that would represent true repeatability in the test. This test has been implemented as a quality check on all fuel cell parts fabricated with the current low volume production process.

Figure 6.2.5-1: H_e permeation test

Figure 6.2.5-2: H_e permeation test

Figure 6.2.5-3: H_e permeation test

6.2.6 Develop Gas Distribution Meshes

Experiments and modeling were performed to verify that relatively small defects in the anode gas flow channels could cause poor stack performance at high-fuel utilization. The objective was to determine whether the “bypass channels” could account for the fall-off of the power density versus fuel utilization curves at fuel utilizations that were ~30% lower than expected.

The device pictured in **Figure 6.2.6-1** was constructed to measure the pressure field induced by flow through a mock-up of the anode flow channel. The results would be used to verify a computational fluid dynamics (CFD) model that would be used to predict flow patterns within the actual stack anode cavities. The tests were conducted using nitrogen at ambient temperature. Wire mesh 0.5 mm thick is sandwiched between flat steel plates. Nitrogen enters at the left and is evenly distributed across the width of the central section by means of a flow spreader. The edges of the mesh are sealed with flexible gasket material. The central section, containing the mesh has a pattern of pressure taps. A pressure gauge can be connected to each tap in succession and the pressure difference between each tap and ambient can be measured while the nitrogen is flowing through the mesh channel.

Figure 6.2.6-1: Device to measure pressure field in mock-up of anode flow channel

To simulate a bypass channel, a 7 mm strip was removed from the mesh (**Figure 6.2.6-1**). **Figure 6.2.6-2** shows the measured distribution of pressures, during an experiment, where nitrogen was introduced at 5 L/min (5000 sccm) to the device. The pressure gauge measurements show that near the entrance (top edge in the figure), the pressure was lowest in the 7 mm gap. A baffle was placed at the inlet and outlet ports to provide even flow distribution. The pressure difference from left to right in the mesh, 372 Pa vs. 440 Pa was due to a very small defect in plate alignment. Pressure drop data were collected for nitrogen flow at 1, 2, 3, 4 and 5 L/min.

Figure 6.2.6-2: Map of pressure field in the device shown in Figure 4.3.7.1 during an experiment when nitrogen was flowed at 5L/min (5000 sccm)

A CFD model was defined to simulate the nitrogen flow through the wire mesh and slit regions to allow for benchmarking the code predictions. This region was 152 mm deep and 146 mm wide, (**Figure 6.2.6-2**) with a plate-to-plate gap of 23 mil (0.58 mm). **Figure 6.2.6-3** compares the calculated pressure drop to the data in the slit region between the furthest two taps. These are the first and fourth taps (from left to right) in the middle row of taps (**Figure 6.2.6-1**). The nitrogen flow rate is converted to velocity (**Figure 6.2.6-3**), referenced to the superficial velocity at the inlet to the wire mesh (i.e., the velocity for the unobstructed mesh inlet area of 0.58 mm x 146 mm). The calculated pressure drop is approximately 15% higher than the data over the entire flow range. The model was defined as symmetric about the slit axis and could not predict the asymmetric pressure drop behavior (left to right pressure gradient) seen in the data. The pressure drop is dominated by laminar pressure losses (pressure drop is nearly linear with velocity). A 15% error in pressure drop would correspond to nearly a 15% error in velocity (mass flow through the slit/bypass region).

Figure 6.2.6-3: Plot of pressure drop along the slit axis versus inlet flow velocity

The CFD model was modified to simulate an actual cell plate configuration. The model used actual cell dimensions, bypass channels at the outer edges (sized to match measured plate distortions) and prototypic fuel flow at ~973 K. **Figure 6.2.6-4** shows the calculated velocity distribution at 0.01 g/sec per cell inlet flow along the wire mesh region (flow direction is indicated in the figure). Within ~30% along the flow axis, the average velocity has dropped ~26%, and stabilizes at ~30% below the inlet velocity by mid-plane (50% along the flow axis). **Figure 6.2.6-5** shows the velocity distribution within the bypass region at mid-plane. The average velocity in the bypass corresponds to ~30% flow bypass at this location. The velocity is maintained until the mesh region exit. If the 15% error is included from the benchmark results (15% too high a bypass flow) the predicted bypass flow would be >25%. This is consistent with measured cell stack data, as discussed in section 4.3.9.

Figure 6.2.6-4: Predicted flow distribution

Figure 6.2.6-5: Predicted flow distribution in the bypass channel

6.2.7 Develop Mesh/Electrode Interface Materials

Delphi continued to develop an interconnect via concept that, in conjunction with the use of silver-coated fccralloy meshes as a current collector, should overcome this problem. The via employs an alumina forming ferritic stainless steel that is perforated, and each hole is filled with a conductive material to minimize the ASR in the separator. Delphi has examined three types of vias: (1) the simple via, (2) the offset via, and (3) the dimpled via.

Work on the simple and offset vias showed good ASR and hermiticity with 2000 hour dual atmosphere testing. The simple via design used a glass-silver composite as the conduction path. SEM analysis of early samples showed a mechanically weak bond that would not hold up to thermal cycling (**Figure 6.2.7-1**). The offset via design had fabrication issues due to the complex design, as well as porosity and gaps forming in the glass-silver composite layer resulting from shrinkage problems (**Figure 6.2.7-2**). This led Delphi to the development of the dimpled via design. A small dimple is mechanically pressed into the separator plate, and the via is formed at the bottom of the hole. The via is then filled with a silver-copper braze, and the dimple then covered with the glass-silver composite. This design allows the glass to protect the via from dual atmosphere degradation and allows the use of the more compliant braze as a conduction path through the separator (**Figure 6.2.7-3**). After initial samples exhibited cracked and porous glass, YSZ fibers were introduced into the glass-silver composite resulting in a hermetic seal (**Figure 6.2.7-4**). ASR tests run on the dimpled via show very good ASR, well below the maximum design limit during the entire test. Dual atmosphere tests have been completed at 100 hours and are continuing out to 1000 hours. The SEM results of the 100-hour test show good hermiticity and minimal degradation (**Figure 6.2.7-5**). Continued testing is underway to rapidly thermal cycle several samples 50 times. Delphi will test to determine the density of vias required in a separator plate to yield an optimum conduction path.

Figure 6.2.7-1: SEM of via showing weak interface with glass

Figure 6.2.7-2: SEM of offset vias showing gaps and porosity in glass layer

Figure 6.2.7-3: The dimpled via concept

Figure 6.2.7--4: Dimpled via samples without (left) and with (right) YSZ fibers in the Ag-glass composite

Figure 6.2.7-5: SEM of dimpled via sample after 500 hour IRU test

6.2.8 Fabrication Developmental Stacks

Single cell testing of both intermediate sized cells (33 cm² active area) and full-sized Gen 3 cells (105 cm² active area) were used extensively to locate problems and evaluate their potential solutions.

Fuel utilization in excess of the 70% was seldom achieved in the Gen 3 cells and stacks but had been achieved in the both the intermediate and 3-piece Gen 3 single cassettes. The 3-piece Gen 3 cassettes are made of 3 flat sheet metal pieces and are constructed differently from the stamped sheet metal cassettes. A series of tests were conducted to determine the critical differences that influenced fuel utilization. The tests were conducted on the 3-piece cassettes since the changes in the gas channels can be easily implemented. Delphi established that the low fuel utilization in the stamped cassettes was the result of poor flow uniformity in the anode channel. This was caused by a “by-pass” channel that was formed between the ends of the anode mesh and the cassette walls (**Figure 6.2.8-1**). This by-pass area had originally been thought too small to have a significant effect on the fuel utilization since it only constituted 4.5% of the cross sectional area. Upon modeling of the flow distribution, as discussed in Section

4.3.7, it was found that approximately 30% of the anode gas flow was going through the by-pass area. The modeling and the experimental data showed good agreement in that cells with the by-pass blocked showed approximately a 30 percent improvement in fuel utilization. **Figure 6.2.8-2** shows the fuel utilization curves of two 3-piece Gen 3 cells with and without the by-pass blocked. The third curve in the figure is a sheet metal cassette single cell with the by-pass open. The different size of the by-pass between the two types of cells is most likely the cause of the slight difference between the curves. During the post mortem of the cassettes, it was determined that the 3-piece Gen 3 had a slightly smaller by-pass area. This explains why the 3-piece curve rolls over at higher fuel utilization than the sheet metal cassette. Engineering efforts are ongoing to effectively block the by-pass area in the sheet metal cassettes.

Figure 6.2.8-1: Cross section of a 4 cell Gen 3 stack

Figure 6.2.8-2: Fuel utilization of tested cells with and without the by-pass area blocked

6.2.9 Evaluate Stack Performance

Multiple Gen 3.1 30-cell stacks were built and tested in the stack laboratory. **Figure 6.2.9-1** shows an IV curve from a Gen 3.1 30-cell stack. The stack produced 1821 Watts at 21 Volts (0.7 Volts/cell) with 48.5% H₂, 3% H₂O, rest N₂ simulated reformat (power density of 578 mW/cm², 42% fuel utilization).

Figure 6.2.9-1: IV curve from a Gen 3.1 30-cell stack

Further improvements were demonstrated in power density by improving fuel distribution within the cassette. Prototype 5-cell stacks were built and tested. **Figure 6.2.9-2** shows power density of 730 mW/cm² at 0.7 Volts/cell with 48.5% H₂, 3% H₂O, and the rest N₂ simulated reformat (50% fuel utilization).

Figure 6.2.9-2: IV curve from a Gen 3.1 5-cell stack with improved fuel distribution in the anode

Multiple 5-cell stacks were used to develop and demonstrate improved durability. The data shows a 5-cell stack operated under constant current for greater than 2000 hours. The stack showed an initial degradation of about 8% in the first 500 hours after it stabilized, and the degradation was about 1% for the next 1500 hours. The stack experienced two unplanned thermal cycles due to the facility shutdown during the course of this run. At the end of the test (2200 hours), there was an abrupt loss of performance in one of the cells. This resulted in shutting down the stack. An autopsy is being carried out to find the root cause of failure in the repeating unit. The test demonstrated encouraging results for durability with Gen 3.1 stack at a reasonable power density.

Figure 6.2.9-3: Gen 3.1 5-cell stack on continuous durability

Improvement in fuel utilization was also demonstrated in 5-cell stacks by blocking fuel flow bypass in the cassettes as described in the previous sections. The data below shows a 5-cell stack tested for fuel utilization at constant current of 66 Amperes. The stack produced 400 mW/cm² at 65% fuel utilization (0.66 Volts/cell) and 350 mW/cm² at 70% fuel utilization (0.6 Volts/cell) with 48.5% H₂, 3% H₂O, and the rest N₂.

Figure 6.2.9-4: Fuel utilization test with Gen 3.1 5-cell stack

6.3 Task 3: Reformer Development

6.3.1 Develop Endothermic Reformer

6.3.1.1 Gen 2P / NG1 FDU Reformer Assembly Testing

The Gen 2P reactor, with Feedstream Delivery Unit (FDU) Natural Gas One (NG1), was tested on methane fuel in both POx and endothermic reforming modes. Tests were undertaken to establish the potential of the Gen 2P reactor independent of the additional factors of liquid fuel atomization, evaporation, and mixing. The NG1 FDU is a proven design and has demonstrated good results when coupled together with the Gen 4T reactor operating on methane fuel. The test setup is illustrated on **Figure 6.3.1-1**.

Figure 6.3.1-1: Gen 2P with NG1 FDU Test Setup

6.3.1.1.1 Partial Oxidation

POx reforming operating conditions are shown in **Figure 6.3.1-2**. The three operating points represent conditions demonstrated with the Gen 4.1T reformer. All tests were performed with a one-half inch thick pre-catalyst directly in front of the endothermic reactor.

Gen 2P POx Test Conditions

Condition	T _{air} [C]	T _{methane} [C]	Ref Eff [%]	O/C [-]	Fuel Flow [g/s]
1	20	20	83.6	1.3	0.2
2	20	20	84.5	1.25	0.2
3	20	20	79.7	1.45	0.2

Figure 6.3.1-2: Gen 2P POx Test Conditions

Figure 6.3.1-3 shows the performance trends vs. O/C in POx mode. Equilibrium predicted Ref Eff w/o CH₄ is virtually flat versus O/C as is the actual reforming Efficiency with CH₄ indicating little change in H₂ and CO in the product despite increased reactant

O₂. CH₄ in the reformat was measured and decreases as O/C increases. Methane was ~1 mole % at O/C = 1.25, was 0.5 mole % at O/C=1.30, and further decreased to 0.1 mole% at O/C = 1.45. Additional O₂ in the reactant stream is believed to 1st react with residual CH₄ rather than participating in reacting with H₂ and CO to form H₂O and CO₂. One can see that at the ~OC between 1.45 and 1.5 that Ref Eff w/ CH₄ and reforming Efficiency without CH₄ curves would meet, indicating zero methane. Both curves would, at this point, decline as O/C was further increased.

Figure 6.3.1-3: Gen 2P POx Efficiency with CH₄

The performance of the reformer with varying O/C, but at constant space velocity, is independent of O/C. The fraction of equilibrium efficiency reached remains constant for all O/C's tested. This is consistent with similar tests of POx with Gen 4.1T reformer, only that efficiencies without methane were generally 1.5% to 2% higher.

Figure 6.3.1-4 shows the reformat temperatures. The difference between equilibrium and measured temperatures is significantly higher than in the adiabatic tests with Gen 4.1T which explains the slightly lower reforming efficiency.

Figure 6.3.1-4: Gen 2P POx Reformate Temperature

Water in the reformate stream is essential to avoid carbon formation in the reformer outlet area and within the Integrated Component Manifold (ICM) and stack inlet. Water-to-methane ratios are presented in **Figure 6.3.1-5**. Apart from the O/C of 1.25, where the water-to-methane ratio reaches the lower limit of carbon margin, water-to-methane ratios are well above the required operating ratio of 3.

Figure 6.3.1-5: Gen 2P POx Water to Methane Ratio

6.3.1.1.2 Endothermic Reforming

Endothermic reforming tests were performed (with and without a pre-catalyst in place) and at space velocities of 25,000 and 50,000 hr⁻¹. The operating conditions are detailed in **Table 6.3.1-1**. The reformer is operated using simulated recycle based on a constant stack fuel utilization of 60%. The test points represent operating conditions of increasing recycle fraction from 13.6% to 50.3%. The flow rates shown in **Table 6.3.1-1** represent the case of 25,000 hr⁻¹ space velocity. The tests at a space velocity of 50,000 hr⁻¹ simply doubled the flow rates. The target reformat outlet temperature was 850 °C. The reactant inlet temperature was varied to preheat the reactants, avoid front edge carbon formation, and ensure sufficient endothermic reforming at increasing levels of recycle.

Table 6.3.1-1 Gen 2P Endothermic Test Conditions

Endothermic Test Conditions at 60% Stack Fuel Utilization

Condition	Eq Eff [%]	m _{air} [g/s]	m _{fuel} [g/s]	m _{recycle} [g/s]	m _{total} [g/s]	T _{air} [C]	T _{fuel} [C]	T _{recycle} [C]	Target T3 [C]	Recycle Fraction
1	107.9%	0.366	0.111	0.111	0.58724	20	20	20	850	0.136
2	118.3%	0.288	0.120	0.180	0.58702	20	20	20	850	0.210
3	127.2%	0.220	0.122	0.245	0.58704	20	20	20	850	0.277
4	136.4%	0.150	0.125	0.312	0.58703	150	150	150	850	0.343
5	146.0%	0.077	0.128	0.383	0.58696	350	350	350	850	0.407
6	156.1%	0.000	0.130	0.456	0.58668	450	450	450	850	0.503

Gross reformer efficiencies with and without methane are presented in **Figure 6.3.1-6** and **Figure 6.3.1-7**. At a space velocity of 25,000 hr⁻¹ the measured efficiencies are much closer to the calculated equilibrium levels than at a space velocity of 50,000 hr⁻¹. For the given geometry, a space velocity of 10,000 hr⁻¹ would be required to reach gross reformer efficiencies of 99% of the equilibrium levels at the tested reforming temperatures. Stationary Power Unit 2 (SPU2) flow requirements translate into a space velocity of 92,000 hr⁻¹ if applied to the Gen 2P planar reformer. The pre-catalyst did not have any significant impact on the overall reforming performance as shown in **Figure 6.3.1-6** and **Figure 6.3.1-7**. Note that in **Figures 6.3.1-7 through 6.3.1-9** condition 5 could not be achieved in the lab for the conditions SV=25,000 with no precat and SV=50,000 with precat.

Figure 6.3.1-6: Gen 2P Endothermic Gross Efficiency with CH₄

Figure 6.3.1-7: Gen 2P Endothermic Gross Efficiency without CH₄

Reformate outlet temperatures are presented in **Figure 6.3.1-8**. The desired reformate outlet temperature of 850 °C was only achieved at condition 1. For all other test conditions, the reformer outlet temperature was significantly lower than 850 °C. The test will be repeated with the emphasis of constant outlet temperature for all test

conditions and will investigate the impact of temperature on reforming efficiency and fuel conversion.

Figure 6.3.1-8: Gen 2P Endothermic Reformate Temperature

Fuel conversion was poor for all conditions tested and is evident in the large discrepancy between measured gross reformer efficiencies without methane and equilibrium predictions (**Figure 6.3.1-7**). This is partially due to the relatively low reforming temperature (below 800 °C) and high space velocity (SV=50,000 hr⁻¹). This may indicate insufficiencies in the conversion efficiency and the kinetics of the washcoat formulation applied to endothermic reforming. Practical applications with the reformer operating at 1000 °C and above, and space velocities of 10,000 hr⁻¹, are challenging. This is because of materials and packaging requirements. The amounts of methane break through are shown on **Figure 6.3.1-9**.

Figure 6.3.1-9: Gen 2P Endothermic Methane Breakthrough

6.3.1.2 Gen 3P Planer Reformer

6.3.1.2.1 Pressure Drop Testing

The flow versus pressure drop for each side (reforming and combustor) of the Gen 3P planar reformer was characterized using room temperature air. The reformer had no washcoat applied for this testing. The results were adjusted to approximate corresponding pressure drops at reformer operating temperatures using a correction for gas density (Figures 6.3.1-10 and 6.3.1-11).

Figure 6.3.1-10: Gen3P Reactor Reforming Side Pressure Drop Adjusted to 900 °C

Figure 6.3.1-11: Gen3P Reactor Combustor Side Pressure Drop Adjusted to 950 °C

6.3.1.2.2 Flow modeling (Combustor Pressure Drop / Heat Transfer)

Computational fluid dynamics (CFD) combustion analysis was performed on the Gen 3P reformer (**Figure 6.3.1-12**). The extracted flow volume is shown in **Figure 6.3.1-13**. Air and combustor fuel (anode tail gas) are supplied to a mixing unit below the combustor. The combustor itself is housed inside the reactor. Details of the computational mesh are illustrated in **Figure 6.3.1-14**.

Figure 6.3.1-12: Gen 3P Reactor Assembly with Internal Combustor

Figure 6.3.1-13: Gen 3P Reactor CFD Flow Model

Figure 6.3.1-14: Gen 3P Reactor Computational Mesh of Combustor Flow Path

Large re-circulations inside the combustion chamber (**Figure 6.3.1-15**) are responsible for temperature variations within the combustion chamber and subsequently throughout the interlaced reformer and combustor layers (**Figure 6.3.1-16**).

Figure 6.3.1-15: Gen 3P Reactor Velocity Distribution (Combustor)

Figure 6.3.1-16: Gen 3P Reactor Temperature (Combustor)

Figure 6.3.1-17: Gen 3P Reactor Temperature (Combustor)

The multi-jet mixing unit beneath the combustion chamber sits in close proximity to the chamber itself and cannot support sufficient mixing prior to combustion to guarantee a uniform temperature distribution. Due to the large variation in velocity and dynamic pressure along the multi-jet mixing unit, pressure conditions exist that supported airflow into the fuel manifold. Combustion will occur inside the fuel manifold (**Figures 6.3.1-16 and 6.3.1-18**).

Temperature variations inside the combustion chambers, due to the proximity of the multi-jet mixing unit, are shown (**Figure 6.3.1-18**). The effects are three-dimensional and more pronounced than can be demonstrated in **Figures 6.3.1-17 and 6.3.1-18**. An external combustor that supplies a uniform temperature to the endothermic reactor may reduce this variation.

Figure 6.3.1-18: Gen 3P Reactor Temperature (Combustor)

6.3.1.3 Gen 5T – Reformer Design

Due to continued difficulties with planar reactor fabrication, an initiative to create a substantially more manufacturable endothermic design was initiated.

6.3.1.3.1 Reformer Sub-System

The Generation 5 Tubular (Gen 5T) reformer is a staged reformer concept for system start-up, transient operation, and high efficiency at full load conditions. The reformer subsystem is comprised of an adiabatic POx reformer in series with an endothermic heat exchange reformer (**Figure 6.3.1-19**). Fuel and recycle are metered individually, mixed, and fed to both reactors. All fluids can be pre-heated. System start-up begins with combustion start-up in the FDU of Reactor 1 followed by POx operation in Reactor 1 at an O/C that prevents carbon formation. Recycle from the SOFC stack fuel is introduced into the recycle stream and is reacted to H₂ and CO inside the endothermic Reactor 2. Reformer efficiency increases with the fraction of fuel metered to Reactor 2.

Figure 6.3.1-19: Gen 5T Reformer System

Figure 6.3.1-20 shows the components of the Gen 5T reformer sub-system. NG1 FDU is a gas/gas mixer that supplies fully mixed fuel and air (and recycle when required) to the adiabatic POx Reactor 1. NG2 FDU is a gas/gas mixer that mixes fuel and recycled anode tail gas with the output of Reactor 1 and feeds the mixture to Reactor 2. Preheat devices are not shown. A combustor provides hot combustion products to the endothermic Reactor 2. An assembly drawing is shown in **Figure 6.3.1-21**.

Figure 6.3.1-20: Gen 5T Reformer Subsystem Components

The NG2 FDU gas-gas mixer was developed for the Gen 5T reformer with the requirements of equal or better mixing than the NG1 FDU, a mixing distance of less than one inch, low pressure loss, scalable geometry for various applications, and with little or no recirculation flow field. The concept, consisting of a multitude of micro-ejectors, is illustrated in **Figure 6.3.1-22**. Fluid 2 is entrained into Fluid 1 and the subsequent re-circulations support mixing.

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Figure 6.3.1-22: NG2 FDU

Figure 6.3.1-23: NG2 FDU Analysis

The design is detailed in **Figure 6.3.1-24** and outlined in **Figure 6.3.1-25**. Multiple small tubes are pressed in a plate with holes. A second plate with tightly controlled larger holes is placed at a set distance from the tubes. A ring manifold supplies Fluid 2 to the cavity between the plates uniformly around the circumference through an array of holes.

Figure 6.3.1-24 : NG2 FDU Design

Figure 6.3.1-25 : NG2 FDU Assembly

6.3.1.3.3 Gen 5T Reactor 1

Reactor 1 is essentially a ceramic foam brick catalyst contained in a tubular housing (Figure 6.3.1-26). The reactor is connected via flanges to NG1 FDU and NG2 FDU. An igniter boss is attached to Reactor 1 to support ignition and system start-up. The assembly of Reactor 1 is shown in Figure 6.3.1-27.

Figure 6.3.1-26: Gen 5T Reactor 1

Figure 6.3.1-27: Gen 5T Reactor 1 Assembly

6.3.1.3.4 Gen 5T Reactor 2

Reactor 2 is an endothermic heat exchanger-type reactor with interlaced reforming (cold) and combustion (hot) flow paths for gross reforming efficiencies of 130%. The reactor is tubular, rather than planar, and consists of six fuel-reforming tubes in a counter-flow heat exchange arrangement.

The stringent heat transfer requirements to support the endothermic reforming kinetics are met by augmented heat transfer rather than maximizing surface area as in a planar micro-channel design. Foam substrate is brazed on the inside and outside of the reforming tubes. Sketches of single cell and multi cell foam structures are illustrated in **Figure 6.3.1-28**.

Figure 6.3.1-28: Gen 5T Foam Heat Transfer

An example of the heat transfer enhancement in laminar flow is shown by the increase in Nusselt number for a given flow rate when compared to Nusselt numbers of 3.5 to 6 for typical laminar pipe flows (**Figure 6.3.1-29**).

Figure 6.3.1-29: Gen 5T Foam Heat Transfer - Nusselt Number

The design is sketched (**Figure 6.3.1-30**) and consists of six tubes of one-inch outer diameter contained within 10 ppi Fecralloy foam. The reforming tubes themselves contain a 20 ppi Fecralloy foam substrate.

Figure 6.3.1-30: Gen 5T Reactor 2

The interior of the reactor assembly is shown in **Figure 6.3.1-31**.

Figure 6.3.1-31: Gen 5T Reactor 2 Foam Assembly

6.3.1.4 Gas Phase Combustor Module 1 (GPCM1) Combustor

A combustor was designed to support Gen 5T and Gen 4P endothermic reformers with hot combustion products. Twenty design and development iterations were performed. The original design was then packaged. **Figures 6.3.1-32** and **6.3.1-33** highlight the differences between optimized and packaged designs

Figure 6.3.1-32: GPCM1 Design Study

The combustor concept is comprised of fuel and air supplies, an air pre-swirl to minimize pressure losses, a fuel swirler surrounded by an air swirler (**Figure 6.3.1-34**) and combustion stability zone centered on a vortex breakdown due to swirl over a bluff body (**Figures 6.3.1-33** and **6.3.1-33**). GPCM1 assembly drawings are shown in **Figure 6.3.1-35**.

Figure 6.3.1-33: GPCM1 Section View

Figure 6.3.1-34: GPCM1 Swirler Arrangement

Figure 6.3.1-35: GPCM1 Assembly Drawing

6.3.2 Develop CPOx Reformer

6.3.2.1 Gen 4.2T Design & Modeling

6.3.2.1.1 CFD of recycle inlet / mixing pre- stack

The Gen 4.2T tubular reformer consists of the Gen 4.1T tubular reformer with additional fuel and recycle-injection into the output of its POx reactor. The concept is illustrated in **Figure 6.3.2-1**. The mixing performance at the second stage fuel/recycle-injection port was investigated for various strategies through computer simulations. The flow volume (**Figure 6.3.2-2**) consists of the flow paths of the reactor; the reformer outlet manifold; the second stage fuel and recycle injection; and the ICM manifolding between the reformer and the two fuel cell stack anode inlets. **Figure 6.3.2-3** shows methane mass fraction contours and the location of a plane ("flow split" plane) just upstream of the split into two separate streams for the two stacks. The evolution of temperatures along the flow path is shown on **Figure 6.3.2-4** for a rated power of 6.3kW and NOC of 1.7kW. The analysis indicates that temperature variations at the inlet to the stacks are very low.

Figure 6.3.2-1: Gen 4.2 T Reformer Concept Illustration

Figure 6.3.2-2: Gen 4.2 T Second Stage Fuel Injection – Flow Model

Figure 6.3.2-3: Gen 4.2 T Mixing - Methane Mass Fractions Post-Second Stage Injection Port

Figure 6.3.2-4: Gen 4.2 T Temperature Distribution in ICM

6.3.2.1.2 CH₄ Metering System Development

The past development on gaseous fuel reforming (i.e., CH₄, Natural Gas) was accomplished using lab-grade gas flow controllers for fuel metering. To incorporate the

fuel metering function into the SPU packaging, work began on selecting an appropriate metering device.

Table 6.3.2-1 is a compilation of flow requirement for both SPU1A and SPU1B. Of significance is the decreased minimum flow (and resulting turndown increase) from previous requirements. A number of logistical requirements were modified due to the time constraint for completion of SPU1B development and subsequent testing, such as:

- The need to use same metering approach for both SPU1A and SPU1B (single development path)
- Supply pressure was limited to 650 kPa
- Preferable to be Saturated Switch-type Driver (ECU capacity for new driver schemes is limited)
- Need to be robust to temperature due to open-loop control scheme

Devices that were investigated included:

- Delphi Multec Topfeed (TF) CNG (compressed natural gas) Prototype Injector
- Delphi SCPI (Sequential Central Port Injection) Base CNG Prototype Injector
- Delphi Evaporative Emission Control Solenoid – Production
- Delphi Multec2 / Multec 3.5 Topfeed Gasoline Injector – modified from production
- AFS (Alternative Fuels Systems Inc.) GS series Injector – prototype
- Quantum Topfeed CNG Injector – prototype
- Teknocract Proportional Flow Control Valve - production

Table 6.3.2-1: CH₄ Metering Requirements - SPU1A and SPU1B

mode/metric	calc or input?	units	reqt importance	Inj Pt 1 (Main Reformer Inlet)	Inj Pt 2 (Recycle Inlet)	Prim Inj for SPU1A
				SPU1B	SPU1B	SPU1 (aka SPU1A)
Min Flow	input	g/s CH ₄	would like	0.015	0.015	0.100
Min Flow2	input	g/s CH ₄	must meet	0.025	0.025	0.100
NOC Flow	input	g/s CH ₄	-	0.035	0.035	0.112
NOC DC est.	calc	%		12%	12%	36%
Max Flow	input	g/s CH ₄	must meet	0.300	0.300	0.310
Dyn Range	calc	[-]	would like	20	20	3
Dyn Range	calc	[-]	must meet	12	12	3

The list was reduced to a single device (Teknocract[®] Proportional Flow Control Valve) as the result of several rounds of evaluation. The summary evaluation is shown in **Table 6.3.2-2** and is explained below.

Table 6.3.2-2: CH₄ Metering Devices - Summary of Issues

Design Intent Fuel	NG	NG	Gasoline Vapor	NG	Gasoline	NG	Gases
Name	Multec TF type	NG Inj SCPI type	Purge Sol	AFS Gs33 NG Injector	Multec 2/3.5 DLC; no director	Quantum Inj	Teknocrift Prop Valve
Availability	poor (requires new build)	poor (requires new build)	good (production)	fair (build to order)	good (modified from production)	fair (build to order)	fair (build to order)
Driver Voltage / Type	12V P&H 4a /1a	12V Sat Switch	12V Sat Switch	12V P&H 8a / 2a	12V Sat Switch	12V P&H 4a /1a	12V Saturated Switch (w/ recirculation diode)
Durability	limited validation	unvalidated	good but to less stringent flow resolution	fair	unvalidated on gaseous flow (inadequate when tested)	good per brochure literature	good per brochure literature
Other Issues			very sensitive to outlet pressure	more temperature sensitive due to heat build		no response to RFQ; not clear performance would be acceptable with un-proven low flow design	

6.3.2.1.3 Blocked hole CFD

Manufacturing issues arose from fuel injection holes being blocked by braze material during the manufacturing of NG1 FDU units for Gen 4.2 T. The brazing issues are illustrated in **Figure 6.3.2-5**.

Figure 6.3.2-5: FDU NG1 Braze Failure Assessment

Five of the ten fuel injection holes on one side were blocked by braze material. Computational simulation was used to determine whether the parts were within acceptable limits of performance. **Figures 6.3.2-6** and **6.3.2-7** compare the mixing performance of the original hardware with that of the blocked holes. The braze

blockage has a significant impact on the performance of the part. **Figure 6.3.2-8** explains the evolution of richer and leaner zones within the highly swirling flow field.

Figure 6.3.2-6: FDU NG1 Braze Failure Mixing Analysis

Figure 6.3.2-7: FDU NG1 Original Design Mixing Analysis

Figure 6.3.2-8: FDU NG1 Braze Failure CFD Analysis

The quality of mixing at the catalyst inlet face is compared in **Figures 6.3.2-9** and **6.3.2-10**. The mixture variation increased from $\pm 2\%$ to $\pm 8\%$. An $\pm 8\%$ variation would overheat the catalyst in areas of lean mixture (-8% from mean) and could produce carbon in areas of rich mixtures ($+8\%$ from mean). The variation was deemed unacceptable to maintain performance over time. As a result, the FDU's were rebuilt.

Figure 6.3.2-9: NG1 FDU w/ Blocked Holes - Mixing Analysis

Figure 6.3.2-10: NG1 FDU Original Design - Mixing Analysis

6.3.2.2 Carbon Formation Coldfinger Testing

Carbon formation tests were conducted for various materials and O/C's. Reformer output is cooled over a probe in a controlled fashion. Various materials can be attached to the probe to investigate carbon formation. The results are summarized in **Table 6.3.2-3**. Materials that were investigated include stainless steel, Inconel 625, welded stainless steel, brazed Inconel 625, brazed Haynes, and anode material.

Table 6.3.2-3: Cold Finger Carbon Formation Summary

ORD	What:	OVC Input	OVC back calc	Inlet conditions	SV _{STP, vol}	Cold finger Probe tip Temp	carbon response?	fueling rate	disturbance	H ₂ O (steady state value)	CH ₄ (steady state value)	H ₂ O/CH ₄ ratio (DS calc)
	units				[1/min]	[°C]				[mole%]	[mole%]	
1	January Testing of Gen 4.1T	cold finger only	1.3	leaked	4733.26		none	0.20	ixture A (old)	3.3	0.5	6.60
2		SS	1.3		4733.26	702	YES-welded	0.20		3.6	0.404	8.91
3		welded SS	1.45		4733.26	811	none	0.20		6	0.5	12.00
4		welded SS	1.25		4733.26	690	YES-welded	0.20		4.5	0.5	9.00
5	May/June Testing of Gen 4.2T	welded SS	1.3	leaked	7340.21	723	none	0.30	ixture B (new)	4.6	0.41	11.22
6		welded SS	1.3		7340.21		-	0.30		-	-	#VALUE!
7		welded SS	1.25		7340.21	687	yes	0.30		3.9	0.61	6.39
8		welded SS	1.3		7340.21		yes	0.20		-	-	#VALUE!
9		welded SS	1.3	leaked	47332.57	710	YES-welded	0.20		3.42	0.04	85.50
10		Anode	1.3		47332.57	714	no carbon visible	0.20		3.44	0.04	86.00
11		B size d I/H	1.3		47332.57	718	no carbon visible	0.20		3.45	0.04	86.25
12		Anode	1.25		45645.53	706	no carbon visible	0.20		2.9	0.06	48.33
13		B size d I/H	1.25		45645.53	695	no carbon visible	0.20		2.9	0.07	41.43
14		Anode	1.35		48573.98	730	no carbon visible	0.20		3.9	0.015	260.00
15		B size d I/H	1.35		48573.98	727	no carbon visible	0.20		3.9	0.019	205.26

The test results showed that carbon was found only on welded stainless steel specimen approximately 10 to 20 °C below the temperature where equilibrium predicts the onset of carbon for a given reformat outlet composition.

6.3.3 Fabricate Development Reformers

6.3.3.1 Build out of Gen 4.1/4.2T Reformer and Process Development

A Gen 4.1T reformer was modified to become the first Gen 4.2T reformer with the addition of a recycle induction port and a new methane delivery unit.

6.3.3.2 Gen 3P Reactor - Braze Development

6.3.3.2.1 Log of attempts & results

There had been 7 braze attempts on a total of three reactors which were unsuccessful. Reactor S/N P30- 3 was brazed five different times in an attempt to repair the leaks, which was a result of the previous runs. Reactors serial numbered P30-4 and P30-5 were individually put through a single braze attempt and then sent for dissection and failure analysis.

6.3.3.2.2 Analysis & Explanation of results

The Gen3 Planar (Gen 3P) Reformer was a new reformer design. It is similar to the previous Gen 2P reformer. As with the Gen 2P reactor, Haynes 214 (a high-temperature nickel-based alloy) was the base metal chosen. The Gen 3P Reformer is physically larger than the Gen 2P, and the plates were fabricated using a chemical machining / etch process. The passage heights are narrower than on the Gen 2P, which increases the thermal mass of the unit and enables braze filler metal wicking

between these plates. A heat exchanger is also integrated into the bottom of the brazed assembly that adds significantly to the assembly complexity.

A test stack was brazed using a set of etched plates similar to the actual Gen3P Reformer. This initial sample stack of plates was brazed in order to finalize some of the design features on the Gen3P reformer prior to cutting the actual productive parts. This stack was produced from Haynes 214, chemically etched to produce features similar to that of the proposed Gen3P reformer design, and brazed using BNi-9 (a nickel-based braze-filler-metal with boron and no silicon content) using a vacuum braze cycle.

This initial braze run resulted in the establishment of reasonable wall thickness dimensions on the Gen3P plates. It was Delphi's first attempt at understanding if the internal web supports etched into the plate design were sufficient to prevent "sagging" of the thin etched plate sections (0.010" nominal) during the braze process. The results of this initial braze run were factored into the Gen3P design.

6.3.4 Develop Catalysts

6.3.4.1 Catalyst Formulation

Catalyst supports were prepared and characterized by BET surface area, XRD and diesel POx reaction testing in an effort to further improve catalyst formulations, specifically for high-sulfur diesel fuel. Variables include different sources of alumina, different types of alumina stabilizers, precursors of stabilizers, and calcination temperatures.

Table 6.3.4-1 shows the H_2 concentration as a function of time when different Ba precursors were used for the Ba-based RDRCA0-320:CB formulation. The catalyst performance decreased in the sequence of $BaCO_3 > BaSO_4 > Ba(NO_3)_2$. Characterization results show that they have similar surface areas (**Table 6.3.4-2**). XRD results demonstrate that different materials were formed when different Ba compounds were used as precursors. Besides theta- and delta-alumina phases and $BaAl_2O_4$, $BaCO_3$ was formed when $BaSO_4$ was used. For $Ba(NO_3)_2$ modified alumina, an aluminate, $BaAl_{10}O_{17}$ was formed. Considering the different performances of these materials and different phases formed, it is suggested that $BaAl_2O_4$ plays a positive role in stabilizing alumina, and thus preventing the Rh sintering process under reaction conditions.

Table 6.3.4-1: Addition of 2%Ni and 2%CeO₂ to RDRCA0-360:CM Catalyst, Tested with 2007 Certification Diesel with 50 ppm S. O/C=1.15. GHSV= 67000/hour

Catalyst	H ₂ %
2% Rh	20.4
2% Ni-2% Rh	19.7
2% Rh-2% CeO ₂	18.9

Table 6.3.4-2: Effect of Catalyst Stabilizer Precursors Catalyst: RDRCA0-320: CB

Ba source	BET surface area (m ² /g)	XRD
BaSO ₄	65.0	θ-alumina, δ-alumina, BaAl ₂ O ₄ , BaCO ₃
BaCO ₃	67.1	θ-alumina, δ-alumina, BaAl ₂ O ₄
Ba(NO ₃) ₂	71.3	θ-alumina, δ-alumina, BaAl ₂ O ₄ , Ba ₂ Al ₁₀ O ₁₇

When differently stabilized alumina's (such as those modified with SiO₂ or La₂O₃) were used as the starting material and BaSO₄ was used as a secondary stabilizer, the performance of resulting catalysts were not as good as when using BaSO₄ modified non-stabilized alumina, as seen from the results in **Table 6.3.4-3**. A silica-modified alumina has a very high thermal stability and high surface area, but the catalyst prepared using silica stabilized alumina showed a rather low hydrogen concentration. This is because the catalyst is too acidic.

Table 6.3.4-3: Effect of Catalyst Support Starting Materials Catalyst: RDRCA0-320: CB, Tested with 2007 Certification Diesel with 50 ppm S. O/C=1.15. GHSV= 67000/hour

Catalyst support starting material	H ₂ %
SiO ₂ modified alumina	18.5
La ₂ O ₃ modified alumina	20.1
Alumina	20.5

For the MgO containing RDRCA0-360:CM formulation, a similar series of studies were performed. **Figure 6.3.4-1** demonstrates that different Mg precursors lead to significant difference in catalyst performance. The performance decreased in the following order: Mg(NO₃)₂ > MgSO₄ > MgCO₃. The MgCO₃ modified formulation shows the quickest degradation. The materials made with these three types of Mg showed a similar surface area. The only difference is the material composition. As seen from the XRD results (**Table 6.3.4-4**), Mg(NO₃)₂ and MgSO₄ lead to the formation of a non-stoichiometric spinel Mg_{0.388} Al_{2.408}O₄, and a phase having a hexaluminate magnetoplumbite-type structure, LaMgAl₁₁O₁₉. When MgCO₃ was used, a small amount of LaAlO₃ with a perovskite structure was also formed.

Figure 6.3.4-1: Effect of source of magnesium on performance of catalysts for partial oxidation of diesel fuel.

Table 6.3.4-4: Effect of Catalyst Stabilizer Precursors

Mg source	BET surface area (m ² /g)	XRD phase
Mg(NO ₃) ₂	21.2	δ-alumina, Mg _{0.388} Al _{2.408} O ₄ , MgLaAl ₁₁ O ₁₉
MgSO ₄	27.5	δ-alumina, Mg _{0.388} Al _{2.408} O ₄ , MgLaAl ₁₁ O ₁₉
MgCO ₃	29.6	θ-alumina, δ-alumina, Mg _{0.388} Al _{2.408} O ₄ , MgLaAl ₁₁ O ₁₉ , LaAlO ₃

The effect of slurry particle size was investigated. The results are given in **Table 6.3.4-5**. Three particle sizes have been tested, 2.26 μm, 4.75, μm and 6.42 μm. This catalyst was not tested because of adhesion problems associated with particle sizes of 2.26 μm. No difference was observed for the catalysts with particle size of 4.75 and 6.42 μm. This implies that the slurry particle size is not an important factor to the catalyst performance.

Table 6.3.4-3 demonstrates that if the catalyst is too acidic, its H₂ concentration will be low. In order to reduce the acidity of the catalyst, a sample was made by adding 1 wt. % Potassium (K). The reaction results are shown in **Table 6.3.4-5**. The addition of K did not enhance the catalyst performance. There are two simple explanations. One is that some acidic sites are required for POx reaction. Another reason for the low H₂ concentration maybe due to an electronic interaction between Rh and K.

**Table 6.3.4-5: Effect of Slurry Particle Size And Potassium Addition.
Catalyst: RDRCA0-320: CB, tested with 2007 Certification Diesel with
50 ppm S. O/C=1.15. GHSV= 67000/hour**

Catalyst particle size (μm)	H ₂ %
2.26	Not tested – poor adhesion
4.75	20.8
6.42	20.8
4.75 with addition of 1% K	19.9

The results in **Table 6.3.4-6** indicate that the calcination temperature of the catalyst support is an important factor. When the catalyst support was calcined at 1000 °C, the resulted catalyst gave a reformat containing 20 volume % H₂. If the calcination temperature is increased to 1200 °C, the H₂ concentration increased to 20.8 %, even though the material calcined at 1000 °C has a higher surface area. The material calcined at 1000 °C is composed of alumina and a non-stoichiometric spinel phase. This material is highly porous, and so occlusion of Rh may occur under POx reaction conditions. When the calcination temperature was 1200 °C, a very stable LaMgAl₁₁O₁₉ phase was formed suggesting the presence of this stable material makes the catalyst more stable.

In the POx process, catalysts are typically held at 900 to 1100 °C. Higher temperatures may occur during transient periods, start-up and shut-down or accidental oxygen to carbon (O/C) ratio changes. Catalyst temperatures as high as 1400 °C may occur. It is necessary to investigate the stability and performance of catalysts at these temperatures.

**Table 6.3.4-6: Influence of Catalyst Support Calcination
Temperature --Catalyst: RDRCA0-360: CM, Tested with 2007
Certification Diesel with 50 ppm S. O/C=1.15. GHSV= 67000/hour**

Calcination temperature (°C)	H ₂ (%)	BET (m ² /g)	XRD
1000	20.0	122.9	δ-alumina, Mg _{0.388} Al _{2.408} O ₄
1200	20.8	27.6	δ-alumina, α-alumina, Mg _{0.388} Al _{2.408} O ₄ , MgLaAl ₁₁ O ₁₉

For an accelerated aging testing, the catalyst is usually aged at 1200 °C in air for 10 hours prior to testing. To study the temperature effect, a higher temperature of 1400 °C was used to age the catalysts. Testing results of these aged catalysts are listed in **Table 6.3.4-7**. The results demonstrate that Delphi's catalysts (RDRCA0-320:CB and RDRCA0-360:CM) are of very high thermal stability. For example, the RDRCA0-320:CB catalyst still produced 19.6% H₂ after 1400 °C exposure.

Table 6.3.4-7: Influence of Catalyst Aging Temperature Prior to Testing with 2007 Certification Diesel with 50 ppm S. O/C=1.15. GHSV= 67000/hour

Catalyst aging temperature (°C)	Catalyst type	H ₂ (%)
1200	RDRCA0-320: CB	20.5
1400	RDRCA0-320: CB	19.6
1200	RDRCA0-360: CM	20.9
1400	RDRCA0-360: CM	19.8

The environment is different between Delphi's air aging process and real reaction condition. Under POx conditions, only the front of the catalyst is exposed to oxidative conditions. The rest of the catalyst is in a reducing environment. It is practical to expose catalysts at high temperatures in the reactor at real POx reaction conditions. In Delphi's experiments, the catalyst temperature was raised by increasing O/C ratio, or by reducing the fuel flow. In doing so, temperatures of 1400 °C or higher can be obtained. The testing results are given in **Tables 6.3.4-3 and 6.3.4-4** for RDRCA0-320:CB and RDRCA0-360:CM catalysts. For RDRCA0-320:CB catalyst, when it was aged 1200 °C, the H₂ concentration was 20.8%. Increasing the catalyst temperature to 1350 °C and holding for 30 minutes, then returning to normal POx conditions, the H₂ concentration remained steady. This indicates that this catalyst is of high stability even at 1350 °C. Raising the catalyst temperature to more than 1350 °C resulted in some degradation of catalyst performance. For RDRCA0-360:CM catalyst (**Figure 6.3.4-2**), there was only a slight change in catalyst performance when the catalyst temperature was higher than 1350 °C, indicating better catalyst thermal stability.

Figure 6.3.4-2: High temperature testing with RDRCA0-360:CM catalyst, tested with 2007 certification diesel with 50 ppm S. O/C=1.15. GHSV= 67000/hr

Table 6.3.4-8 gives the catalyst composition for RDRCA0-360:CM catalyst including the starting material, milling with Rh and then washcoating on a substrate, after 1200 °C or 1400 °C aging, and after higher than 1350 °C testing,. After aging at 1200 °C, catalyst support did not change, but Rh₂O₃ phase became detectable by XRD. This implies that the Rh₂O₃ particles become much bigger after this aging process. After aging at 1400 °C, all alumina became alpha-alumina, and part of Rh₂O₃ decomposes to Rh metal. It is interesting to note that Rh₂O₃ is no longer detectable by XRD in the catalyst tested at higher than 1350 °C, although they retain good catalytic performance. This suggests that at these temperatures the Rh₂O₃ becomes re-dispersed.

**Table 6.3.4-8: Catalyst structure change at different conditions.
Catalyst: RDRCA0-360: CM**

Catalyst conditions	XRD phase	BET surface area (m ² /g)
starting powder	α -Al ₂ O ₃ , θ -Al ₂ O ₃ , Mg _{0.388} Al _{2.408} O ₄ spinel, LaMgAl ₁₁ O ₁₉	27.6
add Rh, mill, 540°C dried slurry	α -Al ₂ O ₃ , θ -Al ₂ O ₃ , Mg _{0.388} Al _{2.408} O ₄ spinel, LaMgAl ₁₁ O ₁₉	48.7
1200°C aged, above	α -Al ₂ O ₃ , θ -Al ₂ O ₃ , Mg _{0.388} Al _{2.408} O ₄ spinel, LaMgAl ₁₁ O ₁₉ , Rh ₂ O ₃	25.5
1400°C aged	α -Al ₂ O ₃ , MgAl ₂ O ₄ spinel, LaMgAl ₁₁ O ₁₉ , Rh and Rh ₂ O ₃	39.8 (?)
Tested, >1350°C	α -Al ₂ O ₃ , MgAl ₂ O ₄ spinel, LaMgAl ₁₁ O ₁₉ , Rh	3.9

For RDRCA0-320:CB catalyst, the catalyst composition under similar conditions are given in **Table 6.3.4-9**. The starting material was composed of delta- and theta-alumina and BaAl₂O₄. The BaAl₂O₄ phase changed to BaO and BaCO₃ phases during the milling

and coating process, and changed back to BaAl_2O_4 again after aging at 1200 °C. Rh was not detected probably because Rh or Rh_2O_3 particles are too small to detect by XRD. After aging at 1400 °C, phase changes were observed. All alumina phases became alpha-alumina and Rh metal was detected. A Ba aluminate phase, $\text{Ba}_2\text{Al}_{10}\text{O}_{17}$, was also formed. When the catalyst was tested at higher than 1350 °C, Rh was still in its metallic form, and no Rh_2O_3 was detected. It is important to note that the spinel-structure BaAl_2O_4 phase disappeared, and it became Ba aluminate, $\text{Ba}_2\text{Al}_{10}\text{O}_{17}$. Considering the drastic H_2 % drop and phase change after the high temperature testing, one may suggest that BaAl_2O_4 plays an important role in stabilizing the catalyst.

Table 6.3.4-9: Catalyst Structure Change at Different Conditions.
Catalyst: RDRCA0-320:CB

Catalyst conditions	XRD phase	BET surface area (m ² /g)
starting powder	$\delta\text{-Al}_2\text{O}_3$, $\theta\text{-Al}_2\text{O}_3$, BaAl_2O_4	62.1
add Rh, mill, 540°C dried slurry	$\delta\text{-Al}_2\text{O}_3$, $\theta\text{-Al}_2\text{O}_3$, BaO, BaCO_3	42.9
1200°C aged, above	$\delta\text{-Al}_2\text{O}_3$, $\theta\text{-Al}_2\text{O}_3$, BaAl_2O_4	11.8
1400°C aged	$\alpha\text{-Al}_2\text{O}_3$, Rh , BaAl_2O_4 , $\text{Ba}_2\text{Al}_{10}\text{O}_{17}$	17.1
Tested, >1350°C	$\alpha\text{-Al}_2\text{O}_3$, Rh , $\text{Ba}_2\text{Al}_{10}\text{O}_{17}$	17.3

6.3.4.2 Washcoat - Substrate Adhesion

Delphi tested washcoat adhesion by changing slurry particle size, substrate pre-oxidation temperature and time, and effect of air aging. Aging the washcoated coupons at a high temperature, such as 1150 °C, in air, lead to washcoat loss. Rh migration from the washcoat to the substrate occurs at such high temperatures. A separate earlier experiment confirmed this phenomenon (**Figure 6.3.4-3**). The energy levels of Cl and Rh are close with Cl K-alpha = 2.632 KeV and Rh L-alpha = 2.694 KeV. Energy dispersive analysis of samples with and without Cl shows that Cl will not interfere with Rh (**Figure 6.3.4-4**), indicating that unambiguous characterization of rhodium containing catalysts prepared with chloride salts is possible.

Figure 6.3.4-3: Confirmation Run on Rh migration Upon High Temperature Process

Figure 6.3.4-4: EDAX® Experiment Clarifying the Absence of Cl in Rh/Alumina

At POx reaction conditions, most of the catalyst is in a reductive atmosphere. It is important that the washcoat adhesion be tested in both reductive and oxidative conditions. For this purpose, washcoated samples were tested in a 1000 °C furnace in the presence of H₂. **Figure 6.3.4-5:** shows the washcoated coupons that were heated in 1000 °C furnace in H₂ for 2 cycles at 16 hours for each cycle. It is seen that most of these samples have good washcoat adhesion. The 1050 °C pre-oxidized coupons had best adhesion.

Figure 6.3.4-5: Effect of Pre-treatment Temperature and Time in Reductive Atmosphere. Fresh Samples, Slurry Particle Size 7 μ m

Figure 6.3.4-6 shows the pictures of washcoated coupons oxidized at 1150 °C for 1 hour after washcoating. The 1150 °C calcination step led to a worse washcoat adhesion and some washcoat loss when compared to the fresh samples which were calcined at a lower temperature (538 °C). The washcoat stayed well on the coupon that was pre-oxidized at 1050 °C for 2 hours.

The slurry particle size is an important factor to washcoat adhesion. By comparing the pictures in **Figure 6.3.4-6** with those in **Figure 6.3.4-7**, it is concluded that particle size of 7 μm is better than 5 μm . Particle sizes smaller than 5 μm will lead to poor adhesion.

Figure 6.3.4-6: Effect of Pre-treatment Temperature and Time in Oxidizing Atmosphere. 1150 °C Aged Samples, Slurry Particle size 7 μm

Figure 6.3.4-7: Effect of Pre-treatment Temperature and Time in Oxidizing Atmosphere. 1150 °C Aged Samples, Slurry Particle Size 5 μ m

6.3.4.2.1 Reactor Evaluation of Washcoat Adhesion on Metallic Substrates

The best adhesion on metallic substrates, when all other factors are held constant, occurs for the thinnest washcoat coatings, corresponding to the lowest loadings of washcoat on the test coupons (**Figures 6.3.4-5, 6.3.4-6, and 6.3.4-7**). Thinner washcoats may lead to loss of performance and decreased durability due to lesser amounts of catalyst active sites being present. The first of these issues is addressed by the following testing. A very thin layer of washcoat, RDRCA0-320:CB (2), was loaded onto Haynes 214 plates and tested in the single channel planar configuration described previously. Washcoat loading was 0.008 grams per square centimeter.

These were tested for methane POx at an O/C of 1.40, at 850 °C, for 20 hours and at a total reactant space velocity of 36,000/hr. At these processing conditions, equilibrium values of H₂ and CO are about 31 and 15 volume %, respectively. Measured operating temperatures through the length of the reactor were about 850 °C, and the measured outlet H₂ and CO concentrations were very close to equilibrium, 30.5 and 17 volume %, which remained unchanged for the duration of the test (**Figure 6.3.4-8**). The appearance of the plates before and after testing is shown in **Figures 6.3.4-9 and 6.3.4-10**. No visible catalyst degradation was observed, and together with the observation of excellent performance indicates that very thin washcoats can be effective in this application.

Figure 6.3.4-8: Methane Partial Oxidation over Low-Loaded Rh/Al₂O₃ on Metallic Planar Substrate - Product Composition

Figure 6.3.4-9: Low-Loaded Rh/Al₂O₃ on Metallic Planar Substrates Prior to Testing

Figure 6.3.4-10: Low-Loaded Rh/Al₂O₃ on Metallic Planar Substrates After Testing for 20 Hours

6.3.4.3 Catalyst Process Development

6.3.4.3.1 Behaviors Of Different Diesel Fuels For Catalytic Partial Oxidation

Catalyst development work focused on using United States 2007 Certification diesel fuel. Fuel composition exerts a significant influence on the quality of reformat as well as catalyst performance. The aromatics content, boiling point, and sulfur levels are considered the most important performance factors.

Table 6.3.4-10 lists the characteristics of the liquid fuels that were used. The 2007 diesel fuel has a boiling point of 327 °C for 95% vaporization. For best performance, a high temperature is required for the fuel to vaporize and mix well with air. The auto ignition temperature for diesel fuel is ~250 °C. The low auto ignition (homogenous combustion of fuel mixture before reaching catalyst) temperature imposes a limit to the fuel vaporization. As seen from **Table 6.3.4-11**, if auto ignition happens, the resultant H₂ concentration will be much lower than without pre-combustion for the same catalyst.

Table 6.3.4-10: A Comparison Of 2007 Certification Diesel With Other Fuels

	Phase II Gasoline	Swedish Diesel	2007 Certification Diesel	JP8 Surrogate
Vaporization Temp (°C, 95%)	160	284	327	243
Density (g/ml)	0.736	0.8157	0.863	0.812
Composition (vol%)				
Aromatics	24.8	3.9	30.4	20.1
Olefins	5.2	N.A.	1.3	0.7
Saturates	70	N.A.	68.3	79.2
H (%)	13.41	14.1	12.8	13.6
C (%)	83.2	85.6	86.3	85.9

Table 6.3.4-11: H₂ Concentration with and Without Pre-Combustion

	H ₂ %
No Pre-combustion	20.8
Pre-combustion	18.5

Prior work confirmed that the presence of aromatics in fuel decrease the inhibitory impact of sulfur on catalyst performance. Aromatics may increase the rate of catalyst deactivation due to their increased propensity for carbon formation. A model compound study was performed on partial oxidation of either isooctane or a 70/30 wt./wt. blend of isooctane with toluene, using the catalyst formulation RDRCA0-250:CB (2,30), which is prone to deactivation. **Figure 6.3.4-11** illustrates changes in H₂ yield for the two fuels as a function of time. While the isooctane/toluene blend has a lower H₂ yield, due to the fuel having a lower H/C ratio, the rates of deactivation of the catalyst on both fuels is about the same, indicating that aromatics, under ideal circumstances, do not contribute additionally to catalyst degradation.

Figure 6.3.4-11: H₂ Yield for Partial Oxidation of Isooctane and Isooctane/Toluene Blend

Significant efforts have been dedicated to alleviate the auto ignition and vaporization problem. A series of experiments (**Table 6.3.4-12**) found that using an uncoated monolith in front of catalyst could solve the problem. For the other fuels listed in **Table 6.3.4-10**, Delphi did not encounter this problem whether foam or a monolith was used in the front of catalyst.

Table 6.3.4-12: Testing of Pre-combustion in Front of Catalyst

Brick in front of catalyst	Pre-combustion
20 PPI ZTA foam	Yes
45 PPI ZTA foam	Yes
400 CPSI monolith	No
Empty space	Yes
Filled with glass beads	Yes

The effect of space velocity was also investigated (**Figure 6.3.4-12**). Increasing space velocity increases the catalyst temperature, resulting in less sulfur inhibition effect. **Figure 6.3.4-13** gives the H₂ concentration as a function of reaction time for fuels with different sulfur contents. The addition of extra sulfur to the low sulfur Swedish diesel caused a significant drop of H₂ concentration as a function of reaction time. The extreme sensitivity of this fuel to sulfur is due to low aromatics content. This is in line with prior work showing that aromatics in the fuel help alleviate the sulfur inhibiting effect on the catalyst.

Figure 6.3.4-12: Comparison of Diesel Fuels for Partial Oxidation as a Function of Space Velocity

Figure 6.3.4-13: Comparison of Diesel Fuels for Partial Oxidation as a Function of Fuel Sulfur Content

6.3.4.3.2 Sulfur Resistance Of Various Catalysts

Table 6.3.4-13 lists the H_2 concentrations when the sulfur content in the 2007 diesel fuel is changed from 10 ppm to 401 ppm. With the as-received fuel of 10 ppm S, the catalyst produced 21.8% H_2 . By increasing the S content to 50 ppm by adding benzothiophene to the fuel, the H_2 concentration dropped to 20.9%. Further increasing S content to 202 ppm, dropped the H_2 concentration to 20.2%. Further increase of S to 401 ppm did not result in significant changes in the H_2 concentration. This implies that the sulfur effect is saturated at the S content of 200 ppm.

Table 6.3.4-13: Influence of fuel sulfur content. Catalyst: RDRCA0-320: CB, tested with 2007 certification diesel. O/C=1.15. GHSV= 67000/hour

S (ppm)	10	50	202	401
H ₂ (%)	21.8	20.9	20.2	20.2

In an effort to improve the sulfur resistance of catalysts, some additives such as 2 wt. % Ni, 5 wt. % Ni, 2 wt. % CeO₂, or 1 wt. % Pt, (based on total weight of the catalyst), were added to the standard Rh based catalysts. **Table 6.3.4-14** gives the results of various modified RDRCA0-320:CB catalysts. None of the additives improved the catalyst's sulfur resistance. For the MgO modified alumina based catalyst RDRCA0-360:CM additives (2 wt. % CeO₂, 5 wt. % Ni) did not lead to an improvement of catalyst performance (**Table 6.3.4-15**).

Table 6.3.4-14: Addition of 1%Pt, 2%Ni, and 2%CeO₂ to Catalyst RDRCA0-320: CB, tested with 2007 Certification Diesel with 50 ppm S. O/C=1.15. GHSV= 67000/hour

Catalyst	H ₂ %
2% Rh	20.3
1% Pt-2% Rh	19.6
2% Ni-2% Rh	19.8
2% Rh-2% CeO ₂	20.0

Table 6.3.4-15: Addition of 2%Ni and 2%CeO₂ to RDRCA0-360:CM catalyst, tested with 2007 certification diesel with 50 ppm S. O/C=1.15. GHSV= 67000/hr

Catalyst	H ₂ %
2% Rh	20.4
2% Ni-2% Rh	19.7
2% Rh-2% CeO ₂	18.9

A comparison of the catalysts rhodium on barium modified alumina (320:CB) and on magnesium modified alumina (360:CM) is shown in **Figure 6.3.4-14**. Both catalysts were aged at 1200 °C prior to testing with 2007 diesel with added sulfur to 401 ppm. The conclusion is that the Mg containing formulation RDRCA0-360:CM is superior to the Ba formulation when the sulfur content is high.

Figure 6.3.4-14: Comparison of RDRCA0-320:CN with RDRCA0-360:CM, tested with 2007 certification diesel with 400 ppm S. O/C=1.15. GHSV= 67000/hr

6.3.4.4 Catalyst Testing

Four durability tests were conducted, including two that are still in progress. After accounting for catalyst degradation due to test stand / laboratory related upsets; catalysts met performance requirements of greater than 20 vol. % H₂; less than 1 vol. % CH₄; and less than 0.2 vol. % non-methane hydrocarbons.

Figure 6.3.4-15 gives the product concentration for a durability test on catalyst RDRCA0-351:CB//351:EB Rh/Ni (30,2)/(100,5). This was supported on a 20 pores-per-inch (ppi) zirconia-toughened alumina (ZTA) foam substrate. The test operated with partial oxidation of CARB Phase II gasoline at 2.00 ml/min., with an O/C of 1.12, and a total equivalent space velocity of 30,000/hr. Significant events during the test included: Cold shut down and restart at 250 hrs; over-temperature due to fuel flow loss at 1145 hours; and a catalyst regeneration from 1313 to 1337 hours. This was accomplished by changing O/C to 1.32 and catalyst center temperature to 1100 °C. The regeneration step was necessary due to carbon deposition related to prior fuel pump problems. H₂ concentrations increased from 19 to 21.5 vol. % as a result of the regeneration. The low flow rate used in the test may have caused a lower than usual catalyst temperature, increasing the propensity for carbon deposition. This was partially corrected by the regeneration procedure.

Figure 6.3.4-15: Durability of Dual Layer Rh-Ni Catalyst for Gasoline Partial Oxidation

Figure 6.3.4-16 gives the product concentration for a durability test on catalyst RDRCA0-360:C (5,120). This catalyst is formulated by modifying the base La-gamma-alumina support with magnesium to form a thermally stable hexaluminate component. This was supported on a 20 ppi ZTA foam substrate. The test operated with partial oxidation of CARB Phase II gasoline at 3.125 ml/min., with an O/C of 1.05, and a total equivalent space velocity of 45,000/hr. Significant events during test include: Cold shut down and restart at 600 hours; a recalibration of the gas chromatography (GC) at 1387 hours; and a change of O/C to 1.15 at 1478 hours. Based on co-current testing, the original O/C of this run was deemed too low, and the value was adjusted to 1.15 in order to improve performance. The result of this change was a significant decrease in product hydrocarbon concentrations. For example, methane fell from ~1.7 to 0.7 vol. %, with corresponding decreases in C₂, with no impact on production of H₂ from this O/C change. The test was stopped at 1600 hours after repeated failures of the fuel pump resulted in unrecoverable catalyst damage.

Figure 6.3.4-16: Durability of Magnesium-Modified Catalyst for Gasoline Partial Oxidation

Figure 6.3.4-17 demonstrates the product concentration for a durability test on catalyst RDRCA0-320:CB (2,60). This catalyst was the current base rhodium on alumina formulation, supported on 20 ppi ZTA foam substrate. The test operated with partial oxidation of methane at 2.47 standard liters per minute, with an O/C of 1.21, and a total space velocity of 45,000/hour. No significant events during the test were observed. The test is targeted to achieve 2000 hours. Some catalyst degradation was observed. As product H_2 and CO concentrations fall at a decreasing rate, indicating that the catalyst is becoming stabilized. Significant variations in CH_4 concentrations are an indication of some variability in the control of this test, which may be contributing to the catalyst degradation.

Figure 6.3.4-17: Durability of Rhodium-Based Catalyst for Methane Partial Oxidation

6.3.4.4.1 Power-Mode Cyclic Durability Testing

The durability cycle was modified due to some of the power modes, such as minimum power, could not be obtained and so were eliminated from the drive cycle. At minimum power, catalyst temperatures were too low; creating carbon depositions. A three mode drive-cycle has been adopted for testing of gasoline (**Figure 6.3.4-18**). At each mode O/C is held at 1.16.

Figure 6.3.4-18: Power Mode Cycling Fuel Flow Rates and Corresponding Catalyst Center Operating Temperatures, for Gasoline Partial Oxidation

The first durability test using this modified drive cycle was performed using catalyst RDRCA0-320:CB (2,120). This catalyst is the current base rhodium on alumina formulation, supported on the 400 cells-per-square-inch (cps) zirconia-mullite monolithic substrate tested for partial oxidation of CARB Phase II gasoline. Performance of the three operating modes: System-start up; normal operating; and maximum power, is given in **Figures 6.3.4-19, 6.3.4-20, and 6.3.4-21**. The performance of the three modes are compared in **Figures 6.3.4-22 and 6.3.4-23**. No significant changes in product concentrations are noted between the three modes, indicating the catalyst is capable of turndown ratio of at least 1.6:1 with no additional adverse effects. The test plan specifies 250 cycles.

Figure 6.3.4-19: Durability of Rhodium-Based Catalyst for Gasoline Partial Oxidation at the System-Start Mode of Operation

Figure 6.3.4-20: Durability of Rhodium-Based Catalyst for Gasoline Partial Oxidation at the Normal Operating Condition Mode of Operation

Figure 6.3.4-21: Durability of Rhodium-Based Catalyst for Gasoline Partial Oxidation at the Maximum Power Mode of Operation

Figure 6.3.4-22: Hydrogen Performance Comparison of System Start Up, Normal Operating Conditions, and Maximum Power Modes of Operation

Figure 6.3.4-23: Methane Performance Comparison of System Start Up, Normal Operating Conditions, and Maximum Power Modes of Operation

6.3.4.5 Fundamental Catalyst Characterization

6.3.4.5.1 Accelerated Aging Method Development

Although the accelerated aging test was sufficient for the characterization of earlier catalyst washcoat formulations, it was found that newer formulations were much more resistant to this rapid aging test, requiring the development of a more stringent aging test. This was accomplished by increasing the intensity of the thermally damaging exotherm that occurs during reformer shutdown. A variety of methods were used, but changing the method of fuel shutoff was the most successful.

A study of reformer catalyst aging as a function of catalyst location was also performed. The results showed that the location within the catalyst where the catalyst was aged had little effect on the overall catalyst efficiency. This reduces the concern that our rapid aging test might age the catalyst in a location different from that resulting from real-world applications.

Delphi attempted to improve the rapid aging test by incorporating steady state aging effects. It is possible that the aging which occurs during steady state reforming might be due to localized air/fuel transients and/or poor air/fuel mixing. A study is being conducted to evaluate the long term durability of reformer catalysts when less than ideal air/fuel mixing occurs.

6.3.4.5.2 Fuel Sulfur Effects on Reforming Catalysts

Delphi has shown several important features about fuel sulfur effects on reforming. In summary, the impact of sulfur is dependent upon the fuel being used. H_2 generation from complex fuels, like CARB Phase II gasoline, is least affected by sulfur compounds, while H_2 generation from simpler fuels, such as methane, is most affected by sulfur. For isooctane, over a wide range of sulfur contents up to 2000 wppm S, the drop in H_2 production scales directly with sulfur content and for all types of sulfur compounds tested to date, ranging from H_2S to dibenzothiophene. The drop in performance is non-linear with fuel sulfur concentration, with the biggest drop being for the first 100 ppm of sulfur added into the fuel, for all fuels studied. Effects of sulfur appear reversible for all sulfur compounds studied in these experiments. There is no evidence of sulfur storage or irreversible changes to the catalyst as a direct result of exposure to sulfur. This is consistent with catalytic site blocking by sulfur in equilibrium with the gas phase concentration, leading to the conclusion that sulfur results in inhibition of reforming activity.

New findings that relate to the speciation of the reformer output with aging and the presence of sulfur can be summarized as follows: Using a range of fuels including methane, propane, isooctane, CARB Phase II gasoline, Swedish diesel fuel, and dodecane, the minor hydrocarbon species exiting the reformer were measured. No carbon species higher than C7 were observed. Delphi examined which species increased with the introduction of high concentrations of fuel sulfur, (up to 2000 wppm), and found that the loss in H_2 yield went mainly to water formation, with some increase in hydrocarbons. Ethylene, propylene, and benzene increased in concentration with increasing fuel sulfur content, while methane concentrations decreased with increasing fuel sulfur content. For each case, the dominant sulfur species in the reformat was always H_2S , regardless of the form of sulfur added to the fuel, including SO_2 , thiophene, benzothiophene, or dibenzothiophene. Also, aging studies found that the same hydrocarbon species were formed as in reformat produced with a fresh catalyst, regardless of fuel sulfur content.

6.3.4.5.3 Improvements to the Accelerated Aging Test

A study using more recently developed catalyst washcoats revealed that our rapid aging test was insufficient for aging the newer, more durable catalysts formulations. In order to improve the severity of the rapid aging test, attempts were made to increase the shutdown exotherm using a variety of techniques. It is this exotherm, under lean conditions, that is responsible for most of the aging generated by this rapid aging procedure.

Another consideration is the position within the catalyst where aging occurs. If catalyst aging were position dependent, then any rapid aging test would have to take this into account when attempting to mimic the degradation imposed by real-world conditions. An understanding of this dependence would allow for the development of new catalysts tailored to better withstand the effects of long-term catalyst use.

The reactor system was modified to improve reforming efficiency up to more appropriate levels (22% for H₂). The use of a quartz reactor (which allowed for the visual inspection of the catalyst) results in the significant loss of heat by radiation, which lowers reforming efficiency. Changing the position of the catalyst, adding inert pieces of substrate before and after the catalyst to trap generated heat, and doubling the flow rate of air and fuel were sufficient for this purpose. A micro-GC was also added to the reactor system to analyze additional components of the exhaust stream.

In order to increase the exotherm generated during a lean shutdown of the reformer catalyst, the most obvious method was to increase the amount of carbonaceous buildup on the catalyst during steady-state operation. It is the burn off of this material that gives rise to the exotherm, which under lean conditions damages the catalyst. Several methods were proposed and tested:

- Lowering the temperature of the fuel vaporizer
- Lowering the O/C ratio
- Lowering the furnace temperature
- Adding sulfur to the feed stream
- Adding acetylene
- Spending longer times in steady-state mode

Only methods 1 and 5 resulted in significantly increased amounts of carbon on the catalyst along with a resultant rise in shutdown temperature. Unfortunately, their effect on the ability of the rapid aging test to degrade the newer, more durable catalysts was minimal. It was found that the best way to increase the shutdown exotherm was to halt the flow of fuel in a less precise fashion. Instead of using a 4-way valve to quickly and cleanly cut off the fuel, the rotary pump supplying the fuel was simply switched off, allowing diminishing amounts of fuel to enter the reactor for several additional seconds after shutdown, with the reactor now containing excess oxygen. The combustion of this residual fuel resulted in a visibly larger exotherm and the resulting increased damage was sufficient to allow the rapid aging test to age the newer washcoats in a timely fashion. A comparison of the effects on catalyst performance of the older and newer rapid aging methods is given in **Figure 6.3.4-24**.

Figure 6.3.4-24: Catalyst Efficiency as a Function of Startup/Shutdown Cycles. The Newer Test Protocol, with its Higher Shutdown Exotherm, Ages Catalyst Quicker

6.3.4.5.4 Location Based Aging – Effect on Catalyst Performance

In order to develop better washcoats and to facilitate the development of improved rapid aging techniques, a study was undertaken to determine the effect of location on catalyst aging and performance. Fresh and aged (furnace aged in air at 1400 °C) catalysts, along with blank (non-washcoated) substrates were cut into smaller slices and then stacked together to create a variety of catalysts with fresh and aged zones at specific locations. By using only the fresh segments of varying lengths, the product distribution could be measured as a function of catalyst length.

As seen in **Figure 6.3.4-25**, for partial oxidation of gasoline over different lengths of catalyst, less than 50% of the H₂ production occurs within the first 0.1” of the catalyst. The other 50% was produced by shift reactions in the rest of the catalyst, converting the initially produced H₂O into H₂. This suggests that aging that occurs at the front of the catalyst may yield different results than aging which occurs toward the back. The concept was tested using fresh and aged catalysts in a variety of configurations. The results of these tests are presented in **Figure 6.3.4-26**.

Figure 6.3.4-25: Empirically Derived Product Distribution as a Function of Catalyst Length

Figure 6.3.4-26: Catalyst Efficiency for a Variety of Fresh-Aged Catalyst Combinations

The main findings in this study were: 1) Reversing the position of the fresh and aged sections had no significant effect on catalyst efficiency, and 2) catalyst efficiency was

dependent upon the amount of catalyst aged, not on where the aging occurs. Therefore the concern that a rapid aging procedure might be aging the catalyst in the wrong location is eliminated based on the location of aging having no effect on catalyst efficiency. The primary issue is the total amount of aging.

6.3.4.5.5 Hydrocarbon Speciation Of Reformate

Questions are often asked about the minor species exiting a reformer, other than the desired large amounts greater than 20 vol. % of H_2 and CO , and low percent levels of CO_2 and H_2O . Using a range of fuels, (methane, propane, isooctane, CARB Phase II gasoline, Swedish diesel fuel, or dodecane), the minor hydrocarbon species exiting the reformer were measured using mass spectrometry (**Figure 6.3.4-27**).

Figure 6.3.4-27: Medium Energy Mass Spectra of POx reformate, Using Methane, Propane, Isooctane, CARB Phase II Gasoline, Swedish City Diesel, or Dodecane Feed, at a C/O Ratio of 1.07

Note that no mass is detected above the highest carbon number present in each of the fuels, except for methane, where some C_2 species are observed. For dodecane, a C_5 species was barely detectable, and for the commercial fuels that contain aromatics there may be ppm-level concentrations of C_6 and C_7 species. The implication is that the reforming catalyst does a very good job of dissociating hydrocarbon fuels. This data was taken at a Medium Ion Energy (ME) where hydrocarbons are easily observed. Species like CO , CO_2 , and N_2 are not excited.

Delphi next examined which species increased with the introduction of high concentrations of fuel sulfur, to 2000 wppm. Data for SO₂, thiophene (TP), and benzothiophene (BT) are shown in **Figure 6.3.4-28**. Such high concentrations were necessary to easily observe changes, since after volume change due to the reforming reaction, the sulfur levels in the exhaust were in the range of only 100 ppm. One significant result is that the dominant sulfur species in the reformat product is always H₂S, regardless of the form of S added to the fuel such as, SO₂, TP, and BT, and also dibenzothiophene. Delphi found that the loss in H₂ yield went mainly to water formation with some increase in hydrocarbons in the hundred-ppm level. As noted previously, the recovery of activity once sulfur is withdrawn is very rapid.

Figure 6.3.4-28: Medium Energy Mass Spectra for H₂, CO₂, H₂O (uncalibrated), H₂S, and SO₂ for POx of Isooctane During the Addition and Removal of SO₂, Thiophene (TP), and Benzothiophene (BT)

Delphi monitored minor hydrocarbon species, such as methane, ethylene, and benzene (**Figure 6.3.4-29**). Ethylene and benzene increase in concentration with increasing feed sulfur concentrations, while methane is less affected by the presence of sulfur. After each withdrawal of sulfur, hydrocarbon levels increase slightly and H₂ levels are slightly lower, possibly due to carbon that deposits on the catalyst during sulfur exposure.

Figure 6.3.4-29: Medium Energy Mass Spectra for H₂, H₂S, Methane, Ethylene, and Benzene for POx of Isooctane During the Addition and Removal of SO₂, Thiophene (TP), and Benzothiophene (BT)

Delphi has used diesel fuel for catalytic partial oxidation to test the difference in the hydrocarbon product distribution between a fresh catalyst, one that has been aged, and one that is exposed to sulfur. The comparison between a fresh and an aged catalyst is shown in **Figure 6.3.4-30**.

Figure 6.3.4-30: Product Distribution of Hydrocarbon Species During POx of Swedish City Diesel Fuel Using Fresh and Aged Catalysts, Measured with Medium-Energy Mass Spectrometry

The major difference between the reformate produced by the two catalysts is a two-fold increase in water and all of the detectable hydrocarbon species, CH₄, C₂H₄, C₃H₆, C₆H₆.

Any of these products can be tracked as monitors of catalyst aging. The presence of benzene can be used as an indicator of the propensity for carbon formation (**Figure 6.3.4-31**). No different hydrocarbon species were observed; only increases in the existing product distribution. The presence of more water may indicate a shift towards more combustion products, rather than reforming products.

Figure 6.3.4-31: Equilibrium Analysis of the Correlation Between Solid Carbon and Benzene Formation

Figure 6.3.4-32 shows which species were enhanced, with the addition of sulfur to the feed stream. Adding sulfur does not change the product distribution. As with aging, sulfur increases the hydrocarbon species that are already present, along with H_2O . The implication is that we could simulate aging by adding sulfur. This being the case, the deactivation in both cases may reflect the same or similar underlying mechanisms, the loss of catalytic sites.

Figure 6.3.4-32: Product Distribution of Hydrocarbon Species During POx with Swedish City Diesel Fuel with or Without 100 ppm of SO₂ Added, Measured with Medium-Energy Mass Spectrometry

6.3.4.5.6 In-Situ Laser Raman Spectroscopy of Rhodium-Based Catalysts Under Reforming Conditions.

Three sets of experiments were completed: Reference, experimental blanks, and either partial oxidation or autothermal reforming on model catalysts. The reference and experimental blank spectrum were collected in order to determine the behaviors of alumina and rhodium under non-reactive conditions and also to determine if appropriate Raman bands for rhodium oxide and carbon can be observed in the equipment used. Two series of 5 wt. % rhodium on alumina catalysts were employed. Low-temperature (LT), pre-treated at 500 °C for 2 hours, and high-temperature (HT), pre-treated at 950 °C for 16 hours.

Figure 6.3.4-33 is ambient spectroscopy; taken at atmospheric temperature and in air, of rhodium oxide on alumina, using either ultraviolet (UV, 325 nm wavelength) or visible (VIS, 532 nm wavelength) laser sources, on the LT and HT catalysts. The resulting spectra shows a broad band, centered at 557 cm⁻¹, for LT, and distinct bands at 267, 413, 557, and 604 cm⁻¹, for HT. Based on both the UV and VIS spectra, the distinct bands are assigned to rhodium oxide, Rh₂O₃, and the broad band to a poorly-defined rhodium oxide composition, RhO_x.

Figure 6.3.4-33: Ambient Raman Spectroscopy of Rhodium Oxide on Alumina

The alumina support and the LT catalyst were exposed to methane, diluted in helium, and UV-Raman spectra measured at 700 or 900 °C (**Figure 6.3.4-34**). No bands were observed on the alumina, indicating that it is not active for methane decomposition. In contrast, the LT sample had distinct bands at 1410 cm^{-1} and 1590 cm^{-1} , corresponding to graphite, indicating that Rh is active for methane decomposition. The alumina and LT catalyst were exposed to propane at 200 °C or 700 °C (**Figure 6.3.4-35**). Both are active for propane decomposition at 700 °C, as indicated by the observation of graphitic bands. While the LT catalyst is active for propane decomposition at 200 °C, the uncatalyzed alumina support is not. These results show the differences in reactivity of methane and propane in the presence or absence of catalyst. The 1394 cm^{-1} band is assigned to the 'D' band of graphite, while the 1565 cm^{-1} band is assigned to the 'G' bands of graphite. The shift in the G band when measured at 200 °C, curve C, compared to 700 °C, curve B, is attributed to contraction of the carbon framework.

Figure 6.3.4-34: Raman Spectroscopy of Alumina and Rh-Supported Alumina During Exposure to Methane

Figure 6.3.4-35: Raman Spectroscopy of Alumina and Rh-Supported Alumina during Exposure to Propane

The assignment of Raman bands at $\sim 1390\text{--}1410\text{ cm}^{-1}$ and at $\sim 1560\text{--}1590\text{ cm}^{-1}$ is based on literature values for graphite. To confirm that a less-condensed aromatic hydrocarbon would not scatter in this range, a sample of anthracene, was characterized by VIS-Raman under ambient conditions (**Figure 6.3.4-36**). There was considerable fluorescence due to the presence of the aromatic, and a band could be observed at 1605 cm^{-1} . This was at too high of a shift to be graphite. Consequently, a Raman shift due to carbon-carbon bonding can be used to identify graphitic or aromatic carbon on the surface.

Figure 6.3.4-36: Ambient Raman Spectroscopy of Alumina After Exposure to Anthracene

In order to understand the behavior of rhodium during heat treatment, the LT catalyst was exposed to either He or O₂/He blends, from 500 °C to 900 °C (**Figure 6.3.4-37**). The intensity of the 560 cm⁻¹ Raman band decreases with increasing temperature. Curves A-E, indicating that either the Rh oxide is re-dispersing, or thermally decomposing. Since exposure to O₂ regenerates the signal intensity, curve F, and removal of O₂, curve G, shows diminished intensity, Rh₂O₃ is assumed to be only partially stable at elevated temperatures.

Figure 6.3.4-37: Raman Spectroscopy of Rhodium-Alumina during Heat Treatment in He or O₂/He Atmospheres

Figure 6.3.4-38 shows the behavior of the LT (A-C) and HT (D-F) catalysts to oxidizing and reducing atmospheres at 200 °C. Highly dispersed rhodium oxide on the LT catalyst could be repeatedly reduced and oxidized. Well-crystallized Rh₂O₃ on the HT catalyst could be reduced (curves D to E), but upon oxidation, only a lesser amount of dispersed rhodium oxide was observed (F). This is explained by assuming that during the reduction step, relatively large rhodium oxide crystals are reduced to equivalently sized rhodium metal particles, which are then resistant to re-oxidation at 200 °C. The highly disperse rhodium oxide, on the LT sample, forms highly dispersed rhodium metal when reduced, which is then easily oxidized. The presence of rhodium oxide crystals in the HT, but not in the LT sample, is confirmed by XRD, (**Figure 6.3.4-39**). Broad diffraction intensities in the LT sample, curve A, are assigned to gamma-alumina. Based on the width of the (012) peak, Rh₂O₃ particle size in the HT sample is estimated to be 180 Å.

Figure 6.3.4-38: Raman Spectroscopy of Rhodium Alumina, after 500 or 950 °C Treatment, during Oxidation-Reduction Cycling at 200 °C

Figure 6.3.4-39: X-Ray Diffraction Patterns for Rhodium-Alumina, after 500 °C or 950 °C Treatment, and for Rhodium Oxide

While alumina was seen to be active for propane decomposition in the presence of a mixture of propane and oxygen at reforming conditions, O/C of 1.1 and 900 °C, no evidence of carbon is observed by UV-Raman (**Figure 6.3.4-40**). In contrast, the LT catalyst shows the formation of graphitic carbon at these reaction conditions, **Figure 6.3.4-41**. The results also show that the presence of the reaction significantly diminished the rhodium oxide 580 cm^{-1} band, indicating that rhodium oxide is involved in the propane partial oxidation reaction. Repeating this experiment with the HT catalyst, (**Figure 6.3.4-42**) shows the non-reversible loss of well crystallized Rh_2O_3 (**Figure 6.3.4-43**), the presence of graphitic carbon, but to much lesser extent, and the formation of smaller amounts of highly disperse rhodium oxide, consistent with the model of the

HT sample containing larger rhodium metal particles and smaller amounts of highly dispersed rhodium oxide.

Figure 6.3.4-40: Raman Spectroscopy of Alumina during Propane Partial Oxidation at 900 °C

Figure 6.3.4-41: Raman Spectroscopy of Rhodium/Alumina, After 500 °C Treatment, During Propane Partial Oxidation at 900 °C

Figure 6.3.4-42: Raman Spectroscopy of Rhodium/Alumina, After 950 °C Treatment, during Propane Partial Oxidation at 900 °C

Figure 6.3.4-43: Raman Spectroscopy of Rhodium/Alumina, After 500 °C Treatment, during Propane Partial Oxidation at 900 °C and at Varying O/C

The LT catalyst was treated in a mixture of propane and oxygen, diluted in helium, at 900 °C, with O/C varying from 6.0 to 0.8. An O/C greater than 3.3 is required for complete combustion of propane to CO₂ and H₂O; this condition existed for curves A, B, and C, each of which has a strong broad band at 560 cm⁻¹, indicative of dispersed rhodium oxide. Once the reaction stoichiometry enters into a CO and H₂ forming regime, at O/C values less than 3.3, this 560 cm⁻¹ band diminishes, curve D, and disappears, curves E-H, while a band at 1588 cm⁻¹ increases in intensity, curves E-H. This behavior, consistent with the above observations, indicates that Rh oxide participates in the fuel reforming reaction and a graphitic carbon is a surface-phase

reaction intermediate, or that the graphitic carbon is covering the rhodium oxide, preventing it from being observed by Raman spectroscopy.

A slightly different experiment is described in **Figure 6.3.4-44**. The LT catalyst was exposed to autothermal reforming conditions at an O_2 -based O/C ratio of 1.1 and a H_2O to carbon molar ratio of 0.4. The temperature was varied from 300 °C to 1000 °C. At 300 °C, curve A, there is no change to the appearance of the 560 cm^{-1} band, as compared to the LT catalyst at ambient conditions. Once the reaction temperature reaches 400 °C, the broad rhodium oxide band at 560 cm^{-1} diminishes and disappears, while graphitic carbon bands at 1405 cm^{-1} and 1590 cm^{-1} appear. The relative intensity of these bands do not change further at reaction temperatures over 600 °C, curves D-H. Similar to the above discussion, these results indicate the rhodium oxide either participates in the reaction, or is covered by surface-equilibrium graphitic carbon. Additional characterization work with complimentary techniques will be required to determine the bulk behavior of the rhodium containing particles.

Figure 6.3.4-44: Raman Spectroscopy of Rhodium/Alumina, After 500 °C Treatment, during Propane Auto-thermal Reforming at Different Temperatures

6.3.5 Core Activities

6.3.5.1 Detailed 3D Kinetics Analysis Development

Detailed chemical kinetics for methane fuel reforming was implemented. The reactions include heterogeneous surface kinetics as well as homogeneous gas phase reactions. All transport phenomena are being modeled within a 3D finite volume approach.

Initial results do not match with test data and the code requires further debugging. The code objective is to deliver complex computations of detailed finite rate chemistry within complex geometries and foam structures and to be able to address changes in substrate materials, heat transfer, environment, and start-up conditions.

6.3.5.2 Foam Microlevel Analysis of Momentum, Heat, and Mass Transfer

Computer simulation efforts commenced to investigate in detail the behavior of microstructures of foam substrates, and ultimately other assemblies such as rolled wire meshes.

Figure 6.3.5-1 shows an example of a single foam cell representation in Unigraphics. Much insight can be gained from detailed simulation of various pore sizes, substrate materials and thicknesses on temperatures, diffusion processes, and velocities. A multi-cell model is shown in **Figure 6.3.5-2**. Test data could be used to calibrate and validate computer simulations based on single cell and multi-cell micro geometry simulations as well as macro level analyses.

Figure 6.3.5-1: Single Foam Cell

Figure 6.3.5-2: Multiple Foam Cell Conglomerate

Figure 6.3.5-3 shows an example of the computational mesh of a single foam cell. Examples of velocities and heat transfer are presented on **Figures 6.3.5-4** and **6.3.5-5**.

Figure 6.3.5-3: Single Foam Cell Computational Mesh

Figure 6.3.5-4: Single Foam Cell Velocity

Figure 6.3.5-5: Single Foam Cell Temperature

6.4 Task 4: BOP Component Development

6.4.1 Process Air Subsystem

When a particular PAM air control valve is closed, the volumetric airflow sensor measures zero flow because there is no output from the particular passage. The expectation is that the computed MAF sensor flow is zero. This was not the case (**Figure 6.4.1-1**), which illustrates existing flow within the closed passage of the manifold when the other valves are open. Airflow through the open passages causes movement of air within the closed passage. This flow is measured by the MAF sensor because the sensors are located upstream of the valves.

Figure 6.4.1-1: S18 Flow Measurement in Closed V18 passage

Figure 6.4.1-2 shows the results of the CFD analysis of the Version 1 PAM Manifold. The plot shows streamline velocities in one passage and illustrates the phantom flow phenomenon. When the downstream valve is closed, flow enters the passage and passes the mass flow sensor element. It then senses the downstream valve closure and reverses direction, passing the flow element again. The hot-wire flow sensing elements do not discriminate direction of flow. Flow in either direction past the element is indicated as flow. Moving the centerline of the sensor in either direction was investigated and found to have no effect. The only alternative was to change the position of the control valves relative to the mass flow sensors. Version 2 of the Gen 3 PAM Manifold has the mass flow sensor located downstream of the control valves such that when a valve is closed, no flow reaches the sensing element and phantom flow is eliminated. **Figure 6.4.1-3** shows the CFD results of the Version 2 PAM manifold.

Figure 6.4.1-2: CFD of GEN 3 Pam Manifold Version 2

Figure 6.4.1-3: CFD of GEN 3 PAM Manifold Version 1

6.4.2 Integrated Component Manifold

Figure 6.4.2-1 shows the FEA results for steady state.

Figure 6.4.2-1: Steady State Temperature Results

Figure 6.4.2-2 shows the FEA structural results reported as Von Mises stress. A very high stress concentration was indicated and correlated to hardware.

Figure 6.4.2-2: Structural Results - Von Mises Stress

Creep strain is proportional to bending stress in the top plate and results in out-of-plane top plate deflection. Bending stress (s) is inversely proportional to the square of plate thickness (t) by the following relation:

$$s \sim 1/t^2$$

A reduction in stress can be achieved by increasing the thickness of the plates.

If it is desired to reduce out-of-plane deflection by 50% then,

$s_2/s_1 = 0.5 = (1/t_2^2)/(1/t_1^2)$ where: s_1 is current stress, s_2 is stress at reduced rate, t_1 current thickness, t_2 desired thickness

or solving for t_2 , $t_2 = ((t_1^2)/0.5)^{0.5}$

If the existing plate thickness is 1.0 mm, a 50 % reduction in deflection can be achieved by increasing the plate thickness to 1.4 mm. Applying the similar methodology, a 90% reduction in deflection can be achieved by increasing the plate thickness to 3.4 mm.

The final decision on new plate thickness was a trade-off between system packaging and available material. Increasing top and bottom plate thickness would increase the overall height of the brazed ICM assembly and violate its current outline drawing. If it were too thick, the Hot Zone Module (HZM) would not fit in existing insulation enclosures and outer enclosures. In order to avoid the time and cost of remaking enclosures, a top and bottom plate thickness of 2 mm was selected.

Existing Gen 3 ICM's were reworked and salvaged by machining off existing top and bottom plates and replacing with the thick plates. All subsequent hardware will be made with thick top and bottom plates.

Figures 6.4.2-3 and 6.4.2-4 show the proposed production ICM. The concept is a cast version of the design. In this concept the ICM consists of two castings (an upper and lower manifold), one stamped middle plate, and separator plate all brazed together.

Figure 6.4.2-3: Cast Upper Manifold

Figure 6.4.2-4: Cast Lower Manifold

Delphi has selected a development partner for this activity and is proceeding with the initial tooling.

6.4.3 Cathode Heat Exchanger

Figure 6.4.3-1 shows the first coupon of the brazed single layer heat exchanger plates prior to coating application.

Figure 6.4.3-1: Single Layer Brazed CHEX Coupon

Figure 6.4.3-2 shows two pieces of the second coupon set where plates were coated first then brazed with a Cr free braze. The braze appeared to react slightly with the coating; however bond strength of the braze did not appear to be affected.

Figure 6.4.3-2: Pre-coated plates then brazed Coupons

6.4.4 Recycle System

6.4.4.1 Pump/Controller

The NE-2 Recycle Pump achieved the required flow and pressure at pump speeds as low as 9100 RPM. At the nominal pump operating speed (10600 RPM), the NE-2 Pump exceeds the maximum flow requirement of 4.8 cfm. Extended run testing indicated that the pump and modified controller remain within the acceptable temperature limits. **Figure 6.4.4-1** shows the pump characterization.

Figure 6.4.4-1: Recycle Pump Characterization

6.4.4.2 Recycle Cooler

Figure 6.4.4-2 shows the completed recycle cooler.

Figure 6.4.4-2: Re-cycle Cooler

6.4.4.3 Recycle Flow Sensor

Table 6.4.4-1 shows the MRF sensor test matrix, and **Table 6.4.4-2** shows the test results of the sensor mapping in tabular form.

Table 6.4.4-1: MRF Test Composition Matrix

O:C		1.50			1.65			1.80		
Utiliz a tion		30%	45%	60%	30%	45%	60%	30%	45%	60%
Recycle	30%	2 A	2D	2G	3 A	3D	3G	4 A	4D	4G
	40%	2 B	2E	2H	3 B	3E	3H	4 B	4E	4H
	50%	2 C	2F	2I	3 C	3F	3I	4 C	4F	4I

Table 6.4.4-2: MRF Sensor Test Results

O:C Ratio (Reference Only)	Composition	Percent Composition							Temp (°C)	Requested Flow (gps)	Coriolis Flow (gps)	Sensor Volts
		H ₂	H ₂ O	CO	CO ₂	CH ₄	O ₂	N ₂				
1.50	2A	22.1	15.3	10.8	7.9	2.5	0.0	41.4	100	0.75	0.793	3.50
	2B	22.8	15.8	11.2	8.2	5.8	0.0	36.2	100	0.75	0.815	3.62
	2C	24.5	17.1	12.0	8.8	8.3	0.0	29.3	100	0.75	0.828	3.77
	2D	17.4	20.0	8.5	10.3	8.1	0.0	35.7	100	0.75	0.823	3.45
	2E	18.6	21.4	9.0	11.0	12.0	0.0	28.0	100	0.75	0.849	3.62
	2F	21.0	24.4	10.2	12.5	15.9	0.0	16.0	100	0.75	0.874	3.87
	2G	12.7	24.7	6.2	12.6	13.7	0.0	30.1	100	0.75	0.853	3.40
	2H	14.0	27.3	6.8	13.9	18.6	0.0	19.4	100	0.75	0.888	3.62
	2I	15.0	35.0	10.0	15.0	25.0	0.0	0.0	100	0.75	0.936	3.97
	3A	22.0	15.4	10.8	7.9	0.0	0.0	43.9	100	0.75	0.786	3.43
1.65	3B	21.0	16.8	10.3	8.6	1.6	0.0	41.7	100	0.75	0.793	3.43
	3C	22.1	17.7	10.8	9.1	4.9	0.0	35.4	100	0.75	0.811	3.57
	3D	15.4	21.0	8.0	10.8	1.9	0.0	41.9	100	0.75	0.791	3.27
	3E	17.0	21.9	8.3	11.2	7.1	0.0	34.5	100	0.75	0.820	3.42
	3F	18.8	24.3	9.1	12.4	11.3	0.0	24.1	100	0.75	0.848	3.62
	3G	12.0	25.4	5.8	12.9	7.1	0.0	36.8	100	0.75	0.818	3.21
	3H	12.8	27.3	6.2	13.9	13.0	0.0	26.8	100	0.75	0.852	3.41
	3I	14.9	32.0	7.2	16.3	19.0	0.0	10.6	100	0.75	0.900	3.72
	4A	22.8	14.8	11.2	7.5	0.0	0.0	43.9	100	0.75	0.784	3.47
	4B	20.9	16.6	10.2	8.5	0.0	0.0	43.8	100	0.75	0.783	3.40
1.80	4C	19.9	18.3	9.7	9.4	1.7	0.0	41.0	100	0.75	0.791	3.40
	4D	17.0	20.5	8.3	10.5	0.0	0.0	43.7	100	0.75	0.782	3.25
	4E	15.6	22.4	7.6	11.4	2.5	0.0	40.5	100	0.75	0.793	3.25
	4F	15.8	24.2	8.2	12.4	7.2	0.0	31.2	100	0.75	0.818	3.42
	4G	11.3	26.2	5.5	13.3	0.5	0.0	43.2	100	0.75	0.781	3.04
	4H	11.7	27.3	5.7	13.9	7.7	0.0	33.7	100	0.75	0.815	3.22
	4I	13.2	31.1	6.4	15.8	13.6	0.0	19.9	100	0.75	0.853	3.46

Upon completion of the sensor performance mapping, a system control algorithm for recycle was developed and implemented. This control algorithm is based on reading sensor volts and comparing it to a baseline calibration curve, to determine the amount of offset for correction. The scaled, or corrected, sensor voltage is used in an average flow polynomial curve fit to calculate recycle mass flow. This method was able to predict recycle flows within +/- 0.9 percent across all cases. Subsequent work will include confirmation in the stack-reformer test stand and implementation at the SPU system level.

6.5 Task 6: System Fabrication

The SPU 1A SOFC System was successfully integrated through the set 1 level of integration (**See Figures 6.5-1 and 6.5-2**). Details of the laboratory and system testing of the SPU 1A unit will be discussed in Task 7: System Testing.

Figure 6.5-1 : SPU 1A Hot Zone Module

Figure 6.5-2: SPU 1A Set 1 Test

The fabrication of the SPU 1B Set 00 System and Test Stand have been fully completed and initial performance shakedown work has begun. This system has completely decoupled stack, reformer, and recycle pump components, and it may run on reformat from a reformer, or a blend of bottled gasses. The stack furnace installation is shown in **Figure 6.5-3**. The fully constructed system and test stand is shown in **Figure 6.5-4**.

Figure 6.5-3: SPU 1B Set00 System Build

Figure 6.5-4: SPU 1B Set 00 System

Initial fabrication and integration of the SPU 1B Set 1 system was started. Some components were fully integrated and assembled, while some new components were integrated only in mock-up form. This unit is shown in **Figure 6.5-5**.

Figure 6.5-5: SPU 1B Set 1 System Build

6.6 Task 7: System Testing

6.6.1 Testing Analysis

There were five tests conducted on electrochemical systems during this period. The performance target for these systems was three kilowatts of net power at 17.5% efficiency, requiring the gross stack output to be approximately four kilowatts. The SPU 1A Power Analysis table (**Table 6.6.1-1**) is a complete system power analysis, and provides a detailed accounting of the system performance. Each of the five systems tested are accounted in a column in the table. The columns adjacent to the actual performance test numbers are the forecast numbers. Based on the performance of the stack modules in the stack lab, a forecast is developed for a system operating with stacks of the demonstrated performance. To date, the system has not been able to achieve the level seen in the stack lab, however, two of the tests have approached this performance.

6.6.1-1: SPU1A Test Analysis Study

Stationary Power Unit (SPU)		Rated Output	Rated Output	Rated Output	Rated Output	Rated Output	Rated Output	Rated Output
		SPU 1A	SPU 1A	SPU 1A	SPU 1A	SPU 1A	SPU 1A	SPU 1A
Steady State Rated Power Analysis (SSRPA)		2x30G 3.1	03/03/05	03/03/05	03/04/05	04/06/05	05/25/05	06/13/05
		TARGET	FORECAST	ACTUAL	ACTUAL	ACTUAL	FORECAST	ACTUAL
REFORMER (Methane)								
Fuel Power	kW	17.2	19.1	17.7	13.0	11.5	16.7	14.9
Fuel Massflow	g/sec	0.344	0.382	0.35	0.260	0.230	0.334	0.299
Reformer O/C Ratio		1.3	1.3	1.3	1.3	1.3	1.3	1.3
Reformer Efficiency	%	86%	86%	86%	86%	86%	86%	86%
STACK		2 x 30	2 x 30	2 x 30cell	2 x 30cell	2 x 30cell	2 x 30	2 x 30cell
System Fuel Utilization	%	50%	33%	26%	38%	25%	33%	22%
SOFC Stack Conv Efficiency	%	27%	18%	14%	17%	15%	19%	12%
Cell Operating Voltage	V	0.71	0.72	0.69	0.61	0.787	0.75	0.70
Stack Output Power	kW	3.949	2.956	2.060	1.931	1.456	2.669	1.480
Stack Current	A	92.8	68.1	50.1	52.6	30.8	69.6	35.5
PARASITIC LOSSES								
Stack to DC Bus Power Conditioner Efficiency	%	100%	100%	100%	100%	100%	100%	100%
Fuel to Raw DC Conversion Efficiency	%	23.0%	15.5%	11.7%	14.9%	12.7%	16.0%	9.9%
Electric Parasitic Load (-)	kW	-0.949	-0.756	-0.810	-0.430	-0.705	-0.669	-0.519
Reformer Type		TUBE CPOX	TUBE CPOX	TUBE CPOX	TUBE CPOX	TUBE CPOX	TUBE CPOX	TUBE CPOX
NET SYSTEM OUTPUT								
Net System Efficiency @Rated Power	%	17.5%	11.5%	7.1%	11.6%	6.5%	12.0%	6.4%
Rated Output Power	kW	3.000	2.20	1.250	1.501	0.751	2.00	0.961
Number of cells per stack: N		30	30	30	30	30	30	30
System Total Number of Cells		60	60	60	60	60	60	60
Reference Stack Power Density (0.7 V/cell, 50% utilization)	W/cm ²	0.650	0.515	0.309	0.230	0.340	0.515	0.230
Total Parasitic Load:	W	949	756	810	430	705	669	492

Evaluating the first extended test performed in the system lab, the March 3 test of the system fell short of its forecast by nearly one kilowatt, and short of its efficiency target by 4.1%. These shortcomings are the result of two issues, a slightly increased parasitic load, and a significantly lower power density exhibited by the stacks during this experiment.

Following the test, the stacks were removed from the system and leak tested. Both stacks were found to have significant leaks, which mean that fuel was being consumed by burning rather than conversion in the stack. This can leave the stack without the required amount of fuel for the requested power. In addition, if there is a leak in a stack that allows oxygen to pass to the anode side of the stack, degradation will occur. These two factors may have contributed to the reduced stack performance.

The next extended system test was initiated on May 25, 2005. However, due to an issue later determined to be a short between the stack and the insulation enclosure, the test was aborted until the issue was resolved and corrective action could be taken. Therefore, this test ultimately operated from June 13, 2005 through June 16, 2005.

This system was able to achieve nearly 1500 watts of gross power, at a net power of 961 watts and a system efficiency of 6.4%. However, this again was short of its target of 2000 watts of net power and 12% efficiency. This system did operate for nearly 60 hours, and for 40 hours producing power, that is the longest continuous operation of a fully integrated system to date.

The system, having had a thermal cycle developed leaks at the stack, causing its fuel utilization to be higher than desired. The system also experienced the type of leak that allows oxygen to degrade the stack anode, further reducing its overall output. This contributed to the output falling short of the expectations.

The third system was tested from June 28, 2005 through July 1, 2005. However, while testing this system, a short occurred, causing the test to be suspended until the location of the short could be identified and eliminated.

Once this short was eliminated, a sense was added to the system in order to measure the voltage of the chassis. This would give an indication as to whether or not a short occurred, and would subsequently alert the test engineer and allow him to react accordingly.

6.6.2 System Testing Results

6.6.2.1 Fuel Metering

The testing done during this period drove several design changes. These changes included hardware modifications, control algorithm changes, and complete subsystem overhauls.

Upon completion of the testing all systems were assembled with product intent fuel delivery systems, the metering device being a fuel injector. Due to the heat seen in the full product enclosure and the lack of cooling performed by the gaseous fuel, the fuel injectors were not durable. They have been temporarily replaced by mass flow controllers in order to continue system testing, but will be replaced by a completely new fuel delivery system.

6.6.2.2 Stack to Chassis Short Circuit

During three of the system tests performed with electrochemical stacks, a short circuit to chassis was created that ultimately shut down the system. Though the issue was difficult to identify and diagnose, a complement of off line tests verified that the abnormal behavior exhibited by the system was due to a voltage applied to the chassis by the stack.

While the stack chassis had a path to ground, there were no issues with the system. However, once the path to ground had been eliminated, that voltage was driven through the chassis, through the thermocouple sheaths and caused the temperature feedback to the system to be incorrect. With one of the offline tests, it was determined that though the thermocouples were isolated at ambient temperature, their dielectric broke down at operating temperature and began to measure inaccurate readings (**Table 6.6.2-1**). This was consistent with the data observed by the system during testing (**Figure 6.6.2-1**).

Table 6.6.2-1: Thermocouple Measurement Variance: Controlled Experiment

Marchi Output Voltage Indicated Temperature				
No sheath potential (Volts)	65.5V sheath potential (Volts)	No sheath potential (DegC)	65.5V sheath potential (DegC)	
4.37	4.37	1121	1096	Temperature Cycle 1
4.5	4.21	1129	1056	Temperature Cycle 2
4.5	4.16	1129	1044	Temperature Cycle 3

Figure 6.6.2-1: Thermocouple Measurement Variance: System Operation

7 2006 TECHNICAL PROGRESS AND ACHIEVEMENTS

7.1 Task 1: System Development

7.1.1 System Design

7.1.1.1 Define System / Subsystem Requirements

The primary development initiative during this period was a three kilowatt, natural gas fueled, stationary power system. The overall system requirements were generated, leading to requirements for stack and reformer subsystems, as well as the balance of plant components. Additional hardware in this system includes an inverter, an energy storage system to aid in transient load handling, a pump to boost the pressure of the natural gas, a gaseous fuel desulfurizer, and an endothermic reformer rather than a catalytic partial oxidation (CPOx) reformer.

The Quality Functional Deployment process was used to determine the most important requirements, allowing each of the system requirements to be ranked based on relative importance. **Table 7.1.1-1** presents the sixteen system needs and how they were ultimately ordered. The system requirements were generated once the order was established utilizing the system operating metrics. The highlights of these requirements include a gross stack power output of 4400 watts, a reformer output power capability of 8800 watts, an overall system efficiency of 45% at its rated output, and the ability of the system to handle sulfur laden fuel.

Table 7.1.1-1: Customer System Requirements Rankings

Customer System Requirements	Score
Prototype Cost Target (k\$/unit - Assuming 10 Units)	406
Degradation Rate [% Rated/500 hours]	346
Fuel Sulfur Tolerance [ppm]	309
Rated Output Power [kW]	307
Thermal Cycles (-10% of Rated)	288
NOC Fuel to Elec Efficiency	286
NOC Power	277
Rated Fuel-to-Elec (60Hz, single phase AC) Electrical Efficiency [%]	262
Max Ambient Operating Temp [deg C]	254
Package Size [Liters] (not including fuel tank, no dimension greater than 24")	231
Mass Limit [kg]	231
Noise Output [Rated Load: SPL @ 3m, dBA]	181
B10 Life @ 90% Confidence [hours] (Includes load transients and thermal cycles)	164
Gaseous Fuel Supply Pressure [kPa]	129
Start-Up Time (25 Ambient soak to Rated Power) [minutes]	125
Surface Temp Rise (from Ambient) [deg C]	90
Min Ambient Operating Temp [deg C]	47

process air blower and the cathode air heat exchanger. Special attention was given to the cumulative system pressure drop with regard to these major system components specifically, as well as other secondary components in the system. An allocation was made for each system component, with a target max system pressure not exceeding 15 kPa. **Figure 7.1.1–1** illustrates the breakdown of the pressure allocation as it applies to the current system mechanization.

Figure 7.1.1-1: Natural Gas System Pressure Allocation

7.1.2 Develop System Mechanization

The system mechanization for the DPS-3000-NG system has similar characteristics to

the mechanization of the Phase I development system, SPU-1B. However, some marked changes were made in order to reshape the efficiency curve over the output power range, as well as augment the thermal management of the high temperature components.

The most notable change to the system comes from the replacement of the CPOx reformer with an endothermic reformer. This change boosts the system efficiency in the middle of the power range, as well as cause a significant rerouting of flow through the system. The mechanization for this system is shown in **Figure 7.1.2-1**. With the endothermic reformer in place, the anode tail gas recycle is brought to the front of the reformer, rather than the back of the reformer as in the SPU1B system. Additionally, the flow from the burner is routed through the reformer, prior to being routed through the cathode air heat exchanger. This is different from the SPU1B system, as the burner flow is routed directly through the cathode air heat exchanger, without passing through the reformer.

Figure 7.1.2-1: Natural Gas System Mechanization

Two notable changes were incorporated in the fuel processing circuit downstream of the reformer. The first change was the addition of a reformate cooling heat exchanger, and the second was the addition of a hydrocarbon cracker. The reformate cooling heat exchanger serves as a means to bring the anode and cathode fluids closer in temperature prior to entering the stack. The hydrocarbon cracker breaks down the higher hydrocarbons that exist in the portion of natural gas intended to be internally reformed, with the intent to provide methane as the only hydrocarbon to the stack.

7.1.3 Perform System Analysis

The modeling results generated this period were the output of a system model similar to that used in the generation of SPU1B performance forecasts. It contains a stack model with a simply scaled polarization curve, and does not make performance adjustments based on operating parameters such as temperature. However, this model was reconfigured to align with a set of fuel processing equations that are generic with respect to the hardware configuration and fuel input. This means that a natural gas or diesel system, with a CPOx or endothermic reformer, can be analyzed with the same model. The only adjustment occurs in the calibration targets, providing a means for comparing many systems without significant model changes.

Though this model is adequate for steady state operating characteristic predictions, a more detailed transient stack model will be integrated in the next period. This will allow for better predictions of performance to be made with respect to system operating characteristics in transient modes, as well as across a range of operating conditions for a given steady state load.

An initial calibration schedule was developed from the experience of operating the current system hardware. Using this calibration schedule, partially comprised of a stack fuel utilization of 60% and a recycle fraction of 50%, the overall system efficiency peaks at 45%. This calibration was used to develop a curve illustrating system efficiency versus percent of application load. The curve is shown in **Figure 7.1.3-1**. Once the system eclipses the 50% application load, equating to roughly 1500 watts electric, it begins to internally reform a portion of the total fuel. The system efficiency is 31% at this point on the operating curve. The system efficiency improves to greater than 35% beyond 60% application load.

Figure 7.1.3-1: System Calibration and Efficiency

The initial system modeling is focused on two discrete points, the rated power point (RATED), and the normal operating condition (NOC) point. The notable differences in the operation of the two are shown in **Figure 7.1.3-2**. The first difference is that the fuel processing efficiency is 35% higher at RATED operation than at NOC, primarily due to the increase of internal reforming.

Stationary Power Unit (SPU) Steady State Power Analysis		FORECAST	FORECAST
		SPU 3A	SPU 3A
		RATED	NOC
REFORMER			
Fuel Power	kW	7.67	5.07
Fuel Massflow	g/sec	0.153	0.101
Anode Tail Gas Recycle Fraction	%	50%	37%
Primary Fuel Fraction (Ψ_1)	%	1%	100%
Reformer (Fuel Processing) Efficiency	%	172%	137%
STACK			
Stack Fuel Utilization	%	60%	44%
SOFC Stack Conv Efficiency	%	32%	29%
System Effective Air Utilization	%	28%	11%
Cell Operating Voltage	V	0.70	0.86
Stack Output Power	kW	4.177	1.974
Stack Current	A	149.2	57.5
Estimated Internal Reforming Effect	kW	2.300	0.000
Parasitic Load Efficiency	%	90%	83%
Electric Parasitic Load (-)	kW	-0.424	-0.344
DC/AC Inverter Efficiency	%	92%	92%
NET SYSTEM OUTPUT			
Net System Efficiency @Rated Power	%	45.0%	29.6%
Rated Output Power	kW	3.45	1.50

Figure 7.1.3-2: Static System Model Results

The second difference that between the two points is the fuel utilization, being 60% at RATED, and 44% at NOC. The stack is the primary need, while the reformer, operating endothermically at the NOC point, requires a burner with adequate energy available to contribute to the reaction. That burner energy need is not as great at rated power as the full reforming load is carried by the stack, and the duty of the reformer is low.

The third notable difference is the air utilization. While operating at the NOC point, the system air utilization is only 11%. This is due to the fact that the cathode air provides the only means of cooling to the stack. When the RATED power point is evaluated, the system air utilization is increased, to 28%. That increase is possible as the effect of the internal reforming reaction reduces the heat removal duty of the cathode air.

The system airflow characteristics, which aid in understanding the dramatic air utilization increase, is shown in **Figure 7.1.3-3**. The NOC point lies at 50% of the total application load, and requires nearly eleven grams per second of total air, with nine grams per second being cathode air used in cooling the stack. The RATED point lies at 100% of the total application load, twice the electrical output of the NOC point, yet requires total system airflow of ten grams per second, still with nine grams per second of cathode air required to maintain the stack temperature.

Figure 7.1.3-3: System Airflow Characteristics

7.1.4 Develop System Design and Perform Optimization

The design layout effort this period was focused on the three kilowatt system. The layout of this system is a vast departure from the previous generation, with the primary goal being optimal control over the thermal environment of each component. The testing that took place during Phase I, and that has taken place thus far in Phase II, suggests that the thermal environment of all components is critical to their performance. This includes thermal communication not only to the ambient environment, but also communication between components. As the system attempts to achieve higher and higher overall efficiencies across the power band, the ability to isolate and possibly control these component environments becomes a greater concern.

The design effort to date produced the layout shown in **Figure 7.1.4-1**. The notable additions to this system include the desulfurizer beds, the pump used to boost the

natural gas pressure, and the hydrocarbon cracker. These components represent necessary content additions to operate the system on commercially available natural gas, versus the chemically pure methane used today.

Figure 7.1.4-1: System Model Concept

The stack module was upgraded to include an external cooling jacket, as well as an independent insulation enclosure, aiding in the control of the stack thermal environment. The CPOx reformer was replaced with an endothermic reformer, which, as previously mentioned, aids in boosting the fuel processing, and thus system efficiency during the middle of the operating range. The process air module was also upgraded to include a commercially available blower and utilize six valves, rather than the four used in the current unit.

Several hot zone components were given package volume for insulation enclosures in order to aid in the control of the thermal environments. The semi-transparent enclosures that exist around the stack (light blue), the hydrocarbon cracker (light gold), the anode-cathode equalizer (light gold), and the hot zone base (light blue), represent the individual enclosures.

7.1.5 Develop System Controls

Activities within this task involved optimizing and finalizing the system control strategy and safety and diagnostic system software algorithms. This was accomplished through algorithm development and validation. Validation of system control algorithms and safety and diagnostic algorithms were achieved through a process which incorporated virtual dynamic system models, hardware-in-the-loop simulation and finally system

tests.

7.1.5.1 Safety and Diagnostics

A major accomplishment was reached in the safety and diagnostics portion of the control algorithm in 2006. The second level S&DII, which includes state based sensor monitoring, was implemented, tested, and calibrated successfully. The implementation also included sensor warning levels and provided intermediate safety and diagnostics states to indicate the current “health” of the system as well as a user defined timer limit before complete shutdown. The advantages of this implementation has already been seen during system testing with failures caused by slow fuel leaks through fuel lines, as well as defining the operation range of the GPC temperature. This achievement brought the control algorithm a step closer in finalizing production development.

7.1.6 System Integration and Testing

7.1.6.1 System Assembly and Manufacturing Process Development

7.1.6.1.1 Development of Inventory System

The previous inventory system was not functioning as efficiently as it should due to the number of systems being assembled and disassembled. Part tracking was relatively uncomplicated in the past when there was only one or two systems to build at time. In 2006, there were multiple systems being built and tested while others were being disassembled. This increase in testing strained the old phase I prototype part tracking system. To accommodate the increased workload, an inventory system was developed as described below:

- The parts are organized and staged for builds as shown in **Figure 7.1.6-1**
- A manual sign out sheet was used to track the parts. This was eventually replaced by an electronic barcode system linked to the central parts database.
- Parts undergo a conformance measurement phase where they can be rejected or accepted based on key product characteristics (KPC's).

It is an ongoing process to improve the inventory system for accessibility as well as ease of use. Constant improvement will result in a centralized system designed to streamline the assembly and disassembly processes.

Figure 7.1.6-1: Part / Inventory Staging Area

7.1.6.1.2 Redesign of SPU1B for Manufacture

There was a constant drive at the system level to design for manufacturability and ease of assembly. The 2006 design iteration illustrates two key examples of design for assembly:

- The fuel interface on the Application Interface Module was redesigned to allow the technician to tighten fuel fittings before installation. **See Figure 7.1.6-2**
- The stack mounting screws have an access panel. This allows the technician to remove the stacks while all other components remain undisturbed. **See Figure 7.1.6-3**

Figure 7.1.6-2: Fuel Interface

Figure 7.1.6-3: Stack Access Panel

Because the system was so tightly packaged, every effort was made to make the assembly process as easy as possible. These changes greatly reduced the assembly time while improving system analysis during teardown and autopsy.

7.1.6.2 System Performance Testing

7.1.6.2.1 Primary Integration Test Stand Capability

The Primary Integration Test Stand was utilized in all stages of component testing

where isolation of one component is necessary. The versatility of the equipment is what sets it apart from standard test stands. The differences are listed in the following sections. This test stand is capable of testing individual system components as well as determining the effect on the entire system when changing the nature of a single component.

7.1.6.2.2 Stack Isolation Module

The performance test stand was designed such that the stacks could be isolated from all other system components (see **Figure 7.1.6-4**). The isolation module allows the engineer to analyze the performance of individual cells in two separate stacks under different environmental conditions. This assessment allows a better understanding of environmental effects on different areas of the stack. The module also allows confirmation of modeling more effectively by changing one variable at a time.

Figure 7.1.6-4: Stack Isolation Module

7.1.6.2.3 Fuel Blending Capability

The performance test stand has the ability to blend the following gases:

- H₂
- N₂
- CO
- CO₂
- CH₄
- Simulated natural gas (without Sulfur)
- Simulated natural gas (with Sulfur)
- Utility supply line natural gas

By blending the fuels, any simulated reformatte can be chosen. This allows a surrogate hydrocarbon fuel to be employed for testing before a means of producing reformatte is

available. The blending capability allows the engineer to make fueling-based decisions quickly and cost-effectively (see **Figure 7.1.6-5**).

Figure 7.1.6-5: Blend Fuel Module

7.1.6.2.4 Desulfurized Natural Gas

The performance test stand is capable of testing system components with desulfurized natural gas. Natural gas is used from the local utility to carry out the tests. Once it has entered the building, a lift pump compresses the natural gas to 55 psig. It is then run through a point-of-use desulfurizer where it can be utilized as a primary fuel source. The desulfurized natural gas is a requirement to testing system components on a readily available fuel (see **Figure 7.1.6-6**).

Figure 7.1.6-6: Natural Gas Desulfurizer

7.1.6.2.5 Performance Testing Results

7.1.6.2.5.1 Methane Fuel with Internal Reforming

Performance testing was done to determine the maximum power and efficiency that the system could achieve without causing damage to the system components. With the current design, the performance test allowed the engineer to test the internal reforming mode of operation. Performance testing was executed on a methane-fueled SPU1D system to determine the maximum power and efficiency while operating in the internal reforming mode. The results of a performance test can be seen on **Figures 7.1.6-7** and **7.1.6-8**. Test result highlights include:

- Rated net power: 2.2 kW
- Peak net power: 2.6 kW
- Peak System efficiency: 36%
- Run time: 150 hours (see **Figure 7.1.6-9**)
- Fully automatic warm up in <4 hours

Figure 7.1.6-7: SPU1D Performance Test

Figure 7.1.6-8: SPU1D Peak Performance

Figure 7.1.6-9: SPU1D Durability Testing

SPU 1D systems were also tested to verify that modifications to the stack exhaust recycle circuit would perform as expected. The changes requiring validation included:

- Reorienting the recycle pump 90 degrees to prevent problems with the water.
- Decreasing the surface area of the recycle loop heat exchanger to decrease the temperature drop of the recycle gas stream.

Both changes were tested in the system and are operating as expected.

7.1.6.3 System Reliability Testing

7.1.6.3.1 Natural Gas Fueled Durability Test

Reliability testing was done with line natural gas as the fuel source in order to show that the system was ready for a widely available fuel source. The utility company delivers low pressure natural gas to the Delphi facility. Once inside the facility, a compressor boosts the fuel to 55 psi. The pressurized fuel passes through a point of use desulfurizer next to the test stand where it is consumed by the system (**see Figure 7.1.6-6 above**).

The results of the natural gas fueled constant current testing can be seen in **Figure 7.1.6-10**. Note that the power degradation of 2.1% per 500 hours is the same with natural gas as it is with previous methane fueled testing. The details are described below:

- 5.4% degradation over 1280 hours
- 2.1% degradation per 500 hours
- Power at beginning of test= 1.2 kW

Figure 7.1.6-10: SPU1D Durability Testing

7.2 Task 2: Stack Development

7.2.1 SOFC Stack Development Executive Summary

Delphi has continued to build and test 30-cell Gen 3.1 stack modules. Key lessons were learned from the performance of these modules and their post-test autopsy analysis. The next iteration in stack design (Gen 3.2) was completed and prototype parts were validated.

Fundamental development focused on the development of low cost coatings for interconnects, development of robust seals, development of sulfur tolerant anodes and understanding the failure mechanisms within the cell and stack during thermal cycling and long term continuous durability tests.

Process development and improvements were key focus areas for development. This included development of more robust and cost effective formulations and processes for cell manufacturing, and optimization of cassette fabrication and stack assembly processes to improve first time quality of stacks.

7.2.2 SOFC Stack Development Results and Discussion

7.2.2.1 Design Stack

Delphi continued to demonstrate the viability of the Gen 3.1 stack design. 30-cell stacks of this design were tested in the system and met the SECA Phase 1 program requirements. **Figure 7.2.2-1** shows an exploded view of the different parts that constitute a cassette repeating unit in the Gen 3.1 design.

Figure 7.2.2-1: Generation 3.1 Repeating Units in a Stack

The focus was on streamlining and improving the design and manufacturing processes that constitute the building of cassettes and assembly of stacks. A key step forward in that goal was the development of the Generation 3.2 design stack.

The Gen3.1 cassette design utilized a flat plate picture frame (see **Figures 7.2.2-2, 7.2.2-3, and 7.2.2-4**) and a formed separator plate that the fuel cell is brazed onto (see **Figures 7.2.2-5 and 7.2.2-6**).

Figure 7.2.2-2: Generation 3.1 Cassette

Figure 7.2.2-3: G3.1 Cassette / Picture Frame

Figure 7.2.2-4: G3.1 Cassette / Picture Frame

Figure 7.2.2-5: G3.1 Cassette / Picture Frame

Figure 7.2.2-6: G3.1 Cassette / Picture Frame

These two sheet metal plates were welded together to create a sealed cassette. There were two main issues with this design. First, as a result of tolerances there was a narrow channel at each end of the cell, between the cell and the perimeter wall of the separator plate, in the completed cassette assembly which allowed some fuel to bypass the cell. This significantly reduced the fuel utilization capability of the resulting stack assembly. These bypass channels were blocked by drilling a small hole at each end of the channels and filling the channels with glass paste. The glass sinters during the

stack sintering process. This process resulted in a substantial improvement in stack fuel utilization and is now up to 85% utilization with less than 10% loss of power. However, this process compromises the hermeticity of the cassette and is a blind process with much variation.

The second issue was cassette warping due to residual stresses from the laser welding process. The cassette configuration resulted in a significant out-of-flat condition of the welded cassette assembly. In particular, the resulting distortion forced the cell into a concave condition (toward the cathode), which is the opposite of the cell's natural camber placing the cell in stress prior to stack assembly.

The Gen 3.2 cassette retained the same footprint and thickness as the Gen 3.1 cassette. This allowed Delphi to use the same manifold, glass seals, current collectors, and stack load frame as Gen 3.1. It also allowed the use of the same internal cassette components. The differences lie in the two sheet metal plates: the picture frame and the separator plate. The picture frame is now the formed part (see **Figures 7.2.2-7 through 7.2.2-11**).

Figure 7.2.2-7: Gen 3.2 Cassette

Figure 7.2.2-8: G3.2 Cassette / Picture Frame

Figure 7.2.2-9: G3.2 Cassette / Picture Frame

Figure 7.2.2-10: G3.2 Cassette / Separator Plate

Figure 7.2.2-11: G3.2 Cassette / Separator Plate

This allows for the bypass channel to be filled with glass paste prior to welding the cassette. Therefore, no holes need to be drilled into the cassette, and the placement of the glass paste can be observed prior to cassette assembly welding. The second advantage to this configuration is that the out-of-flat condition of the welded assembly will be minimized due to the location of the cell in relation to the perimeter weld. Also, the direction of distortion is convex (relative to the cell cathode), which is the direction of the cell natural camber, resulting in a significant reduction of cell stress (see **Figure 7.2.2-12**). This improvement has been shown in FEA modeling. Actual Gen 3.2 cassette components have been recently received and are in preparation for process development and evaluation.

Gen 3.1 cassette – cell warped in concave direction due to weld stress

Gen 3.2 cassette – cell warped in convex direction due to weld stress

- More favorable to cell
- Reduced displacement for same stress

Figure 7.2.2-12: G3.2 Cassette / Separator Plate

7.2.2.2 Develop High-Performance Anode

The anode development task continued to focus on understanding the H₂S poisoning of the current anode. The primary focal point during 2006 was to understand effects of testing parameters such as voltage, current, and temperature on sulfur poisoning. All H₂S poisoning testing was done in button cells with (La_{0.60}Sr_{0.40})_{0.95}Co_{0.20}Fe_{0.80}O₃

cathode (LSCF- 6428 A/B = 0.95) and standard Ni/YSZ anode using test stands which employ a 1" diameter circular cell sealed to an alumina tube.

It was reported that sulfur poisoning is influenced by operating voltage in electrolyte-supported cells [1]; that for a given concentration of sulfur in fuel, lower operating voltages result in lower power loss. To characterize the effect of voltage on the degree of sulfur poisoning, Ni-YSZ anode supported cells with LSCF cathode were tested following the test cycle shown in **Figure 7.2.2-13**. Each cell was subjected to various operating voltages from OCV to 0.5 V for 10 hours in each testing cycle to see the effect of voltage on sulfur poisoning. After 10 hour operation at various voltages, the cell was kept at an open circuit voltage (OCV) for 3 minutes, and then voltage was maintained at 0.7 V for 2 minutes to check the degree of sulfur poisoning at the same voltage before the cell was returned to its particular operating voltage for another 10 hour cycle.

Figure 7.2.2-13: A Test Cycle to Characterize the Effect of Voltage on Sulfur Poisoning

The power retention of cells operated at different voltages after introduction of 1 ppm of H_2S is shown in **Figure 7.2.2-14**. In this plot, the power retention was measured at the particular operating voltage for each cell. The overall trend was that measuring at lower voltage shows higher power retention (or lower power loss). The cell operated and measured at 0.5 V retains 82% of power at 50 hours after H_2S introduction, while the cell tested at 0.8V exhibits only 49% of power at the same point. The power retention measured at 0.7V however, was almost identical for all of the cells (see **Figure 7.2.2-15**). This result indicated that the degree of sulfur poisoning is fundamentally the same regardless of operating voltage even though the power retention measured at different voltages does vary. In other words, sulfur poisoning is possibly a thermal process rather than electrochemical process and the degree of sulfur poisoning at the given concentration of H_2S and the given temperature is basically unchanged by operating voltages between OCV and 0.5 V.

Figure 7.2.2-14: Power Retention of the Cells Operated at Various Voltages after H₂S Introduction (Power Retention for This Plot was Measured at the Various Operating Voltages)

Figure 7.2.2-15: Power Retention Measured at 0.7 V: from the Cells Operated at Various Voltages

To understand the effects of measurement methods on apparent power retention after H₂S exposure, measurements were made using the IV curves that were collected every 10 hours for the cell tested at the constant voltage of 0.7V. The initial IV curve (blue) and three of the IV curves representing 50 hour intervals after H₂S was introduced are shown in **Figures 7.2.2-16 and 7.2.2-17**. Lines are drawn at various constant voltages in **Figure 7.2.2-16** to show how the power retention was determined. Similarly, lines are drawn at various constant current levels in **Figure 7.2.2-17**. **Figure 7.2.2-18** shows the results of these IV curve measurements. These calculations, all based on the same set of IV curves, show much less apparent power retention at constant current than at constant voltage. Thus, constant voltage measurement is much more sensitive to sulfur poisoning (more power loss) than constant current measurement. It is necessary to maintain the same conditions for measurement in order to compare the degree of sulfur poisoning on anodes. Constant voltage measurement is preferable in detecting sulfur poisoning since power loss under this condition is more sensitive than constant current measurement.

**Figure 7.2.2-18: Power Retention Calculated from IV Sweep Curves:
 Constant Voltage vs. Constant Current**

Second stage degradation was another noticeable effect of current and voltage. The rate of second stage degradation (a flatter region after a rapid drop up to 20 hours after H₂S introduction) was more sensitive at lower voltage or higher current. Thus, measurement at constant voltage of 0.7 V can provide more sensitive information on sulfur poisoning in terms of first and second stage degradation compared to constant current measurement or constant voltage measurement at higher voltage.

Impedance analysis conducted at OCV and with 0.2 V bias also showed the sensitivity of measuring voltage on second stage degradation (see **Figure 7.2.2-19**). Polarization resistance (represented by arcs) drastically increases after the introduction of H₂S, while ohmic resistance (represented by X intercepts) does not significantly change due to the sulfur poisoning, is a general trend observed in impedance analysis. Therefore, a main effect of sulfur poisoning on power loss is increased polarization resistance reflecting changes in catalytic activity of Ni rather than an increase in electrical resistance. The impedance measured at OCV is much larger than that measured with a 0.2 V bias, which is close to the operating voltage. Furthermore, polarization resistance measured at OCV during the second stage degradation (refer to curves collected at 140, 200, and 300 hrs) does not show a consistent trend in polarization resistance in the second stage degradation while polarization resistance measured with 0.2 V bias shows an increase in polarization resistance with time, which is associated with power loss during the second stage. This result also confirms that lower voltage (or higher current) gives more sensitive results in terms of second stage degradation of sulfur poisoning.

Figure 7.2.2-19: Impedance Data Measured at (a) OCV and (b) with 0.2 V Bias

In order to confirm the validity of power retention calculated from IV sweep curves, the calculated values are compared with data directly collected from the cells operated at constant current and constant voltage. Points represented by hollow shapes in **Figure 7.2.2-20** are calculated from the IV sweep curves of the cell operated at 0.7V, and solid lines are real data collected from the cells operated under either constant current ($0.65\text{A}/\text{cm}^2$, initial voltage: 0.8V) or constant voltage (0.8V, initial current: $0.63\text{A}/\text{cm}^2$) conditions. Basically, the values calculated from IV curves are well matched with data directly collected from the cells operated under the conditions compared. Thus, periodic IV sweeps taken from one cell can provide representative data on sulfur poisoning at the given concentration of H_2S and the given temperature.

Figure 7.2.2-20: Power Retention from Direct Measurement vs. Calculation from IV Sweeps

Figure 7.2.2-21 shows the effects of operating temperature on the power retention of Ni/YSZ anode supported cells at 0.7V after exposure to 1 ppm H₂S. Higher operating temperatures produce higher power retention. Power retention at 850°C was 23% at 50 hours after 1 ppm H₂S exposure, while only 51% of power was retained at 650°C. It is not certain at this point whether high power retention at high temperature is due to reduced sulfur poisoning or enhanced power (or current) associated with high temperature. Nonetheless, a similar rate of second stage degradation was observed at various operating temperatures.

Figure 7.2.2-21: Effect of Operating Temperature on Power Retention

7.2.2.2.1 Ref [1] S. Zha, Z. Cheng, and M. Liu, J. Electrochem. Soc., vol.154 (2) B201-6 (2007)

7.2.2.3 Ceramic Tape Formulation Development

Figure 7.2.2-22 is a schematic representing the Delphi Gen 3 planar anode supported SOFC, followed by **Figure 7.2.2-23** which is an SEM micrograph of the ceramic bilayer consisting of the electrolyte (10 microns), active anode (10 microns), and bulk anode (460-480 microns). Delphi was working on improved formulations for the bulk anode (185 microns nominal), active anode (17 microns), electrolyte (17 microns), and anode backing layer (24 microns) tape cast films. 2006 efforts focused on improvements in the bulk anode tape. Bulk anode tape (designated at MP formulation) has been cast at a commercial supplier and is currently undergoing evaluation.

Figure 7.2.2-22: Gen 3 Solid Oxide Fuel Cell

Cathode – 31.0 microns
Interlayer – 3.5 microns
Electrolyte – 10.9 microns
Active Anode – 11.0 microns
Bulk Anode – 490 microns

Figure 7.2.2-23: Gen 3 Solid Oxide Fuel Cell

Figures 7.2.2-24 show SEM micrographs of fracture surfaces of two ceramic bilayers fired at approximately 1400°C. **Figure 7.2.2-24 A** represents the standard set of tape cast materials bonded by isostatic lamination. **Figure 7.2.2-24 B** shows a bilayer fabricated with the improved anode tape (cast at Delphi) and bonded by roll lamination. Both images show well bonded interfaces between the various tape components and microstructures similar in levels of open porosity. A larger volume of commercially supplied bulk anode tape has been cast is expected to be available soon for evaluation.

**Figure 7.2.2-24 A:
Standard Bulk Anode,
Electrolyte, Active
Anode Standard
Isostatic Lamination**

**Figure 7.2.2-24 B: MP
Bulk Anode, Standard
Electrolyte and Active
Anode Roll Lamination**

The new formulations were cast and fabricated into a number of forms to evaluate properties and manufacturability. **Table 7.2.2-1** lists a number of measured comparisons between the new MP formulations and the standard formulations of tape sets. Both material sets produce over 900 mW/cm² of power at 750°C, @ 0.7 Volts, in 50%H₂:50%N₂. The new MP formulation showed high strength while maintaining a high level of permeation. The fired shrinkage of the new MP bulk anode tape was formulated to produce a better shrinkage match to the commercially supplied active anode and electrolyte tapes. A better matched fired shrinkage leads improved cell flatness and less need for a post fired flattening step.

Table 7.2.2-1: Comparisons Between New MP Formulations and the Standard Formulations of Tape Sets

Property	Units	Standard Material Set	MP Material Set
Cell Power Density	mW/cm ²	990 +/- 87	942
Bilayer Mechanical Strength	MPa	118 +/- 4	126
Bulk Anode Permeation	Seconds	39 +/- 1	20 +/- 1
Bulk Anode Porosity (MIP)	%	21.2	21.8
Bulk Anode Mean Pore Diameter	Microns	0.25	0.34
Bulk Anode Linear Shrinkage	%	15	20
Active Anode Linear Shrinkage	%	21	21
Electrolyte Linear Shrinkage	%	21	21

A new carbon pore-former for the bulk anode tape was evaluated due to a loss in commercially available material. Tape with the replacement carbon (modified carbon material set) was cast at the commercial supplier and supplied to Delphi for evaluation. Open porosity of the bulk anode was measured by Mercury Intrusion Porosimetry (MIP) and compared to the baseline bulk anode and the new MP tape cast bulk anode composition and shown in **Figure 7.2.2-25**. The distribution of pore sizes is very narrow with a large population between 0.2 and 0.4 microns and a total open pore volume of 21 to 25%.

The same fundamental changes made to improve the bulk anode were incorporated in the active anode, electrolyte, and NiO anode backing layer tape cast films on an experimental basis. **Figure 7.2.2-26** is a micrograph showing a fired bi-layer that consists of a combination of these new tape materials that have been roll laminated and co-fired. The high density electrolyte and well bonded structure provide evidence of a well fabricated cell successfully co-fired near 1400°C. This new material set is currently being evaluated at the laboratory level.

Comparison Plot of Anode Porosity Results

Figure 7.2.2-25: Comparison Plot of Anode Porosity Results

Figure 7.2.2-26: Micrograph Image of Fired Bi-layer

7.2.2.4 Cell Scale-up

In order to scale up Delphi's capabilities for fabricating "much larger" footprint cells, a number of equipment modifications/changes were required. Undersized equipment in use for cell fabrication included the tape caster, screen printer, and isostatic laminator.

In order to cast wider tape for larger footprint cells, the Unique Pereny 12" wide tape caster rollers were rebuilt to accommodate a 14" doctor blade and 16" wide carrier (Mylar, paper, etc.). An adjustable slitteer was added to the end of the caster for sizing after casting, and a 2 gallon pneumatic slurry tank with integral mixer was added for even distribution of the slurry during the casting operation.

The MicroDEK screen printer used for printing interlayer, cathode, and metal cap layers used a 12" x 12" screen frame. As a rule of thumb for good, high volume printing practice, controllable printing dimensions should be less than one third of the frame dimensions. Therefore, the printer was undersized for fabricating cells of significantly larger footprint. The print squeegee travel length on the current printer is also limited for larger cells. Delphi forecasted the addition of a new screen printer in 2007 that would have the capability of much larger print areas, using 20" x 20" screen frames.

7.2.2.5 Current Cell Evaluation: Process Control Improvements

Laser scribing of Delphi SOFC fired bilayers was formerly conducted by running four separate programs that scribed individual quadrants of the current rectangular Gen 3 design. Multiple runs were necessary because of the travel length limitations of the automated laser scribe. A second laser was located and removed from a Delphi manufacturing facility to be used for the fuel cell program. This laser had similar laser characteristics to the current laser and had an expanded travel range, big enough to scribe the entire perimeter of the current cell design. This eliminated the need for repositioning the laser beam and performing multiple scribe processes to create the desired dimension. The laser met expectations for the cell scribe and snap process, however, it needed refurbishing to get and keep the laser running and improve the scribe. Once refurbished, dimensional measurements on set-up bilayers indicated that the scribed cell dimensions were not consistent. The width dimension was varying greater than ± 1 mm. The length dimension was varying by about ± 0.15 mm. Two refurbished Wheeler Micro galvanometer boards were purchased. The width control board was installed and calibrated. The width control was improved to ± 0.025 mm. **Figure 7.2.2-27** illustrates the improved width dimensional control achievable with the refurbishing of the production laser.

Figure 7.2.2-27: Laser Dimensional Control Study

A measurement study of cell length and cell width was performed to illustrate the difference in capability between the two different laser scribe processes for the current Gen 3 cell design. The first laser scribe process used the original laser that cuts one quadrant at a time, and uses an indexing rotary stage to complete the rectangular pattern of the cell. The second laser (removed from production) is capable of cutting all four sides in one continuous path. Results from the capability analysis show that the second laser provides improvements to the scribe process. The Cpk values for width improved from 1.59 to 8.67 using the second laser. Also, the Cpk values for length improved from 0.90 to 4.46 for the second laser scribe process.

Next, a study was conducted to determine the laser setup that provided the best quality cell scribe in terms of edge shape, edge condition, and cut width-to-depth ratio. A series of scribed lines, fabricated using a different set of laser parameters were evaluated. The effects of pulse density, laser power, and the number of laser passes prior to snap, were the process variables of the study. Optimization of scribe quality was based on visual microscopy and scanning electron microscopy (SEM). **Figure 7.2.2-28** shows optical micrographs summarizing the evaluation of scribed edges. Results from the statistical analysis shows that the best overall combination of process variables for edge condition is:

- pulse density of 25,000 pulses/in
- laser power setting of 32 amps

- use of a two-pass cut program
- Once determined, the optimized scribe settings were employed on Delphi fired bilayers.

Ten bilayers produced at this time were then tested for mechanical properties. The calculated strength from the Delphi ball on ring test was measured at 123 MPa, with a standard deviation of 8 MPa. This compares favorably with the strength measurements recorded on standard Delphi bilayers (mean of 118 MPa, standard deviation of 4 MPa) produced earlier in the year.

Here are three typical sections of SOFC materials exposed to different process variables.

Figure 1, below, shows a cross-section for the optimized settings, currently being used on the Plant 43 laser. The sharp point in the trough helps promote a clean break during the snap operation.

Figures 2 and 3, at right, shows how fewer passes and increase current effect the resulting shape of the laser cut path, respectively. Both have a characteristic "rounded" trough, which produce less desirable edge conditions after the snap operation.

Fig. 1. Section at 32 A, 25k pulses/sec, 1 inch/sec, 2 passes

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Fig. 2. Section at 32 A, 25k pulses/sec, 2 inches/sec, 1 pass

Fig. 3. Section at 35 A, 40k pulses/sec, 2 passes

Figure 7.2.2-28: Evaluation of Laser Scribed Edges

7.2.2.6 Develop Seals

Previously, the Delphi-Battelle team reported high rupture strength results for a "reinforced glass seal (Glass-Fiber Mesh)", developed for the cassette-to-cassette seal, which must remain electrically insulating. Virtually all non-reinforced glass seals that were rupture strength tested failed at the metal-glass interface. The GFM seal reinforces this interface, as illustrated in **Figure 7.2.2-29**. With tension, torsion or bending loads applied to the seal, the stress is transferred from the glass-metal interface to the mesh-metal joints, resulting in substantially increased rupture strengths. The glass powder and ceramic additives (fibers) can be cast and applied as a tape or dispensed as a paste. Upon heating, the glass softens and flows to surround the mesh wires. The ceramic additive increases the viscosity of the glass and help to prevent the

opposite meshes from touching and subsequently shorting across the seal. The GFM seal was evaluated in a 10-cell stack and remained hermetic through twenty five thermal cycles.

Figure 7.2.2-29: GFM Seal

However, the GFM seal is difficult to process and has the propensity to cause shorts between the cassettes. This led to the development of an alternate seal that has ceramic fibers throughout the glass matrix. Initial microscopic analysis demonstrated that the seals with fibers (Glass-Fiber seal) have fewer propensities for forming porosity within the matrix compared to the glass by itself (see **Figure 7.2.2-30**). This may be a positive step in mitigating crack formation.

Figure 7.2.2-30: Comparison of Glass Ceramic and Glass Ceramic with Fibers

A 10-cell cell stack with this seal was built and thermally cycled 16 times successfully (see **Figure 7.2.2-31**) with no loss of power and acceptable leak rates. After 16 cycles, the manifold seal (which is not a GF seal) was found to be leaking. This is a very

encouraging result in seal development as the GF seal is easy to process and has the potential to meet targets for certain applications.

Figure 7.2.2-31: Thermal Cycles Demonstrated by a Stack with Glass-Fiber Seal

7.2.2.7 Fabrication Developmental Stacks

Single cell testing of both intermediate size cells (33 cm² active area) and full size Gen 3 cells (105 cm² active area) was used extensively to identify problems and evaluate potential solutions. The continuing problem of electrolyte delamination was an issue since it was first observed in the coal gas test in 2004. Initially the problem was thought to be due to fabrication; however 2006 tests PNNL showed the failure occurs due to certain test conditions. This was discovered during a test to generate data for modeling stack performance.

The test was run at temperatures up to 825°C, current densities near 1.5 A/cm² and steam content in the fuel stream as high as 35%. During the post mortem of the cell it was observed that the electrolyte had delaminated from the anode. This was the first time delamination had been observed at PNNL. At that time it was still not known if the delamination was caused by a fabrication issue or was due to the unusual testing conditions.

Two tests (I-110 and I-111) were conducted on the intermediated test stands to separate the two potential causes. A Gen 3 bi-layer was cut into two intermediate cells (see **Figure 7.2.2-32**) insuring that both would have the exactly the same processing conditions. Both were initially tested with Delphi's standard anode gas composition of 48.5% hydrogen in nitrogen with 3% water, but at 825°C instead of 750°C. The two had

nearly identical initial performance when held at a constant current of 1.0 A/cm². After establishing a baseline performance, the anode gas composition for I-111 was changed to 50% Hydrogen and 50% steam (see **Figure 7.2.2-33**) while I-110 was not changed to act as a control. The initial fall in performance of I-111 is due to the lower OCV caused by the higher water content. Approximately 50 hours into the test I-111 exhibited a rapid degradation in performance. Both tests were stopped and a cross section of each cell was examined by SEM. The test with the higher water content (I-111) showed delamination of the electrolyte while the electrolyte on I-110 was still attached (see **Figure 7.2.2-34**).

Figure 7.2.2-32: Two Intermediate Cells Were Cut Out of a Single Gen3 Cell to Minimize Processing Variations

Figure 7.2.2-33: Performance of I-110 and I-111 vs. Time

Figure 7.2.2-34: SEM of Cross Section of I-110 and I-111 (Pictures were taken at varying distances from the fuel inlet)

Subsequent tests were conducted to determine the effect of current density and temperature and are summarized in **Figure 7.2.2-35**. The metric measured was the time for delamination to occur. It appears the time delamination occurs is nearly doubled if the test is conducted at 750°C rather than at 825°C. When the current density is decreased to 0.5 from 1.0 A/cm², the test time is extended by nearly a factor of four. However since the same anode flow rates were used for all tests, this relationship is somewhat convoluted because both the water content and fuel utilization change with current density. With 50% water at the inlet, the 1 A/cm² test had 62% water in the exhaust while the 0.5 A/cm² tests only had 56%. Tests are currently ongoing to separate the effect of water content and current.

One possible solution for delamination was to increase the bond strength between the electrolyte and the active anode. This was accomplished by decreasing the nickel content in the active anode from 50% to 30%, thereby increasing the number and size of the yttrium stabilized zirconia (YSZ) "anchors" that bind the electrolyte to the active anode (see **Figure 7.2.2-36**).

The increased amount of YSZ improved the bond to the electrolyte when measured by the scratch test. This did prevent the electrolyte from delaminating, but the failure location moved from the electrolyte/active anode interface to the active anode/bulk anode interface as shown in **Figure 7.2.2-37**. This failure mode was duplicated on the intermediate test with the 30% active anode tested on 50% steam in hydrogen, 1 A/cm², and at 825°C. The test was shut down after 100 hours due to shorting of the glass seals. The time for the delamination to occur is not well known for this test since it was not a catastrophic failure like the electrolyte delamination and therefore had no obvious change on the performance. The ability to reproduce this type of failure improved the confidence in the test.

As mentioned above, the glass seals started to be problematic at 825°C for any test in excess of 100 hours. In order to increase the testing time a number of different seal combinations were tried to prevent the shorting. Ultimately the problem was fixed by using the silver/mica/silver composite seal from the SECA Core Technical Program. The PEN to widow frame seal is still glass and currently limits testing to around 300 hrs before it starts to fail. The failure mechanism for the glass seal is currently being investigated.

The focus shifted to improving the bond strength of the bulk anode to the active anode in order to prevent the active anode from delaminating from the bulk. The initial try was to decrease the porosity in the bulk anode. Hopefully, the increased density would improve the bond strength. The high density anode was achieved by removing the pore former from the bulk anode tape cast. This resulted in an 11% decrease in the open porosity of the reduced bulk anode. The new bulk anode was tested with the 30% active anode in Test I-126 for approximately 300 hours on 50% steam in hydrogen, 1 A/cm², and at 825°C. The test was stopped when the OCV began to fall. It was determined in the post mortem analysis the cause was a PEN to widow frame seal

failure. No delamination at either interface was observed during the SEM analysis of the cell cross section (**Figure 7.2.2-38**). Currently tests are planned to optimize the amount of porosity needed in the bulk anode.

Figure 7.2.2-35: Summary of Test to Determine the Effect of Temperature and Water Content (The metric measured is the time for delamination to occur in hours - the test I-117 did not fail, but was stopped at 500hrs)

Figure 7.2.2-36: Micrographs of Anode Samples (Anode Samples were acid leached to remove the nickel, then sectioned and polished. Only the YSZ phase remains, revealing the extent of “anchors” from the electrolyte into the anode. The standard 50% nickel anode is at

the left, while the 30% nickel active anode is on the right. The micrographs at the bottom are photo-enhanced to emphasize the YSZ anchors.)

Figure 7.2.2-37: When a 30% Nickel Active Anode is Used the Delamination Moves from to the Active Anode / Bulk Anode Interface

Figure 7.2.2-38: Test I-126 had a 30% Nickel Active Anode and High Density Anode (No delamination was detected after 300 hrs of operation)

7.2.2.8 Evaluate Stack Performance

Evaluation of 30-cell stacks included polarization tests at 750°C on standard fuel consisting of 48.5% H₂, 3% H₂O, rest N₂. The IV tests were terminated after applying electrical load up to 60 Amperes. Overall power density and individual cell voltages

were measured to evaluate performance. **Figure 7.2.2-39** shows data from such a recent test.

The power density at 60 Amps (570 mA/cm^2) is 475 mW/cm^2 at 25 Volts (average cell voltage of 0.83 Volts, 30% fuel utilization). Fuel utilization studies (see **Figure 7.2.2-40**) showed minimal ($< 1\%$) lowering of power going from 30% to 70% fuel utilization. Stacks have also been successfully integrated and tested in the system (see Section [insert section number]). Two 30-cell stacks were run for 4600 hours. The degradation observed was 2% per 500 hours.

Figure 7.2.2-39: Typical IV Curve from a 30-Cell Stack Module with H₂ Fuel

Figure 7.2.2-40: Typical Utilization Curve from a 30-Cell Stack Module with H₂ Fuel

Development focused on autopsy of stack parts run in the system and the stack laboratory and understanding failure mechanisms. All stacks are taken apart and analyzed in detail to understand ongoing degradation issues. Some are potted and sectioned for detailed analysis.

A few key observations related to failure mechanism include:

Cell Failure: Cell delamination has been observed after continuous steady state operation in a number of samples. This has led to systems being shut down due to increase in temperatures. Delamination has been observed both at the electrolyte - active anode interface (see **Figure 7.2.2-41**) and/or the cathode interlayer – electrolyte interface (see **Figure 7.2.2-42**). There has been a lot of development to mimic this failure with an accelerated testing and some progress has been demonstrated (see Section 4.3.9) to make the interfaces more robust.

Chromia Contamination: Cr poisoning has been observed in all the stacks tested in the system. Most of the Cr species is observed only at the inlet of the stack and the cell while none is found at the exhaust side. This leads us to believe that the Cr contaminants are coming in the airstream upstream of the stack from the system manifold and or heat exchangers. **Figure 7.2.2-43** shows a layer of Cr based species deposited at the inlet of stack. **Figures 7.2.2-44 and 7.2.2-45** show Cr only in the first few centimeters of the cell in the direction of the airflow and none towards the outlet of the cell. This amount of chrome is never observed in stack s tested in the stack laboratory. Work is ongoing to understand the source of Cr and apply better process of Cr retaining coatings in all sub-systems to prevent Cr volatilization and subsequent poisoning of the cells.

Ag Volatility: Ag used in the interconnects volatilizes over time and is a cause for concern in long term durability tests. Although no failure has been associated with Ag volatilization, it needs to be fixed for longevity of the stack. We are testing an array of AgPd based pastes to develop potential solutions for this issue. As stated in the previous sections, progress has been made regarding this issue and newer pastes will be evaluated in the stack.

Degradation of the Ag-Cu Braze: Autopsy results have show that the braze seal between the cell and the picture frame starting to degrade over time (see **Figures 7.2.2-46 and 7.2.2-47**). The porosity (due to dual atmosphere conditions) and the corrosion observed are both areas of concern. Development is ongoing to develop adequate coatings to prevent the corrosion. Development is also focused to minimize the porosity.

Figure 7.2.2-41: Cell Crack and Electrolyte Delamination (in autopsy)

Figure 7.2.2-42: Cathode Delamination Observed in Autopsy

Figure 7.2.2-43: Visual Observation of Cr Species on the Inlet of Cassettes

Stack 452, Cell#10 Leading edge of cathode,

Figure 7.2.2-44: Cr Species at the Inlet of Cassettes

Stack 452, Cell#1 2.1 cm in from leading edge of cathode

About 1% Cr resides in a band in the middle half of the cathode.
 Neither the outer edge, nor the inner edge contain Cr.

Figure 7.2.2-45: Relatively Lower Amount of Cr Species at 2.1 cm From Leading Edge of Cassettes

- Braze on fuel end contains large, interconnected porosity.
 - This is probably "Type 3" porosity formed by dual atmosphere attack, however, attack is concentrated on fuel side
- Center area of braze joint still appears to be sealed.
- Air side of braze seal shows excessive oxidation of metal frame.

Figure 7.2.2-46: Braze Joint Near Inlet on Cell#10, Stack 452 (4600 hours of operation)

There are three distinct layers of corrosion:

- 1) Next to the intact steel is a layer of chrome and iron oxides with trace manganese. This layer appears to be “internal corrosion”.
- 2) Outside that is a dense layer of iron oxide.
- 3) Between the dense iron oxide and the remaining braze is a layer of lacy iron oxide, containing copper oxide.

Figure 7.2.2-47: Corrosion Between Braze and Intact Steel, Stack 452, Cell#10 Stack 452 (4600 hours of operation)

7.3 Task 3: Reformer Development

7.3.1 Executive Summary

Focused work on diesel (US07) endothermic reforming was conducted in 2006. The benefit of recycle as a reactant to diminish inlet coking was demonstrated. A comprehensive comparison of NCV (non contact vaporizer) versus CV (contact vaporizer) was conducted and the CV approach was a clear winner. The CV concept / hardware was subsequently demonstrated to 500hr w/ no carbon buildup effecting performance. The Gen 5T reactor continues to be evaluated versus the DPS3000D/NG requirements. Initial enthalpy balances and heat exchange analysis revealed areas of improvement in heat management. These Gen 5T deficiencies are being addressed thru a Gen 5.1T brazed core design and a more substantial re-design for Gen 8 (for DPS3000NG SPU – Mar '07). Sources of reforming variation between reforming paths (tubes of Gen 5T reactor) have been investigated and quantified through both empirical

and modeling efforts. A natural gas cracking reactor has been developed to crack or reform C2s to make possible the benefits of internal reforming of Natural Gas.

7.3.2 Reformer Developments Results and Discussion

7.3.2.1 Develop Endothermic Reactor

The requirement for capable Endothermic Reformers has not diminished despite the advent of internal reforming for NG SPUs. **Figure 7.3.2-1** shows the progression of requirements from POx, to POx w/ Internal reforming, to Endothermic Reformers for both NG and diesel. During this reporting period the majority of testing was in the area of endothermic reforming of US07 Diesel fuel. While the next system under development was a Natural Gas SPU (DPS3000NG) it was necessary to focus efforts on the more difficult of the two applications. The burden of fuel processing efficiency must be supported by an endothermic reformer because a diesel fueled APU cannot take advantage of internal reforming. The work done in 2006 on Gen 5T Reactor fits appropriately on the path of meeting DPS3000D requirements as it has shown to be capable to approximately 15kW reformat level.

		Fuel	Type	Reqs#	Unique Title	EWO for Data
		CH4			NG	US07 Diesel
		REQTS		REQTS-est	REQTS	REQTS
		3	4	7	7C	15C
		SPU 1 pre LIR: Rev 8/11/04	SPU 1B LIR: Rev 3/14/05	SPU 2 as NGIS/DPS 3000NG(DS): Rev 8/15/06	DPS3000-A-NG-S1: Rev 10/12/06	DPS3000-D: Rev 11/20/06
Mode	Data	(blank)	?	scaled fr SPU2 3/14/06 col	SOFC System Requirements Workbook_Rev15 CMM 091806.xls	DPS3000-D_Rated_Simulink_smk01.xls
SWU	Average of Ref Pwr Calc [kW]	16.00	16.00	9.60		
	Average of Recycle - Fuel Util [fract]	0.00	0.00	0.00	0.40	
	Average of Recycle - recycle fraction [fract]				0.00	
	Average of Gross Ref Eff: Ref Pwr / Fuel Pwr	0.86	0.86	0.86		
	Average of Net Ref Eff: Ref Pwr / (Fuel+Rec Pwr)					
Idle	Average of Ref Pwr Calc [kW]	4.30	1.60	1.98	2.12	2.43
	Average of Recycle - Fuel Util [fract]	0.13	0.13	0.12	0.20	0.17
	Average of Recycle - recycle fraction [fract]				0.00	0.00
	Average of Gross Ref Eff: Ref Pwr / Fuel Pwr	0.86	0.86	1.33		0.72
	Average of Net Ref Eff: Ref Pwr / (Fuel+Rec Pwr)					
Min	Average of Ref Pwr Calc [kW]	4.30	1.60	1.98		
	Average of Recycle - Fuel Util [fract]	0.13	0.13	0.12		
	Average of Recycle - recycle fraction [fract]					
	Average of Gross Ref Eff: Ref Pwr / Fuel Pwr	0.86	0.86	1.33		
	Average of Net Ref Eff: Ref Pwr / (Fuel+Rec Pwr)					
NOC	Average of Ref Pwr Calc [kW]	4.80	1.70	4.56	8.79	6.91
	Average of Recycle - Fuel Util [fract]	0.50	0.50	0.60	0.48	0.60
	Average of Recycle - recycle fraction [fract]				0.40	0.45
	Average of Gross Ref Eff: Ref Pwr / Fuel Pwr	0.86	0.86	1.33		1.31
	Average of Net Ref Eff: Ref Pwr / (Fuel+Rec Pwr)					
Rated	Average of Ref Pwr Calc [kW]	11.40	6.30	13.32	3.25	13.81
	Average of Recycle - Fuel Util [fract]	0.50	0.50	0.50	0.60	0.60
	Average of Recycle - recycle fraction [fract]				0.50	0.45
	Average of Gross Ref Eff: Ref Pwr / Fuel Pwr	0.86	0.86	1.33		1.31
	Average of Net Ref Eff: Ref Pwr / (Fuel+Rec Pwr)					
Max	Average of Ref Pwr Calc [kW]	13.50	6.70	14.28		
	Average of Recycle - Fuel Util [fract]	0.50	0.50	0.50		
	Average of Recycle - recycle fraction [fract]					
	Average of Gross Ref Eff: Ref Pwr / Fuel Pwr	0.86	0.86	1.44		
	Average of Net Ref Eff: Ref Pwr / (Fuel+Rec Pwr)					

Figure 7.3.2-1: Requirement for Reformer Power & Efficiency - Chronology

7.3.2.1.1 Endo fundamentals

7.3.2.1.1.1 Enthalpy Balance Gen 5T

An enthalpy analysis was computed using several reformer data sets in order to properly understand heat transfer performance and losses to ambient. **Figure 7.3.2-2** shows the enthalpy balance for the Gen 5T reactor on NG at 12 kW reformate power.

Reactor	5T		
	Ref_out_Power_w_CH4_kw F2-[kW] Rp,0	Name	Interpretation
De	12.05		
Average of Fuel + Air + Recycle LHV-[kW]	12.35		chemical enthalpy in reforming stream @ entrance to CV
Average of RefOut LHV w/ CH4 total-[kW] Rp,0	12.04		chemical enthalpy in reforming stream @ exit of CV
Average of del LHV Ref (Rm temp implied) - Net-[kW] Rp,0	-0.32		chemical enthalpy decr of reforming stream
Average of delH sensible RefOut (Rm temp to RefOut Temp)-[kW] Rp,0	2.21		sensible enthalpy in reforming stream
Average of Qref[kW] (+) = heat to CV (-) = heat fr CV	1.90	Qref	enthalpy incr of reforming stream
Average of Comb In - LHV total-[kW] Cr,0	19.19		chemical enthalpy in comb/hx stream @ entrance to CV
Average of Comb Out LHV-[kW] Cp,0	0.00		chemical enthalpy in comb/hx stream @ exit of CV
Average of del LHV comb (Rm temp implied) - Net-[kW] Cr,a,RT -> Cp,0,RT	-19.19		chemical enthalpy decr of comb/hx stream
Average of del H comb (Rm temp to Rm Temp)-[kW] Cr,a,RT -> Cp,0,RT	-19.22		same as above but calc via mdotCpdelT method
Average of abs H comb in fuel + air-[kW] Cr,0	-0.93		total enthalpy in comb/hx stream @ entrance of combustor
Average of abs H Comb Out at Comb out temp (TC14)-[kW] Cp,0	-3.84		total enthalpy in comb/hx stream @ exit of combustor
Average of del H comb Rm temp to CombOut Temp-[kW] Cr,a,RT -> Cp,0,TC14	-2.91	Qloss-Combustor	enthalpy loss at comb (to amb)
Average of del H sensible Comb Out Rm temp to CombOut Temp-[kW] Cp,0 RT-TC14	-16.31		sensible enthalpy in comb/hx stream at combustor exit
Average of del H Reactor CHx in to out-[kW] Cp,1-2	-4.11	Qchx	enthalpy decr of comb/hx stream (some goes to losses; some becomes Qref)
Average of Qchx - delH sensible CHxin - CHx Out-[kW] (mdotCpDelT)	-4.14		same as above but calc via mdotCpdelT method
Average of Qloss to amb-[kW] (+) = heat to CV (-) = heat fr CV	-2.21	Qloss-Reactor	enthalpy loss at Reactor
	-5.1	Qloss (Reactor+Combustor)	total enthalpy loss by full combustor/reformer system

Figure 7.3.2-2: Gen 5T Enthalpy Balance

Most concerning was the fact that less than 50% of the heat transfer from the combustion gas stream arrives as heat transfer into the reforming stream. This shows up as the 2.21 kW Q loss of the reactor. Also of concern is the 2.91 kW loss (out of 16.91 kW evolved by the combustor) from the combustion gas stream prior to arriving at the reactor proper. In total 5.91 kW is loss from a total of approximately 31kW entering the system (reformer + combustor). **Figure 7.3.2-3** shows a diagram of Gen 5T and the location and condition nomenclature used to track enthalpy changes. Follow-up work has involved better insulation methods and better understanding of heat loss paths.

<u>Stream & Location Notation</u>	
R	= Reformer Path massflow
C	= Combustor Path massflow
r	= reactants
p	= products
0	= location: edge of reaction zone, product or reactant side
a	= location: ambient (far away from reaction zone)
<u>Delta Chemical Enthalpy (del U) notation</u>	
Rp,X	= where X is % completion of intended reaction, reactants to products
<u>Delta Sensible Enthalpy notation</u>	
Rp,0,IT->FT	= <Initial Temp> to <Final Temp>

Figure 7.3.2-3: Gen 5T Enthalpy Balance Notation

7.3.2.1.1.2 Heat transfer evaluation

Testing was conducted to better understand the heat transfer performance of the reactor without the presence of reforming reactions in order to address the above enthalpy balance results. **Figure 7.3.2-4** shows the locations of temperature data to determine heat exchanger characteristics. The initial test (MG733C265) involved the insulating the reactor per Delphi's then standard lab practice of locating the reactor inside a zircar board "doghouse" which was then stuffed w/ Kaowool insulation (Alumina). **Figure 7.3.2-5** is a x-section at the reactor body of this configuration. Test results are given in the lower portion of **Figure 7.3.2-6** (lines 4, 5 and 6).

Figure 7.3.2-4: MG733C265 Gen 5T Reactor + NG1 Mixer TC locations

Figure 7.3.2-5: MG733C265 Insulation Cross Section

Ord	EWO		Test Point ID	T2 Ref Path Inlet Temp [deg C]	T3 alt (ref out tube ave) [deg C]	T3 (reactor reforming path outlet) [deg C]	delta T3alt - T3 [deg C]	T6 (actual) reactor comb/ht exh inlet [deg C]	TC16 (reactor comb/ht exh outlet) [deg C]	Effectiv eness	UA [W/C]	Heat Transfer (Comb/Hx) [W]	Heat Transfer (Ref Path) [W]	Ht xfer Ratio
1	MG733C270	w/ Insul	Idle SS0	331	629	472	157	756	574	0.83	0.51	-924	87	0.09
2	MG733C270	w/ Insul	NOC SS50	256	645	571	74	747	555	0.86	2.33	-1398	433	0.31
3	MG733C270	w/ Insul	Rated SS100	234	532	505	27	614	482	0.86	4.59	-1956	647	0.33
4	MG733C265	w/o Insul	Idle SS0	309	538	379	159	674	485	0.79	0.43	-952	64	0.07
5	MG733C265	w/o Insul	NOC SS50	229	551	487	63	667	474	0.82	1.98	-1396	350	0.25
6	MG733C265	w/o Insul	Rated SS100	183	531	501	30	660	473	0.80	3.61	-2808	739	0.26

Figure 7.3.2-6: Gen 5T Heat Exchange Evaluation

Noteworthy findings from this test are that UA values were surprisingly small and needed to be investigated further. Most concerning was the low heat transfer ratio which indicated how much of the heat lost by the combustion gas stream is received as heat input to the reforming stream. Subsequent testing aimed to improve the insulation R value by applying a wet layup form fitting low thermal conductivity insulation layer directly to the reactor casing. **Figure 7.3.2-7** is a cross-section of this new configuration at the reactor body. Test results for this new “w/insulation” configuration are given in the upper portion of **Figure 7.3.2-6** above (lines 1, 2, and 3). While the heat transfer ratio, UA, and heat exchange effectiveness all improved, the improvement was less than anticipated. The more prominent heat loss path is potentially via conduction to the relatively large flanges and port structures. A more rigorous thermal evaluation is now underway.

Figure 7.3.2-7: MG733C270 Insulation Cross Section

7.3.2.1.1.3 Gen 5T Evaluation: Requirements vs. Actual

Gen 5T was evaluated under several tests. Two of the tests involve sampling of reformat from individual reforming tubes to detect differences in reforming between tubes.

7.3.2.1.1.3.1 MG733C246 - Tube Sampling

MG733C246 was conducted with individual tube sampling while the Gen 5T reformer was fueled with JP8 surrogate fuel. Results from this test are shown in **Figure 7.3.2-8** and can be summarized as follows:

- Quality reformat was made by all tubes (Quality Reformat requires <1 mol% CH₄ and <0.1 mol% C₂s+)
- C₂s+ were negligible for all tubes
- Product CH₄ varied by tube and follows tube temperature
- Tube Temperature variation was evident (~ 70 deg C range)

Figure 7.3.2-8: MG733C246 JP8 Gen 5T Tube-Tube Variation in Reforming Composition

The second objective of this test was to determine if this tube composition/temperature variation was a product of feed stream preparation. To test this, the FDU was “clocked”

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through four distinct orientations with parallel data collected at each orientation. The effect of FDU orientation versus reforming temperature is shown in **Figure 7.3.2-9**. It is apparent that no big effect is at work and so data was plotted by tube in **Figure 7.3.2-10**.

Figure 7.3.2-9: Effect of FDU Orientaton on Gen 5T Tube-Tube Variation in Reforming Composition

Figure 7.3.2-10: Effect of FDU Orientation on Gen 5T Tube-Tube Variation in Reforming Composition

7.3.2.1.1.3.2 MG733C261 – Tube Sampling

A second test (MG733C261) involving individual tube sampling was conducted as a test to requirements for DPS3000D (US07 fueled APU). **Figure 7.3.2-11** shows the results of this testing in which eight data points (representing reformat power conditions ranging from 2.3 to 17.3 kWt) are averaged together. A very similar pattern of temperature by tube is evident and nearly identical to that indicated in the previous test (MG733C246). The pattern from low to high temperature by tube is nearly identical to MG733C246 test results (2,1,3,7,6,4,5). **Figure 7.3.2-12** shows this data expanded to present data at all reformat power levels. Tubes 7 and 4 meet quality reformat requirements up to approximately 14 kWt. Other tubes showing C2 inflections at much lower power levels indicates that conditions are appreciably different between tubes. A diagnostic tree was employed to better discuss and explain the variation sources and is shown in **Figure 7.3.2-13**. The status of the tree as more investigations were conducted will be revisited later in this report. The FDU orientation testing discussed above suggests removing box #4 as a source of the variation.

Figure 7.3.2-11: MG733C261 US07 Gen 5T Tube-Tube Variation in Reforming Composition

Figure 7.3.2-12: Gen 5T Tube-Tube Variation in Reforming Composition

Figure 7.3.2-13: Diagnostic Tree: Reformate Composition Variation Between Tubes

7.3.2.1.1.3.3 MG733C269 – Delta P by Tube

The three viable Gen 5T reactors were subjected to individual tube delta P testing given the concern over tube-tube variation. The results shown in **Figure 7.3.2-14** indicate that substantial flow variation could exist between tubes based on the delta P data. This data manipulation involves collecting delta P data with room temperature air at fairly low flows. Data is regressed to create an equation for that particular tube and a flow prediction at a nominal pressure drop (as would be seen in operation) is determined.

Figure 7.3.2-14: Predicted Flow Variation Due to Tube Delta P Variation

7.3.2.1.1.3.4 Tube Samples Variation

The suspicion that tube delta P variation was significant led to a re-examination of some sample tubes that used similar material and processing as that of the reforming tubes used in the Gen 5T reactor. Both involved FeCrAl foam brazed inside a 1" OD Inconel 625 tube albeit at different lengths. Net weight versus delta P data was collected for a group of five pieces of 2" long x 1"OD Inconel 625 tubes having a single 1" long 20 ppi FeCrAl foam. The data is shown in **Figure 7.3.2-15**. The cause of this strong correlation has not been identified. Potential factors are variation in the foam PPI, density of the foam itself, or variation in the amount of braze and braze entrained foam at the junction of the tube ID and the foam OD. Work is in progress with the foam supplier to understand the source of this variation.

Figure 7.3.2-15: Predicted Flow Variation due to Tube Delta P Variation

7.3.2.1.1.3.5 MG733C271 – Total Delta P by path

Gen 5T pressure drop data is shown in **Figure 7.3.2-16** along with a diagram indication pressure tap location in **Figure 7.3.2-17**. It indicates the reforming path was sufficiently free flowing. For the combustor / heat exchange path however total delta P was higher than allowed. Additionally this data was collected with un-heated combustor reactants. Under application conditions, anode tail gas (ATG) and cathode air (CA) will be introduced to the combustor at $\sim 700^{\circ}\text{C}$. The effect on pressure drop, mixing and combustion was deemed significant enough that lab capability to provide reactants to the combustor at these temperatures was requested and is underway. In the interim we concluded that delta P on the heat exchange path would need improvement regardless.

Figure 7.3.2-16: Gen 5T Delta P by Source

Figure 7.3.2-17: MG733C271 – Pressure Tap Locations

7.3.2.1.1.4 Gen 5.1T Development

Given the apparent deficiencies in Gen 5T reactor performance an effort to improve the design was initiated in Aug 2006. This effort eventually split into a modest design iteration in order to produce hardware for the Diesel Integration System (DIS – a development level APU system) and was dubbed Gen 5.1T. A more aggressive design iteration intended to produce a reformer for the upcoming DPS3000NG SPU is also discussed below. Both efforts share the common ground of using knowledge of Gen 5T performance and analysis as a basis.

The Objective of both efforts were to improve the following

- temperature delta at tubes
- peak temperature required in reactor (to improve material durability)
- Temperature robustness (both initial & over life via reduction of temperature gradients and stresses)
- improve heat transfer performance to reforming tubes
- improve reforming performance of reforming tubes
- reduce delta P at rated power (flows) - heat exchange / combustion gas path
- reduce delta P at rated power (flows) - reforming path

7.3.2.1.1.4.1 MG733E63 CFD modeling of Gen 5T type reactor configurations

Several of the objectives mentioned above were at least partially addressed with this round of CFD modeling. **Figure 7.3.2-18** shows the base analytical geometry. As of this writing 2 key variables have been evaluated via four geometries. They are:

1. presence / absence of an insulation in the gap between the outside of the 96mm O.D. combustor path foam
2. presence / absence of enlarged inlet and outlet “ring” manifolds for the combustion gas path.

Figure 7.3.2-18: Analysis Geometry Description for Gen 5T Type Reactor Configurations

This insulation can be seen in **Figure 7.3.2-18** and the modified manifolds can be seen in **Figure 7.3.2-19**. The result of these four configurations is shown in **Figure 7.3.2-20**. This plot shows the temperature variation both between and within tubes x-sectional flow area. For this plot, the plane of interest is the reforming tube outlet plane (a.k.a. the combustor inlet plane) and is indicated in **Figure 7.3.2-18**.

Figure 7.3.2-19: Gen 5T w/ Modified Manifolds

Figure 7.3.2-20: Reforming Tube Temperature Distribution for Gen 5T Type Reactor Configurations

On the x-axis of this plot are the minimum, average and maximum temperatures for particular tubes x-section flow area. The ideal response is a completely uniform temperature across the x-section of each tube and with each tube's data identical. This would plot as a straight line at constant temperature. All four configurations have undesired variation. Data is plotted in order of tubes starting with the tube furthest from the combustion gas inlet through the tube closest, and then followed by the center tube (i.e. 1, 2, 3, 4, 7). The following effects are noteworthy:

Modified Manifold

The use of the modified manifold actually decreases the reforming temperature of the tubes, especially tubes 1 and 2. This is believed to be a result of the increased surface area, the subsequent losses that result, and the less restrictive path to the lower portions of the combustor foam afforded by the manifold. This can be seen in **Figure 7.3.2-21** where both configurations 3.0 and 3.1 (modified manifold w/ and w/o insulation) have reduced core temp at and around the plane of reforming tube exit.

Figure 7.3.2-21: Centerline X-Section Temperature Distribution [deg K] of Gen 5T Type Reactor Configurations

Gap Insulation

The use of insulation appeared to have little effect on either reforming tube temperatures or, on reactor casing temperatures (skin temperature). This is a bit surprising and is still under investigation as this model did not include radiation effects, but rather employed only convective heat transfer at the surface of the reactor casing.

The effects on delta P for both these variables can be seen in **Figure 7.3.2-22** with both delta P and tube temperature responses considered together results in the following assessment:

- Insulation: significant delta P penalty w/ no apparent tube temperature benefit

- Modified Manifolds: minor delta P improvement but a net heat transfer / tube temperature variation penalty

Figure 7.3.2-22: Modeled Skin Temperatures - Gen 5T Type Reactor Configurations

Neither of these variables will be employed in the Gen 5.1T build. Additionally, distribution of combustion gas flow (as a result of manifold arrangement) is most likely not a big contributor to the reforming tube temperature variation experienced with the Gen 5T reactor. Delphi can remove this variable from consideration in the diagnostic tree.

7.3.2.1.1.4.2 MG733E64 FEM modeling of Gen 5T type reactor configuration

During the development of the Gen 5.1T next generation tubular reformer, significant efforts were put forth to yield a reduction in thermally induced stresses on the next generation tubular endothermic reformer. Structural buckling had been encountered on the outer wall of the Gen 5T hardware during high capacity operation. One concept that shows promise was the subject of an FEA study that involved shaping a bead - also known as a tube upset or rib - along the circumference of tubes in a tubular reformer assembly as shown in **Figure 7.3.2-23**.

Figure 7.3.2-23: FEA Bead Detail

A simplified, axi-symmetric FEA analysis involving a single one (1) inch diameter tube concentric to a three (3) inch diameter tube was used to gain a fundamental understanding of the effect of the addition of circumferential beads. A more extreme and more deeply drawn circumferential bead shape was also examined in the FEA analysis. In the analysis, an isothermal, uniform temperature increase from 20°C to 100°C was applied with the tubes constrained in a manner not to allow axial growth. The tubes were free to grow radially. High temperature creep was neglected in the analysis. Linear static stress and Eigen value buckling analyses were both considered. Von Mises stresses from the linear static analysis and critical buckling temperatures from the buckling analysis were used to compare the three cases. The maximum Von Mises stresses were 206 Mpa, 1,278 Mpa and 278 Mpa for the non-upset, upset and extreme upset respectively (see **Figure 7.3.2-24**).

Figure 7.3.2-24: MG733E64 FEA Linear Static Analysis Results

The critical buckling temperatures for the three cases were 592°C, 952°C and 11,480°C respectively (see **Figure 7.3.2-25**). In conclusion, for a given compressive load, addition of a stiff (not deeply drawn) bead results in increased resistance to buckling; however, this also induces high localized stress at the bead which will cause yielding and possible low cycle fatigue failure. A softer (more deeply drawn rib) is shown to significantly reduce the stress concentration and greatly increase axial buckling resistance.

Figure 7.3.2-25: MG733E64 FEA Buckling Analysis Results

7.3.2.1.2 Produce Endothermic Reactor Prototypes

7.3.2.1.2.1 Gen 5.1T Manufacturing Development: Brazed Core effort

It was determined that cycling a wash coated reactor assembly through a nickel braze process would be detrimental to the activation and/or adhesion of the wash coat material. This finding, coupled with the required location of the wash coat material in the reactor, affected the manner in which the originally designed Gen 5T assembly was performed. The original design was assembled by TIG welding the reactor components around a pre-wash coated reactor core. The welding process resulted in high stress points in the reactor shell that resulted in warping and cracking during testing. The endothermic reactor was redesigned to be a brazed assembly in an effort to eliminate some of the manufacturing challenges of previous reactor builds. The redesigned components enabled the brazed Porvair core assembly to be secondarily brazed into the remaining reactor assembly. The redesign separated the flow distribution cone assembly from the reactor assembly by incorporating an additional flanged joint. The reactor assembly would be wash coated after braze followed by the cone assembly being attached using bolts. This activity is ongoing and the redesigned components are in the process of being ordered. **Figure 7.3.2-26** is a view of the redesigned assembly shown below.

Figure 7.3.2-26: Gen 5.1T – Brazed Core Reactor – X-Section View

Braze joints were created where the TIG welded joints cracked in the previous design. The base plate was sectioned into three separate plates to alleviate the buckling that occurred in the previous design due to over constraining caused by the single base plate.

7.3.2.2 Develop NG FDU

7.3.2.2.1 NG metering device development

Work began on developing a more productive metering device for natural gas. The current device, while reasonably accurate, is heavy, large and expensive. The initial effort was to determine what devices currently exist and whether they meet the SPU requirements. The device would need to function at low system pressures, meet the flow range specified (minimum flow = 0.03 g/s of NG, maximum flow = 0.15 g/s NG), and have automotive type durability. A current production NG injector used on Honda Civic for Compressed Natural Gas operation (Honda Part Number 06164-PDN-J00) was identified and ordered for evaluation. **Figure 7.3.2-27** shows initial low pressure flow curves for several periods. These initial tests demonstrate flow metering capability using air. Additional testing is planned for 2007 with natural gas.

Figure 7.3.2-27: Evaluation of Fuel Injector for DPS-3000-NG System

7.3.2.3 Develop Diesel FDU

7.3.2.3.1 Non-Contact (NCV) vs. Contact vaporizer (CV) comparative Testing

The Objectives of testing were as follows:

- Determine reformer start-up characteristics (MG733C258)
- Measure O:C variation (mixing quality) across back face of catalyst (MG733C258)
- Measure O:C variation (mixing quality) after a minimum of 300 hrs run time (MG733C262)
- Document presence of contamination within the mixing zone (MG733C262)

These objectives were to be carried out on each of the two vaporizer configurations as adapted to a Gen 4.2T reformer. The non-contact vaporizer hardware is pictured in **Figure 7.3.2-28** and is comprised of an injector capable of high atomization coupled with a high swirl mixer.

Figure 7.3.2-28: Non-Contact Vaporizer: Injector and Mixer

Atomization is further enhanced through the use of heated fuel. The contact vaporizer hardware consists of Multec 3 injector feeding into a vaporization (heat exchange) tube. This Injector – Tube configuration is duplicated so that both fueling and cleaning modes are alternating between the dual paths to the reformer. Vaporized fuel is fed into the center port of an NG1 mixer where is mixed with air and presented to the catalyst face as diagrammed in **Figure 7.3.2-29**. For all testing, sampling of reformer product gas as the back face of the catalyst was employed. A typical output of this set up is shown in **Figure 7.3.2-30** where the output of interest is local O/C. **Figure 7.3.2-31** documents how the 2 competing systems will be run.

Figure 7.3.2-29: Contact Vaporizer Set-Up

Figure 7.3.2-30: O:C Ratio Sampling Set-Up

<p>◆ Non contact Vaporizer</p> <ul style="list-style-type: none"> - 700 KPA inlet fuel pressure - Air inlet temp 250 Deg C - 0.06, 0.100, 0.200 g/sec fuel flow - US diesel-07 - Injector operating without closed loop control - Inlet fuel temp 80 Deg C 	<p>◆ Contact Vaporizer</p> <ul style="list-style-type: none"> - 300 KPA inlet fuel pressure - Air inlet temp 80 Deg C - 0.06, 0.100, 0.200 g/sec fuel flow - US diesel-07 - Injector operating without closed loop control - Air carrier 0.1 g/sec (10 slpm) - 1 hour cleaning cycle - External mixing
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Figure 7.3.2-31: Test Parameters

Evaluation began with start-up characteristics and results are shown in **Figure 7.3.2-32**. The graph indicates the temporary O/C excursion that occurs with the NCV setup as a result of fuel puddling on insufficiently hot chamber walls. Hydrogen production is stunted as a result. This problem was not evident with the CV setup. **Figure 7.3.2-33** summarizes the performance of the 2 configuration at 0 hours at identical O/Cs. The CV performance is slightly better than that of the NCV. Testing also involved catalyst back face sampling for O/C variation. Data for this technique at several fueling levels is shown in **Figure 7.3.2-34**. The O/C range values for CV configuration are significantly better than the NCV value and in addition the NCV setup suffered from pre-combustion. **Figure 7.3.2-35** shows similar data except after 300 hours of operation. The trend is the same with CV having better O/C range values. **Figure 7.3.2-36** shows that the O/C range advantage is evident in reformat compositions and subsequently in reforming efficiency values. **Figures 7.3.2-37** and **7.3.2-38** show the resulting deposit formation for each of the 2 configurations. Both configurations caused deposits with the NCV

setup resulting in significant accumulations immediately upstream of the catalyst. The CV configuration on the other hand caused a lower amount of deposits and they occurred on the exterior surface of the mixing cone. This cone sees the blend of vaporized fuel and reformer air circulate around its exterior before entering the 2 tangential “mixing ports”. The mixing ports are not active as the vaporized fuel enters just outside the mixer housing (i.e. external “mixing”). While the streams initially meet external to the mixer housing, we know that the homogeneity is poor until they have traveled through the mixer geometry properly.

Figure 7.3.2-32: Test Parameters

Reformer output 0 hrs @ 0.100 (g/sec) fueling				
	H2 %	CH4 %	CO %	Ref efficiency %
NCV	18.7	0.2	22.2	74
CV	20.2	0.12	23.6	76

Figure 7.3.2-33: Start-Up Performance NCV vs. CV Vaporizer

	Start - up Performance		Measured O:C ratio across back face of catalyst at 0 hrs		
			0.06 (g/sec)	0.10 (g/sec)	0.20 (g/sec)
NCV	yes	Fuel rate	0.06 (g/sec)	0.10 (g/sec)	0.20 (g/sec)
		O:C ratio	n/a	1.0 - 1.26	n/a
		range		0.26	
CV	no	O:C ratio	n/a	1.11 - 1.12	n/a
		range		0.01	

Figure 7.3.2-34: MG733C258 Reformer Output Performance – 0 hrs

	Measured O:C ratio across back face of catalyst at 300 hrs			
	Fuel rate	0.06 (g/sec)	0.10 (g/sec)	0.20 (g/sec)
NCV	O:C ratio	0.92 - 1.39	0.99 - 1.28	0.53 - 1.27
	range	0.42	0.29	0.74
CV	O:C ratio	1.11 - 1.13	1.16 - 1.17	1.04 - 1.07
	range	0.02	0.01	0.03

Figure 7.3.2-35: A/F Mixing Performance - 0 hrs

	Reformer output 0.060 g/sec fuel @ 300 hrs.			
	H2 %	CH4 %	CO %	Ref efficiency %
NCV	17.6	0.43	21.2	69.0
CV	19.5	0.38	22.5	75.0

	Reformer output 0.100 g/sec fuel @ 300 hrs.			
	H2 %	CH4 %	CO %	Ref efficiency %
NCV	18.5	0.4	22.3	74.0
CV	18.8	0.06	22.5	73.5

	Reformer output 0.200 g/sec fuel @ 300 hrs.			
	H2 %	CH4 %	CO %	Ref efficiency %
NCV	17.2	0.73	21.1	64.0
CV	21.2	0.38	24.3	79.0

Figure 7.3.2-36: MG733C262 A/F Mixing Performance - 300hrs

Figure 7.3.2-37: MG733C262 Reformer Output - 300 hrs

Figure 7.3.2-38: Non Contact Vaporizer 300hrs.

7.3.2.4 MG733C264 - Air Flow/pressure reduction Testing

The objectives of this testing were to evaluate the effects of carrier gas and fuel vapor temperature on system pressure. Additionally it was expected that test parameters for upcoming durability testing could be established. **Figure 7.3.2-39** shows a diagram of the test configuration. In this figure the (2) contact vaporization (CV) tubes are colored green and red. The tube geometry tested was 4.8mm OD / 3.3mm ID (3/16"OD x 0.035" wall) Inconel 625 tubing at a length of 22". Actual photos of the setup are found in **Figure 7.3.2-40** and **Figure 7.3.2-41**. **Figure 7.3.2-42** shows the effect of Air Carrier flow. A change from 2 to 15 slpm resulted in 12-13 kPa change in pressure (~1 slpm / kPa). Decreasing air carrier flow had the effect of lowering vapor temperature despite constant combustor flow and temperature. It was also noted that system behavior was erratic (unstable pressure & sputtering) at low slpm. **Figure 7.3.2-43** shows the effect

of Vapor temperature change. Here a change of 150 C resulted in pressure change of 6 KPa (25C/kPa). Air carrier flow is involved with cleaning effectiveness and is being studied separately.

Pressure Dependency on Pressure Air Carrier

- Vary Air Carrier flow
- Baseline at 10 slpm, observe 2, 5, 15 slpm
- Tube A and B switched from fueling to cleaning every (2) hours

Figure 7.3.2-39: MG733C264 Air Flow/Pressure Reduction Testing

Figure 7.3.2-40: Evaluation of Fuel Injector for DPS-3000-NG System

Figure 7.3.2-41: Evaluation of Fuel Injector for DPS-3000-NG System

Figure 7.3.2-42: MG733C264 Air Flow/Pressure Reduction Testing

Figure 7.3.2-43: MG733C264 Air Flow/Pressure Reduction Testing

Durability Study 1

An initial durability test was launch based on parameters established above. Air Carrier flow was selected to be 7 slpm while vapor temperatures remained unchanged. This was achieved by increasing combustor temp (from ~900 to ~960 C) which resulted in a 1 kPa pressure reduction (to ~7.5 kPa) over the previous baseline testing using 10 slpm. Testing continued for 196 hours until failure resulted due to carbon buildup (tube pressure out of limits – high). The carbon build-up occurred at the air system merger point, the mixing chamber and elsewhere within evaporation tubes and is shown in **Figure 7.3.2-44**.

Figure 7.3.2-44: MG733C264 Air Flow/Pressure Reduction Testing

Durability Study 2

It was hypothesized that based on behavior of the tubes that the 7 slpm air carrier flow was insufficient to maintain the tubes cleanliness. This second study evaluated vaporizer performance with 10 slpm air carrier flow. New Tubes created to replace those fouled from prior tests. The vaporization system displayed an increase in pressure of 1 kPa over nearly 500 hours operation with no significant carbon build-up.

7.3.2.4.1 DIS FDU Design

The contact vaporizer strategy described above was revised to attach to the SOFC system using a Gen 5T Reformer. It utilizes two Multec 3.5 fuel injectors and is integrated into the system via manifold blocks, tubing and Swagelok fittings. The design can be seen in the **Figures 7.3.2-45 and 7.3.2-46** below.

Figure 7.3.2-45: Diesel FDU Configuration for Diesel Integration System

Figure 7.3.2-46: Diesel FDU Configuration Shown in Diesel Integration System

7.3.2.5 Develop NG POx Reformer

In 2006 efforts were focused more on endothermic reforming and little development occurred on the Gen 4.2T POx reformer. Four (4) additional reformers were however built to support systems activities. Efforts for NG POx reforming were focused on development of the NG Cracking Reactor and catalyst.

7.3.2.5.1 Development of NG Cracking Reactor

7.3.2.5.1.1 MG733H1 Requirements

Figure 7.3.2-47 represents key operating points for the NG Cracking Reactor. The function of this reactor is to ingest an ATG-like stream and together with a secondary reactant of Natural Gas create a product streams that is essentially free of C2s and higher HC's+. As a secondary requirement it is desirable that the reactant CH₄ be left largely un-reformed. Current system approach is to have the cracking reactor downstream of the NG Endothermic Reformer such that the ATG-like reactant is the product stream of the reformer, whether or not it is actually reforming (i.e. being fueled) or only serving only as heat exchanger to conduct the stream. A key aspect of this process is that no heat is to be brought to the process other than the sensible heat present in the reactants (assumes adiabatic Cracking reactor). Here we will discuss the reactor development, specifically the modeling conducted to insure adequate mixing at reasonable pressure drop.

	DPS3000A- NG Precat operating points_rev5 .xls			
	Reqs			
Data	SS54	SS65	SS84	SS100 (Rated)
Average of atg mdot [g/sec]	0.720	0.500	0.580	0.690
Average of atg temp [deg C]	700	700	700	700
Average of atg O/C [-]	1.298	1.522	2.663	3.313
Average of sf mdot [g/sec]	0.000	0.036	0.096	0.160
Average of sf temp [degC]	250	250	250	250
Average of react O/C all []	1.298	1.268	1.652	1.650
Average of cat SV @ stp,void vol [hr-1]	17,321	13,938	12,943	14,281
Average of cat SV @ stp,react vol [hr-1]	13,857	11,150	10,354	11,425

Figure 7.3.2-47: NG Cracking Reactor Reactant Specifications

7.3.2.5.2 MG733E61 Flow Modeling

As a starting point for design a reactor shape (cylindrical) size (2"OD) and substrate (Cordierite) were selected based on prior experience with reforming processes. Based on expected pressure drop characteristic of the catalyst, an allocation for the delta P of the mixing section of reactor of 0.75 kPa was selected. **Figure 7.3.2-48** shows several configurations for reactor feed mixing. Secondary fueling (CH₄ for this modeling) is shown as the red stream and the blue represents the ATG stream. Mixer performance was measured by the CH₄ mass fraction at catalyst face and the delta P from Anode Inlet to catalyst (monolith) face. **Figure 7.3.2-49** show the results for both metrics of this modeling. The "rev3 modified" design was selected as it was the best compromise between pressure drop and good mixing.

Figure 7.3.2-48: NG Cracking Reactor Mixer Designs & Results

Figure 7.3.2-49: NG Cracking Reactor – Distribution Modeling Results

7.3.2.6 System SOT Characterization and SOT/EOT test development

In 2006 a number of POx reformers were evaluated either for the start of systems testing or as EOT. In particular the reformer that ran 4600hrs on phase was evaluated. Unfortunately systems data collected for the reformer during testing was found to be less than 100% accurate. Additionally a full characterization was not collected for all POx reformer put into service for Phase 1. As a result in order to determine Reformer Performance at EOT (end of test) a separate EOT characterization was conducted in the reformer lab. Concurrently we were preparing a number of POx reformers for SOT (start of test) and had noticed some short term performance changes, specifically CH₄ changes. A standardized test regimen was created and used to investigate “de-greening” phenomena and is shown in **Figure 7.3.2-50**.

Figure 7.3.2-50: SOT/EOT Characterization Test Schedule

Figure 7.3.2-51 shows Data for temperature through these runs. It is apparent that SOT1 data is fairly different than the SOT2 data during the initial SWU mode (same conditions run sequentially over 2 days). Similar behavior is shown in **Figure 7.3.2-52** for product CH₄. A long thermal equilibrium time especially on power decrease events is evident and even when thermal equilibrium is reached in test it was noted that CH₄ concentration would continue to drift down slowly. This is suspected to still be a temperature effect as it is theorized that inner catalyst temperature is still not in equilibrium, both radially and axially, despite fairly stable reformat temperatures. The de-greening phenomena had been theorized as possibly being the effect of Rh oxide converting to metal oxide.

Figure 7.3.2-51: SOT/EOT Characterization Test Schedule

Figure 7.3.2-52: SOT/EOT Characterization Test Schedule

Catalysts from selected EOT reformers are being evaluated separately from the POx Reactor under Test MG733F34 and are discussed in the Catalyst section of this report.

7.3.2.7 Develop Diesel Endothermic Reformer

7.3.2.7.1 MG733C261 Test to DPS3000D requirements

The objective of the test was to evaluate the reformer to current DPS3000D requirements. Reformer configuration was a Gen 5T Reactor with NG1 mixer and internally mixed single tube contact vaporizer with ~500 hrs of operation logged. Much of the data from this specific test was discussed earlier in this report as it also involved individual reformer tube sampling. Additionally flow rates at rated and NOC power modes, scaled up and down, were run to see the limits of reformer performance. **Figure 7.3.2-53** shows results for some key measures. While full requirements for DPS3000D are still being formulize it is anticipated that reformat quality (driven by stack requirement) and efficiency will be in line with current DPS3000NG requirements. Reforming Efficiencies near 130% and C2s+ at less than 0.1 mol% are expected. Given this, this reformer configuration did not meet these levels. Given the rough service that this particular sample has undergone and as yet unresolved concerns over heat loss management our intentions are to re-test with a fresh reactor as soon as the opportunity present itself.

Figure 7.3.2-53: Gen 5T – US07 Reforming

7.3.2.7.2 MG733C263 Durability w/ CV (contact vaporizer) - Carbon Deposits

The objective of this test was to evaluate a revised mixing strategy referred to as 'externally mixed' on a full reactor and log additional test time w/ the Gen 5T reactor on US07 diesel fuel. The earlier test (MG733C261) used a contact vaporizer / mixing strategy that required periodic cleaning of the CV tube that inadvertently also had the benefit of removing potential carbon deposits in the FDU & reactor inlet. The intent of this test is also to compare the effect of recycle as a reactant on the carbon formation that typically occurs in a FDU when run with a POx reactor. **Figures 7.3.2-54** and **7.3.2-**

55 show the difference in carbon formation that occurs when recycle is added as a reactant. In all other respects the performance of the reformer was similar to that in MG733C261 indicating that the “external mixing” approach appears to be on par with “internal mixing”.

Figure 7.3.2-54: EOT NG1 Mixing Cone

Pox Test shows significantly more carbon deposition

Figure 7.3.2-55: EOT Mixer Housing

7.4 Task 4: BOP Component Development

7.5 Task 5: Project Management

7.6 Task 6: Hybrid System Evaluation

8 2007 TECHNICAL PROGRESS AND ACHIEVEMENTS

8.1 Task 1: System Development

8.1.1 Define System / Subsystem Requirements

For SECA Phase II, Delphi aggressively pursued Phase II performance targets which drove SOFC stack and subsystem performance, including cost reduction. Delphi also utilized technical progress and market research to focus effort on development of a Diesel Truck SOFC APU. A composite view of both SECA Phase II performance requirements for a Stationary Natural Gas system, and Delphi's Diesel APU product are given in **Figure 8.1.1-1**. 2007 development testing status for natural gas systems is also shown **Figure 8.1.1-1**.

Target Metric		DOE/SECA Ph II (CONTRACT)	North America Heavy Duty Truck APU	Current Development Status
Target Date		4Q 2008	2012	3Q 2007
Fuel		Nat Gas	S15 Diesel	Nat Gas
Net Rated Power	kW	3-10	3	3.4
Fuel to Electric Efficiency (Peak)	%	40%	25%	38%
Cost	\$/kW	\$600	700	670**
Cycle Durability	cycles	50	250	31
Operation Life	hrs	1500*	22000	1000*
Degradation Rate	%/500 hrs	1.0%	0.15%	0.84%

* Limit of test duration
** Projected

Figure 8.1.1-1: System Requirements Summary

In the first half of SECA Phase II, emphasis was placed on achievement of Phase II performance metrics on natural gas. Progress was made with respect to Phase II system targets in the area of durability; with thermal cycling and power degradation rate. Delphi has developed several system platforms that are configurable for both natural gas and Diesel fuel operation. These are shown in **Figure 8.1.1-2**

Figure 8.1.1-2: Delphi Phase II SOFC Systems

The Set 00 development platform allowed for controlled integration and testing of SOFC stacks, fuel reformer, controls, electronics, and balance-of-plant components. The SPU 1 platform was used for Phase 1 exit testing at the “B” revision level. During Phase II, this platform was revised to the “D” level for natural gas, and an “E” level for Diesel fuel. Improvements were made in each area of the SOFC system, specifically in the areas of controls and the anode tail-gas recycle loop. SPU 2 included technology and several components from SPU 1. SPU 2 allowed for increased power and efficiency by utilizing four SOFC stacks instead of the two in an SPU 1 unit. These 4 stacks were arranged in series-parallel configuration for both flow and electrical connection. This configuration allowed for increased air utilization in the system and overall higher efficiency and power. Delphi’s Phase II strategy was to migrate Set 00 and SPU 1 platforms to Diesel fuel development and continue Phase II performance testing on natural gas with the SPU 2 system.

8.1.2 Develop System Mechanization

The Delphi natural gas systems operated in Phase II had a CPOx/Internal fuel reforming strategy as shown in **Figure 8.1.2-1**. This mechanization allows for high fuel processing efficiencies (without an endothermic reformer) and enhanced SOFC stack cooling through direct natural gas injection into the recycled tail gas. The blending between CPOx reformat and natural gas & recycle varied depending on desired system operation characteristics (balance between system power, efficiency, and stack voltage). This configuration was used in the SPU 1D system.

Figure 8.1.2-1: Delphi Natural Gas System Mechanization – Internal Reforming Mode

A similar mechanization is used for Diesel systems except that the secondary fuel path is removed (no internal reforming), and the precat is replaced with a hot-reformate desulfurizer. Also, this system does not employ a liquid fuel desulfurizer. The Delphi Diesel system mechanization is shown in **Figure 8.1.2-2**.

Figure 8.1.2-2: Basic Diesel APU System Mechanization

All Delphi systems have a 12 VDC bus to support the system controller and its sensors and actuators. Diesel systems have 12 VDC application power output, and so a Stack DC to 12 VDC power converter was required. Parasitic loads in the system such as blowers, pumps, and heaters also run on this 12 VDC power circuit. For natural gas systems, application power output is 120 VAC. Parasitic loads in the natural gas systems are driven by a 120 VAC circuit.

8.1.3 Perform System Analysis

System analysis was performed to support Delphi's Diesel SOFC APU design designated DPS3000-D. Per the system requirements in **Figure 8.1.3-1**, this system is required to have a rated power of 3 kW on Diesel fuel. A system operation map was generated for Diesel fuel. The map contains predictions of output power, system efficiency, and cathode airflow required as a function of SOFC stack gross power capacity at 0.7 V/cell reference and actual cell operating voltage point. A rated operating point may be chosen anywhere along the 3000 W line net output power. There is a trade-off between high cathode airflow and parasitic load at low cell voltage and efficiency vs. high stack power capacity required at higher cell voltages and efficiency. Based upon evaluation of this trade-off, a rated power operating point was chosen at a stack power capacity of 4700 W (at 0.7 V/cell) and an operating point of 0.77 V/cell. This choice of operating point allowed for lower stack power capacity than needed at higher cell operating voltages and less cathode air than required at lower cell operating voltages.

Figure 8.1.3-1: Diesel SOFC System Operating Analysis

Figure 8.1.3-2 shows the behavior of actual stack gross power and parasitic efficiency on the same coordinates. Parasitic efficiency is the fraction of stack gross power that is available at the output after parasitic loads are served within the system. From **Figure 8.1.3-2**, the actual stack output power at the operating point is 3700 W, and the system parasitic efficiency is approximately 0.82 which is acceptable for a small Diesel APU.

Figure 8.1.3-2: Diesel SOFC System Operating Analysis

A 3 kW Diesel APU will generally have less output power than a natural gas system for the same number of cells. This is due to the reduced hydrogen content in the reformat, which is driven by the hydrogen-to-carbon ratio of the fuel, and the increased parasitic loads in the system due to less efficient cooling methods for the stack due to the absence of internal reforming. **Figure 8.1.3-3** estimates the number of cells required for a SOFC system based upon stack power capacity (at 0.7 V/cell) and stack specific power density. For design purposes, a power density of 0.450 W/cm² at 0.7 V/cell is used. From **Figure 8.1.3-3**, this results in 100 cells required for a 3 kW Diesel APU. The DPS3000-D will require development of SOFC stacks with between 40 and 50 cells each.

8.1.4 Develop Power Architecture and Electronics Design

The application requirements of the North-American Heavy-Duty Truck platform dictate a 12 VDC nominal system output. The Delphi electrical system mechanization for this application is shown in **Figure 8.1.4-1**. In this mechanization, two SOFC stacks comprised of 40-50 cells each are configured in electrical parallel and fed to a wide-range input, controlled-current output DC/DC converter. This converter has an output voltage range of 9-14.7 VDC, with a nominal steady value of 13.5 V. The converter has a dynamic current limit which may be used to buffer large current demand spikes from the SOFC stacks. The system's internal electrical components are powered with the output of this converter which is attached to the truck electrical system that includes a battery and alternator. The vehicle battery serves as the energy storage device to handle large transient demands of electrical power. Start-up power is supplied to the system from the truck electrical system. The truck engine must operate to supply the start-up power to the APU, but after the APU comes online, the truck engine may be either on or off without impacting the power availability of the APU.

Figure 8.1.4-1: Truck APU Power Architecture

A North-American stationary power/CHP system application requires a nominal 120 VAC power output. The Delphi electrical system mechanization for this type of system is given in **Figure 8.1.4-2**. In this mechanization, the output of the SOFC stacks are fed through an A/C inverter to create the 120 VAC single phase. The A/C inverter does not operate in a controlled-current mode, so a SOFC stack bus support is employed using a storage battery and a boost converter, which creates a voltage floor for the SOFC stack bus and protects against stack under-voltage in the presence of large load transients. Since the SOFC system sensors, actuators, and controller are 12 VDC components, a power converter is employed to create an internal system 12 VDC bus. High power components such as the system blower, recycle pump, and heaters, are powered with the A/C power circuit. Start power is supplied via the electrical grid connection until

such time that the system is online and able to supply power to the grid. Grid synchronization would be part of future development for this APU system.

Figure 8.1.4-2: Stationary Power Architecture

Delphi has specified and procured power converters to support development for the North-American Heavy Duty Truck and North-American Stationary/CHP application. The converters for producing the regulated system output power are shown in **Figure 8.1.4-3**. Each converter is rated at 3 kW continuous output. In order to serve a full-scale 3kW net application, the converters needed to have increased capacity to 4 kW.

- **Stack Power Bus to 12 VDC Buck Converter**

- Wide input voltage range (24-63V)
- 3 kW Rated Output (250 A @ 12 VDC)

- **Stack Bus DC/AC Inverter**

- Wide input voltage range (24-63V)
- 3 kW Rated Output.
- >90% efficiency

Figure 8.1.4-3: System Power Electronics

8.1.5 Develop System Design and Perform Optimization

Delphi worked on developing two new Diesel system designs, shown in **Figure 8.1.5-1**. The first was an upgrade of the SPU 1D level prototype, which was designed for natural gas, to SPU 1E, which was zero-sulfur Diesel fuel compatible. This upgrade required

the addition of a pair of Delphi fuel injectors, a pair of fuel vapor carrier air valves, and a high-pressure reformer air pump. This system utilized the same Gen 4.2 T CPOx fuel reformer as used in the natural gas application. Anode tail gas recycle is used in the system to reduce catalyst temperatures in CPOx operation and to introduce water vapor to the reforming process to reduce carbon formation. The system package was increased in length by 125 mm to handle the additional content. In this system, the fuel pump and output power electronics are external to the system package. This system is restricted to zero-sulfur Diesel fuel since a hot-reformate desulfurization sorbent is not being packaged in the system.

Figure 8.1.5-1: Delphi Diesel APU Systems

Detail of the SPU 1E system assembly is shown in **Figures 8.1.5-2 and 8.1.5-3**. The initial integration and operation of the reformer on Diesel fuel was successful.

Figure 8.1.5-2: Delphi SPU 1E Diesel System

Figure 8.1.5-3: Delphi SPU 1E Diesel System Detail

The external dimensions of the DPS3000-D system are representative of a comparable output commercial Diesel internal combustion generator sets. The extended package is required to allow for the packaging of power electronics, desulfurizer, Diesel fuel handling subsystem, and also to accommodate larger SOFC stacks (2 x 50-cell) in an isolated thermal enclosure which optimizes the thermal stack environment. The layout of the DPS3000-D system is shown in **Figure 8.1.5-4**.

Figure 8.1.5-4: DPS3000-D General Layout Features

Additional features of the system design are shown in **Figure 8.1.5-5**. The SOFC stacks are isolated from the remaining the SOFC plant in a separate thermal enclosure.

This reduces the interaction and radiant heat transfer between the surface of the stacks and other system components. Additionally, the stack enclosure insulation is vented so that active cooling air can be used to pull additional heat out of the SOFC stacks during high-load operation.

Figure 8.1.5-5: DPS3000-D Cut-away View 1

The reformer shown in the design is an endothermic reformer based upon the Gen 5.1T reformer design. The system combustor is positioned coaxially with the reformer reactor to reduce heat loss and improve endothermic reforming performance. A single-layer, cast, Integrated Component Manifold (ICM) is used to route gas flows throughout the system while reducing system cost.

A second cut-away view is shown in **Figure 8.1.5-6**. In this view, an integrated heat exchanger assembly is shown. This heat exchanger integrates cathode air preheat, recycle cooling, and reformate cooling functions. The design is adapted from Delphi's current high-volume automotive heat exchanger product line. The heat exchanger is constructed from stamped plate assemblies, die-formed fin centers, and high temperature braze operations developed at Delphi.

Figure 8.1.5-6: DPS3000-D Cut-away View 2

The SPU 2 natural gas system was in the hardware integration stage, and the Hot-Zone Module Assembly is shown in **Figure 8.1.5-7**. This system employed 4x30-cell Gen 3.2 SOFC stacks in a parallel-series electrical, and flow configuration. It was targeted to produce 5 kW net at over 40% system efficiency.

Figure 8.1.5-7: SPU2 Hot-Zone Module Assembly

8.1.6 Develop System Controls

Delphi control development continued in several areas including:

- Simplification and streamlining of software algorithms to improve reliability and function
- Addition of fault-code reporting and history to improve diagnostic function
- Implementation of Diesel system reformer control functionality
- In initial integration of system dynamic plant model and hardware-in-the-loop (HIL) function

The hardware-in-the-loop (HIL) development system is described in **Figure 8.1.6-1**.

- Entire SOFC System Dynamic Plant Model running in Real-Time
- Simulator translates plant model outputs to real electrical inputs to the system controller.
- Full diagnostic feedback and overrides available
- Control algorithm development and testing
- Fault injection to test safety and diagnostic functions on controller and software

Figure 8.1.6-1: Hardware-In-Loop Simulator

In this simulator, Delphi's Simulink-based dynamic SOFC system plant model operated inside the Opal-RT simulator. The simulator received electrical control commands from the system controller and translated these into plant-model inputs. The plant-model outputs were translated by the simulator to analog, digital, and PWM outputs that are read by the system controller. This creates an environment where the system software and controls may operate under very realistic conditions without having to operate a real SOFC system. This functionality allows for more-rapid software and electrical interface development, as well as an automated system for testing the fault-handling capability of the software and controller hardware.

8.1.7 System Performance Testing

For SECA Phase I, Delphi met the 3 kW power target by achieving a peak net output power of 4.24 kW by combining the operation of two SPU 1B SOFC systems with output of approximately 2.1 kW each. These systems combined had a peak efficiency of 36%.

A dramatic increase in power and efficiency performance was demonstrated in Phase II. The 3 kW net power target and 35% efficiency target was met with a single SPU 1 unit using methane as a fuel.

Under high-load operating conditions, where greater than 80% of the fuel is being internally reformed in the SOFC stacks, it was observed that the inlet edge of the stacks tended to run too cold and the outlet edge too hot. The low temperature region at the inlet resulted in a lower overall voltage and power of the stack at a given electrical load. The high temperature region at the outlet of the stack limited the maximum electrical load that could be applied before overheating the stacks.

A modification to the SOFC stack manifold was made that allowed for an internal reversing of the anode-side flow in the stack without requiring any change to the system design or ICM configuration. With this change, the anode and cathode were oriented in counterflow. During high-load operation, the internal reforming endothermic heat load was shifted to the hot cathode outlet side of the stack. This helped to cool the cathode outlet edge of the stack, and increase the cathode inlet edge temperature as well because heated anode tail gas is redirected toward the cathode inlet edge of the stack. The improved temperature profile of the SOFC stack resulted in an increase in power of the system as shown in **Figure 8.1.7-1**.

Figure 8.1.7-1: SPU 1D – Set 6 System Performance with Counterflow Stacks

8.1.8 System Reliability Testing

During the first two quarters of 2007, thermal cycling and continuous durability tests were conducted on SPU 1 systems using local utility supplied natural gas (Rochester

Gas & Electric) and a gaseous fuel desulfurizer sorbent from TDA. The Set 5 SPU 1 system was operated for 1423 hours in CPOx reforming mode with utility-supplied natural gas that was externally pressurized to 240 kPa and supplied to the inlet of the system. The feed gas was sampled post desulfurizer periodically and verified to be less than 10 ppb by volume H_2S . During this test, the internal parasitic loads in the system were externally powered, and a constant current load was applied to the stacks via an external load bank. This configuration was done to improve the overall stability of the stack current, and made the measurement of stack power degradation more accurate.

The resulting system (stack) power degradation performance is shown in **Figure 8.1.8-1**. The results are shown along with Phase I system performance (Set 2 and Set 3) on methane fuel with zero sulfur content. Set 2 and Set 3 were operated at constant system output current. Since parasitic loads tend to vary slightly over time, stack current was not as steady during these tests, and this added complication to the measurement of power degradation. The points shown in **Figure 8.1.8-1** are selected so as to be within ± 0.5 amps from a nominal current. From **Figure 8.1.8-1**, it appears that SPU 1 system power degradation on utility supplied natural gas fuel is consistent with demonstrated system performance on pure methane.

Figure 8.1.8-1: SPU 1 Power Degradation at Constant Stack Current

Additional degradation performance testing was conducted on Delphi's Set 00 development system shown in **Figures 8.1.8-2 through 8.1.8-5**. This system was constructed with a Gen 4.2 T CPOx fuel reformer, 2 x 30-cell Gen 3.1 SOFC stacks, Delphi standard SOFC system controller, and an enhanced high-pressure process air system. The system was constructed such that SOFC stacks and fuel reformer were in

isolated thermal enclosures, and an electric furnace was used to regulate stack in-feed temperatures. It should be noted that the SOFC stacks were operated outside of the furnace to better represent the intended system operating environment.

Figure 8.1.8-2: Set 00 Development System (Natural Gas Configuration)

**Figure 8.1.8-3: Set 00 Development System (Natural Gas Configuration):
Fuel Reformer**

Figure 8.1.8-4: Set 00 Development System (Natural Gas Configuration): Process Air System

Figure 8.1.8-5: Set 00 Development System: Control Cabinet

The Set 00 development system in the natural gas configuration was operated for 1006 hours on utility supplied natural gas using a gaseous fuel desulfurization sorbent from TDA. The stacks were loaded directly with an external load bank and held at a constant current load of 29.5 amps.

The resulting power degradation performance of this system is shown in **Figure 8.1.8-6**. This system demonstrated excellent power stability over the 1006 hour period. The overall degradation rate of the two stacks was 0.84% per 500 hours, which met the Phase II performance target of 1% per 500 hours. The stacks showed different degradation rates during the test. The cell voltage distributions of the two stacks are shown at the beginning and end of the durability test in **Figures 8.1.8-7 and 8.1.8-8**.

Figure 8.1.8-6: Set 00 Natural Gas Durability Test

Figure 8.1.8-7: Set 00 Natural Gas Durability Test: Stack 534 Voltage Distribution

Figure 8.1.8-8: Set 00 Natural Gas Durability Test: Stack 535 Voltage Distribution

Stack 534 exhibited a fairly uniform degradation rate across all cells. The composite degradation is 1.22% per 500 hours. Cell 1 had a low cell voltage at the start of the test, and it had the largest degradation rate in the stack. Stack 535 had an overall lower degradation rate of 0.46% per 500 hours. The degradation rate for all cells were calculated using a linear regression of the cell voltage during the degradation test. The results are shown in **Figure 8.1.8-9**. Cells 1, 19, and 21 were low power in the stack, but had an uncharacteristically high recovery rate during the durability test. Autopsy analysis of the stacks is pending.

Figure 8.1.8-9: Set 00 Cell Voltage Degradation Rates

With Delphi's new GF (Glass Fiber) seal technology in the stack, increased thermal cycle durability was made possible. Small scale stacks with this seal were able to successfully complete over 50 cycles. To test seal performance at a full-scale, an SPU 1D system, Set 6, was configured with 2x30-cell SOFC stacks with the GF seals, and cell voltage monitors to help detect leaks. The Set 6 system with the added stack voltage leads is shown in **Figure 8.1.8-10**

Figure 8.1.8-10: Delphi SPU 1 Natural Gas System (Set 6)

This system was operated with a CPOx reformer on utility-supplied natural gas with an external TDA desulfurizer sorbent. The system was thermally cycled following the profile shown in **Figure 8.1.8-11**. The start-up time from a cold-start to normal operation is approximately 3.5 hours. A small load of 15 amps was held on the stacks for 3-4 hours, and then a normal shut-down is performed. A full cool-down to room temperature, with 30 liters per minute of reducing gas concluded the 24 hour test cycle.

Figure 8.1.8-11: Delphi SPU 1 Natural Gas System (Set 6): Thermal Cycle Profile (2 shown)

31 thermal cycles were performed with good temperature and control repeatability and moderate power stability. The resulting temperature profile data for the 31 cycles is

shown in **Figure 8.1.8-12**. In general, the onset of internal seal leaks results in uncontrollable stack outlet temperatures during the warm-up period, or during the normal power output period. The open-circuit voltage of the stacks has shown good stability over the duration of this test. The open-circuit voltage data of the stacks at the end of the start-up period is given in **Figure 8.1.8-13**.

Figure 8.1.8-12: Set 6 Thermal Cycling Results: Temperature Profiles

Figure 8.1.8-13: Set 6 Thermal Cycling Results: Open Circuit Voltages

8.2 Task 2: Stack Development

8.2.1 Design Stack

The Gen 3.2 cassette (**Figure 8.2.1-1**) retains the same footprint and thickness as the Gen 3.1 cassette, allowing the use of the same manifold, glass seals, current collectors, stack load frame, and all internal cassette components. The differences are the picture frame (**Figures 8.2.1-2 and 8.2.1-3**), and the separator plate (**Figures 8.2.1-4 and 8.2.1-5**). The picture frame is now the formed part. Two distinct advantages were realized by making this change. The first being the bypass channel can be filled with glass paste prior to welding the cassette. The second advantage to this configuration is the “out-of-flat” condition of the welded assembly should be minimized due to the location of the cell in relation to the perimeter weld.

Figure 8.2.1-1: Gen 3.2 Cassette

Figure 8.2.1-2: Gen 3.2 Cassette Picture Frame

Figure 8.2.1-3: Gen 3.2 Cassette Picture Frame

Figure 8.2.1-4: Gen 3.2 Cassette Separator Plate

Figure 8.2.1-5: Gen 3.2 Cassette Separator Plate

8.2.2 Develop High Performance Cathode

The cathode development work focused on addressing cathode robustness to delamination observed in stack tests. Analysis of the cell manufacturing process isolated the cathode paste manufacturing at our supplier as the root cause for this failure mode and an alternate manufacturing route has resolved the issue. Structural and mechanical evaluations along with an accelerated test have been developed that reproduces this failure mode in a non-electrochemical environment. These tests were successful in duplicating the failure mode outside of the stack tests and have helped validate the new paste developments.

Delphi worked with Carnegie Melon University (funded by SECA Core) for detailed evaluation of LSCF cathodes in Delphi cells. Cell samples which were operated up to 4600 hours in the system were investigated by Professor Paul Salvador's group using TEM (Transmission Electron microscopy) and FIB (Focused Ion beam) for understanding degradation mechanisms in cathodes.

8.2.3 Develop High-Performance Anode

One of the primary efforts on the anode development task was focused on improving the H₂S tolerance of our current anode supported cells. Work in 2007 was primarily focused on infiltration of additives into the Ni-YSZ anode supported structure. Initial infiltration testing of selected materials into the current cell structure showed significant limitations in regards to selected infiltrates being applied at the triple phase boundaries of the anode. In order to improve the screening process for the selected elemental infiltrates, an electrolyte supported cell was employed in which the active anode composition was screen-printed onto a ~300μm thick 8.0 mole % Y₂O₃ doped zirconia electrolyte. Delphi's active anode composition was screen-printed to yield a 20-30 μm print of our active anode composition (50 vol% Ni in reduced anode) after sintering at 1375°C for 2 hours in order to simulate our anode supported conditions. Key to the usefulness of these electrolyte supported experiments is that the H₂S response shows the same behavior as observed in our anode supported cell tests. **Figure 8.2.3-1** shows that while the power density of the electrolyte support cells are significantly lower than the standard anode supported cells (0.2W/cm² vs. ~0.8W/cm² for anode supported), both the magnitude of the 1st stage degradation and the degree of 2nd stage degradation were similar when tested at 0.7V under 1.0 ppm H₂S and 750°C.

Figure 8.2.3-1: Comparison of 1.0 ppm H₂S behavior of anode and electrolyte supported cells. Initial power for electrolyte supported cell ~ 200 mW/cm² vs. ~750mW/cm² for anode supported cells.

Infiltration studies were carried out by preparing 1.0 mole/kg aqueous solutions from nitrates and chlorides of Ce, Pr, Ru, Ru+Ce, and Cu. The samples went through multiple cycles of room temperature infiltration and drying at 600°C until ~ 2 wt% infiltration was achieved. The cells were tested in a standard button cell test stand with a 48.5% H₂/48.5% N₂/3% H₂O fuel mixture. The cells were operated at a constant 0.7V for ~ 100 hrs prior to introduction of 1.0 ppm H₂S. The key metrics were: Impact of infiltration on initial power; degree of 1st stage degradation; and 2nd stage degradation rate reported in %/hr. **Figure 8.2.3-2** shows the key data of each of the infiltrated materials along with the baseline performance of the non-infiltrated cell. Baseline cells start out with a power densities ~ 180 mW/cm² under the previously described conditions and retain ~ 66% of the initial power 10 hrs after introduction of 1.0 ppm H₂S.

The second stage degradation rate for this baseline case is 0.017%/hr. Infiltration with a Ce containing solution was observed to lower the initial power by 40% but the cell also retained ~ 88% of that lower initial power. The second stage degradation was slightly higher at 0.026%/hr. The biggest improvements observed were with incorporation of the Pr alone and with a combination of Ru+Ce. In both cases, the initial power is not impacted by the incorporation of the infiltrated species and the power retained after introduction of 1.0 ppm H₂S is roughly 90% of the initial power. The second stage degradation rate for the Pr does appear to be double of the baseline at 0.047%/hr. The initial 2nd stage degradation rate of the Ru+Ce infiltration is also higher than the baseline 0.030 %/hr during the first 60 hrs of operation; however, the 2nd stage degradation stabilizes with extended testing at 0.001%/hr. Our current research efforts are focused

on optimizing the microstructure of the anode supported cells to enable infiltration in a manner that is consistent with current manufacturing methods.

Figure 8.2.3-2: Summary of electrolyte supported H₂S testing. Effect of selected infiltrates on 1.0 ppm H₂S tolerance

8.2.4 Development Cell Fabrication Techniques

Cell fabrication process development continued to be a key focus of ongoing efforts in the development of the solid oxide fuel cell system. Continued progress has been made in ceramic tape formulation development, scaling up material improvements with industrial suppliers, and efficiently producing more consistent cells. Key process improvements were made in the area of producing flatter cells with a reduced degree of cell edge curl. This was achieved by closely monitoring incoming raw materials as well as reduced part to part variability through the initial bi-layer firing operations. Also, much focus was put on improving the cell fabrication process by implementing the fundamental principles of the Delphi Manufacturing System Design (MSD) and gaining improved control of each manufacturing step of the cell fabrication process. A manufacturing quality system has been developed and implemented at Delphi for the production of solid oxide fuel cells. This system currently supports low volume production of cells, but has all the elements to support the scale up to mass production of the fuel cell product.

8.2.4.1 Gen 3.1 Solid Oxide Fuel Cell Description

Photographs of the Delphi Gen 3.1 planar anode supported cell and 30 cell stack assembly are shown in **Figure 8.2.4-1** while the primary components of the multi-layered structure of the cell are illustrated in the schematic shown in **Figure 8.2.4-2**. The SEM micrograph, shown in **Figure 8.2.4-3** provides an image of the microstructure of multiple layers of the fired ceramic cell consisting of the electrolyte (~10 microns), active anode (~10 microns), bulk anode (~500 microns), interlayer (~4 microns) and

cathode (~30 microns). The anode backing layer, bulk anode, active anode, and electrolyte layers are all produced by the tape casting forming process. These tapes are stacked, laminated and co-fired to form the ceramic bilayer. The interlayer, cathode, and cap layer are produced by screen printing, drying, and sintering onto the pre-fired bi-layer. Recent standard button cell data generated with a button of 2.5cm² active are shown in **Figure 8.2.4-4** and **Figure 8.2.4-5** with a stable cell power density of nearly 900mW/cm² at 750deg.C, 0.7V, and 50H2:50N2.

Gen 3.1 Cell

Generation 3.1 30-cell stack
 (2.5 liters, 9 Kg)

Figure 8.2.4-1: Gen 3.1 Solid Oxide Fuel Cell and 30 Stack

Figure 8.2.4-2: Gen 3 Solid Oxide Fuel Cell

Figure 8.2.4-3: Gen 3 Solid Oxide Fuel Cell Microstructure

50H2:50N2, 750degC, 0.7V
 Active Area: 2.5cm²

Figure 8.2.4-4: Recent Gen 3 Button Cell Characterization

50H2:50N2, 750degC, 0.7V
 Active Area: 2.5cm²

Figure 8.2.4-5: Recent Gen3 Button Cell Characterization

8.2.4.2 Ceramic Tape Formulation Development

Material development efforts continued to focus on implementing an improved tape cast film formulation for the bulk anode, designated as formulation MP. The transition of scaling up from laboratory size quantities of tape to commercially supplied, high volume / high quality tape required cooperation and combined efforts between Delphi and a commercial supplier of tape. The MP bulk anode tape was successfully cast by the tape supplier and is currently undergoing evaluation. The benefits of the formulation are summarized below:

- MP material set is much tougher and more robust to handling
- Different binder/plasticizer/solvent system
- Risk of thin tape defects (electrolyte, active, backing) is greatly reduced
- MP material set is easier to process
- Improved dispersion decreases milling from 24 hours to 5 hours
- Much easier to cast and clean
- Greatly reduced susceptibility to aging
- MP material set allows for cost reductions
- Drying rate allows continuous casting of thin tapes on small, cheap tabletop casters
- Designed to be cast on paper (large savings vs. Mylar)
- Can cast new bulk anode much thicker for fewer layers in final cell
- Reduced bulk anode stack from 3 to 2 layers has been demonstrated, 3 to 1 is realistic
- MP formulations are cheaper and greener
- Can roll laminate (eliminating indirect material costs and operations)
- MP formulations are designed for roll lamination
- Allows for common processing and material sets for UTRC (large footprint) and Delphi (small footprint) cells
- Allows for better lamination quality
- Can get high temperature (~150C) melting of binder/plasticizer system
- Less contamination forecasted
- Allows for commonality with PNNL processing and material set
- MP formulations better matched for shrinkage than standard formulations
- Potential for improved electrolyte density and a decrease in sintering temperature.

A comparison of measured properties of cells made from the MP formulation and standard Gen 3.1 cells are shown in **Figure 8.2.4-6**. An SEM micrograph of the MP formulation bulk anode is shown in **Figure 8.2.4-7** after being co-fired with standard active anode and electrolyte layers. The next step is to transfer the fundamental formulation changes of the bulk anode to the active anode, anode backing layer, and electrolyte to obtain a bilayer structure with a highly compatible and optimized organic system for the complete bilayer. From the micrograph, very good bonding was achieved when using the MP formulation anode in the co-fired product.

Property	Units	Standard Material Set	MP Material Set
Cell Power Density	mW/cm ²	990 +/- 87	942
Bilayer Mechanical Strength	MPa	118 +/- 4	126
Bulk Anode Permeation	Seconds	39 +/- 1	20 +/- 1
Bulk Anode Porosity (MIP)	%	21.2	21.8
Bulk Anode Mean Pore Diameter	Microns	0.25	0.34
Bulk Anode Linear Shrinkage	%	15	20
Active Anode Linear Shrinkage	%	21	21
Electrolyte Linear Shrinkage	%	21	21

Figure 8.2.4-6: Measured Properties of Standard vs MP Material Sets

Figure 8.2.4-7: SEM Microstructure of MP Bulk Anode Material Set

The commercial tape supplier cast a production trial of standard width bulk anode tape (~ 8 inches wide) and a production trial of a wider version of bulk anode tape (~13 inches wide) with the MP formulation and delivered to Delphi for evaluation.

Delphi completed the validation process of implementing a new carbon black, poreformer material into the bulk anode tape formulation. The need for a new carbon pore-former was due to the discontinuation of a commercially available material. Tape with the replacement carbon (*modified carbon material set*) was cast at the commercial supplier and supplied to Delphi for evaluation. Validation of the tape with the new carbon black consisted of making and characterizing bi-layers, fabricating full size cells, and performing electrochemical tests in the solid oxide fuel cells stack at the 30 cell level. Performance tests included initial IV curves, durability, and thermal cycling.

8.2.4.3 Cell Scale-up

In order to scale up Delphi's capabilities for fabricating "larger" footprint cells, a number of equipment modifications/changes were implemented into the cell fabrication process. A new screen printer was installed at Delphi for the purpose of being capable of making larger footprint cells. As a rule of thumb for good, high volume printing practice, controllable printing dimensions should be less than one third of the frame dimensions. The new screen printer utilized screen frames as large as 20" X 20" accompanied by increased squeegee travel length to aid in very well controlled print dimensions.

Delphi continued to produce cells fabricated with isostatic lamination equipment. The isostatic laminator used was capable of fabricating bilayers with fired areas of up to approximately 450 cm² (cell active area is projected to be about 300 - 350 cm²). The bilayer size is limited by the dimensions of the pressure vessel. In order to fabricate cells of larger footprint, the lamination process needed to be changed to a continuous, roll lamination process capable of handling wider rolls of tape. Initial trials were conducted to determine the feasibility of laminating wider rolls of tape cast film on a continuous roll laminator using the current material set.

8.2.4.4 Cell Fabrication Process Improvements

The following improvements to the manufacturing process were implemented:

- Delphi advanced manufacturing engineers completed documentation of standardized work instructions to provide improved repeatability of the cell fabrication process.
- Statistical control limits on all firing operations were implemented.
- Process control charts for the laser scribing process were implemented to ensure that cell dimensions remain within acceptable operation limits.
- Along with process temperature control rings, additional thermocouples were implemented that can track firing conditions to peak sintering temperatures and allow for firing process optimization and variability reduction.

8.2.4.5 Implementation of Manufacturing System Design

Manufacturing system design (MSD) is a disciplined method of utilizing product, process, equipment, operating system and plant performance data to design and evaluate new and revised manufacturing system concepts. The manufacturing system

design for Delphi is made up of several key components as shown in **Figure 8.2.4-8**. These components include:

- Technical Requirements
- Product Definition
- Process Definition (Includes process flow diagram, PFD)
- Failure Mode Analysis (PFMEA)
- Control Strategy (Control Plan, Error Proofing)
- Manufacturing (Process Monitoring, Standard Cell & EOP, Layered Audit)

Figure 8.2.4-8: Manufacturing System Documentation

Figure 8.2.4-9 provides a general *process flow diagram (PFD)* for the basic cell fabrication process. As part of Delphi's manufacturing system design, work instructions were clearly documented in detail to assure proper procedures are followed. Over 90% of the work instructions for the cell fabrication process steps were completed and available to the operators of each process step.

Figure 8.2.4-9: Basic Cell Fabrication Processes

Delphi has completed and documented the *process failure mode and effects analysis (PFMEA)* for the manufacturing process, along with the *process control plan (PCP)*. A *process monitoring form* has also been established that provides working specifications, control limits, and documented process changes for the cell fabrication process.

Project gate charts are being fully utilized and updated weekly as well. These gate charts track the standard build of parts and record product fallout. The defects are identified along with the failure mode and recorded for statistical analysis. Information from gate charts that track defected parts also gets reported in the form of a Pareto Chart.

8.2.5 Fabrication Developmental Stacks

One of the developmental tasks on this effort focused on optimizing the seal heights for fiber loaded glass seals currently being developed for improved thermal cycling. Glass seal materials are formed into a “gasket” between each repeat cassette. This gasket is prepared via a tape casting operation and consists of the powdered glass component and a flexible binder system (PVB). During stack assembly the binder system is vaporized before the glass-ceramic seal is formed via nucleation and crystallization of the glass melt. Fiber additions to glass-ceramic seal designed to improve the seal strength and improve thermal cycling ability, impact both the nucleation and crystallization of the glass ceramic seal as well as the final height of the seal. In order to determine the effect of fiber additions on the resulting seal thickness, an experimental

matrix was established focused on % fiber content, heating rate through the glass crystallization region, and hold time at the glass sealing temperature.

Testing was done with a Perkin-Elmer Thermal Mechanical Analyzer (TMA) using the same physical load and thermal profiles encountered during stack assembly. A representative family of curves is shown in **Figure 8.2.5-1** for 7.5 and 45 wt% fiber loadings at heating rates of 1°C/min and 3°C/min from 600°C to 850°C. After heating to 850°C, the samples were then held for up to 4 additional hours. In **Figure 8.2.5-2**, we observe that in addition to the 25% reduction in seal height due to the increased fiber loading, there is a consistent difference in seal behavior as a function of heating rate as the isothermal hold temperature of 850°C is approached. Samples heated at 1°C/min reach a maximum compression even before the isothermal hold segment is reached, whereas samples heated at 3°C/min show an increased amount of compression. This effect is more clearly seen in **Figure 8.2.5-3** where the change in seal thickness is plotted vs hold time at 850°C. A 3°C/min heating rates results in an additional ~ 10% compression of the glass seal over the standard 1.0°C/min. The increased heating rate inhibits crystallization of the ceramic component, retaining a larger percentage of glass at higher temperatures which can then be compressed further by the applied load. **Figure 8.2.5-3** compares the seal thicknesses at 1°C/min and 3°C/min across multiple fiber loadings and shows; that as a general rule of thumb, we can achieve an additional 10% compression with the increased heating rate.

Figure 8.2.5-1: Final glass-ceramic seal height as a function of heating rate and fiber content. Heating rate changed between 600°C and 850°C sealing temperature

Figure 8.2.5-2: Final glass-ceramic seal height as a function of heating rate and fiber Content. Additional compression observed with higher heating rate

Figure 8.2.5-3: Final glass-ceramic seal height as a function of fiber content for both 1°C/min and 3°C/min heating rates. Results show ~ 10% additional compression for each fiber loading with the increased heating rate

5-cell stacks were fabricated for testing the effects of H₂S. **Figure 8.2.5-4** shows data from a 5-cell stack tested on simulated diesel reformat (28% H₂, 30% CO, 6% H₂O, rest N₂) and 2.5 ppmv H₂S. The stack was initially operated at constant current of 570 mA/cm² for 100 hours. 2.5 ppmv of H₂S was added to the stack. A rapid drop of power

(26%) was observed, as expected, from poisoning of the anode. The stack current density was reset to 190 mA/cm^2 to bring the voltage back up and the stack was evaluated for steady state continuous durability. The stack ran for 3600 hours showing no degradation and the test was stopped intentionally for facilities upgrade.

Figure 8.2.5-4: Data from 5-cell stack tested with simulated diesel reformat and 2.5 ppmv H₂S

5-cell stacks with improved cells were also evaluated for steady state continuous durability. **Figure 8.2.5-5** shows data from stack tested at 570 mA/cm^2 with 35% H₂, 30% H₂O, rest N₂ fuel at 750°C at 50% fuel utilization. The stack showed no degradation in 1300 hours.

Figure 8.2.5-5: Data from 5-cell stack tested for durability

Delphi developed a specialized test stand for thermal cycling that mimics heat-up of stacks as in the system. This thermal cycling test stand was used to evaluate

performance of stacks. A 28-cell stack with improved seals and cells is being thermally cycled in this stand (see **Figure 8.2.5-6**). After 7 thermal cycles the stack showed virtually no degradation in power (450 mW/cm^2 @ 570 mA/cm^2).

Figure 8.2.5-6: Data from 28-cell stack being thermally cycled

8.2.6 Evaluate Stack Performance

30-cell stacks continued to be built with excellent performance and minimal cell-to-cell variation. **Figures 8.2.6-1** and **8.2.6-2** show a 30-cell stack with excellent power density (at 60 Amps) and 0.04 Volts cell to cell variation.

Figure 8.2.6-1: Data from 30-cell stack

Figure 8.2.6-2: Data from 30-cell stack - cell to cell voltage

8.3 Task 3: Reformer Development

8.3.1 Develop Endothermic Reformer

8.3.1.1 Endothermic Reactor Development

8.3.1.1.1 Gas Phase Combustor (GPC) Overfueling Impact

Reformer testing worked toward getting the exact environment and inputs seen by a reformer in systems applications. A major improvement was the addition of combustor reactant heaters. These are high power heaters (18kW) for the ~12 g/s of Cathode air and ~5kW for the ~1.5 g/s of GPC fuel. This allows both GPC fuel (a.k.a. combustor fuel) in the form of ATG (anode tailgas) and CTG (Cathode Tail Gas i.e. Oxygen depleted air) to be delivered to the systems combustor at or near the true temperature experience in the APU/SPU assembly.

Figure 8.3.1-1 lists the latest data collected with un-heated combustor reactants vs. DPS-3000-D requirements. While performance appears good, although not yet meeting requirements, it was collected with inappropriate GPC reactant enthalpies. Prior to heating combustor reactants we delivered higher than specified amounts of GPC fuel (i.e. higher LHV) but at 0.0 kW sensible enthalpy due to the fact that these were at room temperature. Row 6 of **Figure 8.3.1-1** shows the net (chemical LHV) delivered to the combustor. It is evident that this is in excess of the enthalpy specified in the requirements column 4.

	FUEL =	US07 Diesel			
	REFORMER GRP REQTS ID# =	15		15C	
	R,A,M (Reqs, Actuals, Model) =	ACTUALS		REQTS	
	EWO for Data =	C271		DPS3000- D_Rated_Simulink_smk01.xls	
	Data	NOC	Rated	NOC	Rated
1	Average of Gross Ref Efficiency w/o CH4 [-]	1.26	1.14	1.33	1.33
2	Average of Net Ref Efficiency w/o CH4 [-]	1.02	0.97	1.08	1.09
3	Average of RefOut LHV w/o CH4 [kW]	5.87	11.93	6.90	13.79
4	Average of Comb In LHV [kW] Cr,0	10.73	15.02	1.52	3.04
5	Average of Comb In sensible del H [kW] Cr,0,RT => Cr,0,T act	0.00	0.00	4.72	9.55
6	Average of Comb In LHV + sens [kW] Cr,0,T act	10.73	15.02	6.24	12.59
7	Average of Comb Inlet Fuel mdot [g/s]	0.20	0.28	0.66	1.31
8	Average of Comb Inlet Total Air mdot [g/s]	7.90	10.48	4.90	9.87
9	Average of Comb Inlet Fuel temp [deg C]	25	25	792	796
10	Average of Comb Inlet Air Mix temp [deg C]	25	25	792	796
11	Average of Comb Inlet Fuel + Air expected temp [deg C]	750	750	792	796
12	Average of Qref [kW] (+) = heat to CV (-) = heat fr CV	0.48	1.05	1.57	3.09
13	Average of Qchx del H sensible CHx In - CHx Out [kW]	-1.69	-2.59	-1.86	-3.67
14	Average of Q loss Comb del H [kW] Cr,a, RT => Cp,0,TC14	0.63	-0.27	-0.18	-0.25
15	Average of Q loss Comb+Piping del H [kW] Cr,a => Cp,2	-0.67	-0.97	-0.18	-0.25
16	Average of Qloss Reactor [kW] (+) = heat to CV (-) = heat fr CV	-1.19	-1.52	-0.26	-0.53
17	Average of H2O/CH4 ratio [-]	14	2	1226	754
18	Average of C2's sum [molfrac]	0.0002	0.0011	0.0500	0.0500
19	Average of Ref Out CH4 [molfrac]	0.002	0.007	0.500	0.500
20	Average of Ref In temp T12 [deg C]				
21	Average of Reactor Inlet Stream temp T2 [deg C]	741	599	250	250
22	Average of Ref Out at Outlet Flange temp T3 [deg C]	866	880	951	926
23	Average of Reactor Hx Inlet at Flange temp T6 [deg C] Cp,1	1068	1114	986	996
24	Average of Reactor Hx Outlet at Flange temp TC16 [deg C] Cp,3	907	930	713	729
25	Average of Recycle Fraction of ATG [-]			0.45	0.45
26	Average of Recycle Fuel Util [-]			0.60	0.60

Figure 8.3.1-1: Reformer Requirements vs. Actual Pre-Combustor Heated Reactants

This finding launched a concerted effort to further understand the enthalpy and heat transfer flow within our reforming systems (reformer + combustor + insulated box). Data for EWO C271 (columns 1 & 2) were with a mixture of H2 and CH4 as the GPC fuel. This mixture was done for economic reasons to limit use of expensive bottled gases. It does, however, reduce flow on the combustor heat exchange (CHx) path which has some effect on heat transfer. **Figure 8.3.1-2** shows the relationship for recent testing between reforming efficiencies and combustor reactants chemical and “sensible” enthalpies.

Figure 8.3.1-2: Reformer Efficiency & Comb Power

8.3.1.1.2 Gen 5T Reactor in Set00 Configuration - w/ Heated Reactants - Mapping of Recycle Fractions / Utilization

Based on the situation describe above, an effort was launched to understand the effects of system recycle fraction and utilization on reformer performance. Recycle composition and mass flow are very dependent on system operating conditions and parameters optimized to achieve a variety of objectives (e.g. cathode air maximization for stack cooling and or heating, best stack fuel utilization etc.). Both tests in this series (C292 and C295) used the Set 00 Insulation Enclosure which is depicted in various states in **Figures 8.3.1-3** through **8.3.1-5**. This entire reformer enclosure assembly was then tested in the systems lab while connected to electrochemical stacks. The benefit of this approach is that disparities between the systems environment and the reformer lab environment are eliminated.

Figures 8.3.1-3: Zircar Wet-Lay Application

Figures 8.3.1-4: Inside Enclosure

Figures 8.3.1-5: Enclosure on Stand w/ Top

Figure 8.3.1-6 shows various ACTUALS and REQUIREMENTS columns for comparison. Columns 1 and 2 show reformer requirements and columns 3 and 4 show the actual generated from testing when using the inputs as specified in the requirements. Rows 12 and 13 show the values for combustor chemical (LHV) and “sensible” enthalpies, respectively. The “mode” designation now reflects that the reformer is operating in “GPC Limited” mode as we are now constraining combustor “sensible” enthalpy to the requirements value.

		1	2	3	4	5	6	7	8	9
		R,A,M	Ref Data: In-Out- Calc A=actual R=requ E=equil C=calc	Eval. to Reqs =	EW0 for Data	Recycle Fraction of ATG [-]	Recycle Fuel Util [-]	Sub-Test Objective	Mode	
1		REQTS		ACTUALS						
2		RRC		AAC						
3		15C				15D				
4		DPS3000- D_Rated_Simulink_sm k01.xls	C292			C295				
5		0.45				0.325		0.35		
6		0.6				0.5				
7		(blank)		w/ inner insul			0.325 Recycle Fract		0.350 Recycle Fract	
8	Data	NOC	Rated	NOC - GPC ltd	Rated - GPC ltd	NOC	.325 Recycle Rated Point, GPC Limited, 8 g/s Comb mdot	.325 Recycle Rated Point, GPC Limited, 12 g/s Comb mdot	.35 Recycle Rated Point, GPC Limited, 8 g/s Comb mdot	.35 Recycle Rated Point, GPC Limited, 12 g/s Comb mdot
9	Average of Gross Ref Efficiency w/o CH4 [-]	1.35	1.35	0.73	0.83	1.13	1.11	1.10	1.14	1.11
10	Average of Net Ref Efficiency w/o CH4 [-]	1.08	1.09	0.58	0.66	0.90	0.93	0.91	0.93	0.90
11	Average of RefOut LHV w/o CH4 [kW]	6.89	13.77	3.73	8.29	5.75	16.75	16.57	16.57	16.02
12	Average of Comb In LHV [kW] Cr,0	1.52	3.04	1.57	3.14	2.98	6.32	6.32	5.99	5.99
13	Average of Recycle H2O+CO2 Enthalpy [kW]	-2.90	-5.70	-2.90	-5.73	-2.90	-4.41	-4.41	-4.79	-4.79
14	Average of Sum of Recycle Endotherm + Combustor LHV [kW]	-1.38	-2.66	-1.34	-2.59	0.08	1.91	1.91	1.19	1.19
15	Average of Comb In sensible del H [kW] Cr,0,RT => Cr,0,T act	4.72	9.55	0.99	2.42	1.89	5.22	8.09	5.24	8.18
16	Average of Comb In LHV + sens [kW] Cr,0,T act	6.24	12.59	2.56	5.56	4.87	11.54	14.41	11.23	14.16
17	Average of Comb Inlet Fuel mdot [g/s]	0.66	1.31	0.66	1.31	1.25	2.38	2.38	2.22	2.22
18	Average of Comb Inlet Total Air mdot [g/s]	4.90	9.87	1.00	2.50	1.80	5.62	9.62	5.78	9.78
19	Average of Comb Inlet Total mdot [g/s]	5.56	11.19	1.66	3.81	3.05	8.00	12.00	8.00	12.00
20	Average of Comb Inlet Fuel temp [deg C]	792	796	346	393	391	411	408	384	385
21	Average of Comb Inlet Air Mix temp [deg C]	792	796	703	701	702	702	702	712	713
22	Average of Comb Inlet Fuel + Air expected temp [deg C]	792	796	750	750	750	750	750		
23	Average of Qref [kW] (+) = heat to CV (-) = heat fr CV	1.57	3.09	-1.78	-2.37	0.15	1.02	0.44	1.14	0.54
24	Average of Qchx del H sensible CHx In - CHx Out [kW]	-1.86	-3.67	-0.63	-1.29	-1.26	-2.21	-1.92	-2.22	-1.95
25	Average of Q loss Comb del H [kW] Cr,a,RT => Cp,0,TC14	-0.18	-0.25	-0.41	-0.62	-0.59	-0.90	-0.40	-0.93	-0.45
26	Average of Q loss Comb+Piping del H [kW] Cr,a => Cp,2	-0.18	-0.25	-0.67	-0.85	-1.01	-1.00	-0.33	-1.02	-0.46
27	Average of Qloss Reactor [kW] (+) = heat to CV (-) = heat fr CV	-0.26	-0.53	-2.41	-3.65	-1.10	-1.17	-1.46	-1.05	-1.39
28	Average of C2's sum [molfrac]	0.0000	0.0000	0.0194	0.0183	0.0066	0.0003	0.0004	0.0003	0.0010
29	Average of Ref Out CH4 [molfrac]	0.000	0.000	0.018	0.021	0.012	0.003	0.004	0.004	0.005
30	Average of Ref In temp T12 [deg C]			206	250	220	264	274	252	263
31	Average of Reactor Inlet Stream temp T2 [deg C]	250	250	573	648	618	521	558	469	484
32	Average of Ref Out at Outlet Flange temp T3 [deg C]	951	926	793	891	868	967	935	918	894
33	Average of Reactor Hx Inlet at Flange temp T6 [deg C] Cp,1	986	996	968	1049	1058	1131	1039	1102	1016
34	Average of Reactor Hx Outlet at Flange temp TC16 [deg C] Cp,3	713	729	677	791	750	920	913	889	888
35	Average of Space Velocity Reformer STP,void vol [1/hrs]	7470	14932	7488	14960	7488	23326	23329	22572	22570
36	Average of Ht xfer Ratio Qref / Qchx	-0.84	-0.84	2.81	1.83	-0.12	-0.46	-0.23	-0.51	-0.28
37	Average of Ref In Recycle mdot [g/s]	0.540	1.070	0.540	1.070	0.540	1.140	1.140	1.190	1.190
38	Average of Comb AFR actual [-]	7.46	7.52	1.52	1.90	1.44	2.36	4.04	2.60	4.41
39	Average of Comb AFT [deg C]	1012	1014	1265	1215	1299	1226	1061	1200	1047

Figure 8.3.1-6: Recycle Impact on Reformer Performance

Reforming efficiencies (Rows 9, 10) were decreased as a result of reduced enthalpy for heat exchange. Despite having excess enthalpy available in the form of hot cathode air, this air cannot be digested by the combustor without lowering the combustor out temperature. This then lowers heat exchange to the reactor. Row 38 shows the high AFRs existing in the requirements system model.

The result is a lower combustor inlet temperature (Row 33 - T6) to the reactor which is acceptable provided the Heat Exchange ratio (Row 36) is 0.85 or greater. The heat

exchange ratio experienced in recent Gen 5T testing is 0.5 and lower. The essential fix for this is improving the heat transfer from combustor stream (Q_{chx}) to the reformer stream (Q_{ref}). The Heat Exchange ratio is a function of the control volume selected for the reactor.

The control volume shown in red in **Figure 8.3.1-7** was used to analyze and improve the Reactor Heat exchange performance. Given that fuel and air enter the FDU at near room temperature and recycle enters at $\sim 250^\circ\text{C}$ we typically experience T12 temperatures of $\sim 270^\circ\text{C}$. Reactant temperature rises as it passes the T2 thermocouple to $\sim 500^\circ\text{C}$ or greater (see **Figure 8.3.1-8** Row 31). The FDU is shown to have significant heating effect on incoming reactants. Delphi is in the process of recompiling the enthalpy calculations to separately compute the enthalpy rise between T12 and T2 locations (the heating effect of the FDU) so that it is quantified.

Figure 8.3.1-7: Gen 5T Enthalpy Balance Notation

This heat is considered part of the Q loss of the reactor (see **Figure 5.3.1.2.2-4** Row 27) as depicted in **Figure 8.3.1-8**. Recognizing the gap in capability, system modeling was executed to determine revised requirements reflecting lower endothermic load placed on the reformer. **Figure 8.3.1-6**, Columns 6 through 9, represent a sample of the recycle fraction and fuel utilization combinations. Each of these test runs used the specified combustor LHV. Not all the cathode air (and its enthalpy) can be used by the combustor. The effect of limited combustor fueling can be seen by the reduced

reforming efficiencies (columns 9 through 10). The test setup was different for tests C292 and C295 as they used different reactors and C295 benefited from better insulation installation and “fit-up”. C295 also has alumina “kaowool” insulation packed in the voids between the insulated enclosure and the insulated hardware.

Figure 8.3.1-8: Gen 5T Heat & Power Flow

Figure 8.3.1-9 shows another mapping approach employed to understand reactor capability. For each of the four cases shown, the red line represents the combustor capability given the fixed combustor fueling. This shows decreasing temperature as additional air is added for combustion as the combustor runs only on the lean side of stoichiometry. The blue line represents a line of constant reforming performance as represented by constant C2s (in mole fraction equal to specified limit) in the reformer outlet stream. The area between these two curves represents the effective operating window of the reformer given combustor and reforming capability limits. It's clear from the graphs that:

- The two reactors are not identical in performance as the operating window for SN4 at 0.325 recycle is larger than that of SN3, and
- As recycle fraction increase the operating window closes, and for this hardware is effectively limited to 0.35

Reactor = SN3

Reactor = SN4

Figure 8.3.1-9: Reformer Requirements for DPS3000-D (from modeling to date)

Figure 8.3.1-10 through 8.3.1-11 show a schematic view of the enthalpy calculator. This schematic is driven by a spreadsheet where input data is compiled. The schematic is essential in interpreting heat flows in particular losses.

Figure 8.3.1-10: Enthalpy Balance DPS3000-D Requirements – Mode=Rated

Figure 8.3.1-11: Enthalpy Balance C271 Rated

Figure 8.3.1-12: Enthalpy Balance Actuals; Mode=.325 Recycle Rated, 8 g/s GPC Limited

8.3.1.1.3 Insulation Improvement

Figure 8.3.1-13 shows the results of two tests conducted to evaluate the heat transfer of the Gen 5T reactor without reacting flows present. Rows 4 through 6 refer to “w/o

insulation” which corresponds to the configuration shown in **Figure 8.3.1-14** while rows 1 through 3 refer to the configuration shown in **Figure 8.3.1-15**.

Ord	EWO		Test Point ID	T2 Ref Path Inlet Temp [deg C]	T3 alt (ref out tube ave) [deg C]	T3 (reactor reforming path outlet) [deg C]	delta T3alt - T3 [deg C]	T6 (actual) reactor comb/ht exh inlet [deg C]	TC16 (reactor comb/ht exh outlet) [deg C]	Effectiv eness	UA [W/C]	Heat Transfer (Comb/Hx) [W]	Heat Transfer (Ref Path) [W]	Ht xfer Ratio
1	MG733C270	w/ Insul	Idle SS0	331	629	472	157	756	574	0.83	0.51	-924	87	0.09
2	MG733C270	w/ Insul	NOC SS50	256	645	571	74	747	555	0.86	2.33	-1398	433	0.31
3	MG733C270	w/ Insul	Rated SS100	234	532	505	27	614	482	0.86	4.59	-1956	647	0.33
4	MG733C265	w/o Insul	Idle SS0	309	538	379	159	674	485	0.79	0.43	-952	64	0.07
5	MG733C265	w/o Insul	NOC SS50	229	551	487	63	667	474	0.82	1.98	-1396	350	0.25
6	MG733C265	w/o Insul	Rated SS100	183	531	501	30	660	473	0.80	3.61	-2808	739	0.26

Figure 8.3.1-13: Gen 5T Heat Exchange Evaluation

Figure 8.3.1-14: Insulation Cross Section

Figure 8.3.1-15: Insulation Cross Section

Figure 8.3.1-16 shows the effect of the insulation on reforming performance. Rows 1 and 2 clearly show a benefit in reforming efficiencies, particularly at NOC. Qchx (Row 18) and Qloss of the Reactor (Row 21) were both reduced more than 1 kW while Qref (Row 15) Heat transfers to the reforming stream improved by 0.3 to 0.6 kW. This improvement is similarly seen in the lower combustor inlet temperatures (Row 27) required for this improved level of reforming.

		ACTUALS			
		15			
		C261		C271	
		w/o wet layup insul		w/ wet layup insul on reactor	
Data		NOC	Rated	NOC	Rated
1	Average of Gross Ref Efficiency w/o CH4 [-]	1.17	1.12	1.26	1.14
2	Average of Net Ref Efficiency w/o CH4 [-]	0.95	0.92	1.02	0.97
3	Average of RefOut LHV w/o CH4 [kW]	5.74	11.82	5.87	11.93
4	Average of Comb In LHV [kW] Cr,0	9.30	13.42	10.73	15.02
5	Average of Recycle H2O+CO2 Enthalpy [kW]	-1.66	-3.53	-1.69	-4.19
6	Average of Sum of Recycle Endotherm + Combustor LHV [kW]	7.64	9.89	9.04	10.83
7	Average of Comb In sensible del H [kW] Cr,0,RT => Cr,0,T act	0.00	0.00	0.00	0.00
8	Average of Comb In LHV + sens [kW] Cr,0,T act	9.30	13.42	10.73	15.02
9	Average of Comb Inlet Fuel mdot [g/s]	0.17	0.25	0.20	0.28
10	Average of Comb Inlet Total Air mdot [g/s]	8.08	11.35	7.90	10.48
11	Average of Comb Inlet Total mdot [g/s]	8.26	11.60	8.10	10.75
12	Average of Comb Inlet Fuel temp [deg C]	25	25	25	25
13	Average of Comb Inlet Air Mix temp [deg C]	25	25	25	25
14	Average of Comb Inlet Fuel + Air expected temp [deg C]	750	750	750	750
15	Average of Qref [kW] (+) = heat to CV (-) = heat fr CV	0.15	0.32	0.48	1.05
16	Average of QrIn Net del LHV [kW] Rr,0,RT => Rp,0,RT	-0.27	-0.65	0.17	0.06
17	Average of Qr2 sensible del H [kW] Rp,0,T2 => Rp,0,T3	0.42	0.97	0.32	0.99
18	Average of Qchx del H sensible CHx In - CHx Out [kW]	-2.68	-3.76	-1.69	-2.59
19	Average of Q loss Comb del H [kW] Cr,a, RT => Cp,0,TC14	2.25	3.22	0.63	-0.27
20	Average of Q loss Comb+Piping del H [kW] Cr,a => Cp,2	1.34	2.33	-0.67	-0.97
21	Average of Qloss Reactor [kW] (+) = heat to CV (-) = heat fr CV	-2.49	-3.40	-1.19	-1.52
22	Average of C2's sum [molfrac]	0.0001	0.0015	0.0002	0.0011
23	Average of Ref Out CH4 [molfrac]	0.001	0.006	0.002	0.007
24	Average of Ref In temp T12 [deg C]				
25	Average of Reactor Inlet Stream temp T2 [deg C]	649	601	741	599
26	Average of Ref Out at Outlet Flange temp T3 [deg C]	289	388	866	880
27	Average of Reactor Hx Inlet at Flange temp T6 [deg C] Cp,1	1115	1165	1068	1114
28	Average of Reactor Hx Outlet at Flange temp TC16 [deg C] Cp,3	863	915	907	930

Figure 8.3.1-16: Effect of Improved Reactor Insulation: C261 vs C271

8.3.1.1.4 POx Operation of Gen 5T

During the initial shakedown of the Gen 5T on US07 Diesel a preliminary POx operation test was conducted. The objective of the test was to run the reactor in the 2 modes (idle and system warm up) that require POx operation (i.e. no recycle available). During these periods, temperature management of the reformer inlet was taxed due to the fact that the system combustor was still operating and its stream must still be routed through the endothermic reformer. Therefore, Delphi was unable to turn off the heat transfer to the reactor but rather must manage combustor operation to limit and/or pull heat from the POx reforming reaction. **Figure 8.3.1-17** shows results of all testing.

Figure 8.3.1-17: Gen 5T POx Operation – Flame Arrestor Effect

Testing was conducted at both idle fuel flows (0.066 g/s) and SWU fuel flows (0.400 g/s). The first observation was that T2 temperatures were uncomfortably high at ~1000C. Varying O/C and altering combustor conditions did not have significant effects. A teardown at this point also revealed significant carbon deposits in the reformer outlet manifold as shown in **Figure 8.3.1-18** and some carbon deposits on the reactor inlet catalyst face, as shown in **Figure 8.3.1-19**. After rebuild (without cleaning) the reactor was re-run in endothermic mode w/ recycle for ~5 hrs to see if the recycle gases would clean up the carbon deposits.

Figure 8.3.1-18: Reformer Outlet Manifold – 1st POx Operation

Figure 8.3.1-19: Reformer Inlet Catalyst Face – 1st POx Operation

Figure 8.3.1-20 shows the reformer outlet manifold with no discernable change in the deposit amount. However, **Figure 8.3.1-21** does show appreciable improvement in the reformer inlet cat face deposit amount.

Figure 8.3.1-20: Reformer Outlet Manifold – Post Recycle

Figure 8.3.1-21: Reformer Inlet Catalyst Face - Post Recycle

The reactor was then reconfigured with a radiation shield / flame arrestor similar to ones used in Delphi's previous POx reformer configurations as a means to lower reformer inlet temperatures. A view of the radiation shield / flame arrestor from the reactor inlet is shown in **Figure 8.3.1-22**. The results show a reduction of more than 100 °C in T2 temperatures when the radiation shield was used.

Figure 8.3.1-22: Pre-Test – Radiation Shield/Flame Arrestor

Delphi discovered problems with the hardware that shortened the test. **Figure 8.3.1-23** shows the mass balances for C, O, and H (as C, O, H endo recovered) for this testing

and the big fluctuation in H and C recovered that correlate to combustor operation changes indicate a cross leak between combustor and reformer passages. Final teardown did reveal leaks in the reactor as shown in **Figure 8.3.1-24**. (Note: this leak path has been addressed with the creation of the Gen 5.1T reactor)

Figure 8.3.1-23: Gen 5T POx Operation – Flame Arrestor Effect

Figure 8.3.1-24: EOT Cross Leak Location

Delphi also discovered that the radiation shield / flame arrestor had disintegrated, as shown in **Figure 8.3.1-25**.

Figure 8.3.1-25: Post-Test – Radiation Shield / Flame Arrestor

8.3.1.2 Diesel POx Reformer Design & Testing

8.3.1.2.1 Diesel POx Reformer (FDU) Design for SPU1E

Design work was completed to adapt the CV for Gen 5T Endothermic Reformer to the SPU1E (diesel) POx application. Compromises in packaging had to be made because the SPU1 architecture already existed.

8.3.1.2.2 Evaluate Performance of reformer using Electrically Heated Contact Vaporizer (EHCV) Vaporized Feed

Figure 8.3.1-26 shows the test arrangement for the reformer being started and maintained using an electrically heated contact vaporizer (EHCV). The EHCV evaluated for this design was the heater cartridge which was capable of vaporizing the largest amounts of fuel for the reformer. The flame was quenched and fueling restarted for reformat generation after the combustor test. **Figure 8.3.1-27** shows the quality of the reformat at start up with the EHCV and transitions to the contact vaporizer. No discernable change in H₂, CO and/or un-reformer HC's is evident. Work continues in developing the controls for the transition from EHCV fuel and the normal running of a combustor heat exchange CV fuel.

Figure 8.3.1-26: EHCV Combustor and Reformer Start Set-up

Figure 8.3.1-27: EHCV Combustor and Reformer Start

8.3.1.3 Natural Gas (NG) POx Reformer Testing

Five (5) separate catalysts were evaluated in Gen 4.2T POx reformers. All catalysts were characterized in Gen 4.2T POx reformers on the Reformer lab's POx Characterization Cart. The reformers were then assembled into various SOFC Systems and tested under various test schedules. After the completion of system testing, the reformer performance was re-evaluated in the reformer lab on the POx Characterization Cart. If the catalyst performance did not degrade significantly, the reformer (and catalyst) would be placed back on SOFC systems test.

Figure 8.3.1-28 shows a synopsis of systems testing that the five selected reformer/catalysts were subjected to. **Figure 8.3.1-29** through **Figure 8.3.1-31** show the SOT (Start of Test) characterization results all five catalysts for efficiency, methane break through, and reformer output power.

MG736C144	A-B-A Test: 50/50 Start, Methane POx Start, 50/50 Start
MG736C145	POx Performance Evaluation on DeS Natural Gas - 1500hrs
MG736C146	High Load Durability, Test Start.Ran 172hrs.
MG736C146	Desulfurization Test
MG736C162	Rebuild with stacks in doghouse (top of furnace) and soft-start. TDA Desulfurizer test, A-B-A-C-A-B
MG736C162	Desulfurization Test - New Stack
MG736C162	NG Baseline Test
MG733C284	Characterization Test for Demo System

Figure 8.3.1-28: Table of Selected Tests for Reformer Evaluation

Figure 8.3.1-29: NG POx Reformer Testing – Start of Test, Efficiency (without Methane)

Figure 8.3.1-30: NG POx Reformer Testing – Start of Test, Methane Breakthrough

Figure 8.3.1-31: NG POx Reformer Testing – Start of Test, Net Power

8.3.1.4 Gen 5.1T Development - Modeling

Thermal modeling of Gen 5T, 5.1T and derivatives continued in 2007. While empirical data was the mainstay of reformer development it became necessary to develop correlated models for heat transfer knowledge and insight. Several modeling approaches were used, including:

1. Conventional heat transfer CFD (non-reacting flows)
2. Heat transfer CFD using a volume based distributed “endothermic” load to create equivalent net heat sink
3. Heat transfer CFD using integrated “reacting flow” kinetics solver (i.e. Chemkin)

8.3.1.4.1 CFD Modeling of Gen 5T type Reactor Configurations

The objective of this work was to both establish correlation between modeling results and test results, and to apply the correlated model to new derivatives of the Gen 5T and Gen 5.1T configurations. Specifically of interest was the heat transfer improvement that would be possible with a corrugated combustor/heat exchange substrate. Test data was compiled as input conditions for our current model, see **Figure 8.3.1-32**.

	R,A,M	Eval. to Reqs =	EWO for Data	Sub-Test Objective	Mode	
	REQTS		ACTUALS			
	15C		15		15C	
	DPS3000-D_Rated_Simulink_smk01.xls		C271		C292	
	(blank)		w/ wet layup insul on reactor		w/ inner insul	
Data	NOC	Rated	NOC	Rated	NOC - GPC ltd	Rated - GPC ltd
Average of Gross Ref Efficiency w/o CH4 [-]	1.33	1.33	1.26	1.14	0.73	0.83
Average of Net Ref Efficiency w/o CH4 [-]	1.08	1.09	1.02	0.97	0.58	0.66
Average of RefOut LHV w/o CH4 [kW]	6.90	13.79	5.87	11.93	3.73	8.29
Average of Comb In LHV [kW] Cr,0	1.52	3.04	10.73	15.02	1.57	3.14
Average of Recycle H2O+CO2 Enthalpy [kW]	-2.90	-5.70	-1.69	-4.19	-2.90	-5.73
Average of Sum of Recycle Endotherm + Combustor LHV [kW]	-0.69	-1.33	9.04	10.83	-1.34	-2.59
Average of Comb In sensible del H [kW] Cr,0,RT => Cr,0,T act	4.72	9.55	0.00	0.00	0.99	2.42
Average of Comb In LHV + sens [kW] Cr,0,T act	6.24	12.59	10.73	15.02	2.56	5.56
Average of Comb Inlet Fuel mdot [g/s]	0.66	1.31	0.20	0.28	0.66	1.31
Average of Comb Inlet Total Air mdot [g/s]	4.90	9.87	7.90	10.48	1.00	2.50
Average of Comb Inlet Total mdot [g/s]	5.56	11.19	8.10	10.75	1.66	3.81
Average of Comb Inlet Fuel temp [deg C]	792	796	25	25	346	393
Average of Comb Inlet Air Mix temp [deg C]	792	796	25	25	703	701
Average of Comb Inlet Fuel + Air expected temp [deg C]	792	796	750	750	750	750
Average of Qref [kW] (+) = heat to CV (-) = heat fr CV	1.57	3.09	0.48	1.05	-1.78	-2.37
Average of Qr1n Net del LHV [kW] Rr,0,RT => Rp,0,RT	0.54	1.10	0.17	0.06	-2.10	-3.01
Average of Qr2 sensible del H [kW] Rp,0,T2 => Rp,0,T3	1.03	1.99	0.32	0.99	0.31	0.64
Average of Qchx del H sensible CHx In - CHx Out [kW]	-1.86	-3.67	-1.69	-2.59	-0.63	-1.29
Average of Q loss Comb del H [kW] Cr,a, RT => Cp,0,TC14	-0.18	-0.25	0.63	-0.27	-0.41	-0.62
Average of Q loss Comb+Piping del H [kW] Cr,a => Cp,2	-0.18	-0.25	-0.67	-0.97	-0.67	-0.85
Average of Qloss Reactor [kW] (+) = heat to CV (-) = heat fr CV	-0.26	-0.53	-1.19	-1.52	-2.41	-3.65
Average of C2's sum [molfrac]	0.0500	0.0500	0.0002	0.0011	0.0194	0.0183
Average of Ref Out CH4 [molfrac]	0.500	0.500	0.002	0.007	0.018	0.021
Average of Ref In temp T12 [deg C]					206	250
Average of Reactor Inlet Stream temp T2 [deg C]	250	250	741	599	573	648
Average of Ref Out at Outlet Flange temp T3 [deg C]	951	926	866	880	793	891
Average of Reactor Hx Inlet at Flange temp T6 [deg C] Cp,1	986	996	1068	1114	968	1049
Average of Reactor Hx Outlet at Flange temp TC16 [deg C] Cp,3	713	729	907	930	677	791
Average of Space Velocity Reformer STP,void vol [1/hrs]	7470	14932	7684	14976	7488	14960
Average of Ht xfer Ratio Qref / Qchx	-0.84	-0.84	-0.29	-0.40	2.81	1.83
Average of Ref In Recycle mdot [g/s]	0.540	1.070	0.420	0.880	0.540	1.070
Average of Comb AFR actual [-]	7.46	7.52	39.52	37.43	1.52	1.90
Average of Comb AFT [deg C]	1012	1014	1132	1183	1265	1215

Figure 8.3.1-32: CFD Test Data for Correlation

Columns 4, 5 and 6 were selected for correlation for several reasons. Row 4 – Test C271 used an insulation enclosure that encased only the reformer (i.e. not the combustor as well as in the Set 00 enclosure) and this test showed net endothermic reforming. Row 5 & 6 – Test C292 used a more insulating enclosure although it includes the combustor. This data was also collected at GPC limited fueling. These conditions, as a first iteration, should give a reasonable range of thermal conditions that a model would need to predict. The CFD modeling used the value for Qr1n shown in Row 16 the chemical enthalpy change of the reforming stream from reactor inlet to reactor outlet and distributed this heat throughout the volume of the reforming substrate.

Figure 8.3.1-33 shows results for both CFD modeling and actual test data with respect to Reformer Tube Outlet temperatures. The model assumes initial convective heat transfer coefficient of 25 W/m²-K, a surface emissivity at 750⁰C of ~ 0.72 for Inconel 625 and a free stream temperature of air of 750⁰C. With these conditions we can see

there is disagreement when there is a significant reaction; in this case an exotherm for C292 data within the reactor.

Figure 8.3.1-33: CFD Tube Temperature Correlation

8.3.1.4.2 Corrugated Core Analysis, Modeling & Manufacturing

The Gen 5T reformer design successfully reformed fuels without producing excessive amounts of carbon, as was produced with the earlier flat plate reformer designs. However, the heat transfer properties of the Gen 5T reformer design still required optimization. A new multi-tube reformer core Gen 6T was designed to enhance the heat transfer of the Gen 5T reformer design as shown in **Figure 8.3.1-34**.

Figure 8.3.1-34: Gen 5.1T Reformer Design Features Corrugated Metal on the Combusting Path and Fecralloy Foam in the Reforming Path.

There were two paths to increasing the heat transfer properties of Gen 5T. One was to choose materials with higher thermal conductivities than those materials used in Gen

5T, or change the geometry. In this version, of the reformer core, Delphi changed the materials and the design of the substrate used in the combustion path of Gen 6T. Gen 6T used a corrugated metal substrate, shown in **Figure 8.3.1-35**, on the combustion path of the reformer and metallic foam on the reforming path of the reformer as shown in **Figure 8.3.1-36**.

Figure 8.3.1-35: The Picture shows the Corrugated Metal Substrate used in the Combusting Path of the new Reformer Design.

Figure 8.3.1-36: Picture clearly show the placement of the metallic foam in the reforming path and the corrugated metal in the combusting path of the new reformer design

The metallic foam, used in the reforming path of the Gen 5T reformer design, was shown to be superior at keeping catalyst washcoat adhered during operation when compared to several other metallic substrates, including corrugated metal substrates. The thermal conductivity of the metallic foam was shown to be very low at 3.7 W/m-K at

1000°C compared to 24 W/m-K at 1000°C for the corrugated metal substrate. Since the metallic foam material had such superior properties for retaining catalyst washcoat compared to all other metallic substrates tested, the metallic foam was also used as the catalyst washcoat substrate in the reforming path of the Gen 6T design. Because the thermal conductivity of the metal foam was so low, a new material was chosen for the combustion path of the new reformer design.

Figure 8.3.1-36 shows the placement of the metallic foam and the corrugated metal substrate in the Gen 6T reformer design. The corrugated metal substrate has far better thermal properties than the metallic foam as shown in **Table 8.3.1-1** which contains data from Emitec, Inc. and Porvair, Inc. The data indicates that the heat transfer coefficient of the corrugated metal substrate is far greater than the heat transfer coefficient of the metallic foam. The corrugated metal substrate was chosen for use on the combustion path of the new reformer design since the combustion path has no duties to carry catalyst washcoat. The corrugated metal substrate was not utilized in the reforming path due to its inability to keep catalyst washcoat adhered. The corrugated metal substrate also has a smaller pressure drop for the same flow compared to the metal foam, which is of particular importance on the combustion path due to the high flow rates of that path which are typically around 12 g/s compared to 0.5 g/s on the reforming path.

Table 8.3.1-1: A comparison of thermal properties of metal foam and corrugated metal substrate materials. The corrugated metal data is from Emitec, Inc. and the metal foam data is from Porvair, Inc.

Substrate Type	Heat transfer coeff		Thermal Conductivity	Geometric Surface Area
	700°C W/m ² /K	1000°C W/m ² /K	1000°C W/m-K	GSA (m ² /L)
Metal Foam	34.8	1.29	3.74	0.88
corrugated metal at 600 cpsi	283.7	346.6	24.1	3.31
corrugated metal at 1000 cpsi	339.2	450.9	24.1	4.16

Figure 8.3.1-37 shows that the pressure drops of the combustion substrates of a 300 and 600 cpsi (cells per square inch) corrugated metal substrate are ten times smaller than the pressure drop of the metal foam at the same flow rates.

Figure 8.3.1-37: Graph shows the pressure drop variation versus flow for the metal foam and two different densities of corrugated metal substrate. Cpsi is an anagram for cells-per-square-inch.

The Gen 6T design required several studies to determine the most promising processes to manufacture the corrugated metal combustion path substrate. A process using laser cutting finally proved to be the best choice. After careful selection of the laser parameters such as power level, angle of cut, cutting speed, etc., a successful process was developed. The laser cut holes were stable and did not suffer from the unraveling syndrome that was seen with other cutting processes such as CNC milling or wire EDM.

Figure 8.3.1-38 shows the finished hole through the corrugated metal substrate after laser cutting. This manufacturing process was exciting because of its potential for high volume and low cost. Next the reforming tubes were installed into the holes and physically attached. The joint between the hole and the tube must have excellent heat transfer properties. Brazing was chosen as the most reasonable process to successfully achieve this goal. However, the substrate of the corrugated part is an alumina-forming alloy called Aluchrom YHf®. It was determined that the laser cutting process did cause an alumina layer to form on the surface of the hole. Alumina layers are particularly difficult to braze and generally requires precious metal brazes such as silver or gold. A brazing process that was both low cost (no precious metals) and able to wet the alumina layer needed to be found or developed. A braze and brazing process was developed and successfully used to produce the new Gen 6T reformer core design. The testing of The Gen 6T reformer core has not yet taken place.

Figure 8.3.1-38: The laser cut hole of the corrugated metal combustion substrate. The hole has been welded during the cutting process which negates the possibility of the corrugate metal substrate unraveling.

8.3.2 Develop Catalysts

8.3.2.1 Catalyst Formulation

8.3.2.1.1 Evaluation of Standard Rhodium Catalyst for Natural Gas Pre-Reforming

Delphi's standard rhodium on alumina catalysts (RDRCA0-320:CB (2,120)) was evaluated for natural gas pre-reforming with the goal of determining which operating conditions will be most effective for reducing non-methane hydrocarbon content while maintaining or improving CH₄ content of the reformat. This catalyst consists of a barium-stabilized, primarily delta-alumina, washcoat containing 2 wt. % Rh, supported on a 400 cells-per-square-inch (cps) 4 mil wall thickness cordierite substrate, with a total loading of 120 g/ft³ rhodium. Testing conditions, including simulated anode recycle flow rates, are listed in **Figure 8.3.2-1**. Modes 54, 65, 84, and 100 are based on system-level requirements; points 0.5, 1.0, and 2.0 are additional test points selected to further understand the performance of catalysts in this reaction mode. Note that operating mode 54 is 100 % recycle – operating at this point can test the catalyst's ability to reach water-gas shift equilibrium and the catalyst's activity for CO or CO₂ methanation.

operating mode	N ₂ (SLPM)	H ₂ (SLPM)	H ₂ O (SLPM)	CO (SLPM)	CO ₂ (SLPM)	natural gas (SLPM)	H ₂ O (g/min)	total flow (SLPM)	space velocity (1/hr)	fuel/ recycle ratio
54	1.70	4.17	0.51	2.07	0.16	0.00	0.407	8.60	40,112	0.000
65	0.28	3.62	0.61	1.58	0.45	0.39	0.490	6.93	32,329	0.059
84	0.00	1.93	1.71	0.52	1.26	1.03	1.372	6.46	30,118	0.190
100 (Rated)	0.00	1.21	2.40	0.03	1.78	1.72	1.931	7.15	33,311	0.317
point - 0.5	0.31	3.95	0.67	1.73	0.49	3.58	0.535	10.73	50,000	0.500
point - 1.0	0.23	2.96	0.50	1.30	0.37	5.36	0.402	10.73	50,000	1.000
point - 2.0	0.15	1.98	0.33	0.86	0.25	7.15	0.268	10.73	50,000	2.000

furnace temperature : 500 – 800 °C, in 50° increments

PS584F-33

Figure 8.3.2-1: Processing conditions for natural gas pre-reforming. Space velocities used in testing were adjusted to 50, 100 or 200 % of listed values

Results were also obtained at each of the six operating points employing fuel, however only the results for operating mode 84 are presented in **Figures 8.3.2-2** and **5.3.2.1.18.3.2** and space velocity, indicating that the catalyst under these conditions is not active for methane reforming. Only at the lowest space velocity and at temperatures over 700 °C was ethane and propane conversion noted. At these conditions, close to 100 % conversion was obtained. These results indicate that either rigorous reaction conditions will be required or improved catalysts need to be employed for natural gas pre-reforming; work in this area during the next reporting period will focus on selecting known catalysts and optimizing their usage.

Figure 8.3.2-2: Methane conversion measured during natural gas pre-reforming at operating mode 84 for three flow rates

Figure 8.3.2-3: Ethane and propane conversions measured during natural gas pre-reforming at operating mode 84 for three flow rates. A negative value indicates species formation

8.3.2.1.2 Testing of Argonne National Lab Ruthenium-Perovskite Fuel Reforming Catalyst

A novel Ruthenium Perovskite based washcoat formulation was received from Argonne National Lab. This was washcoated onto a 20 pores-per-inch reticulated foam 1" x 1" cylindrical monolith, for performance evaluation with methane partial oxidation and natural gas endothermic reforming and for durability testing with diesel fuel endothermic reforming.

Due to the limited amount of material, 6.0 grams, and unusual washcoat slurry properties, the washcoating proceeded with difficulty. A washcoat containing 6.1 wt. % solids was employed; normally, about a 30-40 wt. % solids content is used for alumina-based washcoats. The dip method was used for coating; after 13 passes, a loading of 4466 g/ft³ of washcoat, dry basis, was achieved. In comparison, usually one or two washcoating passes are required to reach a loading of 6000 g/ft³ for alumina-based washcoats.

The ANL catalyst has slightly better performance for methane POx, as compared to our standard Rh-based formulation, **Figure 8.3.2-4**. The catalyst was tested at an O/C molar ratio of 1.07, 90,200/hr space velocity, and at a furnace external temperatures ranging from 700 to 1000 °C, in 50° increments. The performance was compared to previously tested Delphi Rh-alumina based catalyst. Under the same processing conditions, the ANL catalyst operated at higher temperatures; consequently product H₂ and CO concentrations were higher, while reformat CH₄ content was lower. As seen

in **Figure 8.3.2-5**, the ANL catalyst has slightly better activity as compared to the Delphi catalyst, operating closer to equilibrium conversion.

Figure 8.3.2-4: Comparison of Argonne and Delphi catalyst performance for methane partial oxidation

Figure 8.3.2-5: Comparison of Argonne and Delphi catalyst activity for methane partial oxidation

The ANL catalyst was then tested for natural gas endothermic reforming, at a total O/C molar ratio of 1.3, 55,200/hr space velocity, and at furnace external temperatures ranging from 700 to 1000 °C, in 50° increments. The catalyst was also tested at 27,500

and 112,500/hr space velocities. Simulated anode recycle flow rates employed and the results of testing are given in **Figure 8.3.2-6**, and the results compared to the same Delphi Rh-alumina catalyst formulation. Regardless of flow rates, similar comparative data was obtained. The ANL catalyst exhibited unusual behavior, perhaps indicative of rapid change in structure or loss of active sites, finally testing consistently much less active than our standard catalyst. The behavior of the experiment suggests that one cause of the degraded performance of the ANL catalyst may be due to drifts in flow controller calibrations, resulting in operations in carbon forming regimes.

Figure 8.3.2-6: Comparison of Argonne and Delphi catalyst performance for natural gas endothermic reforming

Finally, the catalyst was evaluated for diesel fuel endothermic reforming durability at a total O/C mole ratio of 1.24 and at 45,000/hr space velocity. This was measured at standard temperature and pressure and based on external catalyst volume. An external furnace was used to control catalyst temperature to about 960 °C. Results were compared to the Delphi Rh-alumina catalyst, in this case placed on a 1/2" diameter substrate for improved heat transfer. While the selectivity of the ANL catalyst was lower as compared to the Delphi catalyst, it maintained good durability during testing, as seen in **Figure 8.3.2-7**. Hardware issues may have been involved in the diminished performance of the ANL catalyst. In contrast, the standard catalyst maintained good performance for over 600 hours.

Figure 8.3.2-7: Comparison of Argonne and Delphi catalyst durability for diesel fuel endothermic reforming

8.3.2.2 Catalyst Process Development

8.3.2.2.1 Substrate Selection for Natural Gas Pre-Reforming

Several substrates were evaluated for natural gas pre-reforming, use operating mode point 1.0 as described in **Figure 8.3.2-8**. As seen in **Figure 8.3.2-8**, no significant performance differences were noted between cordierite honeycomb or cordierite foams, in terms of ethane or propane conversion, suggesting that the reaction rate is chemical kinetics controlled. Prior results, for partial oxidation, have shown that a foam substrate exhibits significant increased amounts of mass transport rate limitations, as compared to a honeycomb, making them not useful for partial oxidation. This difference was not observed for pre-reforming, suggesting that the substrate should be selected for best heat transport characteristics. Since the operating temperature of pre-reforming is lower than that used in other types of reforming for SOFC, the result of predominant chemical kinetics control of reaction rate is sensible.

Figure 8.3.2-8: Comparison of ethane conversion for honeycomb or foam substrates during synthetic natural gas pre-reforming using Rh-ZRQ2 based washcoat and natural gas to recycle ratio of 1:1

8.3.2.3 Catalyst Testing

8.3.2.3.1 Natural Gas Pre-Reforming Process Optimization

The Delphi Rh-alumina based catalysts were evaluated for natural gas pre-reforming using the processing conditions listed in **Figure 8.3.2-9**. Catalyst temperatures were typically 100 – 300 °C less than the furnace temperature set point, indicating significant resistance to conductive heat transport into the catalyst bed, as in **Figure 8.3.2-9**. As previously discussed, regardless of space velocity, little to no methane conversion or formation was noted (see **Figure 8.3.2-10**). Only at temperatures above 700 °C, and at the lowest flow rates, was any significant amount of ethane or propane conversion noted. Although, lesser conversions were obtained at lower temperatures or higher flow rates (see **Figure 8.3.2-11**). Of significance is the formation of considerable amounts of ethylene at the reaction conditions most favorable for ethane conversion (see **Figure 8.3.2-12**). Note that equilibrium concentrations of C₂H₆, C₂H₄, and C₃H₈ approach zero under all of the conditions tested. These results indicate that the catalyst is highly non-selective for the desired reactions.

Figure 8.3.2-9: Catalyst center and back face temperatures measured during natural gas pre-reforming testing at operating mode 100 for three flow rates

Figure 8.3.2-10: Methane concentrations measured during natural gas pre-reforming testing at operating mode 100 for three flow rates

Figure 8.3.2-11: Ethane and propane concentrations measured during natural gas pre-reforming testing at operating mode 100 for three flow rates

Figure 8.3.2-12: Ethylene concentrations measured during natural gas pre-reforming testing at operating mode 100 for three flow rates

Results from testing at operating mode 54 indicate some activity for methanation of CO or CO_2 , see **Figure 8.3.2-13**, as well as formation of higher hydrocarbons, see **Figure 8.3.2-14**, perhaps from a Fischer-Tropsch mechanism. At higher temperatures the amounts of ethane and propane decrease accordingly. A similar pattern for ethylene formation is also noted; see **Figure 8.3.2-15**, indicating that in the absence of methane or higher hydrocarbons, ethylene formation will not occur. This raises a selectivity issue, for when operating at mode 100, there will be some residual amounts of C_2H_6

and copious quantities of CH_4 , providing precursor species for undesirable C_2H_4 formation.

Figure 8.3.2-13: Methane concentrations measured during natural gas pre-reforming testing at operating mode 54 for three flow rates

Figure 8.3.2-14: Ethane and propane concentrations measured during natural gas pre-reforming testing at operating mode 54 for three flow rates

Figure 8.3.2-15: Ethylene concentrations measured during natural gas pre-reforming testing at operating mode 54 for three flow rates

A comparison of the six tested operating modes, at the lowest flow rates studied, is presented in **Figure 8.3.2-16**, **Figure 8.3.2-17**, **Figure 8.3.2-18**, and **Figure 8.3.2-19**. Operating modes which result in little to no higher hydrocarbons also yield the lowest amounts of CH₄, such as mode 65.

Figure 8.3.2-16: Methane performance of different operating modes during natural gas pre-reforming

Figure 8.3.2-17: Ethane performance of different operating modes during natural gas pre-reforming

Figure 8.3.2-18: Propane performance of different operating modes during natural gas pre-reforming

Figure 8.3.2-19: Ethylene performance of different operating modes during natural gas pre-reforming

8.3.2.3.2 Impact of Substrate on Catalyst Durability during Methane Endothermic Reforming

A methane endothermic reforming 1500 hour durability test was completed using a zirconia-toughened alumina (ZTA) 20 pores-per-inch (ppi) ceramic foam substrate. The test was similar to the one previously reported using a FeCrAlY 10 ppi foam substrate. The test cycled through four operating modes:

- System start-up: partial oxidation, O/C molar ratio 1.30, 50,000/hr space velocity, 925 °C, for 1 hour,
- Minimum power: with recycle, 21,000/hr space velocity, 850 °C, for 0.5 hours,
- Normal operating: with recycle, 25,000/hr space velocity, 925 °C, for 15 hours, and
- Dwell (no flow) for 0.5 hours.

Recycle composition was 21.61 % H₂, 25.51 % H₂O, 10.07 % CO, 13.43 % CO₂, and 29.38 % N₂. The test was completed to a total of 1500 hours running time, which corresponds to about 88 cycles.

In system start up mode, the catalyst supported on the ZTA substrate had little measurable degradation, in comparison to the FeCrAlY substrate, see **Figure 8.3.2-20**. Under normal operating conditions, the ceramic supported part exhibited increased rates of degradation during the first 500 hours of testing, but subsequently more stable performance, eventually performing as well or better, depending on the operating mode, than the FeCrAlY part, see **Figure 8.3.2-21**.

Figure 8.3.2-20: Comparison of ceramic and FeCrAlY substrate performances for methane endothermic reforming durability in system start-up mode

Figure 8.3.2-21: Comparison of ceramic and FeCrAlY substrate performances for methane endothermic reforming durability in normal operating mode

Both catalysts were tested for methane partial oxidation activity before and after durability testing, see **Figure 8.3.2-22**. While both exhibited loss of activity, there was little change in the activation energy slope, indicating the predominant rate limiting step did not change during the reaction. The catalyst on the ZTA substrate lost 53 % of its original activity, while the FeCrAlY lost 73 %, as measured at 900 °C. Post test visual analysis of the substrates revealed that the FeCrAlY substrate lost considerable amount of material, while the ZTA substrate was intact.

Figure 8.3.2-22: Comparison of ceramic and FeCrAlY substrate activities for methane partial oxidation before and after methane endothermic reforming durability. Vertical line at 900 °C indicates position of activity comparisons. FeCrAlY parts tested at 57,300/hr (fresh) and 48,400/hr (aged) space velocity, ceramic foam parts tested at 97,000/hr (fresh, aged).

These results indicate that FeCrAlY foam is not suitable for fuel reforming applications, regardless of the final physical state, as activity loss was measured almost immediately after start-of-test in the system start-up operating mode.

8.3.2.3.3 High Temperature Durability of Reforming Catalysts

A series of catalysts were tested continuously, for a total of 500 hours, at constant temperatures of 1000 °C, 1100 °C, or 1200 °C, in order to determine rates of deactivation at high temperatures. Substrates used in this testing were all 1" diameter by 1" in length. Flow rate, space velocity, and air/fuel ratio, O/C molar ratio, were adjusted through the test to maintain the indicated catalyst center temperatures, the average values of which are reported below. A summary of testing conditions and end-of-test activity losses are also listed below **Tables 8.3.2-1** and **8.3.2-2**. End-of-test activity was measured by methane partial oxidation at O/C 1.30 molar ratio and 96,000/hr space velocity, and compared to corresponding fresh catalyst activity, as measured at 900 °C.

Tables 8.3.2-1: Evaluated with natural gas, initial activity about 25% less than that for methane

rhodium loading (g/ft ³)	operating temperature (°C)	substrate	O/C	space velocity (1/hr)	activity loss (%)
30	1200	honeycomb	1.69	95,200	88
60	1200	honeycomb	1.69	95,700	82
120	1200	honeycomb	1.74	98,100	51
120	1200	foam	1.73	96,700	24*

T

Tables 8.3.2-2: Significant carbon deposition, due to flow controller failure, occurred at ~200 hours into test, untowardly degrading catalyst.

catalyst	Generation 3 120 g Rh / ft ³			Generation 4 120 g Rh / ft ³		
operating temperature (°C)	O/C	space velocity (1/hr)	activity loss (%)	O/C	space velocity (1/hr)	activity loss (%)
1000	1.44	87,000	51	1.35	81,000	66
1100	1.60	90,200	62*	1.62	117,700	62
1200	1.74	98,100	51	1.73	114,100	60

Catalysts supported on ZTA reticulated foam substrates exhibited a nearly identical rate of deactivation, as compared to catalysts supported on honeycomb monolith substrates, see **Figure 8.3.2-23**, suggesting that provided that the ZTA substrate remains intact, with no loss of material or disintegration, the supported washcoat can maintain its activity.

Figure 8.3.2-23: Catalyst performance measured during durability testing, at 1200 °C, for methane partial oxidation using generation 3 Catalyst on reticulated foam or honeycomb monolith substrates

The results indicate minimal change in performance at the tested temperatures regardless of catalyst generation or temperature; see **Figure 8.3.2-24** and **Figure 8.3.2-25**.

Figure 8.3.2-24: Catalyst performance measured during durability testing, at different catalyst center temperatures, for methane partial oxidation using generation 3 Catalyst on honeycomb substrate

Figure 8.3.2-25: Catalyst performance measured during durability testing, at different catalyst center temperatures, for methane partial oxidation using generation 4 Catalyst on honeycomb substrate

Rhodium loading strongly impacts durability, as seen in **Figure 8.3.2-26**. While the observed performance of the 60 and 120 g. Rh per ft^3 parts was steady, the 30 g/ ft^3 part exhibited increased rates of degradation. Activity losses measured after testing show that only the 120 g/ ft^3 part retained significant activity after testing at 1200 °C.

Figure 8.3.2-26: Catalyst performance measured during durability testing, at different catalyst rhodium loadings, for methane partial oxidation using generation 3 Catalyst on honeycomb substrate

8.3.2.3.4 Substrate Durability

Visual examination of catalyst removed from SECA Phase I testing revealed that all substrates exhibited significant mechanical degradation via embrittlement. A summary of catalysts tested and end-of-test age factors are listed in **Figure 8.3.2-27**. Catalyst washcoats were supported on 45 pores-per-inch zirconia-toughened alumina reticulated foam substrates, 1-13/16" diameter, 2-3/8" length, with 60 g/ft³ Rh, and 2 wt. % Rh in the washcoat. Typical operating conditions were about 850 °C with minimal thermal or flow rate cycling. Catalysts were tested from 1 to 4660 hours; post-test age factors were evaluated with methane partial oxidation, at an O/C 1.3 molar ratio, and 19,600 or 49,000/hr space velocity, with activity compared at 900 °C.

catalyst	System Test Set#	time on stream (hr)	catalyst age factor
902719-11	---	1	1.000
902719-7	4	150	0.716
902719-1	1	910	0.443
902719-3	3	2440	0.401
8655202-14	2	4692	0.263

Figure 8.3.2-27: Summary of Catalysts Evaluated from System Durability Testing. Age factor is fraction of initial activity remaining.

Regardless of the time of test, the substrates had become extremely fragile. Appearances of the catalysts after testing are given in **Figure 8.3.2-28** through **Figure 8.3.2-32**.

Figure 8.3.2-28: Appearance of catalyst 9027-19-11, after 1 hour of testing, corresponding to a 1.0 age factor. A minor amount of chipping is evident.

Figure 8.3.2-29: Appearance of catalyst 9027-19-7, after 150 hours of testing, corresponding to a 0.72 age factor. Substrate is cracked and material is missing from both the front and back faces.

Figure 8.3.2-30: Appearance of catalyst 9027-19-1, after 910 hours of testing, corresponding to a 0.44 age factor. Substrate is cracked and significant amounts of material are missing from both the front and back faces.

Figure 8.3.2-31: Appearance of catalyst 9027-19-3, after 2440 hours of testing, corresponding to a 0.40 age factor. Substrate shows extensive deterioration.

Figure 8.3.2-32: Appearance of catalyst 8655-202-14, after 4692 hours of testing, corresponding to a 0.26 age factor. Substrate is cracked, and significant amounts of material are missing from both the front and back faces

8.3.2.3.5 Further Investigation into Substrate Durability

The employed zirconia-toughened alumina reticulated foams failed due to embrittlement under a wide range of reforming and mixing zone conditions. Three catalyst samples supported on ZTA foam, zirconia-mullite honeycomb, and alumina honeycomb monolithic substrates, were tested according to the rapid age test. The three samples were exposed to approximately 8000 of these cycles each. The results of the testing are given in **Figure 8.3.2-33**.

Figure 8.3.2-33: Performance of different substrates for natural gas partial oxidation, tested at 0.45 g/s natural gas flow rate and a 1.7 O/C molar ratio

Honeycomb monoliths proved more robust to these conditions with the alumina composition showing no apparent failures. Zirconia-mullite compositions exhibited cracking. Regardless of composition, smaller parts of 1" diameter or less, did not

exhibit these types of thermal stress related failures. A summary of measured catalyst age factors, the activity remaining after testing, and visual appearances, are given in **Figure 8.3.2-34**, **Figure 8.3.2-35**, and **Figure 8.3.2-36**.

SIDE VIEW

Figure 8.3.2-34: Appearance of catalyst 9001-39-6, 45 ppi ZTA foam substrate containing 100 g/ft³ Rh, after 8524 cycles, corresponding to a 0.41 age factor measured at 900 °C. Substrate is friable, with material breaking away during post-test handling of catalyst.

TOP FACE

SIDE

Figure 8.3.2-35: Appearance of catalyst 9039-7-C, 400 cpsi / 20 mil wall thickness zirconia-mullite honeycomb substrate containing 60 g/ft³ Rh, after 8492 cycles, corresponding to a 0.61 age factor measured at 900 °C. Substrate has cracked during testing, with material falling away during post-test handling.

Figure 8.3.2-36: Appearance of catalyst 9029-141-4, 484 cpsi / 12 mil wall thickness alumina honeycomb substrate containing 60 g/ft³ Rh, after 8194 cycles, corresponding to a 0.59 age factor measured at 900 °C. Substrate exhibits no apparent damage on visual examination, and retains original structural integrity.

8.3.2.4 Fundamental Catalyst Characterization

8.3.2.4.1 Raman Spectroscopy Catalyst Surface Mapping

A demonstration project was completed at Lehigh University in order to show that *in-situ*, or *operando*, laser Raman spectroscopy, operated in a mapping mode, can provide useful information on catalyst surface species under realistic high-temperature fuel reforming conditions. Use of the mapping mode will allow for measurements of changes in surface species as a function of position, so that difference in catalyst surface behavior can be measured with respect to changing gas phase chemistry, for example. Three tests were completed with propylene partial oxidation, at O/C molar ratios of 1.1, 1.1, and 1.5, and total flow rates of 30, 60, and 60 cm³ per minute, respectively. Analysis was primarily by UV-laser Raman. Gas compositions and the presence of reaction products were confirmed by micro gas chromatography and mass spectroscopy. For this purpose a 5 wt. % Rh on non-Raman active alumina was used, calcined at 500 °C, and then deposited on a heated flat plate held in a flow cell having a quartz observation window. Raman mapping was done in 30 µm increments, from 0 to 570 µm, in the direction of flow. Data was normalized by benchmarking with minimum response and window background peak intensities, artifacts were removed, and a 10 point moving average was used to smooth out the data.

A summary of the inlet compositions, operating conditions, propylene conversions and measured product compositions, and thermodynamic equilibrium predicted outlet compositions, are listed in **Figure 8.3.2-37**. Each of the three reactions operated at low conversions, far from equilibrium, indicating significant reactant bypass in the flow cell.

O/C	1.1	1.1	1.1	1.1	1.5	1.5	1.5
temperature		850	850	850		850	850
flow cm ³ /min	inlet	30	60		inlet	60	
C ₃ H ₆ conversion	---	41%	30%	equil.	---	32%	equil.
Methane	0.000	0.000	0.000	0.004	0.000	0.000	0.000
Ethane	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ethylene	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Propane	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Propylene	0.377	0.193	0.250	0.000	0.308	0.199	0.000
Oxygen	0.623	0.000	0.107	0.000	0.692	0.238	0.000
Nitrogen	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Helium	0.000	0.000	0.000	0.000	0.000	0.000	0.000
CO	0.000	0.066	0.000	0.474	0.000	0.000	0.379
CO ₂	0.000	0.337	0.321	0.026	0.000	0.282	0.121
Hydrogen	0.000	0.061	0.000	0.468	0.000	0.000	0.370
H ₂ O	0.000	0.342	0.321	0.028	0.000	0.282	0.130

Figure 8.3.2-37: Test conditions, and inlet, predicted, and equilibrium concentrations for reaction conditions employed during laser Raman mapping experiments

Typical Raman spectra for this series of measurements are listed in **Figure 8.3.2-38**, for cases in which oxygen only is flowing and under propylene partial oxidation conditions. In both cases helium is used as a diluent. Significant features in the first spectrum are the presence of the quartz window background, arising from silicon-oxygen bonds, at 494 cm⁻¹, bulk Rh₂O₃, at 555 cm⁻¹, and bulk Rh sub-oxide, expressed as RhO_x, at 610 cm⁻¹. Upon the introduction of reactants the rhodium oxide species are suppressed and new species appear; tentatively identified as a surface rhodium-alumina-oxygen species, expressed at Rh_xAl₂O₃, at 990 cm⁻¹ and surface carbon at 1560 cm⁻¹. Of note is the presence of the interaction of Rh and alumina, which has not been noted previously and only occurring under reaction conditions. This may prove to be significant in terms of quantifying active sites for elementary step reaction modeling.

Figure 8.3.2-38: Typical single point response measured by laser Raman spectroscopy during oxygen only and propylene partial oxidation reaction conditions

For each of the three reaction conditions, twenty of these spectra were collected from the front edge of the catalyst inward to about 570 microns. Since the results from each run are similar, only the results from the last run are presented in **Figure 8.3.2-39**. This distance, 0.5 mm, represents only the leading edge of the reaction zone, but is sufficient to establish some trends, as it is in this zone that the rapid decreases in reactant concentrations occur.

Figure 8.3.2-39: Normalized laser Raman mapping data measured for propylene partial oxidation at O/C 1.5 and 60 cm³/min total flow

The major bands, at 600, 990, and 1560 cm⁻¹, were normalized and the trends are presented in **Figure 8.3.2-40**. Little or no trends are observed in the surface Rh sub-Delphi SECA Final Report Oct 2011 v.6.doc

oxide, at 600 cm^{-1} or in the Rh-Al-O surface species, at 990 cm^{-1} . However, surface carbon shows a significant increase, as shown by the changes to the intensity of the band at 1560 cm^{-1} . These results suggested that even under oxygen rich conditions that exist at the leading edge of the catalyst, carbon surface species, such as CH_3^* play a role in the reaction. This result underscores the value of direct measurements of surface chemistry that high-temperature *in-situ* Raman can allow for.

Figure 8.3.2-40: Correlation of selected Raman bands with axial position of catalyst, measured during Raman spectroscopy mapping of propylene partial oxidation. Bands arise from RhOX (600 1/cm), RhXAl₂O₃ (990 1/cm), and carbon (1560 1/cm).

8.3.2.4.2 *In-Situ* Gas-Phase Analysis Under Partial Oxidation Conditions

Oak Ridge National Lab continued to demonstrate their *in-situ* capabilities for measuring gas-phase compositions and temperatures inside of catalyst honeycomb channels during actual fuel partial oxidation conditions. The work was extended to study propane partial oxidation. Prior work, shown in **Figure 8.3.2-41**, was done with methane partial oxidation at an O/C molar ratio of 1.09 using Delphi standard Rh-alumina catalyst on a 400 cpsi honeycomb monolith, 1" diameter, 1" long. The catalyst was externally heated to $700\text{ }^{\circ}\text{C}$ prior to reforming. Gas phase compositions were monitored by a capillary probe connected to a mass spectrometer, "SpaciMS", and temperatures measured by a micro-thermocouple probe.

Figure 8.3.2-41: Experimental and predicted axial concentrations and temperatures for methane partial oxidation. Solid lines with symbols are experimental data, dashed lines are model predictions. Operated at 27.6 % CH₄, 15.1 % O₂, balance Ar, at 47,000/hr space velocity.

For the purpose of elementary step reaction modeling, the reactor is considered to be adiabatic and operate in a plug flow mode. No mixing is assumed to occur in the axial direction but perfect mixing is assumed in the transverse direction. There is reasonable agreement between the model and actual experimental measurements in the high conversion region, close to the catalyst back face. In the region of rapid transitions, towards the front portion of the catalyst, the model significantly miscalculates reaction conversions and selectivities, especially to H₂, and overestimates temperature. This limits the usefulness of the model for modeling and reactor design at realistic thermal environments.

The model predicts high levels of surface carbon, essentially 100 % coverage, while direct experimental measurements with Raman do not confirm this or match the predicted trends in carbon coverage. At this stage of development, there is insufficient knowledge to further improve the understanding of carbon coverage and how this impacts on the model's ability to accurately predict reformer behaviors.

A similar series of measurements were completed with propane partial oxidation, using the same catalyst and experimental set-up as before, except that light-off was achieved at 400 °C and the reaction was operated at an O/C molar ratio of 1.02. The results of this test are given in **Figure 8.3.2-42**. Compared with the CH₄ partial oxidation measurements, propane is consumed faster, H₂ production is more gradual, and H₂O is consumed after C₃H₈ depletion. Additionally, dry reforming is more apparent and some

amount of intermediate CH_4 is measured. These differences may reflect the lack of a primary $\text{CH}_4 \rightarrow$ to CH_3 step in a C_3H_8 reaction mechanism, and additional C-C bond breaking steps that would be required in a C_3 reaction network.

Figure 8.3.2-42: Experimentally observed axial concentrations and temperatures for propane partial oxidation and indication of major reaction regimes. Operated at 12.04 % C_3H_8 , 18.43 % O_2 , balance Ar, at 30,000/hr space velocity. Missing hydrocarbons (HC) determined by mass balance.

Clearly in the C_3H_8 partial oxidation is the presence of distinct reaction zones, as indicated in **Figure 8.3.2-43**. The first regime is an oxidation zone, about 0.6 mm wide, in which the concentrations of H_2O and CO_2 are at a maximum and likewise temperature reaches its highest value. In this zone syn-gas is generated and both combustion and reforming reactions appear to occur simultaneously. This is followed by a C_3H_8 depletion zone, again about 0.6 mm wide, in which steam and dry reforming occur.

Downstream of this zone is additional steam and dry reforming, as evidenced by the continuous decrease in CO_2 and H_2O content, and increases in H_2 and CO content. Likely more H_2 is generated by the water-gas shift equilibrium, as temperature continues to fall in this zone. Also in this zone is the formation and consumption of CH_4 . This behavior of methane may be due to either methanation of CO or CO_2 , or methanation of surface carbon species.

A carbon and hydrogen balance was performed on the measured data, the results being that insufficient amounts of these species were found, especially in the catalyst front. Independent detailed analysis of propane partial oxidation reformat compositions, at

different conversion levels, indicates significant formation of ethylene and propylene. By assuming the presence of C_2H_4 and C_3H_6 , all of the missing carbon and hydrogen can be accounted for. These species are not detectable by the experimental apparatus used by ORNL in this work. The presence of these species is also consistent with the observations of increased than decreased CH_4 , as these C_2 's and C_3 's are consumed, and accounts for the additional dry and steam reforming observed in the downstream zones.

In summary, spatially resolved intra-catalyst measurements give detailed insights to reformer chemistry, which will lead to better models that reflect chemistry throughout reformer. Propane reforming is much more complex than methane, as more reactions and intermediate hydrocarbons are present. Broader mass monitoring is needed to measure these intermediate hydrocarbons. A time-of-flight mass spectrometer would provide a solution.

8.3.2.5 Chemical Reaction Reforming Modeling

The chemical reaction rate model was further developed with improvements in both gas- and surface-phase chemistry. The gas phase chemistry was extended to include many components up to C_8 , consisting of 421 gas-phase species. The surface chemistry included species up to C_3 and selected radicals. These changes enabled chemical kinetics models to accurately predict experimental observations of partial oxidation of octane-toluene mixtures.

Olefins are important byproducts during partial oxidation of propane. These unsaturated hydrocarbons can play a very important role in reforming chemistry and are important coke precursors. The latest surface kinetics has been extended to include the kinetics for C_3H_6 and C_2H_2 oxidation on rhodium, as well as intermediate steps responsible for lateral interaction between surface carbon species and other adsorbates. **Figure 8.3.2-44** and **8.3.2-45** show the simulations for propylene oxidation with gas-chemistry only and with both gas-phase and surface mechanism, respectively. The formation of gaseous hydrogen is higher and faster for the case with surface kinetics than for the case with just gas-phase kinetics.

Figure 8.3.2-44: Gas-phase chemistry predicted mole fraction distribution of reactants and products in gas phase (average values in radial direction) as a function of axial position along the monolith channel at 2D steady state simulation for propylene oxidation, $T = 1318$ K, 90,000/hr space velocity, $O/C = 1$.

Figure 8.3.2-45: Surface- and gas-phase predicted mole fraction distribution of reactants and products in gas phase (average values in radial direction) as a function of axial position along the monolith channel at 2D steady state simulation for propylene oxidation, $T = 1318$ K, 90,000/hr space velocity, $O/C = 1$.

Due to the rapid dehydrogenation and destruction of olefin hydrocarbons on rhodium surface, the surface was covered with a monolayer of carbonaceous species (atomic carbon), as shown in **Figure 8.3.2-46**. The formation of a carbon monolayer prevents the following adsorption and reaction of hydrocarbons from the gas phase, resulting in the catalyst deactivation. The lack of catalyst activity allows the homogeneous reaction to take control, resulting in the increase in the formation of coke precursors, namely poly-aromatic hydrocarbons, as evidenced in **Figure 8.3.2-47**.

Figure 8.3.2-46: Surface- and gas-phase predicted surface coverage of species along the monolith channel: 2D steady state simulation for propylene oxidation at $T = 1318\text{K}$, 90,000/hr space velocity, $O/C = 1$

Figure 8.3.2-47: Surface- and gas-phase predicted mole fraction distribution of carbon precursors in the gas phase (average values in radial direction) as a function of axial position along the monolith channel at 2D steady state simulation for propylene oxidation; $T = 1318\text{ K}$, 90,000/hr space velocity, $O/C = 1.0$.

It is important to take the radial mass transport of all species into account. Since the overall destruction rate of radicals formed in the gas phase depends on the diffusion of those species to the catalytic surface, radial mass transport becomes crucial. Therefore two-dimensional simulations were needed to understand the coupling between gas-phase, surface and chemistry; and, hence, the reactor behavior. This is illustrated in **Figure 8.3.2-48** and **Figure 8.3.2-49**.

Figure 8.3.2-48: 1D steady state simulation: mole fraction distribution of radicals in gas phase (average values in radial direction) as a function of axial position along the monolith channel; T = 1434 K, 90,000/hr space velocity, O/C = 1.3

Figure 8.3.2-49: 2D steady state simulation: mole fraction distribution of radicals in gas phase (average values in radial direction) as a function of axial position along the monolith channel; T = 1434 K, 90,000/hr space velocity, O/C = 1.3

8.4 Task 4: BOP Component Development

8.4.1 Integrated Component Manifolds

The brazing of a cast manifold was a significant accomplishment in 2007. The braze trials performed on scrap cast pieces proved to be valuable as the lessons learned during the trials were directly applicable to full size cast parts. Delphi's Thermal Division, the brazing vendor, in conjunction with the SOFC Team made many small changes that greatly aided in the success. The thickness of the material in the mid-plate was increased which enabled a much flatter part that helped to create a solid leak free joint to both the upper and lower halves of the ICM. The mating geometry between the GPC tubes and the mid-plate was revised into a lap joint instead of a butt joint for a more robust interface. These small changes enabled the successful first braze of Delphi's Cast Inconel ICM. The remaining challenge with the Cast ICM is to correct a minor shrinkage problem which will produce dimensionally accurate parts (See **Figure 8.4.1-1**).

Figure 8.4.1-1: Brazed Cast Manifold

The old style 5 piece water-jet cut and brazed ICM, made by conventional prototype processes, continues to perform well under all testing. Additional units have been ordered for systems testing as a back-up should the Cast ICM's fail durability testing.

8.4.2 Heat Exchangers

Three different heat exchanger configurations were tested to determine their potential as replacements for the existing prototype units. A formed plate prime surface heat exchanger was purchased. Prime surface implies that there are no fins to enhance performance. The surfaces in this unit had a ribbed pattern stamped in them as a mechanism to improve heat transfer. Heat transfer performance was compared to the

existing cathode preheat heat exchanger. An approximately 30% larger core volume yielded approximately 25% less heat transfer. The main advantage of this type of heat exchanger is ease of manufacture and thus relatively low cost. The increase in size to meet performance requirements is undesirable.

Figure 8.4.2-1: Oil Cooler Type Heat Exchanger

A formed plate heat exchanger, similar to an automotive oil cooler, was fabricated and tested (See **Figure 8.4.2-1**). The configuration and size of the actual heat transfer section of the unit is similar to the existing cathode air preheat heat exchanger. Heat transfer (in counter-flow configuration) was found to be lower than expected. The geometry of this design necessitates that the flow path on hot side be directed around an obstruction created by the cold side manifold. It was suspected that flow was not redistributing by the time it entered the heat transfer core. A simple flow visualization model (See **Figure 8.4.2-2**) of a singular hot side flow passage was fabricated. Small lengths of thread mounted across the passage width to show streamlines confirmed that flow was not redistributing in the heat transfer fins after the obstruction.

Figure 8.4.2: Flow Visualization Model

An annular passage heat exchanger was built as a possible replacement for the recycle heat exchanger. (See **Figure 8.4.2-3** and **8.4.2-4**) This design consisted of two finned

annular passages manifolded such that hot fluid in one passage flowed in a counterflow direction to the cold flow in the adjacent passage. Testing compared well with the heat transfer prediction model. A negative feature of this configuration is that it is not as compact as the oil cooler type heat exchanger configuration or the existing recycle cooler. It is simpler to build than the existing recycle cooler. Another feature of this type of design is that its manifolding and symmetry provide for uniform flow distribution which in turn provided for a more uniform thermal stress distribution. Yet another unique feature of this construction is that the annular walls are free to move relative to one another reducing stress due to axial thermal expansion.

Figure 8.4.2-3: Annular Type Heat Exchanger

Figure 8.4.2-4: Annular Type Heat Exchanger Cross Section

8.4.3 Diesel Carrier Air Pump

The Parker Hannifin pump model T2-01 was tested. The performance curves (pressure versus flow) are shown in **Figure 8.4.3-1**. As can be seen on the chart, the capacity of

this pump was far greater than the required flow and pressure. The power consumption was 40 watts.

Figure 8.4.3-1: Parker Hannifin T2-01 Pump Performance

A down side of positive displacement pump technology is pressure pulsations. Tests were conducted to measure the pressure pulsations of this pump. This data is shown in **Figure 8.4.3-2**.

Figure 8.4.3-2: Parker Hannifin T2-01 Pressure Pulsations

The pressure pulsations were at a frequency of 50 Hz. The magnitude of the pulsations was approximately 0.8 kPa or 0.45% of the mean pressure value.

8.4.4 Hot Reformate De-Sulfurization

A concern of thermal cycling of the hot sorbent bed was that coking might occur, increasing pressure drop across the bed. Pressure drop during testing was monitored

and some increase in pressure drop was observed. **Figure 8.4.4-1** shows the recorded pressure drop.

Figure 8.4.4-1: Pressure Drop

Although pressure drop increased, there was no visual evidence of coking on the internal reactor surfaces, the ZTA monoliths or the quartz frits that were placed in the reactor tube to hold the sorbent particles in place, after test (see **Figure 8.4.4-2**).

Figure 8.4.4-2: Reactor Parts / Reactor Parts and Coking Results

The DOE test results can be seen in **Figure 8.4.4-2**. Delphi found that higher temperatures, longer reduction times and higher percentage flow rates strongly affect the oxidation step.

Figure 8.4.4-3: Regeneration Test Results / Regeneration Test Results

One of the sorbent samples was also run for 80 cycles at what was determined to be one of the optimal regeneration conditions. This sorbent sample retained 0.3 mg/grams capacity after 80 cycles.

8.4.5 Chromium Volatility and Transport

The first series of test were intended to demonstrate the viability of the test method. 5 grams of Crofer mesh were installed into a 3/8" quartz tube. Tests were run at 700°C, 800°C and 900°C. The 900°C test was repeated in order to determine if the test method was repeatable. 5% water was added to the dry air feed of the test stand as the literature indicated that increased moisture content of air increased Chromium volatility. This amount of water is equivalent to 70% humidity at 27°C. The test results are listed in **Table 8.4.5-1**. Cr content is listed in mg/liter. This is total Cr captured and detected by ICP.

Table 8.4.5-1: Chromium Transport Test Results

Sample Type	Air Flow Rate	H2O	Sample Tube	Flow Through HCl	HCl Quantity	Test Time	Test Temp	Cr mg/l
	liters/min	%		liter/min	ml	hours	C	mg/l
crofer	10	5	quartz 3/8	1	200	115	900	0.220
crofer	10	5	quartz 3/8	1	200	115	800	0.150
crofer	10	5	quartz 3/8	1	200	115	700	0.182
crofer	10	5	quartz 3/8	1	200	115	900	0.181

Additional tests were run to further evaluate the effects of water content in air. This was of interest because the literature sources indicated that moisture content had a large effect on Cr volatility. These results can be seen below. The value of 5% water content in air was chosen because 70% humidity at 27°C was a reasonable maximum operating point. The water contents of 0% and 10% were chosen as high and low bracketing, boundaries. The results of this test can be seen in **Table 8.4.5-2** which show that dry air, 0% moisture had very little Cr, while air w/ 5% moisture showed increased Cr. The test with 10% moisture in the air does not agree. The 10% water content created a considerable amount of water precipitation prior to the exhaust stream entering the HCl bubbler. The water captured contained 2.6 mg/liter Cr. It is possible that this condensate picked up some Cr from the exhaust piping system in addition to the Cr vaporization of the Crofer mesh. Delphi believes that the lower level of Cr found in the 10% water content sample is due to Cr being trapped in the condensate.

Table 8.4.5-2: Chromium Transport –vs– % Moisture

Sample Type	Air Flow Rate	H2O	Sample Tube	Flow Through HCl	HCl Quantity	Test Time	Test Temp	Cr mg/l
	liters/min	%		liter/min	ml	hours	C	mg/l
crofer	10	0	quartz 3/8	1	200	115	900	< 0.010
crofer	10	5	quartz 3/8	1	200	115	900	0.181
crofer	10	10	quartz 3/8	1	200	115	900	0.0265

In addition to the Cr bench testing conducted above, Delphi also placed an HCl bubbler on System Set00 test stand and sampled a portion of cathode feed air to actual stacks

running a Set 00 test. This was a system test already running in the system lab. It is interesting to note that the results of this system test showed very stable performance having run for several hundred hours with only a 0.5% degradation rate for stack power. Interestingly, it was also found that the Cr level was also very low (see **Table 8.4.5-3**).

Table 8.4.5-3: Set 00 Chromium Volatility Performance

Sample Type	Air Flow Rate	H ₂ O	Sample Tube	Flow Through HCl	HCl Quantity	Test Time	Test Temp	Cr mg/l
	liters/min	%		liter/min	ml	hours	C	mg/l
Set 00	630	0.5	N/A	0.5	100	215	N/A	0.02

8.5 Task 6: System Modeling & Cell Evaluation for High Efficiency Coal-Based Solid Oxide Fuel Cell Gas Turbine Hybrid System

8.5.1 Modeling of MW-scale IGFC Hybrid Power Systems

The system-level modeling effort focused on generating power plant concepts for: (1) a 1 MW SOFC demonstration power plant operating at near-atmospheric pressure and integrated with a UTC Rankine cycle power generator, and (2) a pressurized, 100 MW-scale SOFC system integrated with a stationary Pratt & Whitney (P&W) aeroderivative gas turbine generator set. Exploration of detailed system configurations focused on prime mover sizing, parameter selection, overall performance assessment, and Pratt & Whitney FT8 gas turbine design change requirements. Modeling and design of the SOFC systems also included integration and evaluation of CO₂ capture methods (mono-ethanol-amines and oxygen combustion).

The results of the study indicated that pressurized utility scale (>100 MW) hybrid SOFC systems could achieve electric efficiencies as high as 55% (HHV), including carbon capture using oxygen combustion, when integrated with the low-pressure turbine spool of the P&W FT8-3 gas turbine and a scaled-up, water-cooled version of the UTC Power PureCycle organic Rankine cycle (ORC) power generator. In order to integrate the P&W FT8 into the SOFC system, the high-pressure turbine spool is removed which lowers the FT8 capital cost by up to 15% and increases the expected life of the gas turbine engine. A high-level engineering design assessment on the FT8 was made to gauge the magnitude of the changes required. It was found that most changes needed were minor to medium in nature and could be done economically. The impact of integrating an ORC bottoming cycle was found to be significant and can add as much as 7 percentage points of efficiency to the system. Furthermore, pressurized hybrid SOFC systems using MEA-based CO₂ capture, could potentially reach 49% (HHV) system efficiency.

Demonstration-scale integrated gasification fuel cell (IGFC) systems with ORC bottoming cycles have the potential to reach 48% (HHV) efficiency without carbon capture and 44% (HHV) with CO₂ capture. Additionally, the use of cathode gas recycle is strongly relevant to efficiency performance when integrating with ORC bottoming cycles.

The parameter sensitivity analysis revealed that SOFC power density is strongly influenced by design cell voltage, fuel utilization, and amount of anode recycle. To maximize the power output of the FT8, SOFC fuel utilization should be reduced to 70%. Cathode side design parameters, such as pressure drop and temperature rise only mildly affect efficiency and power density.

Aside from the SOFC stack, high temperature recycle blower technology also represents a technology gap for realization of the efficiency advantages demonstrated by these system concepts. Thermal management of the oxygen combustor, allowable combustor equivalence ratios, and high temperature heat exchanger technology represent significant technical challenges to enabling carbon capture via oxy-combustion.

8.5.1.1 System Modeling Overview

The system-level modeling effort focused on two power plant concepts: (1) a 1 MW SOFC demonstration power plant operating at near-atmospheric pressure and integrated with a UTC Rankine cycle power generator, and (2) a pressurized, 100 MW-scale SOFC system integrated with a stationary Pratt & Whitney aeroderivative gas turbine generator set. Exploration of detailed system configurations focused primarily on prime mover sizing, parameter selection, overall performance assessment, and Pratt & Whitney FT8 gas turbine design change requirements.

System concepts may also vary depending on the type of CO₂ capture strategy employed. Two different methods for carbon capture were evaluated herein: (1) post-combustion cleanup via a mono-ethanol-amine processing plant and (2) post-combustion separation via oxygen-combustion of the anode tail-gas followed by water knockout. Pre-combustion CO₂ separation processes via water gas shift membrane reactors or other concept strategies were not examined in this study and are left for a future effort.

8.5.1.2 Pratt & Whitney Gas Turbine Product Line Screening Study

Prior work reviewed the results from a preliminary screening study of P&W gas turbine product lines aimed at matching the pressure ratio and flow range for a 100MW SOFC stack with that of a Pratt & Whitney (P&W) gas generator. The two leading candidates identified were the stationary, aeroderivative FT4 and FT8 gas turbine product lines. **Figure 8.5.1-1** shows a simplified schematic of a P&W aeroderivative gas turbine power generator. The operating pressure of the combustor is typically on the order of 18-19 atm. This pressure elevation necessitates the removal of the high-pressure spool of turbine when integrating with the SOFC. One of the challenges in matching a gas turbine power generator with an IG-SOFC topping plant is in the potential flow mismatch

between compressor and expander due to the use of the low-Btu coal fuel gas in the system. When the SOFC capacity is selected to match the design flowrate and pressure ratio (PR) of the low-pressure compressor (LPC) section of an available gas turbine product line, the mass flow delivered to the low-pressure turbine (LPT) section is likely to be too large for the unit. Another challenge is that the inlet pressure to the low-pressure turbine is 2 bars higher than the outlet pressure of the low-pressure compressor. Thus, removal of the high pressure spool presents an off-design aerodynamic inlet condition even if the flowrate is matched properly. If the mismatches in flow and pressure ratios are large enough, significant speed differences between turbine and compressor may exist which necessitate the addition of a gearbox or other workaround solution. Matching the SOFC exhaust gas flow to the maximum LPT flow capacity was considered to be the best approach as it avoided the need to reject exhaust mass flow to the surroundings, while the off-design flow delivered to the LP compressor still enabled a high-efficiency operating point to be achieved.

Figure 8.5.1-1: Simplified schematic of PW FT8-series gas turbine power generator

Prior preliminary analysis indicated that the FT4C-3F product line was nearly a perfect match. However, the FT4 product line was no longer in production by 2007 and the analysis was confined to an approach where the flow and pressure ratio requirements were matched to a 100 MW SOFC stack power output. In a refined approach, the basic requirements established for the low-pressure compressor (LPC) were a *range* of PRs (3-5) and a *range* of flowrates (60-120 kg/s [132-265 lb/s]). The low-pressure turbine (LPT) requirements were examined in the same range of conditions as the LPC and the SOFC stack power was left to be determined by matching the cathode airflow with that of the LPC. The maximum gas flow for the LPT on a single FT8-3 gas turbine engine is about 84 kg/s (185 lb/s). This flow of product gases translates into an approximate airflow of 70 kg/s for the LPC. The turbine inlet pressure is about 200 kPa (30 psi) lower than its design condition with the high pressure gas turbine spool in-place, but high efficiencies are still possible with the high turbine inlet temperatures provided by the SOFC exhaust gas. When using (2) FT8-3 gas turbine engines in an IG-SOFC power plant configuration, the SOFC stack sub-system power output is about 115 MW_{dc}.

A detailed gas turbine engine performance map was generated for the FT8 as a function of mass flow, PR, and turbine inlet temperature. Operating at LPC PRs between 4 and 5, both the LPC and LPT are capable of isentropic efficiencies greater than 90%. Furthermore, the speed of the LPC and LPT can be matched to avoid the use of a gearbox. Two-parallel FT8 engine power plants are offered by P&W in a 'TwinPak' configuration and were selected as the best option for stationary power generating stations.

8.5.1.3 Engineering Design Change Analysis of the FT8-3 Gas Turbine Engine

This section details a high-level engineering design change analysis carried out by P&W to assess both the number and magnitude of changes required to modify an FT8-3 generator for integration with a pressurized IG-SOFC power plant. **Figure 8.5.1-2** illustrates an aeroderivative gas turbine engine mounted on a stand inside its enclosure. The engine is mainly comprised of a low-pressure compressor, high pressure spool, power turbine, and synchronous 60 Hz generator. **Figure 8.5.1-3** depicts a more detailed cross-section of a jet engine (i.e., FT8 without the power turbine and generator) with the main bearings and their positions given. The high-pressure spool employs a concentric shaft and contains the high-pressure compressor, diffuser, combustor, and high-pressure turbine components. The high-pressure spool operates at a speed greater than the low-pressure spool. Removal of the high-pressure spool includes consideration of the following:

- Shaft and bearing lubrication systems
- LPC exhaust and LPT inlet volute aerodynamic and mechanical designs
- Engine gearbox/startup skid requirements
- Secondary air systems management (bleed streams)
- Engine enclosure modifications
- Engine operability and rotor-dynamics

Figure 8.5.1-2: Schematic of aeroderivative gas turbine with synchronous generator

Figure 8.5.1-3: Cutaway view of P&W FT8 gas turbine with bearing locations

An example of the level at which the engineering change assessment was made is given in **Table 8.5.1-1**. As **Figure 8.5.1-3** shows, there are seven shaft bearings in the engine. Bearings 3, 4, and 5 were identified for removal and **Table 8.5.1-1** illustrates some of the implications of such a change.

Table 8.5.1-1: Sample of bearing design changes anticipated for FT8-3 system

Design Change	Type
Remove #3, #4, #5 High Spool Bearings	Medium
Add off-mounted lube pump to replace gearbox pump to supply #1, #2, #4.5, #6 bearings	Minor
Re-design #2 bearing gravity scavenge & breather from IMC to gearbox (no gearbox)	Minor
Re-design #6 bearing rotor driven scavenge pump to connect w/ new #4.5 scavenge pump, or rout it out some other way	Minor
#4.5 bearing scavenge pump currently driven off HPC internally. Need to re-design #4.5 scavenge pump	Minor

The most significant change was the design and incorporation of LPC exhaust and LPT inlet gas scrolls. The available space envelope for the scrolls was limited to the volume formerly occupied by the HP spool as **Figure 8.5.1-4** shows. Considerations in this design change include exit and inlet gas aerodynamics, structural and mechanical design, rotor-dynamics, durability of the high temperature inlet scroll, and main shaft support.

Figure 8.5.1-4: Sectional view of modified FT8 with inlet and exhaust gas takeoff scrolls

Changes to the existing FT8-3 engine design were considered to be significantly simpler and more cost-effective than either making design changes to a different product line or to beginning a new turbine development program. Additionally, the effect of the design changes on FT8 capital cost is about a 40% reduction on the engine itself and a 10-15% overall capital cost reduction of the gas generator is expected when considering the supporting hardware, sub-system, and parts count reduction. Other synergies, such as a reduction in turbine maintenance and an increase in engine life, are also anticipated due to the design changes outlined above.

8.5.1.4 Performance Mapping of the FT8

An integral part of the system component models are the performance maps for the LPC, LPT and PT hardware. Conventional turbine and compressor performance maps typically involve speed as one of the inputs, and the outputs include quantities such as pressure ratio and efficiency. As speed is more of a design variable and is not of interest as far as system studies are concerned, the functional input/output format of the performance map was reversed.

The LPC inputs consist of the mass flow through a compressor, and the pressure ratio associated with the compressor. The conditions for the inlet air are fixed at 15 °C and 1 atm pressure. Given these two inputs, the performance maps predict the compressor efficiency from which quantities, such as power required for compression and compressor outlet temperature can be obtained using simple thermodynamic calculations. Based on tests with residuals obtained using different polynomial functions, the following functional form was deemed most suitable:

$$\eta_{LPC} = \sum_{i=0}^2 \sum_{j=0}^2 a_{i+j} (PR)^i (Mass Flow)^j \quad (1)$$

The advantage of the above functional form is that the process of obtaining the polynomial coefficients can be cast as a linear-least-squares optimization problem, which is easily solved using MS-Excel's SOLVER tool.

In the case of the LPT, the operational speed can be adjusted so as to maintain a constant isentropic efficiency of 91.8%, but at the cost of altering the expansion pressure ratio (PR) with different inlet conditions. Thus, the expansion pressure ratio of the LPT is defined as a function of the inlet temperature. If the inlet stream conditions (mass flow, temperature and pressure) are specified, then efficiency and pressure ratio can be calculated, which in turn can be used to calculate the outlet stream properties and the power obtained from the expansion process. **Figure 8.5.1-5** presents a comparison of the actual PR of the LPT versus inlet temperature data and the corresponding polynomial fit. In this case the pressure ratio was expressed as a cubic polynomial in the inlet temperature, where the coefficients of the polynomial were obtained by solving a linear-least-squares optimization problem using the SOLVER tool in MS-Excel. A cubic polynomial was selected because it revealed the right trends even outside the range of available data.

Figure 8.5.1-5: Plot comparing the P&W LPT performance data and the corresponding polynomial fit

In the case of the power turbine (PT), the outlet pressure is fixed at close to 1 atm and the inlet pressure is determined by the outlet pressure of the LPT. The PT efficiency is observed to be a function of inlet temperature (in K) and pressure (in atm). The functional form for the efficiency curve is given by:

$$\eta_{PT} = \left(\sum_{i=0}^4 a_i P_{in}^i \right) \left(\sum_{i=0}^3 b_i \left(\frac{T_{in}}{1000} \right)^i \right) \quad (2)$$

The above functional form was chosen after several trials with different functional forms. The optimization problem in this case is a nonlinear-least squares problem, which was also solved using MS-Excel's SOLVER tool. Given the inlet pressure and temperature the performance map predicts the PT efficiency from which quantities such as power obtained from the expansion process and PT outlet temperature can be obtained using simple thermodynamic calculations.

8.5.2 Modeling/Analysis of Utility-scale IGFC-GT Power Generation Systems

The modeling effort in this section was focused on generating system concepts for utility-scale hybrid power plants that involve solid oxide fuel cells integrated with stationary P&W gas turbine (GT) generator sets, and a UTC organic Rankine cycle (ORC) power generator. Initial studies established the DC power rating of the SOFC sub-system near 115 MW and focused on integrating the SOFC power section with a ~25 MW gas turbine power generator developed by P&W. Additionally, as the quality of the waste heat exiting the gas turbine is sufficiently high, a bottoming cycle using a scaled-up version of the PureCycleTM ORC system was incorporated and analyzed for its impact on overall system efficiency.

Special emphasis has been placed on system concepts that effectively handle the issue of CO₂ capture and compression. Two particular system configurations have been studied in detail. Both of these configurations involve a pressurized IGFC system with both gas turbine and Rankine bottoming cycles, but differ in the way the CO₂ capture is accomplished:

8.5.2.1 IGFC-GT-ORC-OxyC System

This system concept is comprised of a pressurized SOFC power module with a bottoming FT8 gas turbine engine, followed by a bottoming organic Rankine cycle power system. A flow-sheet of this configuration is presented in **Figure 8.5.2-1**. The system makes use of a pure oxygen stream from the gasifier air-separation plant in a combustor which oxidizes the anode tail-gas, thereby producing only CO₂, H₂O, and a small amount of N₂. The anode tail-gas is not mixed with the cathode exhaust gas stream and thereby, makes the process for CO₂ separation and capture a simple one through the use of condenser to knock-out the water vapor present in the stream. The system also employs hot cathode gas recycle.

Figure 8.5.2-1: IGFC-GT-ORC-OxyC System Process Flow-sheet

8.5.2.2 IGFC-GT-ORC-MEA System

This system concept makes use of the excess O₂ in the cathode tail-gas to oxidize the anode tail-gas, thereby producing CO₂, H₂O and retaining the large amount of N₂ that is associated with the cathode tail-gas stream. A flow-sheet of this configuration is

presented below in **Figure 8.5.2-2**. The presence of a large amount of N_2 eliminates the option of an exhaust gas condenser for the purposes of CO_2 separation. Instead, a mono-ethanol-amine (MEA) based CO_2 capture unit is installed downstream of the ORC unit. Chemical absorption based on mono-ethanol-amine (MEA) appears to be the most advanced and industrially practiced process of all CO_2 capture methodologies. It is suitable for dilute concentrations of CO_2 (3-15 % by volume) and operates at ordinary temperatures and pressures. Also, there is a major worldwide effort to improve the process using better absorbents, energy integration and optimization. The main drawbacks with chemical absorption are: (1) the thermal energy requirement for the heat of regeneration of the solvent for chemical absorption is high, which significantly reduces system efficiency, and (2) the large amount of process hardware and the associated cost and footprint required to enable separation and sequestration.

Figure 8.5.2-2: IGFC-GT-ORC-MEA process flow-sheet

8.5.2.3 IGFC-GT-ORC-OxyC System Analyses

Utility-scale (>100 MW) system analyses have focused on integration of the SOFC stacks with the P&W FT8-3 TwinPak system and a scaled-up, high-efficiency version of the UTC Power PureCycle product. **Figure 8.5.2-1** above depicts a process diagram of a baseline IGFC-GT-ORC-OxyC system concept and **Table 8.5.2-1** shows its expected performance. The power plant concept is projected to have a capacity of 149 MW at 59.1%-HHV (~63%-LHV) efficiency without considering the CO_2 capture, and 139 MW

at 55.1%-HHV efficiency with CO₂ capture and compression to sequestration-ready pipeline conditions [i].

The incoming system air at station (1) is split (split fraction = 0.5) into two streams and each stream is compressed to the system pressure ratio of 5.2 using the LPC from the modified P&W FT8 engine. The LPC has a well-defined performance map where the efficiency is a function of the mass flow rate of air through the system and the compressor PR. The conditions (flow, temperature and pressure) of stream (2) are such that when mixed with the cathode recirculation stream (6), the conditions of the resulting stream (3) meet the inlet requirements of the cathode compartment of the SOFC stack. Part of the stack cathode exhaust stream is re-circulated (5) with a high-temperature cathode recycle blower. The balance of the flow (7) receives thermal energy transferred from the oxygen burner outlet stream. Burner product gases transfer heat to the cathode exhaust in a high-temperature heat exchanger. The constraint on the heat-exchanger is that it should maintain a pinch temperature of at least 15 °C and at the same time ensure that the outlet temperature of stream (8) is as close (and less than) to 950 °C as possible. Here 950 °C is the maximum allowable LPT inlet temperature. The modified FT8 TwinPak requires a flow split for the two sets of parallel turbines. As described previously, each turbine set is comprised of a low-pressure turbine whose expansion pressure ratio is on the order of 2.5, a power turbine whose outlet pressure is close to atmospheric pressure, and synchronous 60 Hz electric generator. The thermal energy accompanying the turbine exhaust gases (9) is transferred to the bottoming ORC heat engine via a heat recovery refrigerant evaporator/superheater before being vented out as exhaust gas at a temperature of 100°C (10).

The fuel (11) is supplied to the plant from the gasification clean-up processes at elevated pressure (~15 bar) and near ambient temperature (20°C). In the fuel preheater, the fuel-gas is preheated to a temperature (12) such that, when mixed with the re-circulated anode exhaust stream (15), its temperature matches the temperature and pressure (13) of the stack anode inlet while maintaining a steam-to-carbon ratio of 0.5. While a portion of the anode tail-gas is re-circulated (15), the thermal energy accompanying the balance of the flow (16) is used to preheat the coal gas in the fuel preheater. The residual fuel in the anode tail-gas stream is then burned in the oxygen combustor using O₂ supplied by the air

Table 8.5.2-1: Performance summary for IGFC-GT-ORC-OxyC system

System	
Net Power, MWac (incl. CO ₂)	149 (139)
SOFC, MWdc	115
P&W FT-8 TwinPak, MWac	21.8
ORC@20% effic., MWac	19.3
CO ₂ compression power, MW	10.1
Net efficiency on coal gas (w/o CO ₂ compr), %HHV (%LHV)	59.1 (62.6)
Net efficiency on coal gas (with CO ₂ compr), % HHV (%LHV)	55.1 (58.3)
Blower efficiencies, %	50.0
S/C ratio at anode inlet	0.50
SOFC Stack	
Cell voltage, V/cell	0.75
Fuel utilization per pass, %	80
Operating pressure, bar	5.2
Cathode □T, °C	100
Cathode □P, kPa	2.5
Cell electroactive area, cm ²	396
Cell power density, W/ cm ²	0.45
No. cells in stack	300
No. stacks in plant	2151

The use of pure oxygen in the combustor generates gas temperatures higher than 1500°C depending on the amount of fuel utilization and presents material and durability issues in combustor design. The concept was to employ an actively-cooled burner tube which would limit combustor temperatures to 1100°C. Heat rejection from the burner tube would then be transferred to the ORC unit in a separate heat exchanger (not shown). The inlet gas temperature of the LPT can be as high as 950°C. To take advantage of this capability, a regenerative heat exchanger is shown above in **Figure 8.5.2-1** to boost the cathode tail-gas temperature from 825°C and making it as close to 950°C as possible. This heat exchanger has severe temperature requirements and is envisioned to be a rotating, ceramic core regenerative heat exchanger type currently being developed for 300 kW microturbines in distributed generation applications. Finally, the remaining thermal energy associated with the burner outlet stream at station (20) is transferred to the ORC in a lower-temperature heat exchanger (750-800°C) made from high-grade stainless steel or a high temperature alloy. This oxygen

combustor product gas stream contains mostly CO_2 and H_2O . After condensing out the water, the CO_2 can be compressed to 150 bar (2200 psig) and piped to a sequestration location. Thus, the ORC has three primary heat addition sources: (i) thermal energy transfer from the cooled oxygen combustor tube, (ii) the hot exhaust gas from the PT of the modified FT8, and (iii) the high temperature heat exchanger located between stations (20) and (21).

The power plant process design has been implemented in gPROMS and **Figure 8.5.2-3** shows the GUI model flow-sheet implementation in gPROMS where the CO_2 separation and compression processes are performed in a post-processing step.

Figure 8.5.2-3: Flow-sheet of SOFC system involving oxy-combustion in gPROMS

Table 8.5.2-1 also summarizes the overall impact to the system when accounting for the energy requirements of the CO_2 compressor. The overall system efficiency (not including the CO_2 compression parasitic power) of the power plant is 62.6%-LHV with the re-designed FT8 and the UTC Power PureCycle sub-systems contributing nearly 20 MW each. The SOFC operates nominally at 775°C with an average cell voltage of 0.75 V, a fuel utilization of 80%, a power density of 0.45 W/cm^2 , a 100°C temperature rise across both the anode and the cathode, and a 2.5kPa pressure drop across the cathode. The percentage of power delivered by each prime-mover sub-system is shown in **Figure 8.5.2-4**. The SOFC power section provides about 73% of the total power from the plant, and the redesigned FT8 and scaled-up ORC systems supply approximately 14% and 13% of the remaining power output, respectively.

Figure 8.5.2-4: Percent power supplied by each of the IGFC-GT-ORC sub-systems

The LPC pressure ratio is fixed at 5.2. The compression of CO₂ to sequestration-ready pressure levels requires nearly 10 MW of power, which lowers the overall system efficiency by 4 percentage points to 58.3%-LHV. The LPC, LPT and PT operate at 84.0, 91.8 and 85.8 % efficiencies, respectively. The recycle blower operates at 50% efficiency and consumes about 2.4 MW of power for a cathode recycle ratio of 4.6 and a cathode recycle loop pressure rise requirement of 3 kPa.

Having established the baseline performance, a few selected system parameters were varied, and the sensitivity of these parameters to the system performance was evaluated. Cell voltage, fuel utilization, system pressure ratio, anode S/C ratio, cathode-side pressure drop, and stack ΔT were the system parameters that were varied. The DC power from the stack was fixed at 115 MW throughout this study.

Figure 8.5.2-5 illustrates the effect of cell voltage on system efficiency, power density (as reflected by the number of cell-stacks), and parasitic power in the system. An increase in voltage results in lower blower parasitic power, as well as, as a reduction in total power produced by the FT8 and ORC systems. Reductions in power output from the bottoming cycles occurs because increasing cell voltage translates into increasing cell-stack efficiency, and correspondingly lower quantities of waste heat in the product gas.

Figure 8.5.2-5: Effect of cell voltage on various system parameters associated with the IGFC-GT-ORC-OxyC system

The effect of fuel utilization on performance is shown in **Figure 8.5.2-6**. System efficiency is correlated with fuel utilization as is ORC power production. The increase in net system efficiency is off-set by reductions in FT8 and ORC power production. The power density of the SOFC is also lowered with increasing fuel utilization as revealed in **Figure 8.5.2-6** by the increasing number of SOFC stacks required. Interestingly, net power from the FT8 gas turbine system reaches a maximum near a fuel utilization of 70%. Further increases in gas turbine power production with decreasing fuel utilization are constrained by turbine inlet temperature limits. The bottoming ORC power output is directly correlated with fuel utilization and as expected, decreases with increasing fuel utilization due to lower available thermal energy associated with the burner outlet stream.

Figure 8.5.2-6: Effect of fuel utilization on various system parameters associated with the IGFC-GT-ORC-OxyC system

Operating the power plant system at elevated pressure is very important to achieving SOFC power density goals of 0.45 W/cm^2 , as **Figure 8.5.2-7** shows. Net system efficiency also benefits substantially (~ 3.5 percentage points) when increasing the system pressure from 3 to 5.2 bar operation. The cathode recycle blower power parasitic decreases substantially ($\sim 43\%$) in response to increases in system operating pressure due to reductions in hot gas density and hence, volume flowrate. However, the primary factors that enable higher system efficiency from increasing the system pressure arise from higher efficiency SOFC and FT8 gas turbine operation. Higher efficiency SOFC operation in response to elevated pressure is well-documented. The FT8 produces some 57% more net power by increasing the system pressure by 2 bars. This increase in power production occurs because the PR of 5 is much closer to the FT8 design point allowing the LPT shaft power to increase incrementally more than the increase in the LPC power consumption.

Figure 8.5.2-7: Effect of system pressure ratio on various system parameters associated with the IGFC-GT-ORC-OxyC system

The presence of carbon monoxide (CO) in the dry coal-gas stream delivered to the power plant requires consideration of coking formation side reactions within piping runs and hardware. The Boudouard coking mechanism can be inhibited and/or controlled with steam injection. The approach taken in the system design efforts to limit the potential for undesirable coke formation is centered on a two-pronged strategy where (1) fuel gas piping is lined with copper or oxide layers that minimize nucleation sites for coke formation and (2) injecting steam (albeit at a lower steam-to-carbon ratio) into the fuel gas stream via an ejector and anode gas recycle. Since the coal fuel gas provided by the gasifier is significantly pressurized, the ejector can be effectively driven to provide the desired recycle flows. **Figure 8.5.2-8** relates the effect of steam-to-carbon (SC) ratio on system performance. One of the main effects of increasing SC ratios is the reduction in SOFC power density due to dilution of the anode gas feed and hence, a lowering of the Nernst potential. This dramatically increases the number of fuel cell stacks required to deliver 115 MW of power. The overall system efficiency is also correlated with the amount of anode recycle (and hence, SC). Interestingly, the increase in SC ratio produces an increase in system efficiency even though the bottoming cycle power production is reduced. The root of this performance change is related to an increase in effective *system* fuel utilization. In this analysis, the per-pass (or in-cell) fuel utilization was held constant at 80%. The increase in recycle actually increases the overall *system* fuel utilization. Thus, the system efficiency trends with increasing SC are not unlike those of increasing per pass fuel utilization within the SOFC (although the concavity of the plots is different).

Figure 8.5.2-8: Effect of anode S/C ratio on various system parameters associated with the IGFC-GT-ORC-OxyC system

Figure 8.5.2-9 and **8.5.2-10** depict the sensitivity of cathode side pressure drop and temperature rise on system performance, respectively. While the recycle blower parasitic power appears to be strongly influenced by cathode loop pressure drop, it is actually a relatively mild effect when considering pressurized gas flows and the percentage of net power production from the plant. There is a much stronger system-level efficiency effect associated with cathode pressure drop in near-ambient pressure SOFC systems, such as the demonstration power plant. Cathode temperature rise has a direct influence on SOFC power density due to increases in per pass oxidant utilization as **Figure 8.5.2-10** shows, but the system efficiency and net power production from the ORC are only mildly affected. The net FT8 power production is slightly decreased due to the reduction in mass flow through the unit.

Figure 8.5.2-9: Effect of cathode-side pressure drop on various system parameters associated with the IGFC-GT-ORC-OxyC system

Figure 8.5.2-10: Effect of stack ΔT (cathode and anode) on various system parameters associated with the IGFC-GT-ORC-OxyC system

Table 8.5.2-2 provides a qualitative summary of the trends observed in **Figure 8.5.2-5** through **Figure 8.5.2-10**. Overall, while efficiency was reasonably correlated to fuel utilization, system pressure and anode S/C ratio, the number of stacks required to achieve 115 MW from the SOFC system is sensitive to each of these parameters.

Given that the analyses did not include the cost of air separation, the study revealed that the oxy-combustion system configuration could indeed lead to high system efficiencies. It also revealed that there is a clear advantage in going for pressurized systems. It is worthwhile to note that these results were obtained by using calibrated single cell V-I data from Delphi, and realistic FT8 performance maps from P&W. In this study, parametric sensitivity study was conducted on a given system configuration.

Table 8.5.2-2: Summary of parametric sensitivity study results

Parameter	Range	Figure #	Comments
Cell Voltage	0.68 – 0.79 V (range set by FT8 performance map)	10	<ul style="list-style-type: none"> Power and current densities with increase in voltage → increase in # stacks to produce same stack DC power, and decrease in coal gas and air flow-rates Number of stacks increases by 2x An increase in voltage results in lower blower parasitic power and a reduction in total power produced by FT8 and ORC systems Efficiency changes by 3-points over the range
Fuel Utilization	66 – 86%	11	<ul style="list-style-type: none"> Efficiency changes by 3-points over the range of fuel utilization studied Coal gas flow rate decreases with increase in utilization Reduction in power from FT8 and ORC systems with increase in fuel utilization is off-set by lower coal gas flow. This boosts the system efficiency Net power from FT8 system decreases with increasing utilizations because of lower turbine inlet temperatures, which in turn is due to lower energy associated with burner outlet
System PR	3.00 – 5.17	12	<ul style="list-style-type: none"> Power density increases favorably with increase in PR due to increase in current density for a given voltage Increases in PR produce increases in FT8 power Fairly strong correlation with system efficiency
Anode S/C ratio	0.25 – 1.15	13	<ul style="list-style-type: none"> Power density decreases with increase in S/C ratio, and hence the # stacks increases Coal gas flow rate decreases with increase in S/C ratio Fairly strong correlation with system efficiency Fuel cell efficiency and lower coal gas flow-rate boost efficiency even though ORC power and FT8 power decrease with increase in S/C ratio
Cathode pr. drop	2 – 10 kPa	14	<ul style="list-style-type: none"> Blower parasitic power increases by 4.2x over the range studied Net power from FT8 weakly correlated Other parameters (excluding efficiency) almost uncorrelated
Stack ΔT (Cath $\Delta T = \text{An. } \Delta T$) Outlet T = 825 °C	100 – 150 deg. C	15	<ul style="list-style-type: none"> Cathode recycle ratio decreases rapidly with increase in ΔT. This in turn results in a decrease in the blower parasitic power Air flow decreases slightly with increase in ΔT LPC power increases slightly with decreased air flow in the region of operation Net power produced by the LPT and PT turbines decreases with increase in ΔT because the air flow decreases

8.5.2.4 IGFC-GT-ORC-MEA System Analyses

The flow-sheet of the IGFC-GT-ORC-MEA hybrid system is shown in **Figure 8.5.2-11**. The system configuration is similar to the oxy-combustion case with the primary difference being that the cathode and anode tail-gases are allowed to mix in the combustor rather than maintaining the gas separation and using externally supplied O₂. This increases the difficulty of employing low-energy intensive CO₂ capture solutions since the cathode tail-gas contains predominantly N₂. Another important consequence of this decision is that the mass flow through the turbines (LPT and PT) in the FT8 is higher than the flow rate through the LPCs, whereas in the oxy-combustion case the mass flow through the turbines is less than the flow rate through the LPCs. The flow-sheet in **Figure 8.5.2-11** has been implemented in gPROMS and **Figure 8.5.2-12** shows the GUI model flow-sheet as implemented in gPROMS.

System	
Net Power, MWac (incl. CO₂)	156 (146)
SOFC, MWdc	115
P&W FT-8 TwinPak, MWac	32.5
ORC@20% efficiency, MWac	15.8
CO₂ compression power to 2200 psig, MWac	10.1
Net energy required for Sorbent regeneration, MWth	37.8
Net efficiency on coal gas (w/o CO₂ capture), % HHV (%LHV)	62 (65.6)
Net efficiency on coal gas (with CO₂ capture), % HHV (%LHV)	49.3 (51.7)
Blower efficiencies, %	50.0
S/C ratio at anode inlet	0.50
SOFC Stack	
Cell voltage, V/cell	0.75
Fuel utilization per pass, %	80
Operating pressure, bar	5.2
Cathode □ T, °C	100
Cathode □ P, kPa	2.5
Cell electroactive area, cm²	396
Cell power density, W/cm²	0.45
No. cells in stack	300
No. stacks in plant	2151

Table 8.5.2-11: Performance summary for IGFC-GT-ORC-MEA system

The system parameters were fixed at the same levels as in the oxy-combustion case i.e. the SOFC operates nominally at 775 °C with an average cell voltage of 0.75 V, a fuel utilization of 80%, a power density of 0.45 W/cm², a 100 °C temperature rise across both the anode and the cathode, and a 2.5kPa pressure drop across the cathode. The stack power was fixed at 115 MW_{dc}. The LPC pressure ratio was fixed at 5.2 as in the oxy-combustion system. The total power produced by the FT8 system in this case is higher than that obtained in the oxy-combustion case, and this can be attributed to the fact that the mass flow through the turbines is much higher. On the other hand, the

ORC power production was lower than the oxy-combustion system due to the reduction in thermal energy available in the system.

Figure 8.5.2-12: IGFC-GT-ORC-MEA process flow-sheet

Figure 8.5.2-13: gPROMS Model GUI flow-sheet of the IGFC-GT-ORC-MEA system

The CO₂ absorption system based on MEA technology is generally very effective for dilute CO₂ streams up to 14% (mol) [ii]. This system requires that the process gas temperature be at about 50°C for the absorber, but the thermal energy to regenerate the sorbent is significant. The compression work required to make the CO₂ effluent stream sequestration-ready is about 10 MW, which is close to the CO₂ compression cost in the IGFC-GT-ORC-OxyC case. But the energy associated with the regeneration of the MEA is nearly 38 MW_{th}, which is significant and lowers the overall system efficiency. Thus, the energy associated with CO₂ capture and compression reduces the overall system efficiency by 14 percentage points from 66%-LHV to 52%-LHV.

8.5.3 Modeling of Demonstration-scale IGFC Hybrid Power Systems

8.5.3.1 IGFC-ORC-Oxycombustion System Analysis

Analysis of demonstration-scale IG-SOFC power plants focused on ambient pressure, 1-MW hybrid configurations due to their simplicity and ease of integration with existing bottoming cycle hardware. As with the pressurized hybrid systems, waste heat power generation was accomplished with an organic Rankine cycle bottoming cycle. These concepts are illustrated in **Figure 8.5.3-1** and **Figure 8.5.3-2**, with the difference between the two flow-sheets being the presence (or absence) or a cathode recycle loop and the associated recycle blower.

Figure 8.5.3-1: IGFC-ORC-OxyC with cathode recycle blower

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anode inlet. The amount of recirculation of the anode exhaust stream (12) coupled with the driving pressure available from the gasification process enables the use of an ejector to accomplish the recycle. The balance of the flow (14) is used to preheat the cold coal gas. This anode tail-gas stream (15) is then burned using oxygen (16) from the air-separation plant associated with the gasifier. The thermal energy accompanying the burner hot exhaust gases (17) is transferred to a bottoming Rankine cycle heat engine via a heat recovery steam generator or an organic fluid evaporator/superheater. The cooled stream (18) consists primarily of CO₂ and water vapor from which the water is condensed out. The CO₂ stream (19) is then compressed to ~ 150 bar and piped to a sequestration location.

Table 8.5.3-1 summarizes the performance of the system when accounting for the energy requirements for CO₂ compression. The CO₂ compression requires nearly 90 kW, which lowers the system efficiency by about 4 percentage points to 47 %-LHV. The operating parameters such as cell voltage, system pressure, number of stacks and fuel utilization are also specified in **Table 8.5.3-2**. It is also worth noting from **Figure 8.5.3-1** that the power associated with the re-cycle blower is ~100 kW, which is a significant amount of energy. To analyze the impact of the recycle loop, a system configuration without the cathode-side recycle loop is proposed in **Figure 8.5.3-2**. In this configuration, the cathode exhaust stream (4) is used to preheat the compressed air (2). As a result, the cathode exhaust stream loses a lot of its thermal energy, which would be otherwise available to the Rankine cycle-based heat engine. Thus, for the same set of operating parameters, this configuration results in a lower power output from the ORC.

Table 8.5.3-1: Performance summary for IGFC ORC-OxyC system with cathode recycle

System	Recycle	No Recycle
Net Power, kWac (incl. CO₂)	1061 (974)	975 (887)
SOFC, kWdc	1000	1000
ORC@20% effic., kWac	216	127
CO₂ compression power, kW	88	88
Net efficiency on coal gas (w/o CO₂ compr), % LHV	51.2	47.1
Net efficiency on coal gas (with CO₂ compr), % LHV	47.0	42.8
S/C ratio at anode inlet	0.50	0.50
SOFC Stack		
Cell voltage, V/cell	0.75	0.75
Fuel utilization per pass, %	80	80
Operating pressure, bar	1.1	1.1
Cathode □ T, °C	100	100
Cathode □ P, kPa	2.5	2.5
Cell power density, W/ cm²	0.274	0.3
No. cells in stack	300	300
No. stacks in plant	34	31

The salient features on the fuel-side of the system with the recycle loop depicted in **Figure 8.5.3-1** include fuel preheat to 534°C, an anode recycle ratio (ARR) of 1.92 with a S/C of about 0.5, and a fuel utilization of 80%. On the air-side of the power plant, the amount of cathode recycle required to adequately preheat the air is significant and results in a cathode recycle ratio of nearly 5.3. The cathode side air temperature rise is assumed to be 100°C and the pressure drop is about 2.5 kPa. The cathode recycle generates the largest single parasitic power in the system at 97.5 kW. The primary benefit of the recycle is to eliminate the air recuperator and reduce the size of the fresh air turbo-blower at the expense of the recycle device.

8.5.3.2 Performance Sensitivity of IGFC-ORC-Oxycombustion System to design parameter variation

The baseline demonstration system design operates at an average single-cell voltage of 0.75V. The sensitivity of the system performance to design voltage selection is shown in **Figures 8.5.3-3 (a) and (b)**. The efficiency plot shows a linear relationship with cell

voltage, however, it is clear that there is a highly non-linear dependency between cell voltage and the required number of cell-stacks to generate 1 MW_{dc} power. As **Figures 8.5.3-3** illustrates, the number of cell-stacks required increases by a factor of 2.5 when moving from a cell voltage of 0.7 V to 0.8 V, and increases by a factor of 10 when moving from 0.65 V to 0.85 V. Increases in cell voltage (and hence system efficiency) result in decreases in parasitic blower power requirements, but also a lowering of the net power output from the ORC system as is shown in **Figures 8.5.3-3 (b)**. A 100 mV increase in design cell voltage translates into a reduction of 23% in ORC power output and a 26 % decrease in turbo-blower parasitic power. The optimal cell voltage from an overall cost and efficiency standpoint can be obtained by optimization studies, and will be performed in future.

Figure 8.5.3-3: Effect of cell voltage on various system parameters associated with the IGFC-ORC-OxyC demoscale system with cathode recycle

The performance impact due to variation in system fuel utilization is shown in **Figure 8.5.3-4**. The sensitivity of system efficiency and parasitic power with changes in fuel utilization was not as strongly correlated as it is with cell voltage. In general, an increase of about 1 system efficiency percentage point is possible with every 5% increase in fuel utilization. While blower parasitics are relatively insensitive, the ORC power output is strongly influenced by the amount of fuel utilized. This was expected as the thermal energy available in the exhaust gas after combustion is directly proportional to the unused fuel content in the anode tail gas.

Figure 8.5.3-4: Effect of fuel utilization on various system parameters associated with the IGFC-ORC-OxyC demoscale system with cathode recycle

The performance impact due to variation in the allowable cathode air temperature rise (maintaining average cell temperature at 750°C) is shown in **Figure 8.5.3-5 (a) and (b)**. The number of stacks required is insensitive to this parameter. The sensitivity of system efficiency is non-linear and fairly dramatic in the 50-100°C temperature difference range. This non-linearity is attributable primarily to the recycle blower power requirements. As the allowable cathode temperature rise increases, the blower parasitic power reduces, and **Figure 8.5.3-5(b)** shows the non-linear sensitivity of the blower parasitic power to the cathode temperature rise. In contrast, the ORC power output decreases only slightly with increasing cathode ΔT and approaches an asymptotic limit.

Figure 8.5.3-5: Effect of cathode temperature rise on various system parameters associated with the IGFC-ORC-OxyC demoscale system with cathode recycle

8.5.4 Conceptual Design of SOFC Cell Stack and Stack-Module

8.5.4.1 Airflow Distribution in Module Concepts

Two module concepts, one unpressurized the other pressurized, were selected to verify that adequately uniform airflow could be achieved with acceptably low pressure drops.

The unpressurized concept was the annular module shown in **Figure 8.5.4-1**. In this configuration airflow enters the center of the module from underneath and then flows radially outwards through the annulus of stacks and is then directed upwards and out through the top. In the first configuration the inlet and outlet ducts are 30cm in diameter and there is a 10cm radial clearance between the outside of the stack annulus and the module casing (air exhaust ducting).

Figure 8.5.4-1: Unpressurized annular stack module concept

Airflow distribution was modeled using the CFD code Fluent and the flow was assumed to be axisymmetric. The cell stacks were represented as porous media which provided similar pressure drops to those calculated across the stack (approximately 170Pa). The media was assumed to have isotropic properties which theoretically permit unrealistic flow vertically in the stack, but in practice airflow follows the path of least resistance which is a predominantly radial direction as can be seen in **Figure 8.5.4-2**. The resulting flow distribution in **Figure 8.5.4-3** shows the air velocity variation with axial position in the stack at the entrance point and half way across the cell. As can be seen the velocity profile is highly non-uniform which is attributed to the recirculation zones illustrated in **Figure 8.5.4-2**.

Figure 8.5.4-2: Geometry and streamlines for annular case 1

Figure 8.5.4-3: Velocity distribution in cathode cells for annular case 1

In an attempt to improve uniformity the inlet and outlet duct diameters were increased to 60cm and the outer radial clearance was increased to 20cm. This has the effect of reducing the air velocity entering and exiting the module which should reduce the extent of flow recirculation. **Figure 8.5.4-4** shows that the recirculation zones form lower down the inlet duct, moving away from the stack which does result in substantially improved flow uniformity (**Figure 8.5.4-5**).

Figure 8.5.4-4: Geometry and streamlines for annular case 2

Figure 8.5.4-5: Velocity distribution in cathode cells for annular case 2

Further improvements were achieved by introducing a low pressure drop (100Pa) screen immediately upstream of the stack in the inlet duct. The effect of the screen is to cause the recirculation zone to occur further upstream and away from the stack face, the beneficial results of which are seen in **Figure 8.5.4-6**. The overall pressure drop for this last case from air duct inlet to outlet is only 480Pa which is well within the 1-2kPa target. For reference, the equivalent pressure drop for the first case (**Figure 8.5.4-2**) was 4700Pa. Although these models don't include the precise conditions, e.g. the air is assumed to be at a constant temperature of 700°C, the results indicate that sufficient flow uniformity is feasible with low pressure drops.

Figure 8.5.4-6: Velocity distribution in cathode cells for annular case 3

An equivalent study for airflow distribution was done on the pressurized linear module is shown in **Figure 8.5.4-7**. In this concept air enters between the diverging ends of two nonparallel rows of stacks, flows in a normal direction through the stacks and then turns and flows out towards a channel at the converging end of the stack rows. Similar assumptions were used to those applied to annular module analyses but here 2D planar models were employed. Although this concept was designed as a pressurized system, the air was defined to be at atmospheric pressure which is a worst case as it results in the highest gas velocities. An initial model was run for the geometry in **Figure 8.5.4-7** but this resulted in poor airflow distribution due to the recirculation zones caused by the sudden expansion where the air initially enters between the two rows of stacks.

Figure 8.5.4-7: Pressurized linear module concept with angled rows of stacks

The geometry was thus modified so the air entrance channel was the same width as the distance between the two stack rows (**Figure 8.5.4-8**), but even in this case, some recirculation occurred. The resulting flow distribution for the two stack rows in **Figure 8.5.4-9** shows that although flow is evenly distributed between the two rows there is some variation along them. Using a similar technique to that employed in the annular module to control the recirculation zones, a 100Pa pressure drop screen was inserted on the inlet. The plot of streamlines in **Figure 8.5.4-10** shows this to be effective at inhibiting recirculation with the expected flow uniformity benefit illustrated in **Figure 8.5.4-11**. Although there is still an approximate 20% variation in airflow from one end of the stack rows to the other, the overall pressure drop was calculated to be only 400Pa (including the screen) and therefore there is still some margin to increase the pressure drop across the stacks to further improve flow uniformity.

Figure 8.5.4-8: Linear stack baseline case - Air-side streamlines

Figure 8.5.4-9: Linear stack baseline case - Normal velocity (mass flux) distribution in cathode cells

Figure 8.5.4-10: Linear stack design - screen added to improve flow uniformity

Figure 8.5.4-11: Linear stack design - Normal velocity in cathode cells with & without screen

8.5.5 Cell Size / Geometry and Flow Configuration Effects on Temperature

A user defined function for SOFC electrochemistry was developed for use with the CFD code Fluent to enable thermal / electrochemical analysis of individual cells with differing size, geometry and flow configuration. The models were calibrated using V-I data for Delphi cells and were run using coal gas compositions that included a surface catalyzed water gas shift reaction. Solutions were run with the cell voltage specified and the current and power densities being outputs. Uniform gas distribution was assumed along the inlet and outlet edges of the cell and the remaining external boundaries of the

model were assumed to be adiabatic. Although heat transfer to the stack frames may be significant, it was not expected to substantially alter the conclusions of the study and inclusion of such a mechanism would have greatly increased the complexity of the modeling effort. The purpose of the exercise was to better understand the advantageous / deleterious effects of certain parameters that can be readily altered in the design of a stack. The principal parameters of interest were, cell area and aspect ratio, and flow configuration (cross, co, counter). The baseline case was for a 19x19cm active area cell running off a coal gas composition, details of which are given in **Table 8.5.5-1**. Solutions were obtained for the baseline with cross, co and counter flow configurations, results of which are in **Figure 8.5.5-1**. One thing that became immediately apparent when trying to compare solutions was the number of variables meant there were multiple ways of making comparisons. In this first case the cell voltage and cathode inlet temperature was defined to be the same, but the anode flows were adjusted to maintain approximately same fuel utilization (55%). Under these conditions cross-flow resulted in the highest average power density and co-flow the lowest, which correlates with the average cell temperatures. Because average cell temperature is calculated from the solution, it is not possible to directly define this as a fixed condition. In order to try and match this parameter it would be necessary to adjust something else, such as the cathode inlet temperature, flow rate or cell voltage. **Figure 8.5.5-2** shows the results of increasing the cathode flow to 155% of nominal and reducing the cathode inlet temperature by 25°C to 675°C for the counter-flow case. In either case the average power density is reduced to a similar level of the cross-flow solution. What can be concluded is that cross-flow seems to be the least desirable configuration as it has the highest maximum cell temperature for equivalent average power density. It is interesting to note that the current density distributions (**Figure 8.5.5-3**) do not directly correlate with the temperature distributions (**Figure 8.5.5-1**), which is due in part to the variation in fuel concentration which in turn is dictated by the anode flow direction.

Table 8.5.5-1: Baseline cell flow conditions & geometry for CFD / electrochemistry analyses

anode	IN
Temperature, C	700
Flow rate, kg/s	6.50E-05
mole frac. H2	0.183
mole frac. H2O	0.157
mole frac. CO	0.315
mole frac. CO2	0.316
mole frac. N2	0.030
cathode	
Temperature, C	700
flow rate, kg/s	4.55E-04
mole frac. H2O	0.016
mole frac. O2	0.207
mole frac. N2 (N2 + Ar)	0.778
anode channel height, mm	1
cathode channel height, mm	2
MEA thickness, mm	0.5
cell width, mm	190
cell length, mm	190

Figure 8.5.5-1: Baseline cell temperature contours and results summary for cross, co & counter-flow

Figure 8.5.5-2: Baseline cell temperature contours and results summary for counter-flow with hi flow & lo temp

Figure 8.5.5-3: Baseline cell current density contours and results summary for cross, co & counter-flow

The effect of cell size and geometry was investigated for cross, co and counter-flow conditions using the baseline geometry (19x19cm), a square cell double the baseline area (26.9x26.9cm), and a rectangular cell with a 4:1 aspect ratio having the same area as the baseline (38x9.5cm). Similar conditions to those reported in the previous paragraph were used, namely a cell voltage of 0.75V, 700C gas inlet temperatures and air and fuel flow rates were kept constant, albeit doubled for the larger area cell. These conditions resulted in power densities of approximately 0.25W/cm² and fuel utilization of 52%. Summaries of the results for cross, co and counter-flows are shown in **Figures 8.5.5-4, 8.5.5-5 and 8.5.5-6** respectively, and included cell temperature contour plots and tables of key data, e.g. maximum cell temperature. Note that two cases were run for the rectangular cell, one with the air flowing in the short direction and the other in the long. With the exception of the far right contour plot, the air flow direction is from right to left as indicated by the blue “A” arrow. Fuel flow direction is indicated by the red “F” arrow.

Figure 8.5.5-4: Baseline, large & rectangular cell temperature contours and results summary for cross-flow

Figure 8.5.5-5: Baseline, large & rectangular cell temperature contours and results summary for co-flow

Figure 8.5.5-6: Baseline, large & rectangular cell temperature contours and results summary for counter-flow

Examination of figures indicates that for any one particular flow configuration the cell area and aspect ratio had little or no effect on the average power density, nor the maximum cell temperature and cathode temperature rise. The key implication being that if cell temperature is independent of size for a given power density (assuming fixed flow rate to area ratio) then thermal gradients should be reduced by flowing air in the direction of the longest cell direction. Plots of thermal gradients in the direction of fuel and airflow are shown respectively in **Figures 8.5.5-7** and **8.5.5-8** for cross-flow. **Figures 8.5.5-9** and **8.5.5-10** show thermal gradients in air / fuel flow direction for co and counter-flow. The nominally one dimensional variation in temperatures for co and counter-flow mean that thermal gradients in the direction normal to the gas flow are very small and therefore have not been plotted. Examination of the thermal gradient plots highlights markedly different responses for the three flow conditions. For cross-flow the largest thermal gradients occur in the direction of fuel flow not air flow, and the longer the fuel flow path the smaller the gradients. Counter-flow shows similar maximum thermal gradients irrespective of cell size and geometry (**Figure 8.5.5-10**). Co-flow exhibits the lowest overall thermal gradients and lengthening the flow path does reduce the gradient as comparison of the two rectangular cell contour plots in **Figure 8.5.5-9** indicates.

Figure 8.5.5-7: Baseline, large & rectangular cell temperature gradient contours and results summary for cross-flow

Figure 8.5.5-8: Baseline, large & rectangular cell temperature gradient contours and results summary for cross-flow

Figure 8.5.5-9: Baseline, large & rectangular cell temperature gradient contours and results summary for co-flow

Figure 8.5.5-10: Baseline, large & rectangular cell temperature gradient contours and results summary for counter-flow

8.5.6 Cell Evaluation and Benchmarking

8.5.6.1 V-I Characteristics of the Radial Modules

Table 8.5.6-1 lists characteristics of the seven different radial module electrochemical tests. The voltage current characteristics (V-I curves) of the four representative radial module tests measured at 750°C are shown in **Figure 8.5.6-1**. For comparison, the V-I curve of a Delphi's 30-cell stack tested at 750°C is also shown in the same plot. All the radial module tests have demonstrated consistent polarization performance. The radial module performances are comparable to that of the Delphi's 30-cell stack at low current density. At high current density, the radial modules tested at UTRC have exhibited a slightly lower voltage compared with that of the Delphi's 30-cell stack, likely due to variation in local temperature distribution as well as the total ohmic resistance. Overall, the Delphi cells performed well at 750°C, exhibiting a power density greater than 0.45W/cm² with an output voltage of 0.75V.

Table 8.5.6-1: Radial module electrochemical tests

	RM-D-1	RM-D-2	RM-D-3	RM-D-4	RM-D-5/ RM-D-5A	RM-D-6
Test configuration	Radial module	Radial module	Radial module	Radial module	Radial module	Radial module
Cell	Anode-supported cell with LSCF cathode	Anode-supported cell with LSCF cathode	Anode-supported cell with LSCF cathode	Anode-supported cell with LSCF cathode	Anode-supported cell with LSCF cathode	Anode-supported cell with LSCF cathode
Cathode surface	Without metal cap layer	With metal cap layer	Without metal cap layer	Without metal cap layer	Without metal cap layer	Without metal cap layer
Cathode interfacial materials	UTRC's ceramic past	Delphi's metal paste	Delphi's metal paste	UTRC's ceramic paste	UTRC's ceramic past	UTRC's ceramic past
Testing temperatures	First at 700C, then at 750C	750C	700-800C	First at 700C, then at 750C	650C-800C	750C
Thermal cycling	9 TCs	10 TCs	3 TCs

Figure 8.5.6-1: V-I curves of representative radial module tests at 750°C

8.5.7 Steady-state Cell Performance

Radial module tests using cells with cathode metal cap and metal paste as cathode interfacial materials showed rapid decays during the initial period of steady-state tests (2% degradation over the first 50 hours). However, the degradation rate decreased over time and stabilized after ~150 hours with a rate of 3.7 %/1000hrs. Using cells without cathode metal cap and UTRC's ceramic paste as the cathode interfacial materials, very stable and reproducible steady-state performance has been observed in the radial module tested at 750°C as shown in **Figure 8.5.7-1**. Post test analysis, as

shown in **Figure 8.5.7-2**, revealed that there was a Cr rich layer between the Delphi metal contact material or the metal cap layer and the LSCF cathode surface. Cr-rich layer formation probably caused the relatively high degradation observed for RM-D-2 and RM-D-3. For radial modules using cells without the metal cap layer and ceramic interfacial paste, slight Cr-enrichment was observed at the surface of the interfacial layer where it is in contact with the metallic interconnect, as shown in the Cr-map from RM-D-1. However, there is no evidence of Cr-diffusion into the cathode layer, indicating a successful chromia-containment strategy employed by UTRC's coated interconnect design.

Figure 8.5.7-1: Steady-state performance of RM-D-1 and RM-D-6

Figure 8.5.7-2: Cr maps for cells in RM-D-1, RM-D-2 and RM-D-3

8.5.7.1 Temperature Effect on Cell Durability

In order to study the temperature effect on cell performance, a radial module (RM-D-5A) was tested under constant current load at different operating temperatures of 650, 675,

700, 750 and 800°C, respectively. As shown in **Figure 8.5.7-3**, stable module performance was obtained at all these different testing temperatures. This test provides information on operation boundaries of cells in a system environment where temperature gradient exists across the stack.

Figure 8.5.7-3: Load performance as a function of time at different temperatures for RM-D-5A

8.5.8 Cell Fracture Issues

Cell mechanical robustness was a concern, especially for large footprint cells. In order to determine whether cell structural integrity is affected by cell surface flatness, 5 cells from the same batch of cells as that of SM-D-2 were white-light scanned to study their surface flatness. These cells demonstrated different characteristics as shown in **Figure 8.5.8-1**. Practice runs of square module assembly were then conducted using these five cells to evaluate their mechanical robustness. Four out of the five cells survived the dry runs while cell #27 fractured. As shown in **Figure 8.5.8-2**, the cell fractured in the region where there was a high localized curvature. Apparently, to avoid cell fracture during square module assembly, local curvature near cell edges needs to be minimized. Both the Delphi team and the UTRC team are working on cell manufacturing process optimization and stack design modification to address this issue.

Figure 8.5.8-1: Cell Contour Scanned using White-light (Dimensions in mm)

Figure 8.5.8-2: Cell #27 Fractured during Cell Assembly Trial

9 2008 TECHNICAL PROGRESS AND ACHIEVEMENTS

9.1 Task 1: System Development

9.1.1 Define System / Subsystem Requirements

Delphi developed several system platforms that were configurable for both natural gas and Diesel fuel operation. These are shown in **Figure 3.2.1-1**.

Figure 3.2.1-1: SOFC Systems

The SPU 1 system was configured to operate with diesel or natural gas fuels. It utilizes a CPOx fuel reformer and has a maximum stack output power of 3400 W. This limits the net output of this system to approximately 1500 W at 15% efficiency. This system also does not contain the required power electronics, and fuel processing (pump, desulfurizer) required to interface directly with an application. The DPS3000D system design is intended to resolve these issues by allowing for increased fuel reforming efficiency (with an endothermic high-efficiency reformer) and integrated power electronics and fuel desulfurization. The key requirement contrasts between Delphi's current and future Diesel SOFC systems is shown in **Figure 3.2.1-2**.

		SPU 1E GAP	DPS 3000 ENHANCEMENT
System Efficiency	Power Level (3.5kW net)	60 cells (105 cm ²) - 1-1.5 kW Stack cooling limited	40-50 cells (270 cm ²) - 3-4 kW Improved cooling environment around stacks
	Parasitic power losses	High parasitic loads due to high-pressure drop components and high stack cooling airflow required	Opportunities for reduced pressure drop and improved stack cooling.
	Fuel Processing Efficiency	Lower efficiency with CPOx reformer with low recycle flow	Improved efficiency with "Endothermic" reformer and high recycle flow
	Heat Loss	High heat loss due to thin insulation and high internal thermal communication (undesirable)	Increased insulation thickness and thermal component compartmentalization
	Fuel Compatibility	Zero sulfur Diesel fuel restricted (no reformat desulfurizer)	US 07 Ultra-Low-Sulfur Diesel compatible (internal, integrated reformat desulfurizer)

Figure 3.2.1-2: Feature Comparison

9.1.2 Develop System Mechanization

System mechanizations for both SPU 1 and DPS3000D Diesel systems were developed and analyzed. Both systems utilize anode tail-gas recycle to bring water vapor and excess hydrogen and carbon monoxide gas back to the front of the reforming process. The DPS3000D design uses a reformer with an integrated heat exchanger to support the reformer temperature in high-efficiency (endothermic) reforming modes. A non-regenerative desulfurizer sorbent is placed in the reformat stream to reduce H_2S in the reformat to below 10 ppb by volume. A heat exchanger is employed between the outlet of the reformer and the desulfurizer that allows for cooling of the reformat with the cathode air feedstream to the stack. This “equalizer” heat exchanger serves two important functions: First, it cools the high temperature reformat to below $800^{\circ}C$ (which is the maximum inlet temperature allowed by the desulfurizer sorbent), and secondly, to recover heat from the reformat stream back to the cathode air. This allows for adequate cathode air preheating during high-efficiency reforming operation. The DPS3000D system mechanization with supporting rated power analysis is shown in

Figure 3.2.2-1.

Figure 3.2.2-1: DPS3000-D Model Predictions

2008 Delphi SOFC systems had a 12 VDC bus to support the system controller, sensors and actuators. The DPS3000D system also had a 12 VDC application power output, and thus a Stack DC to 12 VDC power converter. Parasitic loads in the system like blower, pumps, and heaters also run on this 12 VDC power circuit.

A simplification of this mechanization is used in the SPU 1E systems. The endothermic reformer is replaced with a CPOx reformer. Anode tail-gas recycle strategy is used to

allow for water vapor and nitrogen diluent input to the reforming process which improves margin against precipitation of solid carbon in the reformat. The SPU 1E system mechanization with supporting rated power analysis is shown in **Figure 3.2.2-2**.

Figure 3.2.2-2: System Model Predictions

9.1.3 Perform System Analysis

System analysis was performed on both SPU 1E and DPS3000 Diesel SOFC Systems. The SPU 1E system has low system efficiency (14.4%) and lower net power output (1590 W) due to low efficiency CPOx fuel reforming, reduced number of cells, and limitations on stack cooling capacity. The DPS3000 system design has several advantages when compared to the SPU 1E system that increase power output (3625 W) and improve system efficiency (25.5%). These advantages include: endothermic fuel reformer, additional solid oxide fuel cells, and auxiliary stack cooling.

Results of system simulation using MATLAB/SimulinkTM, for DPS3000 and SPU 1E are shown in **Figures 3.2.3-1** and **3.2.3-2**. The SPU 1E system assumes 60 SOFC cells with an active area of 105 cm² per cell, and a power density of 0.379 W/cm² at 0.7 V/cell. These assumptions are consistent with anticipated performance on recycle-diluted diesel CPOx reformat. Under these assumptions, the SPU 1E system will generate up to 1590 W at 14.4 % efficiency. Most of the inefficiency is caused by lower fuel processing efficiency (85% with recycle) and high parasitic loads on the system. A majority of the parasitic load is due to high cathode airflow required to cool the SOFC stacks with a small allowable cooling temperature gradient, and the high pressure drop of the SOFC stacks requiring a high blower pressure.

Figures 3.2.3-1: Trends in Stack Power Density

Figure 3.2.3-2: Projected Performance Comparison

The DPS3000 system was originally designed with 100 SOFC cells with an active area of 105 cm^2 per cell, and a power density of 0.450 W/cm^2 at 0.7 V/cell . Under these assumptions, the DPS3000 system will generate up to 3400 W at 25% efficiency, and peak efficiency of 30% at 2400 W net output. The 2008 DPS3000 design incorporated a large single 40-cell stack. For the analysis shown in **Figure 3.2.3-1**, 40 cells at $270 \text{ cm}^2/\text{cell}$ active area and $0.450 \text{ W/cm}^2 @ 0.7 \text{ V/cell}$ power density was assumed. The result is a net increase output of power 3625 W and 25.5% system efficiency.

Figure 3.2.3-1 shows data from several stacks for a mixture of $50\% \text{ H}_2$ fuel $50\% \text{ N}_2$ fuel as a function of temperature at a fixed voltage. This data indicates that stack power density is a function of average cell temperature with a slope of $85 \text{ mW/cm}^2 \text{ C}$. For a target average cell temperature of $800\text{-}810^\circ\text{C}$, stack power densities of 550 mW/cm^2 at

0.825 V/cell should be expected. **Figure 3.2.3-2** shows an update of system efficiency projections for DPS3000D based upon the original 2x50-cell stack ($0.450 \text{ mW/cm}^2 + 0.7 \text{ V/cell}$) and the original 1x40-cell, 270 mW/cm^2 ($@582 \text{ W/cm}^2 + 0.8 \text{ V/cell}$). Commercial diesel generator efficiency and SPU 1E efficiencies are shown for reference. The yellow field between the two DPS3000 projections represents the probable efficiency boundary for the DPS3000D design based upon worst-case and best-case estimates.

For heavy-duty commercial vehicle applications, internal-combustion diesel engine generators are the incumbent technology. At each net electric output load in **Figure 3.2.3-2** above, Delphi's diesel SOFC systems have higher electrical generation efficiency than the diesel generator. Over a significant portion of the load profile, the Diesel SOFC system could save between 40% and 60% of fuel consumption compared to the diesel generator.

9.1.4 Develop Power Architecture and Electronics Design

The application requirements of the North-American heavy-duty commercial vehicles dictate that the SOFC system interface with a 12 VDC power bus. This requires a high-current stack-to-12 VDC converter. The stack should experience a voltage range of 36–63 V; the converter must have high input voltage range compatibility and also high conversion efficiency especially at high system output.

To support commercial vehicle application system development, Delphi has procured and tested a high-output, high efficiency, wide-input-range 12 VDC converter. The converter has very high conversion efficiency (>96%) across most of the output power band and at input voltages consistent with high stack output power (40-50 V).

To support near-term commercial vehicle application development, the 12 VDC converter has been integrated into a commercial vehicle electrical architecture that allows for start-up power flexibility. The integrated electrical interface hardware is shown in **Figure 3.2.4-1**. The interface allows for supply of input power to the SOFC system via 120 VAC input source, or 12 VDC vehicle electrical power. Both inputs are converted to a nominal 42 VDC input which is required to operate SPU 1E Diesel SOFC systems. The DPS3000 systems are 12 V systems and do not require 120 VAC-to-42 V on 12 – 42 V converters. DPS3000 systems use vehicle 12 V bus power supplied by the alternator to supply start-up power.

Hardware

- Transient Truck Bus Load Support
- Lab Grade Safety Circuit
- Electrical Interface
- A/C Start-Up Power Support

Software

- Transient Truck Bus Load Support
- Power enable buffering
- Safety & Diagnostic

Figure 3.2.4-1: Electronics - Truck Demonstration Electronics Application Interface

9.1.5 Develop System Design and Perform Optimization

The basic design for the DPS3000D Diesel SOFC APU is shown in **Figure 3.2.5-1**. The outline dimensions and arrangement of components were chosen to be consistent with current rail-mounted heavy-duty truck APUs.

Figure 3.2.5-1: Diesel SOFC APU Conceptual Design

Several changes have been implemented in the original system design and layout. The most significant change is the move from 2x50-cell Gen 3.1 stacks (105 cm² active area) stacks to a single 40-cell stack (270 cm² active area). This change simplified the feed and return flow plumbing requirements, reduces electrical terminals and cabling, and includes a slight increase in stack active area. Next, a dedicated air and fuel supply system was implemented for the reformer subsystem. In the previous design, reformer air inputs were sourced from two independent sources: Main process air blower and carrier air pump. In the updated design, all reformer air inputs are sourced from the carrier air pump, the fuel and air control actuators are integrated into the modified Delphi SECA Final Report Oct 2011 v.6.doc

Reformer Air/Fuel Module (RAFM). This facilitates pre-build and validation of this input control module before system assembly. The allowed volume of desulfurizer sorbent has also been increased from 3 liters to 4.5 liters. This 50% increase in sorbent volume will allow for a six month service interval on desulfurization sorbent which is consistent with application service interval requirements. Lastly, the power electronics package was expanded and partitioned to allow for 12 V power output, dual DC voltage output, or AC/DC output power. This is accomplished through use of a dual converter package. The pair of converters can be configured as 2 x 3 kW DC/DC (12 V), or 3 kW (12 V) and 3 kW (24 V), or 3 kW (12 V) and 3 kW (120 VAC) depending on the converters installed in the system. These features are described in **Figures 3.2.5-2, 3.2.5-3, and 3.2.5-4.**

Figure 3.2.5-2: Diesel SOFC APU Conceptual Design

The SPU 1E diesel system has been integrated and successfully tested.

Figure 3.2.5-3: Diesel SOFC APU Conceptual Design.

Figure 3.2.5-4: DPS3000-D Hot-Zone-Module

9.1.6 Develop System Controls

System controls were developed and validated for natural gas and diesel fuel reformers used in Delphi's SOFC systems. One key area of control development is power electronics, Delphi's SOFC system. The reformer air and fuel inputs cannot respond instantaneously when rapid electrical loads are applied to an SOFC stack. For large changes in current, the stack fuel utilization may be driven unacceptably high. Electrical storage devices in the form of batteries and capacitors have been employed to help buffer fuel cells from rapidly changing electrical loads. For Delphi's heavy-duty commercial vehicle applications, the vehicle lead-acid battery will serve as an energy storage device to deliver currents to loads primarily during transient periods. Delphi's strategy is to buffer the rate of load increase with its power electronics so that the battery handles instantaneous demand (reduced load impedance), and the SOFC stack transitions to the load at a controlled rate.

To handle electrical transients and protect the stack from excessive fuel utilization demand, a dynamic current-limit control scheme was developed for the DC/DC converter. At any given load current, the DC/DC converter current limit is set to a safe margin above the current load. For the onset of a transient current demand, the output current of the DC/DC will rise to this buffer limit, and only allow increased current demand over time via a pre-defined slew-rate. This reduces the rate of change of the stack current demand and allows the fuel reformer air and fuel inputs to keep pace with the instantaneous demand during the transient. During this transient period, the output voltage of the converter must drop. A battery system employed in parallel with the fuel cell powerplant supports the bus voltage during the low output voltage period and excess current is supplied by the battery. As dynamic current limit ramps up to the new demand point, the DC/DC converter output voltage increases and the batteries resume charging. 100% of the steady state load is then supplied by the fuel cell system.

The electrical interface hardware has been integrated and successfully tested with both resistive and reactive loads. The results of a typical load transient are shown in **Figure 3.2.6-1**.

Figure 3.2.6-1: Transient Load Handling

9.1.7 System Integration and Testing

9.1.7.1 System Integration

The truck demonstration chassis unit is comprised of the SPU 1E diesel SOFC unit shown in **Figures 3.3.1-1** and **3.3.1-2**, and a chassis/enclosure comprising power electronics and fuel supply hardware. The chassis and enclosure also provides mechanical support for vehicle installation. The demonstration chassis enclosure system is shown in **Figures 3.3.1-3** and **3.3.1-4**.

Figure 3.3.1-1: SPU 1E – Diesel SOFC Powerplant

Figure 3.3.1-2: SPU 1E Diesel SOFC Powerplant

Added to SECA System for Truck Demonstrator:

- Diesel fuel vaporizer
- Electric start vaporizer
- Carrier air pump
- Carrier air control manifold
- Injection air controller
- Check valve assembly
- Fuel pump and filter asm
- Truck output power converter
- Truck input power converter
- AC input power converter
- Power interface controller
- Truck mounting frame and enclosure with vibration isolators
- Electronics housing with vibration isolators
- Reducing gas supply and controller
- User interface panel
- Remote user interface head
- Wireless remote PC monitoring system

Demonstrator Chassis (362 Liters)

Q1-2008

1.25 kW / 14% Efficiency (No Sulfur Diesel)

991 mm long x 533 mm wide x 686 mm tall
 39 in long x 21 in wide x 27 in tall

SPU 1E Powerplant (79 Liters)

Q4-2007

1.25 kW / 14% Efficiency (No Sulfur Diesel)

790 mm long x 400 mm wide x 250 mm tall
 31 in long x 15.8 in wide x 9.8 in tall

Figure 3.3.1-3: Delphi Diesel SOFCAPU Technology Demonstration

Figure 3.3.1-4: Class 8 Truck Diesel System Demonstrator

The demonstration chassis system is able to draw diesel fuel from a tank with an integrated fuel pump and execute an automatic cold-start warm-up using either 12 V input power (from a vehicle) or 120 VAC input power. During start up period, the diesel reformer vaporizes diesel fuel, first with electric heat, then with recuperated burner heat. The diesel reformat travels through the system until it joins the cathode tail gas in the burner. The cathode air is heated with recuperated heat from the burner, and the cathode air heats the stacks and other hot zone system components until the target operating temperature of the system is obtained (750 °C). Once operating temperature is obtained, the 12 V DC/DC converter is enabled and the stacks then provide power to both internal and external loads through the 12 VDC power bus. For system shut-down, the system performs a controlled cool-down with the reformer continuing to make reformat. The system cools the stacks to 380°C, and then executes a full shut-down by cutting off fuel to the reformer. This controlled cool-down period is required to prevent anode oxidation of the stacks during the shut-down period. On the event of an unintended stoppage when the stacks are at operating temperature, a small bottle of reducing gas is on-board the unit and will purge the system during an unpowered cool-down.

9.1.7.2 System Performance Testing

Delphi built and tested three demonstration chassis units: One natural gas fueled, and two diesel fueled. The natural gas unit has been used primarily for power electronics integration testing and software development. It logged over 1000 hours, 9 thermal cycles, and over 160 transient load cycles with each cycle representing one-day's anticipated usage. The power degradation experienced by the natural gas unit is approximately 6%. There were several diesel reforming challenges encountered in 2008:

1. Fuel/Air mixture pre-combustion: The fuel and air mixture has been susceptible to combustion ahead of the reforming catalyst during some system modes, particularly the end of the system warm-up period where some system components run the hottest, or during hot restarts where the reformer body has been allowed to soak-up to a higher operating temperature. When the fuel and air mixture burns ahead of the catalyst, poor reformat and high reformer temperatures result, leading to a shut-down of the system. The solution implemented was the addition of an insulating sleeve liner in the air/fuel mixture duct area ahead of the catalyst. This liner prevents the high temperature walls of the reformer from igniting the air/fuel mixture.
2. Reformer plugging during cold-starts: To execute a reformer cold-start, an electrically-heated fuel vaporizer provides fuel, then the main blower provides metered air to the mixer of the reformer, and an igniter initiates combustion ahead of the catalyst. This combustion mode lasts for several seconds, and it heats the leading edge of the catalyst substrate. After quenching the flame by interrupting fuel flow, reforming is initiated by providing fuel at the target air/fuel ratio required of the reforming reaction. Due to sooting in the

- combustion phase, the fibrous radiation shield ahead of the catalyst can be fouled and high pressure-drop may result. The solution implemented was a change in the mixer geometry from a perforated-plate style, to the swirl-cone type used for natural gas applications. The improved mixing of the air/fuel mixture reduced the propensity for sooting and plugging of the radiation shield.
3. Stack plugging during system-warm up: After successful reformer cold-start, it was found that carbon deposits were forming downstream of the reformer in the SOFC stacks. This is due to cooling the reformat in the presence of the nickel anode. The carbon deposits caused increasing pressure drop of the SOFC stacks. The solution was to increase the oxygen to carbon ratio (O:C) of the reformat to increase the water vapor content and suppress low-temperature carbon-forming reactions. High O:C ratio in a fuel reformer can lead to excessive reforming temperatures and damage to reforming catalysts. The solution implemented in the system was to use moderate O:C ratios in the reformer, but inject supplemental air consistent with the higher target O:C downstream of the reforming catalyst. This supplemental air reacts with the reformat to form additional water and carbon dioxide by sacrificing some hydrogen and carbon-monoxide (reduced reforming efficiency). The resulting high O:C reformat has been confirmed to have less carbon-formation in the stacks during system warm-up.

After implementation of the aforementioned reforming solutions, the integrated demonstration chassis systems were tested to up to 4 thermal cycles, and 135 hours of continuous operation (**see Figure 3.3.2-2**). Rated power of the integrated system (12V DC output) on diesel fuel with 1.2 ppm total sulfur (by weight) is 1250 W at 14% fuel-to-electric efficiency (**see Figure 3.3.2-1**). **Figure 3.3.2-3** shows the effect of anode-side pressure drop (P12 pressure in system) as a function of stack temperature during sequential thermal cycling. Blue and orange curves show rising pressure drop due to carbon formation cycle-to-cycle, while the blue curves show consistent pressure (reduced carbon formation rates) with air injection implemented.

Figure 3.3.2-1: SPU 1E Diesel System Performance

Figure 3.3.2-2: SPU 1E Diesel SOFC Powerplant 135 Hour Test

Figure 3.3.2-3: SPU 1E Diesel SOFC Carbon Deposition during Warm-up

With the ability to demonstrate power, thermal cycling, and several days of stable operation, Delphi's diesel SOFC system was taken outside of the laboratory and connected to a full-size diesel pick-up truck (see **Figure 3.3.2-4**). The system was fueled with an auxiliary fuel tank next to the truck containing low-sulfur diesel (1.2 ppmw total sulfur max). The system was started, and powered during the warm-up using the truck generator power with the truck running. After approximately three hours, the truck was shut off and all loads were powered by the diesel SOFC system. Power output was between 500 W and 860 W during the period of operation. After the loading period, the truck was re-started, and the system executed its automatic cool-down mode.

Accomplishments:

- First operation of Delphi SOFC outside of a laboratory
- First complete start-up on truck generator power
- Automatic transition of truck loads to fuel cell system (truck engine off)
- SOFC Fuel Cell System support of truck loads ($860W_{net}$):
 - HVAC Blower
 - Radio
 - Interior lights and dashboard lights
 - Headlamps & running lights
 - Windshield wipers
 - Battery charging
 - Fuel pump
 - 12V cooler accessory

Figure 3.3.2-4: Delphi Diesel SOFCAPU Technology Demonstration

This test procedure was repeated with the system installed on a full-size Class 8 diesel truck. The results of the test are shown in **Figure 3.3.2-5**. The system, once online, successfully powered the truck's HVAC blower, radio, lights, and battery re-charge for a ten hour period simulating a typical day's operating condition for the system.

Figure 3.3.2-5: Diesel System Operation on Class 8 Truck

9.2 Task 2: Stack Development

9.2.1 Stack Design

The Generation 3+ stack design was the starting platform for the development of a large footprint productive design where changes could be implemented quickly at low relative costs and will allow for the evaluation of a larger cell. While there are numerous changes from the Gen3.2 design, some of the same proven technologies were to be carried over into Gen3+ design. One such technology is the fiber filled glass seal, which had shown excellent results in improving stack thermal cycling capability. Delphi also used the same interconnect contact pastes, as well as the same wire mesh interconnects. Delphi replaced the wire mesh interconnects with integrated interconnects within the anode plate and cathode plate. The integrated interconnects will give more consistent repeating unit spacing, improved electrical contact, better fuel utilization, and lower pressure drop.

The Gen3+ repeating unit has a larger footprint, 204mm x 320mm, compared to a Gen3.2 at 150mm x 155mm. There are two repeating unit configurations: one uses a single large cell (see **Figure 4.3.1-1**) and the other uses two cells similar in size to the current G3.2 cells in one retainer (see **Figure 4.3.1-2**).

Figure 4.3.1-1: Gen3+ Single Cell Repeating Unit

Figure 4.3.1-2: Gen3+ Twin Cell Repeating Unit

The new Gen3+ design yields a high length-to-width aspect ratio allowing for minimum pressure drop and promoting a more uniform cell temperature. The Gen3+ will retain the co-flow configuration with proven performance from Gen3. For ease of manufacturing, both anode and cathode ports are round in the Gen3+ design. Another significant change was that the cell is mounted into a recess in the retainer plate (see **Figure 4.3.1-3**).

This recessed feature has several advantages; it enables self-location of the cell, it provides braze containment, and decouples the sealing and mechanical retention function that the braze joint served in Gen3.2. The recess provides retention by clamping to the anode spacer (see **Figure 4.3.1-4**). Another advantage of this design is it minimizes shear stress into the cell. The flat Gen3 retainer allowed the thermal shear stresses to translate directly to the electrolyte. In the Gen3+ design, the recessed cell frame significantly decouples shear stress. Because of the way the Gen3+ repeating unit is constructed, it eliminates one of the major problems of the Gen3.2 design, namely fuel bypass. The fact that the cell will lie flat against the anode spacer will prevent fuel bypass, yielding optimal fuel utilization.

Figure 4.3.1-3: Gen3+ Cell Retainer

Figure 4.3.1-4: Gen3+ Repeating Unit – Cross Section

The Gen3+ repeating unit assembly is a laminated structure, consisting of four “layers”: The cell retainer, anode plate, separator plate, and cathode plate (see **Figures 4.3.1-5** and **4.3.1-6**). These parts are fabricated from flat sheet stock using low cost, quick turn-around forms of tooling, which greatly facilitates any change requirements. The assembly can be welded or brazed together. The Gen3+ manifold is designed to allow for stack “modules” which can be combined to yield the desired power output with serviceable connections between modules (see **Figure 4.3.1-7** and **Figure 4.3.1-8**). The manifold can be fabricated by machining and brazing, as well as casting. The stack load frame utilizes the same basic concept as Gen3.2, where a spring system is used to keep the stack in compression at all times.

Figure 4.3.1-5: Gen3+ Repeating Unit

Figure 4.3.1-6: Gen3+ Repeating Unit – Exploded

Figure 4.3.1-7: Gen3+ Stack Module Assembly, Gen3+ Stack Assembly (5 kW)

Figure 4.3.1-8: Gen3+ Stack Module Assembly, Gen3+ Stack Assembly (10 kW)

9.2.2 Stack Modeling

The distribution of cell voltages within a stack under electrical load is determined by individual cell performance and thermal environment. The voltage of each cell "floats" to the point where that cell can support the current flowing through the stack. Cells

which are less electrochemically active than the average will float to lower than average voltage in order to pass the required current. Similarly, cells that are cooler than the rest of the stack will float to lower voltages. The general shape of the voltage distribution will be determined by the temperature distribution within the stack, whereas the detailed "scatter" of voltages will be determined by the relative cell performances. This is illustrated in **Figure 4.3.2-1**, which shows the voltage distribution for the 30-cell stack (C625) under load at two different conditions. The red data was at 60 amps load and low fuel utilization of 30%. The blue data is also at 60 amps, but at high fuel utilization of 70%. The average temperature $((\text{inlet } T + \text{outlet } T)/2)$ of the stack at 70% utilization was higher, at 784°C than for the stack at 30% utilization, 772°C. However, because the fuel was more depleted in the 70% utilization case, the cells had to float to lower voltages to produce 60 amps. Note that the pattern of scatter is closely similar between each data set, indicating that the relative performance of the cells did not change. Also note that the general shape of the two data sets is similar, as indicated by the dashed lines which are 3rd order polynomial fits. This indicates that the thermal profile of the stack (cooler on the lower numbered bottom cells) was similar during these tests.

Figure 4.3.2-1: Voltage distributions for stack C625 under two different conditions

The general shape of the voltage distribution can be used to calibrate the finite element/finite volume (FE/FV) stack model, as illustrated in **Figure 4.3.2-2**. The blue line is the voltage distribution produced by the stack model. In order to reproduce the general "downward sloping to the right", a thermal gradient was introduced into the model, so that the incoming cathode air and anode fuel cool from 745°C as cell #1 to 723°C at cell #30. The downward curvature on the left was produced by simulating increased heat loss through the bottom of the stack, which is mounted on a relatively massive hearth plate. The resulting temperature and current density profiles produced by the FE/FV model are shown in **Figure 4.3.2-3**. The predicted maximum cell temperature was near the outlet of the middle cells (red line for cell #15 in lower right plot).

Figure 4.3.2-2: Voltage profile produced by FE/FV stack model (blue curve) compared to polynomial fitted to actual stack voltage data

Figure M3..

Figure 4.3.2-3: Temperature, current density and voltage profiles predicted for stack C625 by FE/FV model

Voltage profiles of stacks C625 and C600 are compared in **Figure 4.3.2-4**. These data sets were each obtained at 60 amps and 30% fuel utilization on the same test stand with the same insulation package. The difference between them is that stack C600 contained layered mesh in the cathode flow cavities, whereas stack C625 contained “bed-of-nails” (BON) plates. Apparently, the BON plates promote increased thermal vertical conductivity within the stack.

Figure 4.3.2-4: Voltage profiles of stacks C600 (blue) and C625 (red). Stack C600 contained layered mesh in the cathode flow cavities, whereas stack C625 contained “bed-of-nails” (BON) plates

The FE/FV model was used to evaluate the effect of changing cell size and shape. Six cases were modeled, as explained in the caption of **Figure 4.3.2-5**. In each case, a 30 cell stack was modeled. Air and fuel flow rates were scaled to the active areas: air flow rate was 8.541e^{-2} slpm per cm^2 of active area and fuel flow rate was 9.821e^{-3} slpm per cm^2 of active area. Air and fuel inlet temperatures were 732 °C at cell #1 and 702 °C at cell #30. Voltage was constant at 0.787 volts/cell. The thermal environment and heat transfer parameters were the same as those that were found to replicate stack C625 voltage profile. Insulation was 10 cm thick, with a conductivity of 0.04 W/mK. The results listed in **Figure 4.3.2-5** indicate strikingly similar performance for all cases in terms of power density, fuel utilization and maximum cell temperature. **Figure 4.3.2-6** shows the predicted temperature profiles for four of the modeled cases.

Results	Power Density W/cm ²	Fuel Utilzn. %	Max Cell Temp
Standard 1:1.56, Wide	0.321	49.96%	813.6
Standard 1.56:1, Long	0.316	49.15%	811.4
Super 1:3, Wide	0.327	50.85%	821.9
Super 3:1, Long	0.321	49.84%	818.8
Super 1:10, Wide	0.329	51.11%	821.2
Super 10:1, Long	0.315	48.94%	814.6

The top line (Standard 1:1.56, Wide) is for the current cell and flow direction. The second line is for the standard size (105 cm^2) and shape cell, but with the flow in the longer direction. The middle two lines are for cells with ten times the current active area (1050 cm^2) and 1:3 aspect ratio and the bottom two lines are for cells with 1050 cm^2 active area and 1:10 aspect ratio.

Figure 4.3.2-5: Results of modeling effects of cell size and shape on stack performance

Figure 4.3.2-6: Predicted thermal profiles for four of the cases modeled to determine effects of cell size and shape

9.2.3 Cathode Development

Cathode development efforts were aimed at gaining a better understanding of the impact that key cathode properties such as stoichiometry, surface area, sintering, and phase have on the power density and stability of LSCF cathodes. Variations in both power density and stability were observed for different lots of $(\text{La}_{0.80}\text{Sr}_{0.20})_{0.95}\text{Co}_{0.20}\text{Fe}_{0.80}\text{O}_3$ (LSCF-6428) cathode powders despite conforming to current specifications ranges. The primary concern with the chemical composition of the LSCF cathode involved the development of an A-site (La,Sr) excess composition which could lead to SrZrO_3 formation at the electrolyte interface. Originally, a 5% A-site deficient composition was selected in order to maintain an A-site deficient cathode by compensating for potential batching errors and/or Co loss occurring during the processing steps. The chemical composition of LSCF cathode used in our tests was determined by Inductively Coupled Plasma (ICP). To improve the accuracy and repeatability of these tests, standards of La, Sr, Co, and Fe were prepared with to an accuracy of $\pm 0.2\%$ and one cathode composition (lot 6168) was chosen as a reference standard to run with each unknown to track machine drift within the machine. Samples of previous and current cathode materials were submitted for analysis as blind unknowns and included multiple replicates. **Figure 4.3.3-1** shows the results of 60+ ICP runs on the 6168 reference standard giving a measurement error on the A/B ratio of 0.963 ± 0.004 . **Figure 4.3.3-2** shows the resulting A/B ratios from all commercial cathode powders batched for the same 5% A-site deficient LSCF composition. While most compositions are close to the desired 5% A-site deficiency, lots 6111, 6168, and 6202 show a higher A/B ratio. These powders, prepared by an alternate process by the supplier, required multiple calcination steps to achieve the desired perovskite phase. However, significant Co loss was only found in lot 6202 which required the most calcination steps (3) to achieve phase purity (**Figure 4.3.3-3**).

Figure 4.3.3-1: A/B ratio determined from ICP for reference cathode lot 6168

Figure 4.3.3-2: A/B ratio determined from ICP for commercial $(\text{La}_{0.80}\text{Sr}_{0.20})_{0.95}\text{Co}_{0.20}\text{Fe}_{0.80}\text{O}_3$ powder lots

Figure 4.3.3-3: Co/Fe ratio of selected cathode powder lots

Of particular note is the ICP analysis on lot 5548. This cathode powder was tested in stack 530 which ran for 3600 hrs at Delphi and has undergone extensive TEM analysis at Carnegie Mellon University (CMU). ICP comparison of the raw powder 5548 with the cathode ran for 3600 hrs (**Figure 4.3.3-4**) reveals a slight depletion of A-site cation which appears to be consistent with SrZrO_3 formation observed in the CMU analysis.

Figure 4.3.3-4: Comparison of A/B ratio for 5548 cathode as-received and tested for 3600 hrs

9.2.3.1 Performance and Robustness to Delamination

Delphi demonstrated that stack performance, specifically stack voltage and cell-to-cell voltage variation, is strongly affected by the quality of the cathode electrode. Poor quality of the cathode layer was linked to low cell voltage output along with catastrophic failures of the cell and stack during operation at elevated temperatures or during the process of thermal cycling. Catastrophic failures typically are caused by delamination of

the cathode electrode, primarily seen between the electrolyte and the cathode barrier layer. Development of improved cathode materials and processes was conducted to develop more robust fuel cells. **Figure 4.3.3.1-1** shows the electrochemical performance of stacks tracked as a function of time and a significant improvement can be seen since June of 2007.

Figure 4.3.3.1-1: Stack Performance Variation Reduction

9.2.4 Anode Development

Efforts to improve the H_2S tolerance of Ni-based anode-supported cells continued to focus on infiltration of various H_2S tolerant materials into anode supported cells. Using a pore reformer to enhance porosity in the active anode layers in an oxide state was found helpful to infiltrate the Ru+Ce solution into the active anode while maintaining good structural integrity. One of problems related to the infiltration into the porous active anode was the leakage of the solution through pin-holes on a thin electrolyte, which damaged the performance of the cathode leading to lower initial power. In 2008, Delphi focused on (1) the elimination of pin-holes to improve the initial performance of infiltrated cells and (2) the infiltration of other sulfur-tolerant elements (Pr-based) into anode-supported cells. To remove the pin-holes, Delphi attempted the use of thicker electrolytes to employ more sinterable YSZ, and to increase the firing temperature of bilayers.

Figure 4.3.4-1 shows the effects of thicker electrolyte on the initial performance and the sulfur tolerance of Ru+Ce infiltrated cells in comparison to non-infiltrated baselines. While a Ru-Ce infiltrated cell with 1X electrolyte ($\sim 7 \mu m$) reveals lower initial power due to pin-holes, an infiltrated cell with 2X electrolyte ($\sim 15 \mu m$) shows higher initial power comparable to the non-infiltrated baseline. However, the power of the infiltrated cell with 2X electrolyte after exposing to 1 ppm H_2S was slightly lower ($\sim 500 \text{ mW/cm}^2$) than that of the 1X electrolyte cell even though both cells exhibited significantly improved

sulfur tolerance compared to the baselines. **Figure 4.3.4-2** lists the sulfur tolerance and the contents of Ru and Ce in the active anode obtained by EDX analysis. The power after sulfur poisoning seems to be related to the content of Ru. Even though the infiltrated cell with 2X electrolyte has higher initial power, its power after sulfur poisoning was lower compared to the cell with 1X electrolyte since the amount of infiltrated Ru in the active anode was lower (0.93~1.09 at%). In the case of anode-supported cells, the Ru and Ce contents were lower compared to the electrolyte-supported cells; possibly due to the limited porosity in the active anode and a long infiltration path. Therefore, processing modification is needed to put more sulfur tolerant elements in the active anodes in order to improve the sulfur tolerance even further.

Figure 4.3.4-1: Sulfur Tolerance of Ru-Ce Infiltrated Cells with Different Electrolyte Thickness

Cell Number	512a	546a	566a	569b
Type	<i>ELSupp</i>	<i>ADSupp</i>	<i>ADSupp</i>	<i>ADSupp</i>
Infiltration	RuCe	RuCe	RuCe	RuCe
Electrolyte Thick	200 μ m	1X (~7 μ m)	2x (~15 μ m)	2x (~15 μ m)
Power bf H2S (mW/cm ²)	211	604	717	600
Power (1st stage, mW/cm ²)	182	532	504	454
Retention (%)	86	88	70	76
Power (1st stage, baseline)	126	393	339	339
Increase vs baseline (%)	44	35	49	34
2nd Degradation (%/h)	0.010	0.010	0.010	0.041
Ru (at%) at AA**	1.93	1.21	1.09	0.93
Ce (at%) at AA**	3.00	1.44	2.05	1.35
Ru+Ce (at%)**	4.93	2.65	3.14	2.28

Figure 4.3.4-2: Sulfur Tolerance of Ru-Ce Infiltrated Cells and the Contents of Ru and Ce in Active Anode

The sulfur tolerance of cells infiltrated with Pr-based sulfur tolerant materials is shown in **Figure 4.3.4-3**. Both cells infiltrated with Pr and Ni-Pr reveal similar or slightly higher

power after sulfur poisoning (~ 550 mW/cm²) compared to the Ru-Ce infiltrated cells. Thus, the sulfur tolerance of Pr-based infiltrated materials (Pr, Ni-Pr, Pr-Ru, Ni-Pr-Ce, etc), which has shown in the electrolyte-supported cells, is also observed in the anode-supported cells. The amount of Pr in the active anode of anode supported cells listed in **Figure 4.3.4-4** is quite limited (0.99 - 1.22 at%) compared to the electrolyte supported cell, leading to lower power retention after 1 stage degradation, especially when the initial power before sulfur exposure was high. This also demonstrates the necessity of processing modification to put more Pr in the active anode of anode supported cells.

Figure 4.3.4-3: Sulfur tolerance of cells infiltrated with Pr-based sulfur tolerant materials

Cell Number	513a	563a	570a	571a
Type	<i>EL-Supp</i>	<i>AD-Supp</i>	<i>AD-Supp</i>	<i>AD-Supp</i>
Infiltration	Pr	Pr	Pr-Ni	Pr
Electrolyte Thickness	200 μ m	1X ($\sim 7 \mu$ m)	2x ($\sim 15 \mu$ m)	2x ($\sim 15 \mu$ m)
<i>Power bf H2S (mW/cm2)</i>	195	697	687	569
<i>Power (1st stage, mW/cm2)</i>	182	475	568	528
<i>Retention (%)</i>	93	68	83	93
Power (1st stage, baseline)	126	393	339	339
<i>Increase vs baseline (%)</i>	44	21	68	56
2nd Degradation (%/h)	0.017	0.036	0.036	0.017
<i>Pr (at%) at AA**</i>	2.23	0.99	1.22	1.21

Figure 4.3.4-4: Sulfur tolerance of Pr infiltrated cells and Pr content in active anode

Another effort to eliminate pin-holes on the electrolyte is to use more sinterable YSZ. The cell prepared with more sinterable electrolyte shows a low initial power of ~ 550 mW/cm², but burn-in to > 700 mW/cm² before sulfur introduction (**Figure 4.3.4-5**). This bilayer infiltrated with Ni-Pr-Ce, reveals the highest power at ~ 600 mW/cm² after first stage sulfur degradation.

Figure 4.3.4-5: Effect of more sinterable YSZ on initial performance and sulfur tolerance of infiltrated cells

The bilayer firing at higher temperature of 1425°C was also attempted to remove pin-holes. The effects of bilayer firing temperature on the initial power and the sulfur tolerance are shown in **Figure 4.3.4-6**. Even though the power before sulfur introduction was stable and high, possibly due to the favorable influence of higher firing temperature on the elimination of pin-holes, the infiltrated cell had lower sulfur tolerance similar to the non-infiltrated baseline. This is because high firing temperature resulted in less porosity in the active anode even with 20% pore former, limiting the infiltration of sulfur tolerant elements into the active anode.

Figure 4.3.4-6: Effect of High Firing Temperature on Initial Performance and Sulfur Tolerance of Infiltrated Cells

9.2.4.1 Cell Flexural Testing

The results of flexural stress testing of standard Delphi fuel cells are shown in **Figure 4.3.4.2-1**. Weibull statistics (Stress vs. Unreliability) were used to plot the results of the

failure stress of multiple cells that were tested in tension. The method for measuring the biaxial flexure stress was a modified ball and ring test. The test apparatus actually used a piston that comes in contact with the test specimen and a ring of 10 balls (ball bearings) supports the sample from the underside. By placing the anode side up and the electrolyte side down, fired bilayers can be measured with fracture occurring mainly at the center of the electrolyte surface. By using this method of piston and ring, the edge effects become negligible and do not have an impact on the flexural stress unlike what is typically experienced in 3 point and 4 point biaxial testing of rectangular samples. Scanning electron microscopy was used to determine the failure origin and provide evidence of the cause of failure. In the plot and micrographs, it can be seen that there are two difference slopes to the plot and a distinct transition between them. Studies showed evidence of defects in the active anode, probably relating the tape casting process, that affect the failure mode for parts making up the bottom portion of the plot. The transition that leads to the slope change of the upper portion of the plot is related to a different failure mode.

Figure 4.3.4.2-1: Flexure Strength of Standard Cells: Electrolyte in Tension

9.2.4.2 Braze Process Optimization

A belt furnace brazing process was developed for the cell to picture frame joint. For consistent quality of the cell to picture frame joint, the braze firing process was optimized for improved efficiency and cell quality. **Figure 4.3.4.3-1** shows the furnace profiles of a batch operation and a continuous brazing operation. The continuous belt furnace was evaluated as an improved method to supply consistent braze quality where every part experiences the same thermal profile and avoids temperature variations that are known to occur in the batch kiln. In support of the braze firing optimization development, real time x-ray (radiography) was used to monitor braze joint quality. **Figure 4.3.4.3-2-A** provides a radiographic image of an acceptable braze joint where

the braze material melted and experienced complete flow. On the right, Figure 4.3.4.3-2-B shows the results of a poor or unacceptable braze joint where the braze material incompletely melted and moved showing practically no flow. Porosity is clearly detected in the two images and is a major area of focus in the formulation of improved braze paste materials.

Figure 4.3.4.3-1: Braze Cycle Adjustment Using Belt Furnace

Figure 4.3.4.3-2-AB: Use of Radiography to Optimize Brazing Process

A braze paste viscosity measurement system was developed to ensure that the flow properties of the paste are optimized. Once the paste formulation was optimized, process control limits were determined and implemented that allow for consistent flow ability of the braze and hence consistent thickness of the braze paste deposited on the periphery of the fuel cell surface.

9.2.5 Development of Cell Fabrication Techniques

The Delphi advanced manufacturing engineering team worked to apply all elements of the Delphi Quality System to the SOFC product. Each element of this product is shown in **Figure 4.3.5-2** and the status of completion of each element is shown in the bar chart. The elements listed in the bar chart and tracked frequently are the following:

- MSD - Manufacturing System Design
- PFD - Process Flow Diagram
- PFMEA - Process Failure Mode and Effects Analysis
- PCP - Process Control Plan
- Work Instructions
- PMF - Process Monitoring Form
- Gate Chart

Except for Gate Charts for the stack builds, all elements of the Quality System are over 90% implemented as seen in **Figure 4.3.5-2**.

Figure 4.3.5-2: Quality System Implementation Progress (%)

Gate charts such as the one shown in **Figure 4.3.5-3** were used to track the SOFC build and inspection process. The first time quality (FTQ) of the batch of bilayers was tracked and compared to historical data. The type and quantity of defects was tracked through the build, firing, and inspection step to monitor the quality of the fired bilayers. If the FTQ has drifted to a point higher than the historical level, the batch was flagged and an investigation initiated to understand the type of defect and the material or process issue causing the issue.

Figure 4.3.5-3: Gate Chart Used to Track Cell Defects and Frequency of Occurrence

9.2.6 Seal Development

The primary focus of seal development work was aimed at gaining a better understanding of: 1) The accelerated corrosion of CroFer during the brazing process and, 2) Crystallization and phase development of fiber containing G-18 glass after exposure to the thermal conditions associated with SOFC heat up and various lengths of operation. Previous investigations using SEM and DSC (Differential Scanning Calorimetry) of aluminized CroFer brazed with Ag-6.6 mol% CuO air brazes indicated that a corrosion product is formed between the braze and CroFer. The corrosion product was shown to be due to the formation of a copper oxide-rich liquid that forms at and above 969°C at compositions containing 2.0 or more mol% copper oxide. This was confirmed as can be observed in **Figure 4.3.6-1**, where DSC traces and SEM of Ag with 2.0 mol% CuO braze composition from mixed powders indicated that corrosion was reduced as compared to the Ag-6.6 mol% CuO braze.

Figure 4.3.6-1: Corrosion of CroFer filings during DSC runs

In addition it was thought that the method of powder fabrication (pre-alloyed vs. mechanical mixing) may influence corrosion behavior. Investigations of aluminized CroFer brazed made from pre-alloyed Ag-Cu powders indicated that corrosion still occurs with pre-alloyed powders as observed in **Figure 4.3.6-2**, where some dissolution of the CroFer material into the braze was seen. The corrosion was thought to be due to a discontinuous alumina layer on the CroFer material. It was observed (**Figure 4.3.6-3**) that iron and chrome phases could be found on top of and through the protective alumina scale even when the braze was not in contact with the aluminized CroFer. The iron and chrome phases present on top of or through the alumina layer can be expected to form a corrosion product when not separated from the braze by the alumina layer. **Figure 4.3.6-4** shows the DSC curves for pre-alloyed powders mixed with untreated (not aluminized) CroFer filings. While the exothermic reaction corresponding to the corrosion may be too weak to be observed with DSC for braze compositions with less than 2 mol% CuO, SEM shows that the corrosion may be significantly reduced but was still present as seen in **Figure 4.3.6-5**.

Figure 4.3.6-2: Aluminized CroFer after brazing with alloyed powder braze

Figure 4.3.6-3: CroFer without braze after brazing cycle

Figure 4.3.6-4: Corrosion of un-oxidized CroFer filings during DSC runs with alloyed braze powders

Figure 4.3.6-5: Alloyed powder braze and un-oxidized CroFer fillings from DSC tests

It was thought that improvements in the protective alumina scale along with low copper oxide content brazes could be used to minimize the corrosion. This is demonstrated in **Figures 4.3.6-6** and **4.3.6-7**. In **Figure 4.3.6-6** the DSC traces and SEM of Ag-6.6 mol% Cu on un-treated CroFer and Fecralloy that has been pre-oxidized at 1200°C for two hours is shown. Here we can see that a corrosion product can be observed for both substrate materials. Corrosion of the pre-oxidized Fecralloy material is due to the copper oxide-rich liquid that interacts with the alumina scale to form copper aluminate and in the process breaks up the protective scale and leaves the remaining iron and chrome phases open to corrosion. **Figure 4.3.6-7** shows the corrosion products for Ag-2 mol% Cu braze with pre-oxidized Fecralloy was significantly reduced if not eliminated. A 2-4 μm fully continuous alumina layer was observed to fully enclose the Fecralloy particles and thus protect the iron and chrome from contact with the braze.

Figure 4.3.6-6: Alloyed powder braze with CroFer and pre-oxidized FeCrAlloy filings

Figure 4.3.6-7: Alloyed powder braze and CroFer and pre-oxidized FeCrAlloy filings

Previous efforts on glass-based seals revealed that 30% or more yttria-stabilized zirconia fibers appears to suppress crystallization in the G-18 glass-ceramic, improving thermal cycling ability of stacks. Thermal Mechanical Analysis (TMA) was employed to study the impact of thermal cycling on the crystallization. **Figure 4.3.6-8** shows the expansion vs. temperature curve for the baseline G-18 glass. During the first heat up, a deviation in the expansion curve was noted near the glass transition temperature of G-18 indicating a significant level of residue glass is left in the sample. After one thermal cycle to 800°C at X°C/min the glass transition temperature was no longer observed. In contrast, the 30% fiber load G-18 sample appears to retain a significant glass phase after sixty thermal cycles, **Figure 4.3.6-9**. Area calculations on the expansion curves

were used to indicate the relative amount of glass remaining compared to initial run and are shown in **Figure 4.3.6-10**. Linear extrapolation of the curve indicates that a significant amount of glass component may remain in the seal for over one hundred thermal cycles.

Figure 4.3.6-8: Crystallization TMA Study with 0% Glass Fiber 5 Cycle Increments

Figure 4.3.6-9: Crystallization TMA Study with 30% Glass Fiber 5 Cycle Increments

Figure 4.3.6-10: Glass Peak Area Calculations for 30% Fiber Loaded G-18 as a Function of # of Thermal Cycles

These new additives in seal technology demonstrated improvements in thermal cycling and overall durability of stacks. The seal between two repeating units (cassettes) and between the cassette and the two current collectors is a glass ceramic seal (G18) that was modified with dopants (30% by wt zirconia fiber). Evaluation of the performance of this seal in multiple stacks demonstrated very encouraging results. An analysis of seal failures in the stack showed very good cassette to cassette sealing. The weaker joint and the root cause for eventual seal failure in current stacks, which was observed to be between the current collector and repeating unit (dummy cassette). This seal was observed to be thicker and has overall more porosity than the cassette to cassette seal. Development is ongoing to improve this seal to make it consistent with the other seal joints (see **Figure 4.3.6-11**)

Figure 4.3.7-1: IV Curve from a 5-cell Stack with Improved Power Density

Figure 4.3.7-2: Cell to Cell Voltage Variation from a 5-cell Stack with Improved Power Density

Stacks with cost-effective coatings for interconnects were also evaluated. A cobalt Co coated (instead of LSC) separator plate was evaluated in a 5-cell stack with very encouraging results. The stack showed good power density and steady state durability. Data from a representative cell with Co-coated interconnect (from a 5-cell stack) is shown in **Figure 4.3.7-3**. The stack was tested with 48.5% H₂, 3% H₂O, rest N₂ fuel and held at steady state under 0.57 mA per cm² at 750°C. The initial degradation for the first 600 hours can be correlated to Cr contamination from the test stand. After the initial degradation, there was minimal degradation (~0.04% per 500 hours) for the remainder of the test (total of 2886 hours). This result fundamentally demonstrates the promise for using low cost coatings like Co for interconnects.

Figure 4.3.7-3: Durability data of a representative cell with Co coated interconnect

9.2.8 Evaluate Stack Performance

Multiple 30-cell stacks were fabricated and evaluated. **Figure 4.3.8-1** shows a typical 30-cell IV curve with 48.5 H₂, 3% H₂O, rest N₂ fuel. It was tested in the stack laboratory in a furnace and produced power of 1.44 kW (450 mW/cm²) @ 60A (570 mA per cm²), 24.6 V (0.82 V / cell avg), 750°C.

Figure 4.3.8-1: IV curve from a standard 30-cell stack

The cell to cell distribution is shown in **Figures 4.3.8-2** and **4.3.8-3**. Both show very tight grouping of cell voltages through the IV curve.

Figure 4.3.8-2: Cell to cell voltage from a standard 30-cell stack

Figure 4.3.8-3: Cell to cell voltage from a standard 30-cell stack

9.2.9 Stack Autopsy Results

Multiple stacks were tested in systems on <3ppm diesel. One observation in the failure analysis of these stacks is the propensity to form carbon on the anode side of the cell. Fundamental evaluation was conducted to understand the root cause of these carbon depositions (not adequate steam, poor quality reformat, aromatics, etc) to be able to mitigate this phenomenon at a system level. Carbon (when formed) was observed to be causing two detrimental effects on the cells. The first effect was fuel starving of the cells due to the build up of carbon within the fuel passageway at the inlet edge of the cell and inlet port areas. The fuel starving of the cell can lead to permanent damage of the cell such as electrolyte delamination (see **Figures 4.3.9-1** and **4.3.9-2**). The second effect was the anode corrosion “dusting” that causes permanent damage to the anode structure of the cell (see **Figures 4.3.9-3** and **4.3.9-4**). This mechanism has the

following effects on the cell: reduced electro-chemical capability, reduced structural integrity, and increased interconnect resistivity.

Figure 4.3.9-1: Carbon at inlet of cell causing fuel blockage

Figure 4.3.9-2: Electrolyte delamination

Figure 4.3.9-3: Cell cracked at inlet region due to reduced structural integrity resulting from anode corrosion "dusting"

Figure 4.3.9-4: Anode corrosion “dusting” effects on cell structure

Multiple stacks were evaluated in the stack laboratory for durability. Stack 578 was a 5-cell stack tested at 0.57 A per cm² on simulated reformat (28% H₂, 6% H₂O, 30% CO, 5% CO₂, rest N₂) for 1219 hours. During the first 900 hours, H₂S was introduced to the fuel. The stack was observed to have the beginning stages of anode corrosion “dusting” (see **Figure 4.3.9-5**). The cause for this phenomenon is under investigation. Stack 635 was a 5-cell stack tested at 0.57 A per cm² on 48.5% H₂, 3% H₂O, rest N₂ fuel for 1878 hours. Both stacks 578 and 635 exhibited two degradation mechanisms typical with long duration testing (see **Figure 4.3.9-6**). The first is Ag volatilization at the inlet leading edge of the cell. This mechanism resulted in high contact resistance between the cathode and interconnect creating a drop in cell performance and subsequent increased thermal stress on the cell. The second was the braze migration from the outlet braze joint across the inactive cell region. The ultimate result of severely progressed braze migration is the shorting of a cell. This happens when the Ag from the braze migrates across the electrolyte inactive region of the cell, electrically bridging the gap between the cell cap layer and the picture frame.

Figure 4.3.9-5: Anode corrosion “dusting”

Figure 4.3.9-6: Long term testing observations

9.2.9.1 Long Term Testing Effects on Interconnects

Stack 624 was a 5-cell stack tested at 0.57 A per cm^2 on 48.5% H_2 , 3% H_2O , rest N_2 fuel for 2886 hours. This stack was selected for analysis of both the anode and cathode interconnects. The interconnect had Cobalt coating on CroFer for the cathode side and no coating on CroFer for the anode side. The analysis was focused on the interconnect paste contact to the separator plate on the anode and cathode sides. On the anode side, the formation of the Mn, Cr oxide spinel layer was observed between the separator plate and the Ni paste (see SEM line scan in **Figure 4.3.9.1-1**). On the cathode side, the formation of a Mn, Cr and Co oxide spinel layer(s) was observed between the separator plate and contact paste (see SEM line scan in **Figure 4.3.9.1-2**).

Figure 4.3.9.1-1: SEM analysis of separator plate anode side

Figure 4.3.9.1-2: SEM analysis of separator plate cathode side

9.2.9.2 Glass Seal Thermal Cycling

Stack 609 was thermal cycled 25 times with minimal glass seal leaks ($< 0.2 \text{ slpm at } 8''\text{H}_2\text{O}$). Analysis had identified that most of the glass leaks are occurring at the glass seal interface between cassette and current collector. This seems to be due to the quality of the glass seal created during the stack sintering operation (see **Figure 4.3.9.2-1**). Large pores form at this specific location rendering the seal inferior to those in the rest of the stack. The cassette to cassette glass seal interface has not shown to be an issue regarding leaks during thermal cycle testing (stack 609) nor other long term durability testing.

Figure 4.3.9.2-1: Glass seal at cassette to cassette interface

9.3 Task 3: Reformer Development

9.3.1 POx Reformer Development

This period of development was characterized by iterative builds of reformer hardware followed by systems testing and failure mode discovery. A number of failure modes were discovered and a better understanding of Pox Reformer operation was gained with solutions and avoidance strategies implemented.

9.3.1.1 C296 SPU1E Durability Test#1 - Previous Durability Testing – EOT Analysis closeout

Analysis of components that had run ~640 hrs was conducted. **Figure 5.3.1.1-1** shows the SEM analysis of the radiation shield and embedded debris. The photo shows a 'caked mud' like deposit covering a majority of the frontal flow area of the radiation shield. This was believed to be a result of metal dusting of a component exposed to high temperature and Co plus a hydrocarbon rich composition of the vaporized fuel and recycle. The sample's spectra and composition (presence of Mo, Fe, Ni and Cr) were consistent with metal dusting of 316 stainless steel.

Element	Weight %			
	Box 1	Box 2	Box 3	Average
Al	1.50	1.66	0.73	1.30
S	3.19	4.14	3.62	3.65
Cr	24.09	24.38	24.85	24.44
Fe	9.66	11.13	9.42	10.07
M	61.56	58.69	61.38	60.54

Figure 5.3.1.1-1: Radiation Shield Analysis – Location A

Since there was no carbon detected, Delphi believes that the deposit was not nickel carbide. Based on this analysis and research into the metal dusting phenomena, it was deduced that due to the presence of the high number of components made of stainless steel (see **Figure 5.3.1.1-2**), particularly components that see vaporized fuel between 400°C and 600°C, metal dusting was the prominent failure mode. Based on this deduction, all stainless steel components located in areas with a high probability of metal dusting were removed from the reformer assembly and taken out of inventory.

Figure 5.3.1.1-2: Component Materials in the Reforming and Combustion Paths

9.3.1.2 Catalyst Plugging

9.3.1.2.1 Systems Test Results

Figure 5.3.1.2.1-1 shows a compilation of both system and reformer tests in which catalyst plugging was suspected and/or catalyst melting was observed. The table shows the key variables that defined each test and the test results. Catalyst plugging was identified by a rise in P11 pressure (catalyst delta P). P12 increases as the absolute pressure at the inlet to the Feed Stream Deliver Unit (FDU) increase.

Set #	EWO #	Ref EWO (SOT Characterization)	Date Of Systems Run	Reformer Perf / Failure Issue	Pre Cat / Cat (lookup fr DS file)	Catalyst Type (ZTA or ZM)	Cat S/N
7	MG735C187-02	C300_8	12/14/07, 12/17/07, 12/18/07	Cat Plugging, CV tube leak?	10mm Monolith FA Nextel RS; Cat= 50mm ZTA foam	ZTA	9029-166-3
	MG735C193-01	C300_8	1/9/08	Cat Plugging (P11) in ~20 hrs	10mm Monolith FA + 1X Nextel RS; Cat= 50mm ZTA Foam	ZTA	?
			1/11/08	CV tube leak; suspect Cat Plugging but reformer saw air during shutdown and presumed burn-off occurred	10mm Monolith FA + 1X Nextel RS; Cat= 50mm ZTA Foam	ZTA	?
	MG735C197-01	C300_11	1/24/08	Sawtooth rise in P11 over 20 hrs of operation;	Nextel RS + 5 mm Mono FA ; Cat= 60mm ZM mono	ZM	17268-2
	MG735C200-04	C300-13	2/21/08	Cat melted	5 mm Mono FA + 2 x Nextel RS ; Cat= 60mm ZM mono	ZM	17268-11
(blank)	n/a	MG733C303	(blank)	Cat melted	(blank)	(blank)	(blank)
		MG733C317 DOE1	(blank)	Attempted to recreate Cat Plugging; not to same degree	10mm Monolith FA + 1X Nextel RS; Cat= 50mm ZTA Foam	(blank)	(blank)
		MG733C317 DOE2	(blank)	No cat plugging during TCs with 3 hr cycle; 24hr test yield Cat Plugging (4 kPa rise) w/ "TC17"	5 mm Mono FA + 2 x Nextel RS ; Cat= 60mm ZM mono	(blank)	17268-9?

Figure 5.3.1.2.1-1: Catalyst Plugging & Over Temping

Figures 5.3.1.2.1-2 and **Figure 5.3.1.2.1-3** show the first instance of catalyst plugging from system testing. Because there was need to keep the system test running, a cleaning cycle was run to remove carbon; and therefore no hardware was available for analysis. Due to the high temperatures at the reformer catalyst and previous pre-combustion problems, a change to the pre-catalyst configuration was implemented. Due to other program needs, the catalyst was changed to a ZM monolith substrate in the same build. Subsequent systems testing showed a similar P11 rise indicating catalyst plugging, but additionally showed a variation between fueling modes. **Figure 5.3.1.2.1-4** illustrates the system test with P11 plotted.

Figure 5.3.1.2.1-2: Cat Plugging

Figure 5.3.1.2.1-3: MG733C193-01 Cat Plugging Day 2

Figure 5.3.1.2.1-4: Systems Test – Catalyst Plugging

P11 rises more when fueling mode B is fueling and mode A is cleaning (BF/AC). Disassembly of the reformer and inspection of the catalyst revealed that approximately 70% of the monolith's passages were blocked (see **Figure 5.3.1.2.1-5**). Cross sectioning of the catalyst revealed carbon deposits biased heavily toward the lead edge (see **Figure 5.3.1.2.1-6**). Further analysis indicated the composition is amorphous carbon. The deposits were thought to be due to pyrolysis of heavy aromatic carbon derived from the feed; or was polymerization and pyrolysis of mixing zone combustion products (fuel =>CH₄ => aromatics => C).

Figure 5.3.1.2.1-5: Catalyst - ZM Monolith SN17268-2

Figure 5.3.1.2.1-6: Section of Catalyst from Testing (SN 17268-2)

Clues were gathered from the systems test data in order to diagnose the cause of the deposits. **Figure 5.3.1.2.1-7** shows the temperature data by fueling mode. A decrease in $T_{3_{alt}}$ temperature (reformate stream at catalyst back face) and a similar increase in T_2 (mixing zone just forward of the pre-catalyst configuration) can be seen over the 20 hours of testing while P11 was rising. It was not clear whether less heat release was occurring at the catalyst. **Figure 5.3.1.2.1-8** shows a comparison of key variables between modes AF/BC and BC/AF. A major difference is the respective fueling and cleaning temperatures. Part of this distinction was later explained by treatment condition (TC) location. The distinction being that CV outlets were not symmetric with tube A's entrance to the mixer being upstream of tube B's TC location. This was corrected on later builds by locating the TCs more directly in the CV tubes' exit path.

Figure 5.3.1.2.1-7: Systems Test – Catalyst Plugging – Temperature

Data	0	1
Average of CTO_LLI_ImeasT12DegC	194	196
Average of CTO_LLI_ImeasT2VapMixZoneDegC	467	469
Average of T6 ALT	1033	1032
Average of T3 ALT	1150	1159
Average of Vaporizer A	386	652
Average of Vaporizer B	407	303
Average of CTO_LLI_ImeasT3RefOutDegC	1103	1106
Average of CTO_LLI_Imeas_CVAirTubeA_kPa	3.53	7.10
Average of CTO_LLI_Imeas_CVAirTubeB_kPa	6.19	3.26
Average of CTO_EXEC_EdesReformerO2C	1.2	1.2
Average of O_to_C_backcalc	1.186	1.196
Average of CTO_LLO_DesiredInj2_Duty	0.41	0.00
Average of Micro-Motion	0.162	0.159
Average of CTO_LLI_ImeasS11RecycleFlowGps	0.017	0.017
Average of CTO_LLI_ReformerAir_Gps	0.964	0.963
Average of CTO_LLI_ImeasS17RefAirGps	0.814	0.813
Average of CTO_LLI_ImeasCVAir_1_Gps	0.075	0.075
Average of CTO_LLI_ImeasCVAir_2_Gps	0.075	0.075
Average of Hydrogen	18.503	17.655
Average of Carbon Monoxide	21.929	21.141
Average of Water	1.514	1.517
Average of CO2	1.922	2.345
Average of Methane	0.133	0.186
Average of Ethane	0.174	0.169
Average of Ethylene	0.186	0.272
Average of Oxygen	0.258	0.260

Figure 5.3.1.2.1-8: Tube A versus Tube B Comparison

9.3.1.2.2 Design of Experiment (DOE) 1

The configuration under study for the first DOE is shown in **Figure 5.3.1.2.2-1** and was identical to that employed in test MG736C197. The test layout is shown in **Figure 5.3.1.2.2-2**. The test involved only two variables: O/C and Contact Vaporizer Outlet Temperature (CV Temp). Levels were selected based on the values seen in the systems tests.

Figure 5.3.1.2.2-1: RP225504 rev 4 MP 1/18/08 DS Pre-catalyst / Catalyst Configuration

Run Ord	TC	TC condions	O/C SP	CV Tube Temp SP	Average of Ref In O/C (-)	Average of CV Fueling Temp (TC at Junction Block)	Max of Cum hrs on Build	incremental duration - hrs
1	1	O/C = 1.25; CV vapor temp = 600	1.25	600	1.250	599	12	12
2	2	O/C = 1.25; CV vapor temp = 400		400	1.254	409	25	12
3	3	O/C = 1.15; CV vapor temp = 600		600	1.163	611	37	13
4	4	O/C = 1.15; CV vapor temp = 400	1.15	400	1.155	408	49	12
5	4-2				1.154	397	16	16
6	3-2	O/C = 1.15; CV vapor temp = 600		600	1.155	595	22	6
7					1.154	594	28	6
8	2-2	O/C = 1.25; CV vapor temp = 400	1.25	400	1.252	404	41	12
9	1-2	O/C = 1.25; CV vapor temp = 600		600	1.251	586	83	42
10	5	O/C = 1.15; CV vapor temp = 650; CV air=0.075 g/s	1.15	650; CV air=0.075 g/s	1.164	642	107	24
11					1.148	645	116	9
12	5R50	O/C = 1.3; CV vapor temp = 650; CV air=0.075 g/s	1.3		1.326	639	131	15

Figure 5.3.1.2.2-2: DOE 1 TC's log

Reassembly of catalyst replacements are time consuming, therefore a sequential approach without rebuilding was adopted (i.e. the catalyst is not changed for each new set of operating conditions). As evidence of plugging become apparent, rebuilding was conducted. Data for all DOE 1 runs is compiled in **Figure 5.3.1.2.2-3** and **Figure 5.3.1.2.2-4**. The initial four runs, labeled as Ord 1 through 4, led Delphi to believe the OC=1.15 (i.e. low) and CV Temp = 600°C (i.e. high) were the cause of the plugging. The reformer was rebuilt and the treatment conditions (TCs) were run in the opposite order (Ord 5 through 9). A forced rebuild, due to an emergency lab shutdown, was conducted after the conclusion of TC = 3-2 due to concern that information would be effected by the shutdown damaging the catalyst. **Figure 5.3.1.2.2-3** shows that on a number of TCs a cool flame, prior to the catalyst inlet (based on T2 temperature at this location), existed. This result did not correlate with the response of increases of P11

due to carbon TC. Run Ord 9 (1-2) was allowed to run 42 hours. Additional runs were conducted as follows:

- TC 5 increased CV temperature to 650°C and reduced CV air (both cleaning and fueling) to 0.075 g/s. The desired result was to push the observed P11 increase closer to the 10 kPa seen in systems testing.
- Previous CV airflow was 0.10 g/s as this was the standard value commanded via the software.
- TC 5 appeared to re-create the sharp increase in delta P previously observed and shows that extended run time would help.
- TC 5R50 was run to determine if recycled ATG could reverse the plugging process. This represents 12% recycle fraction which is ~ 13 mol% water in the recycle.

Figure 5.3.1.2.2-3: DOE1 Pressures vs. TC Plot DS14

Figure 5.3.1.2.2-4: DOE1 - Temperatures vs. TC

9.3.1.2.3 DOE 2: Catalyst Plugging

A second DOE was contemplated in order to clearly identify the source of carbon formation. A key difference between the systems and reformer lab environment was that the reformer is located directly over the ICM base gas phase combustor (GPC) in the system application. This type of setup was not available at that time in the reformer lab. The proximity to the GPC increased the surface temperatures seen at the reformer. Instrumentation of key reformer surface and stream temperatures (see **Figure 5.3.1.2.3-1**) indicated that an important difference existed between the system and reformer tests.

Figure 5.3.1.2.3-1: Configuration 2b; Reformer - Surface TCs

Figure 5.3.1.2.3-2 shows the surface temperature identified in **Figure 5.3.1.2.3-1** plotted in grade line fashion (note there are several planes for TC location in which both top and bottom surface temperatures are recorded). Superimposed on this graph is the typical T2 (thermocouple is in the mixer just upstream of the pre-catalyst) temperature

ranges for both the reformer lab test setup and the systems lab testing. The temperature in the vicinity of the flange is significantly hotter in the systems than the reformer lab setup. A band heater (or flange heater) was used to raise the heat input to the front end of the reformer in order to better simulate the system test. This was subsequently then used to characterize pre-combustion robustness and used as a factor in the proceeding catalyst plugging experiment. The reformer configuration for DOE 2 was used under the same (see **Figure 5.3.1.2.3-3**) conditions as the current configuration which is similar to systems test beds.

Figure 5.3.1.2.3-2: Flange Temp: System versus Reformation Lab

Figure 5.3.1.2.3-3: RP225504 rev 4 MP 1/29/08 DS as Tested in System and DOE 2

This configuration was used for the catalyst plugging issues with the addition of a second layer of the Nextel alumina radiation shield. **Figure 5.3.1.2.3-4** shows the test layout.

	2	3	4	5	7	8	11	12	Run Time				
									Thermal Stab	Data of interest			
Run Ord	Comment / Purpose	TC	Mixer Type	Cat Type	Flange Skin Temp	CV vapor temp	Op Condition	O/C	AF/BC	BF/AC	AF/BC	BF/AC	min / Run
0	Baseline 1	0	RP225524 rev 2	ZM mon	370	650	Recycle 20%	1.45	45	45	45	45	180
1	BOB	5	RP225524 rev 2	ZM mon	370	450	Recycle 16%	1.40	45	45	45	45	180
2	Baseline 1	0	RP225524 rev 2	ZM mon	370	650	Recycle 20%	1.45	45	45	45	45	180
3	WOW	4	RP225524 rev 2	ZM mon	440	650	POx	1.15	45	45	45	45	180
4	Baseline 1	0	RP225524 rev 2	ZM mon	370	650	Recycle 20%	1.45	45	45	45	45	180
5		2	RP225524 rev 2	ZM mon	370	650	POx	1.15	45	45	45	45	180
6	Baseline 1	0	RP225524 rev 2	ZM mon	370	650	Recycle 20%	1.45	45	45	45	45	180
7		6	RP225524 rev 2	ZM mon	370	650	Recycle 16%	1.40	45	45	45	45	180
8	Baseline 1	0	RP225524 rev 2	ZM mon	370	650	Recycle 20%	1.45	45	45	45	45	180
9		8	RP225524 rev 2	ZM mon	440	650	Recycle 16%	1.40	45	45	45	45	180
10	Baseline 2	0	RP225524 rev 2	ZM mon	370	650	Recycle 20%	1.45	45	45	45	45	180
11		1	RP225524 rev 2	ZM mon	370	450	POx	1.15	45	45	45	45	180
12	Baseline 2	0	RP225524 rev 2	ZM mon	370	650	Recycle 20%	1.45					
13		3	RP225524 rev 2	ZM mon	440	450	POx	1.15	45	45	45	45	180
14	Baseline 2	0	RP225524 rev 2	ZM mon	370	650	Recycle 20%	1.45	45	45	45	45	180
15		7	RP225524 rev 2	ZM mon	440	450	Recycle 16%	1.40	45	45	45	45	180
16	Baseline 2	0	RP225524 rev 2	ZM mon	370	650	Recycle 20%	1.45	45	45	45	45	180

Figure 5.3.1.2.3-4: DOE 2 – Test Layout

Delphi adopted a more aggressive problem resolution approach. Due to time constraints, systems data showed that high and low rates of P11 increases could be seen from Tube A fueling to Tube B fueling, therefore it was decided that the phenomena should be observed during a single fueling/cleaning cycle (see **Figure 5.3.1.2.1-4**).

Percent recycle was included as a variable in the test after identifying that recycling would be employed at the system level. Therefore, the O/C ratio was nested with Reforming Mode as an additional variable. A baseline recycle mode using 20% recycle was run between each TC as a means to give equal preconditioning to each TC. The flange heater was used to produce two levels of inlet heating and CV temperature was set to level two (450°C & 650°C) which are similar to levels seen in recent systems testing. Each TC plus baseline would take six hours test time as compared to the overnight runs of DOE 1. Results of this testing are shown in **Figures 5.3.1.2.3-5** and **Figure 5.3.1.2.3-6**. Minor increases in P11 delta P occurred during testing.

Figure 5.3.1.2.3-5: DOE 2 – Tube Pressures and T2 Temperatures versus TC

Figure 5.3.1.2.3-6: DOE2 – Tube Pressures versus TC

Figure 5.3.1.2.3-7 shows a detailed reduction of the data to determine if significant slopes ($\Delta P / \text{time}$) could be identified. Data in columns mean ΔP and ΔP slope (versus time) showed no clear trends. The two TCs expected to be best and worst based on previous testing showed negative slopes (improving ΔP). A final TC ran 43 hours producing plugging similar in magnitude to that of DOE 1, see **Figure 5.3.1.2.3-8**.

Test method limited to 3hr per TC;						Data						
Run Order	Test Condition	CV Tube Temp SP	Operating Point	Flange Skin Temp SP	O/C SP	Average of Catalyst delP (kPa) P11 CORR	Average of Catalyst delP (dP/dt) [kPa/10hr]	Average of CV Cleaning Temp (TC at Junction Block)	Average of CV Fueling Temp (TC at Junction Block)	Average of CV Cleaning Temp	Average of Recycle to Reformer	Average of Recycle_Tot_FB_gps
0	0	650	Recycle 20%		1.45	2.17	0.028	523	662	577	1	0.325
1	5	450	Recycle 16%	370	1.4	2.03	-0.046	392	456	422	1	0.251
2	0		Recycle 20%		1.45	2.20	0.047	515	649	565	1	0.328
3	4		POx	440	1.15	2.06	-0.058	532	652	573	0	0.015
4	0		Recycle 20%		1.45	2.24	0.051	517	645	569	1	0.325
5	2		POx		1.15	1.98	-0.023	525	641	566	0	0.014
6	0	650	Recycle 20%	370	1.45	2.25	-0.006	512	637	563	1	0.325
7	6		Recycle 16%		1.4	2.21	0.010	508	632	555	1	0.251
8	0		Recycle 20%		1.45	2.27	-0.007	505	630	553	1	0.328
9	8		Recycle 16%	440	1.4	2.33	-0.003	508	631	556	1	0.251
10	0		Recycle 20%		1.45	2.28	-0.008	513	630	564	1	0.328
11	1	450	POx	370	1.15	1.83	-0.081	393	452	416	0	0.015
12	0	650	Recycle 20%		1.45	2.27	0.092	499	622	547	1	0.325
13	3	450	POx	440	1.15	2.01	-0.084	393	450	415	0	0.015
14	0	650	Recycle 20%	370	1.45	2.29	0.062	497	618	544	1	0.325
15	7	450	Recycle 16%	440	1.4	2.25	-0.018	392	454	418	1	0.253
16	0	650	Recycle 20%	370	1.45	2.30	0.013	500	622	548	1	0.328

Figure 5.3.1.2.3-7: DOE 2 – Results Table

Figure 5.3.1.2.3-8: DOE 2 – TC 17 Extended Run

The investigation was terminated based on systems testing of the configuration shown in **Figure 5.3.1.2.3-3** running for 135 hours without catalyst plugging. The conclusions of this investigation are as follows:

1. Catalyst substrate (ZM monolith vs. ZTA foam) contributes to plugging
2. Pre-catalyst configuration contributed marginally to plugging

3. Recycle prevents plugging
4. O/C and vapor temperatures are contributory factors to plugging

In summary, based on available data, no single factor studied appears to have caused the problem. Instead, the problem was due to either a combination (interaction) of factors and/or some unknown factor.

9.3.1.3 PP1 Experience: Low T2 at Start Up Problem

9.3.1.3.1 Overview

Systems testing showed unexplained rises in P11 (pre-catalyst + catalyst delta P) shortly after the Perforated Plate 1 (PP1) design was utilized. Teardowns indicated a plugged radiation shield.

Figure 5.3.1.3.1-1 graphically shows the plugged radiation shield problem. A “Best of Best” (BOB) start has a rapid and high ($>600^{\circ}\text{C}$) T2 rise indicating a full combustion event has occurred. A “Worst of Worst” (WOW) start has slow sluggish ($<600^{\circ}\text{C}$) T2 rise; indicating an incomplete or poorly distributed combustion event. Delphi’s experience shows that these low and slow T2 temperature starts will cause carbon to deposit on the radiation shield eventually plugging.

An investigation was initiated to understand the factors that control the variation in T2 during startup. A compare and contrast approach (Shainin Red X) was adopted based on the available reformer hardware. A reformer that had this problem in a systems test was labeled the WOW reformer. A similar reformer that had undergone a test in the reformer lab and had never experienced this issue was labeled the BOB reformer. The WOW reformer was tested in the reformer lab and was confirmed to be a WOW. This confirmed that the test stand and lab were not contributing factors.

Fuels were swapped; both injector mass flow and actual reformer combustion starts were conducted. Neither mass flows nor T2s during start had strong correlation with fuel and therefore was eliminated as a variable for further study.

Figure 5.3.1.3.1-1 Best of Best and Worst of Worst Contrast

Several factors that were found to contribute to the WOW vs. BOB were:

- T2 depth not consistent between builds
- Injector supply voltage not consistent between stands (poor voltage regulation)

These investigation differences were eliminated during the process.

9.3.1.3.2 Dictionary Split Graphs

Figures 5.3.1.3.2-2 through 5.3.1.3.2-8 represent the data for all splits related to hardware and control variables. After a number of parts were swapped without the benefit of balanced events, data was compiled in order to evaluate the effects across the range of disparate levels of background variables. As a result, a sequential judgment call was made on whether an effect can be observed over the other variation in the background. Each successive plot moves one of six variables to be the primary variable. If a distinct effect in T2 temperatures can be observed (between red bars) within this primary pattern, then an effect is evident. Six variables of interest consist of three hardware and three setting:

1. BOB / WOW reactor
2. BOB / WOW / NONE mixer (where “NONE” means not declared as BOB or WOW)
3. BOB / WOW EHCv assembly (note: the “400W Inconel wire wrap” design was made from the WOW EHCv)
4. EHCv position: ranges from +6 to -8 mm
5. EHCv orientation: 0 to 180 degrees
6. Pre-heat Time (of EHCv): 100, 115, and 150 seconds

Initially in the investigation a number of variables appeared to have an effect on the results, but further testing indicated that they did not. As an example, EHCv angle and depth seemed to have an effect on the test data, but additional analysis concluded that they were not primary factors.

Figure 5.3.1.3.2-1: Effect of Injector Lean & Pre-bleed Proc

Figure 5.3.1.3.2-2 shows a split for EHCV angle with significant high and low T2s on both sides of the split. Therefore this cannot be the primary factor. **Figure 5.3.1.3.2-3** shows EHCV depth spanning a range from -6mm to +8mm. This dimension refers to the relationship of the EHCV outlet hole to the incoming airstreams and can be seen in **Figure 5.3.1.3.2-10**. High and low T2s can be seen across the entire spectrum of depths.

Figure 5.3.1.3.2-2: EHCV Angle

Figure 5.3.1.3.2-3: Preheat Time

Figure 5.3.1.3.2-4 shows preheat time effect of 3 levels (100, 115 and 150 seconds). While the data is not well balanced the presence of highs and lows on either end suggest again that this variable is not the primary factor (Red X). **Figure 5.3.1.3.2-5** shows the effect of specific reactor for each of the 3 reactors involved (BOB, WOW, none). As the split was not planned in advance it is confounded with the Mixer. **Figure 5.3.1.3.2-6** shows this same data recompiled to show the mixer as primary variable. In

this instance a clear difference can be seen between the BOB Mixer and the WOW mixer. It appears that the 'none' mixer acts more like a WOW mixer than a BOB in that a fair number of low T2 temperatures were experience. Much suspicion surrounded the EHCV as vaporization and mixing are difficult to quantify.

Figure 5.3.1.3.2-4: EHCV Depth

Figure 5.3.1.3.2-5: Reactor

Figure 5.3.1.3.2-6: Mixer

Inspection of BOB, WOW and other EHCVs indicated that the heating element was not well centered in the fuel carrier tube. A modification was employed that utilized a wire wrap around the heating element in order to better center it within the carrier tube. This modification was initially only done to the BOB EHCV assembly and the modifications effect along with original performance can be seen in **Figure 5.3.1.3.2-7**. While data is superimposed over other variables some improvement in T2 temps can be observed. This modification was employed for subsequent testing and eventually the WOW EHCV assembly was also modified. A breakthrough occurred by chance when testing to determine the settings for an upcoming Systems test using Reformer Lab hardware proved to be disastrous for other hardware of the same design. **Figure 5.3.1.3.2-8** shows on the left how the setting of -8mm and 180 deg were selected on the BOB mixer and then subsequent trial on 2 other mixers. The "none" and WOW mixer both performed poorly at this setting which clearly indicated that mixer is a key source of the variation.

Figure 5.3.1.3.2-7: EHCV

Figure 5.3.1.3.2-8: Mixer with EHCV Depth and Orientation

In the midst of all this hardware swapping a distortion in the perforated plate was noticed on disassembly. The plate is tack welded to the ID of the mixer tube and a both a weld had come undone as well as a distortion on the plate was evident. It is on clear which of these 2 anomalies occurred first. The mixer was repair and data is compared from before and after the repair in **Figure 5.3.1.3.2-9**. Based on the 5 common combinations were before and after data exist it was concluded that the plate repair and its prior condition are the not the primary source of T2 variation at start up.

Figure 5.3.1.3.2-9: Effect of Mixer Plate Repair

Further inspection of the mixers including BOB, WOW & none revealed a difference in EHCV and Igniter fitting angles. **Figures 5.3.1.3.2-10, Figure 5.3.1.3.2-11, and Figure 5.3.1.3.2-12** show the degree to which these fittings were angled on the 3 mixers.

Figure 5.3.1.3.2-10: BOB (FCHX-331) Mixer EHCV and Igniter attitude

Figure 5.3.1.3.2-11: WOW (FCHX-328) Mixer: EHCV and Igniter attitude

Figure 5.3.1.3.2-12: FCHX-326 Mixer: EHCV and Igniter attitude DS62

Figure 5.3.1.3.2-13 shows key dimensions that were noted on the BOB, WOW & NONE mixers. **Figure 5.3.1.3.2-14** summarizes Delphi's conclusions. While a definitive Red X was not identified, a number of contributing factors were. Boxes on this diagram are white indicating an unknown factor. The white boxes without lower branches indicate an area of vulnerability. In particular the fuel type which was US Low Sulfur Diesel (LSD) for the reformer lab testing and near zero sulfur diesel for the systems testing. Sulfur levels are believed to play a role in carbon formation.

Angles are visual estimates					
SN	Designation	Part Type	How Fab'd	Ignitor Splay [deg]	EHCV Splay [deg]
FCHX-331	BOB	Mixer	Brazed	0	0
FCHX-328	WOW	Mixer	Welded (make fr)	2	2
FCHX-326	none	Mixer	Welded (make fr)	2	1

Figure 5.3.1.3.2-13: Mixer Descriptions

Figure 5.3.1.3.2-14: PP1 Reformer Cold Start Red X Solution Tree™

9.3.1.4 NG1 & PP1 Pre-Combustion

A heater was wrapped around the reformer flange assembly in order to rapidly evaluate pre-combustion performance in the Gen 4.2T POx reformer in a test lab environment (see **Figure 5.3.1.4-1**). The heater was controlled from 450°C to 750°C in 50°C increments and allowed to stabilize for 30 minutes at each temperature. During the pre-

combustion test, the reformer was run at a variety of test conditions; with the condition shown in **Figure 5.3.1.4-2** being the most severe; T2 (mix zone) temperature as the measured response.

as tested in:
 MG733C330 Pre Comb Eval

Figure 5.3.1.4-1: RP225504 MP NG1 w/ Ceramic Sleeve v1

Figure 5.3.1.4-2: Objective 1a: Pre-Combustion

The NG1 reformer (**Figure 5.3.1.4-3**) was first tested as a baseline and shown to fully pre-combust between 600°C and 650°C, as shown in **Figure 5.3.1.4-2** above. This result correlates with NG1 reformer performance in full system enclosures. **Figure 5.3.1.4-4** shows external skin temperature correlation plots of three reformers run in systems test enclosures and one reformer run in the test lab enclosure. At the S2 flange skin location (top & bottom) the systems enclosure tests were 200°C higher than the test lab enclosures. The flange heater temperature that caused pre-combustion was the same temperature as the flange temperature system's reformer.

Figure 5.3.1.4-3: NG1 Mixer

Figure 5.3.1.4-4: Flange Temp: System versus Reformation Lab

Figure 5.3.1.4-4 shows that the system test's T2 temperatures are 450°C to 500°C, while the test lab reformer T2 temperatures were 290°C to 350°C. However, there were test lab T2 temperature excursions to 470°C that did match system test temperatures. This phenomenon is "Cool Flame" combustion, and is evident in the plateau in the pre-combustion plot in Figure 5.3.1.4-2.

The PP1 reformer (Figure 5.3.1.4-5 and Figure 5.3.1.4-6) was tested next pre-combustion performance degraded. T2 temperatures were too high with mix zone thermal isolation needed. Figure 5.3.1.4-7 shows the addition of a ceramic sleeve lining the mix zone shell. This resulted in significant pre-combustion performance improvement. T2 temperatures remained below 400°C throughout the heater flange ramp up through 750°C. Due to start up combustion problems associated with the PP1 mixer design, efforts returned to the NG1 mixer.

Figure 5.3.1.4-5: PP1 Mixer (Perforated Plate)

Figure 5.3.1.4-6: PP1 Mixer (Perforated Plate)

Figure 5.3.1.4-7: PP1 v2-1 with Mixer Configuration = Base Configuration

The same ceramic sleeve lining the mix zone shell was attempted with the NG1 mixer. The tested configuration is shown in **Figure 5.3.1.4-8**. However, there was little or no pre-combustion performance improvement compared to the original NG1 design performance. The only noted difference was the absence of the “Cool Flame” pre-combustion phenomenon.

as tested in:
MG733C330 Pre Comb Eval

Figure 5.3.1.4-8: RP225504 MP NG1 w/ Ceramic Sleeve v1

The next design iteration tested involved thermally isolating the NG1 mixing cone from the flange. The resulting design configuration, named NG1_v2, is shown in **Figure 5.3.1.4-9**. The pre-combustion performance of this design nearly matched that of the PP1 mixer with the ceramic sleeve. The NG1_v2 configuration was tested in two separate test and two different NG1_v2 reformers. **Figure 5.3.1.4-2** shows one test pre-combusted when the flange heater was set to 750°C while the other never pre-combusted.

Figure 5.3.1.4-9: RP225504 MP NG1 w/ Ceramic Sleeve v2

Figure 5.3.1.4-10: Pre-combustion Testing Heated Flange – 450°C Vapor Temperature

9.3.1.5 Contact Vaporizer (CV) Plugging

Five CV assemblies were put into service around January 2007, and underwent numerous reformer and systems tests. **Figure 5.3.1.5-1** shows a compilation of system tests employing each of the CV assemblies. The test included a minimum of one start. The analysis suggests that despite the severe thermal environment (1150°C) and axial gradient the CV performance met the requirements.

Sum of # of Starts under Systems EWO #	
CV Asm S/N	Set 7 & 8 Systems Testing since 2/20/08 (does not include testing prior to this date testing)
FCHX-303	5 Start / Tests: developed scar on tube; tube was disected
FCHX-304 (all versions)	60 Start / Tests: developed leak at tube heel; was disected
FCHX-305	40 Start / Tests: had plugging complaint; was subsequently cleaned; still in service; complaint under investigation
FCHX-306	18 Start / Tests: Test 6 was 135 hr run w/o incident; Test 7 thru 13 had no cleaning (~700 minutes) resulting in plugged tube; subsequently cleaned; still in service
FCHX-307	23 Start / Tests: no problems; still in service

Figure 5.3.1.5-1: CV Assembly Systems Starts & Tests

9.3.1.5.1 FCHX-303 Dissection and Analysis: Tube Scarred

Upon disassembly of previously run System Test equipment, the contact vaporizer tubes were found to have significant scoring (see **Figure 5.3.1.5.1-1**). Erosion was evident on the exterior of the tubes at the point of impact with the exhaust from the combustor (see **Figure 5.3.1.5.1-2**). The protective oxide layer was also stripped off of the surface as seen in the microscopic images.

Figure 5.3.1.5.1-1: System Test with CV Erosion

Figure 5.3.1.5.1-2: Contact Vaporizer FCHX-303 Surface Erosion

9.3.1.5.2 FCHX-304 Dissection and Analysis: CV Tube Leak (Breach)

A system test ended when the O/C ratio became uncontrollable resulting in poor reformer performance. Subsequent disassembly led to the discovery of a pin hole sized breach of one of the contact vaporizer tubes into the ICM chamber (see **Figure 5.3.1.5.2-1**).

Figure 5.3.1.5.2-1: Breach of Tube A During Test

Figure 5.3.1.5.2-2 shows a closer view of the hole and locations where SEM analysis was conducted. **Figure 5.3.1.5.2-3** is a chart of the analysis results. Most unusual were the locations showing high zinc content. System components having zinc content such as washers were identified and changed.

Figure 5.3.1.5.2-2: Microscopic Images and SEM Test Locations

SEM Analysis of Surface of Blow Hole (Locations identified in figure 6)										
Element	Location									
	Base Metal Inconel 625	1	2	3	4	5	6	7a	7b	7c
Al	1.77	1.18	1.38	1.80	0.60	2.08		3.65	0.35	26.62
Si	2.35		1.72	1.15	0.61	2.26		2.64	0.49	28.16
Cl	1.13					1.64		1.42	2.45	
Cr	9.27	37.57	5.16	48.86	26.02	10.79	23.37	42.03	3.58	28.24
Fe	8.72	6.72	3.17	3.09	49.27	18.73	6.66	6.93		
Ni	71.40	45.83	8.90	11.23	17.83	58.96	65.50	31.57		5.29
Nb	5.36	2.53		4.04	1.79		1.69	2.62		
Ti		6.18			1.79		2.78	6.97		2.90
Zn			79.68	29.83	2.08	3.09				
K						2.45		2.17	2.06	8.79
C									88.60	
Na									1.59	
S									0.88	

Figure 5.3.1.5.2-3: SEM Analysis Results

Figure 5.3.1.5.2-4 shows a microscopic view of the breach after being cut by a diamond saw. This section was encased in acrylic, ground smooth and etched to examine metallic grain structure.

Figure 5.3.1.5.2-4: Breach of CV Tube during C300-11

9.3.1.5.3 SPU1E CV Tube Pressure Management Optimization

A test to determine tube deposit formation and removal rates as a function of CV fueling and cleaning temperatures was initiated. Due to the difficulty of imposing specific combustor operating conditions and the resulting CV tube temperatures on systems testing, the Reformer labs SPU1E integrated stand was deployed. This stand did not employ stacks but rather shunts reformat flow back to the ICM. Systems tests had difficulty transitioning from EHCv vaporized fuel to CV vaporized fuel due to light off and heat transfer problems in the GPC. Tests were designed to better understand what conditions impact rates of deposit formation and removal.

The stand runs two set of conditions that include simulated startups. The startup conditions vary combustor temperatures as a means to affect CV vapor temps. TC1 was with CV temperatures targeted at 650°C fueling / 525°C cleaning, and TC2 was with CV temperatures targeted at 550°C fueling / 425°C cleaning. TC1 ran ~60 hrs followed by ~50 hrs at TC2.

9.3.2 Develop Endothermic Reformer

9.3.2.1 Gen 5T EOT Analysis

The Gen 5T reformer did not undergo testing during this period in favor of POx system development. Previous Gen 5T analyses involved known failure modes relative to buckling and weld failure, both of which were addressed. On several occasions, debris was collected from either the ref_{out} cavity or the system ICM paths that warranted analysis. **Figure 5.3.2.1-1** shows a compilation in which a key question of whether or not washcoat or substrate was separating from the reactor. In each of the three cases no evidence of separation was found.

EWO #	MG733D153	MG733D158	MG733D159
Description	Debris from RefOut Manifold & MassSpec filter from MG733C272 Gen 5T Pox operation testing on US07	Debris from RefOut Manifold from MG733C295 Gen 5T Pox & Endo operation testing on US07	Debris from RefOut Manifold from MG736C172-02 System testing of Gen 5T Pox & Endo operation testing on US08; deposit is from Combustor Ignitor cavity
Substrate Found?	No	No	No
WC found?	Yes, but only washcoat that was on Inconel 625 was flaked off during disassembly. No evidence of washcoat from substrate.	No	No
Matl Analyzed	black powder WC; broken off however only traces of Rh and Ni incating that washcoat was attached to tubes rather than substrate. white particles WC; broken off during disassembly; had white edge at fracture; black faces due to carbon.	particles Hot corrosion oxide scale from 316 SS and Inconel 625 was predominant in this sample. Chlorine was detected at 3 wt% in this debris	white fibers: some insulation black fibers: insul w/ Cr,Ni, Moly, Fe (fr SS, Inc625) silver particles: oxide scale with Fmica + silver + boron nitride (thd lube)
Results:	Sample was mostly oxide scale. A small amount of washcoat was found that had been on inconel 625 tubing and was displaced during disassembly.	Some washcoat that had been on inconel 625 tubing and was displaced during disassembly	Some washcoat that had been on inconel 625 tubing and was displaced during disassembly

Figure 5.3.2.1-1: Analysis of Debris from Gen 5T Testing

9.3.2.2 Gen8T Reactor

9.3.2.2.1 Generate HYSIS Model of Gen8T Reformer Sub-System

A new flow and pressure drop model was developed to calculate effective flow areas for the different flow passages within the reformer sub-system. A model was developed in MS Excel with a more comprehensive model to be compiled in HYSIS. **Figure 5.3.2.2.1-1** illustrates the combustor flow network of the Gen 8T reformer sub-system. Cathode air and cooling air are fed to the combustor inlet manifold. There are four parallel flow paths that open up: Air swirler and mixer flow; nozzle flow; leakage flow through the sliding seal; and bypass flow. **Figure 5.3.2.2.1-2** shows the calculated effective areas: Mass flow, temperatures, and pressure drops for a 100% load condition. The proper design of all the effective areas is critical to functionality of the design. Temperatures of the hot combustion gases, heat transfer, and metal temperatures strongly depend on accurate flow splits between the parallel flow paths.

Figure 5.3.2.2.1-1: Combustor Flow Network

		Aeff [m²]	Area [mm²]	Area [m²]	Cd [-]	massflow [%]	massflow [kg/s]	Del P [Pa]	Tstatic [K]	Tstatic [C]	Rho [kg/m³]	M [g/mol]		
Cathode Air							0.01517			1073				
Cold Air							0.00054			63				
Air Flow		0.000486					0.01571	1511	1073		800	0.345898	28.84	
ATG Flow							0.00173			1073	800		29.74	
Diesel Flow							0.00000			1073	800		142	
Outlet							0.01744			1250	977	0.298463	28.99	
Cathode Air Inlet Manifold	I	0.001388	1735.0	0.001735	0.8	100.0%	0.01571	185	1073		800	0.345898	28.84	
Swirler/Bypass/NozzleCooling/ bypass holes	II													
II-1	0.000293	450.0	0.00045	0.65	37.1%	0.00582	573	1073	800	0.345898	28.84		28.84	
II-2	6500	1.0E+10	10000	0.65	0.3%	0.00005	0	1073	800	0.345898	28.84		28.84	
II-3	0.000051	85.0	0.000085	0.6	3.6%	0.00056	174	1073	800	0.345898	28.84		28.84	
II-4	0.000953	850.0	0.00085	0.65	59.1%	0.00928	408	1073	800	0.345898	28.84		28.84	
Mixer/Nozzle/Leakages/Bypass	III									1073	800	0.345898	28.84	
leakage ignitor and thermistor	III-1	0.000013	20.0	0.00002	0.65	1.7%	0.00026	601	1073	800	0.345898	28.84		28.84
leaking sliding seal	III-2	2.4E-06	3.0	0.000003	0.8	0.3%	0.00005	602	1073	800	0.345898	28.84		28.84
nozzle cooling holes	III-3	3.25E-05	50.0	0.00005	0.65	3.6%	0.00056	428	1073	800	0.345898	28.84		28.84
mixing of fuel and air	III-4	0.000801	1001.4	0.001001	0.8	59.1%	0.00928	194	1073	800	0.345898	28.84		28.84
	B	0.000747	1149.0	0.001149	0.65	35.4%	0.00556	80	1073	800	0.345898	28.84		28.84
Combustion Chamber	IV	0.001282	8011.8	0.008012	0.16	68.1%	0.01188	164	1422	1149	0.262395	28.99		28.99
Dump Loss from Combustor to Hex	V	0.001075	2500.0	0.0025	0.43	68.1%	0.01188	233	1422	1149	0.262395	28.99		28.99
Heat Exchanger	VI	0.000446	4244.0	0.004244	0.105	68.1%	0.01188	1273	1336	1063	0.279269	28.99		28.99
Bypass/Dumploss	VII									1250	977	0.298463	28.99	28.99
	VII-1	0.000263	350.0	0.00035	0.75	35.4%	0.00556	705	1173	900	0.318055	28.99		28.99
	VII-2	0.001676	5585.8	0.005586	0.3	68.1%	0.01188	84	1250	977	0.298463	28.99		28.99
Outlet Manifold	VIII	0.000758	947.5	0.000948	0.8	100.0%	0.01744	887	1250	977	0.298463	28.99		28.99

Figure 5.3.2.2.1-2: Effective Areas at 100% Load Condition

9.3.2.2.2 Gen 8T DPS3000 - Analysis of Ejector Pump for the Ingestion of Recycle into the Reformer

Ejector pumps are a valid alternative to common displacement pumps. Ejector pumps can be used at high temperatures unlike common displacement pumps. If made from Nickel alloys, ejectors can operate with fluids as hot as 1000°C. This supports the application of ejector pumps as hot recycle pumps in SOFCs. Another positive aspect is the absence of moving parts and with the added benefits of longer life and lower service requirements.

System operating requirements put constraints on the performance of the ejector pump, such as multi fuel operation, turndown the pressure requirements of the working fluid, pressure recovery, cost, and mixing of the fluids. These aspects were investigated numerically. **Figure 5.3.2.2.2-1** shows results from an earlier study of recycle ingestion using an ejector pump with Methane as working fluid. It is demonstrated that an ejector pump with CH₄ as working fluid was capable of attenuating the required flow of recycle from the stack anode. The results assume a 6.5kPa negative pressure differential between the stack anode and the ejector. The ejector in the model was approximately 4 inches in length and 1.5 inches in diameter.

◆ Ejector Pump/Mixer Preliminary Study (MG733E51)

Figure 5.3.2.2.2-1: Ejector Pump with CH₄ Working Fluid

Figure 5.3.2.2.2-2 shows an example of a FOX Mini Adductor. The working fluid which creates the low static pressure by increasing flow velocity is referred to a “motive gas”. The ejector consists of a nozzle, a venturi section, a recovery or discharge section, and a suction region (see **Figure 5.3.2.2.2-2**). For example, FOX Mini Adductors claim to reach a suction vacuum pressure of 80 kPa (**Figure 5.3.2.2.2-2**) which is far beyond the requirements in the SOFC system. The working fluid pressure requirement is 600 kPa and the motive fluid in the test is room temperature air. In DPS3000 the motive fluid is diesel fuel with air with the diesel fuel is vaporizing at ~ 400°C.

Figure 5.3.2.2-2: Commercial Ejectors and Terminology

In an ejector, the vacuum is drawn by increasing the dynamic pressure of the working fluid between the nozzle and the venturi at near constant total pressure, thus lowering the static pressure locally. The dynamic pressure is directly proportional to the local density and square of velocity. The velocity decreases with increasing fluid density. **Figure 5.3.2.2-3** illustrates the strong effect of molecular mass on the sonic velocity of various fuels. Higher density gases create lower vacuums for a given working pressure ratio. This is a problem because the working fluid is diesel (see **Figure 5.3.2.2-4**) as vaporized diesel cannot create enough vacuum to draw the required flow rate of recycle. Mixing the fuel with air solves the vacuum problem and varying the air flow at full fuel flow over the entire range of operation conditions creates the turndown required for system operation.

Fuel Effect on Ejector Vacuum

- Velocity decreases with increasing fluid density. See strong effect of molecular mass on sonic velocity.
- Vacuum is drawn by increasing the dynamic pressure at near constant total pressure, thus lowering the local static pressure. The dynamic pressure is directly proportional to the density and square of velocity.
- Therefore, higher density gases create lower vacuums at a given working pressure ratio.

Figure 5.3.2.2-3: Effect of Fuel on Ejector Vacuum

Figure 5.3.2.2.2-4: Ejector Performance with Diesel as Working Fluid

The contact vaporizer technology used 0.1g/s air as carrier and cleaning gas within the vaporizer tubes. This air flow rate is kept constant over the whole range of operating conditions from idle to full load. **Figure 5.3.2.2.2-5** shows an ejector operation at full load with the nozzle exit Mach number being 1 (sonic flow). The required recycle flow for DPS3000 can only be maintained if the pressure differential (vacuum) between the stack anode and the ejector is less than 6kPa (see **Figure 5.3.2.2.2-5**). The pressure differential is larger in the current system. The suctioned flow rate of hot recycle falls off with lowering the velocity of the working fluid when also lowering the load from full power to idle. This is partially offset by the decrease in pressure differential. However, with a constant air flow the ejector vacuum decreases (due to decrease in fuel flow) stronger than the decrease in pressure differential between stack anode and ejector leading to insufficient turnaround.

Sonic Ejector - Diesel Fuel - SPU1E RATED Condition

Figure 5.3.2.2.2-5: Ejector with Constant Air Flow at Sonic Nozzle Condition

9.3.2.2.3 Start-up Carbon and Pre-combustion Mitigation by Exhaust Gas Ingestion

System start-up provided the strongest challenges to the whole system in terms of carbon formation and deposition. Metal walls are cold and fuel can condense causing carbon to precipitate out. The reformer will operate in CPOx during start up without the carbon suppressing benefit of the water recycle. The CPOx reformat is highly susceptible to carbon formation (e.g. Bodouard) when cooled within the cold flow passage between reformer and stack and inside the stack. Conventional reactor design and operation uses large amounts of water to suppress carbon formation when operating with diesel which is not Delphi's strategy. Carbon suppression is not an issue at normal operation when recycle delivers water to the reformer, but the problem prevails at start-up when recycle is not available.

There was one source of water during start up and that is the system combustor exhaust. The start-up strategy used liquid diesel within the combustor. As soon as startup happens, there is water vapor present in the exhaust. The reforming reactor (heat exchanger) heats up and provides rich fuelling to the reactor in CPOx mode. Recycle is not be available until the stack is at operating temperature of approximately 720°C. Carbon formation and deposition during this time can be sharply suppressed by ingesting water containing system exhaust. In addition, the efficiency will increase due to the increase in reactant's temperature and decreasing the O/C ratio.

Figures 5.3.2.2.3-1 and 5.3.2.2.3-2 illustrate the water content and reactant's temperature when ingesting a certain amount of exhaust into the air stream, with 0% pure air and 100% being pure exhaust. **Figure 5.3.2.2.3-1** shows results of exhaust ingestion into the reformer air only while **Figure 5.3.2.2.3-2** assumes that exhaust is ingested into the entire system air. While 100% exhaust ingestion into the reformer air is possible and desirable for maximum carbon suppression, when ingesting exhaust into the system air the percentage of the exhaust should probably not exceed much beyond 50% due to negative effects on the SOFC stack electrochemistry.

Figure 5.3.2.2.3-1: Exhaust Ingestion into Reformer Air

Figure 5.3.2.2.3-2: Exhaust Ingestion into Systems Air

Figure 5.3.2.2.3-3 and **Figure 5.3.2.2.3-4** show the concentrations of Nitrogen and Oxygen within the reformer reactant stream. The amount of Nitrogen that decreases is another indication of the increase in efficiency as less and less N_2 needs to be recycled through the system (heat addition provides another increase in efficiency). As oxygen content in the reactant stream sharply decreases, are more beneficial in the suppression of pre-combustion (auto-ignition, hot wall forced ignition, flashback) while operating in CPOx mode. At Oxygen levels of 15% combustion will be nearly completely suppressed.

Figure 5.3.2.2.3-3: Exhaust Ingestion into Reformer Air Nitrogen and Oxygen Concentrations

Figure 5.3.2.2.3-4: Exhaust Ingestion into System Air Nitrogen and Oxygen Concentrations

9.3.2.2.4 Gen8T DPS3000 - Momentum and Conjugate Heat Transfer Analysis

Figure 5.3.2.2.4-1 shows a Gen 5T core reactor assembly. It consists of seven tubes of 1 inch diameter and 6 inches in length. Brazed to the inside tube walls are a 20 ppi Fecralloy foam monolith of 5 inches in length. Heat is transferred from the outside through the aid of a heat transfer substrate to the inside of the reforming tubes. The heat transfer medium in the Gen 5T case was 10 ppi Fecralloy foam. The outer substrate core is roughly 4 inches in diameter. Hot combustion gases pass through the 10 ppi foam and is conducted and convected to the tubes. The Gen 8T reactor uses the same technology as the Gen5T. Based on Gen 5T test data Delphi knows that the heat transfer was insufficient for the application. Candidate substrates were laboratory tested for their heat transfer quality to better characterize their heat transfer. This data and other data from literature and tests were used to conduct a CFD conjugate heat transfer study on four conceptual designs. In these designs the reforming tubes are 0.75 inch in diameter and the outer substrate diameter is essentially the same as in the Gen 5T case with approximately 4 inches. The four conceptual designs are shown in **Figure 5.3.2.2.4-2**.

Figure 5.3.2.2.4-1: Gen 5T Reactor Core

Gen 8T Design and Packaging Concepts

Figure 5.3.2.2.4-2: Gen 8T Reactor Packaging Study

Concept A comprised eight reforming tubes of 0.75 inch diameter arranged around an inner cavity of 1.5 inch diameter. The hot combustion products from the combustor enter the heat exchanger through the narrow 1.5 inch diameter center opening and then flow in between the reforming tubes to the outlet. In concept B the hot combustion gases flow around the reformate collector and reformate outlet manifold and then through the outer substrate. Concepts C and D contained a single, donut shaped, reforming substrate instead of a ring of individual tubes. The difference between C and D was in the manifolding. Whereas in C the flows, either combustor or reactor enter from the end then branch off 90 degrees to their individual outlets in concept D the

combustor flow flows straight through the reactor. This would be a superior arrangement in terms of combustor pressure drop. The arrows in **Figure 5.3.2.2.4-2** above indicate the flow directions of reformat stream in blue color and combustion gas stream in red.

Figure 5.3.2.2.4-3 shows results of model A for various substrates. With ceramic substrates the tube interiors become very cold and reformat quality will be very poor. Carbon formation is most likely in this case. In order to improve the performance to adequate levels with ceramic substrates, the tube diameter requires a large reduction, probably to the level of 0.25 inch diameter or smaller. Such a reduction, however, will increase the number of tubes required to achieve the required residence time from 8 to 80. The resulting increase in cost and complexity is inadequate.

Figure 5.3.2.2.4-3: Gen 8T Reactor Packaging Study – CFD

Fecralloy and Alluchrome showed similar behavior in heat transfer. The Alluchrome corrugated sheet substrate delivers a lower pressure loss and a somewhat higher heat transfer when compared to a 20 ppi Fecralloy foam. However, for a tube diameter of 0.75 inch diameter, the heat transfer augmentation of both substrates was not fully satisfactory. For this purpose the tube diameter was further reduced to 0.625 inch diameter and the tube length was increased by 80%. **Figures 5.3.2.2.4-4, 5.3.2.2.4-5, and 5.3.2.2.4-6** summarize the findings from the CFD study. Post analysis test data showed the Alluchrome substrate to be superior in heat transfer although the (not calibrated) CFD analysis does not show this trend. The space velocity of the new reactor design is 30,000/hr at DPS3000 rated conditions.

Gen 8T Reactor Concept Evaluation – Ceramic Foam

Figure 5.3.2.2.4-4: Gen 8T Reactor Study – Ceramic Substrates

Gen 8T Reactor Concept Evaluation – Fecralloy Foam

Figure 5.3.2.2.4-5: Gen 8T Reactor Study – Fecralloy Substrate

Gen 8T Reactor Concept Evaluation – Alluchrome Corrugated Sheet

Alluchrome Substrate Flow Results at DPS3000 RATED Operating Conditions

Concept	Gen8T Baseline		A1 - simple		B1 - simple		C1 - simple		D1 - simple	
	Reactor	Combustor	Reactor	Combustor	Reactor	Combustor	Reactor	Combustor	Reactor	Combustor
Corrugated Sheet Substrate	1000cps	600cps	1000cps	600cps	1000cps	600cps	1000cps	600cps	1000cps	600cps
N tubes	7		8		9		1			
Di tubes	23.62		17.05		17.05					
L substrate	0.128		0.09		0.09		0.098			
mdot	2.586	10.83	2.586	10.83	2.586	10.83	2.586	10.83	2.586	10.83
Vol foam/substrate	3.93E-04	4.33E-04	1.64E-04	3.93E-04	1.85E-04	4.70E-04	2.02E-04	4.66E-04	2.02E-04	4.66E-04
SV STP substrate	18090	70509	43273	77595	38420	64899	35255	65532	35255	65532
Tau res substrate at Tms	55.6	14.3	23.3	13.0	26.2	15.5	27.9	15.0	27.9	15.0
Qdot Endotherm	2500		2500		2500		2500		2500	
	W/m3	6.368E+06	1.521E+07		1.352E+07		1.240E+07		1.240E+07	
Substrate (Foam) Flow Domain										
M	g/mol	29.74	28.99		29.74	28.99		29.74	28.99	
Tin	K		1196	1455	1184	1455	1187	1447		
Tout	K		1266	1237	1265	1231		944	1330	
Taverage in volume	K		1172	1299			1015	1377		
Cp in	J/kgK		1635	1278	1634	1278		1635	1277	
Cp out	J/kgK		1646	1246	1645	1245		1590	1260	
Hdot in	W		5014.2	20128.3	5034.0	20128.3		5020.3	20009.3	
Hdot out	W		5389.7	16680.1	5382.5	16593.8		3680.8	18152.5	
Qdot Heat Transfer	W		2874.5		2878.5		1368.6		496.3	
Qdot Heat Loss	W			573.7		656.0				
HT effectiveness	-									
Ptin	Pa		1834	1596	1600	1396.4		140	1796	
Ptout	Pa		19.4	21.5	16.8	16		3.1	21	
Rho in	kg/m3		0.244	0.276	0.244	0.276		0.243	0.277	
Rho out	kg/m3		0.228	0.324	0.228	0.326		0.306	0.301	
Rho average	kg/m3		0.247	0.305	#DIV/0!	#DIV/0!		0.295	0.291	
L substrate	m	0.128	0.09	0.09	0.09	0.09	0.098	0.088	0.088	0.088
Area Flow	m2	3.07E-03	4.24E-03	3.95E-03	4.37E-03	2.05E-03	5.23E-03	2.24E-03	5.18E-03	2.24E-03
Vel	m/s			8.0	#DIV/0!	#DIV/0!		4.1	7.2	
Del Pht	Pa		1814.6	1574.5	1583.2	1380.4		136.9	1777	
Del Pp-s	Pa									
Del Pts	Pa									
Cd t-s	-									

Improved
pressure loss
– still high

Figure 5.3.2.2.4-6: Gen 8T Reactor Study – Alluchrome Substrate

9.3.2.3 Combustor

9.3.2.3.1 Gen8T Combustor Design, status at time of reporting

The combustor design is presented in Figures 5.3.2.3.3-1 through 5.3.2.3.3-4. Figure 5.3.2.3.3-1 shows a cross section of the combustor indicating the air, anode tail gas, diesel fuel passages, air swirler, air bypass, conical combustor dome, combustion chamber, and nozzle air circuit.

Figure 5.3.2.3.3-1: Gen 8T Combustor Assembly

Figure 5.3.2.3.3-2 details the air swirler and fuel cartridge. Air enters the fuel swirler through radial swirl veins. During fuel cell operation, the anode tail gas is injected into the swirling air through holes from the inner tail gas chamber. Fuel and tail gas mix before entering the combustion chamber. The swirl in the flow generates a double

toroidal flow field with a large recirculation on the centerline in front of the swirler/nozzle assembly. This low velocity recirculation zone acts as the flame stabilizing anchor of the combustion process. During start up, when tail gas is not available, ignition and start up combustion are performed with liquid diesel. Diesel fuel is injected from a pressure swirl atomizer with a hollow spray and 90 degrees cone angle. The nozzle air provided has two functions. One, it will assist in the fuel droplet atomization process during ignition and start-up, and two, it will cool the nozzle during normal operation on anode tail gas as the fuel source. The nozzle and liquid fuel circuit are purged with air when not in operation to prevent fuel from pyrolyzing and gumming up nozzle and fuel lines.

Figure 5.3.2.3.3-2: Gen 8T Combustor Swirler and Fuel Cartridge

The igniter and thermistor designs are shown in **Figure 5.3.2.3.3-3**. The two-shell arrangement of combustion chamber and bypass shell creates a thermal expansion mismatch during operation. A floating collar has been implemented to minimize thermal stresses and to prevent fatal failures of the igniter and/or thermistor. In this design both the igniter and the thermistor are seated inside a tight fit collar. The collar itself is floating within a containment that is attached to the outside of the combustor liner. Also shown in **Figure 5.3.2.3.3-3** is the floating arrangement of the combustor liner and the combustor dome. The dome is attached to the swirler and is free to move on the other end. In the same way is the combustor liner fixed to the reactor and can float within the flange as shown in the figure below. This is necessary for assembly as well as mitigating the large thermal expansions due to temperature differences.

Figure 5.3.2.3.3-3: Gen 8T Combustor Floating Arrangements

Figure 5.3.2.3.3-4 details the air bypass. The bypass has three functions: First, air is removed from the combustion area which increased the combustor exit temperature and thereby the heat transfer within the heat exchanger. Second, the air is used to cool the combustor walls and no thermal barrier coating (TBC) is required. Third, the air bypass acts as an insulation barrier, effectively minimizing the heat loss from the hot reactor and combustor to the insulation and other components. The bypass is designed as a narrow coaxial flow chamber. Air enters the bypass through holes upstream of the combustor dome. The bypass air flows over the combustor and outer reactor wall and meets the combustion gases through holes after these exit the heat exchanger. The heat that is recuperated and prevented from escaping the reformer is now available to the cathode air heat exchanger. It is assumed that up to 1kW of energy can in this way be preserved within the flow stream.

Figure 5.3.2.3.3-4: Gen 8T Combustor Air Bypass

9.3.2.4 Feedstream Delivery Unit (FDU)

9.3.2.4.1 FDU Design and Status at time of reporting

The FDU (Feedstream Delivery Unit) design is shown in **Figure 5.3.2.4.1-1**. The Contact Vaporizer (CV) is attached to the outlet manifold of the combustor, situated in between the reactor and the cathode air heat exchanger. The CV receives conductive heat from the combustor outlet manifold. Two fuel vaporizing tubes are located within the CV block. Fuel and air pass through these tubes causing the fuel to vaporize. The CV contains a cooling air channel to adjust the fuel vapor temperature during turndown to maintain a vapor temperature of 400°C to 450°C.

Figure 5.3.2.4.1-1: Gen 8T FDU

The fuel enters the junction block after vaporization. The purpose of the junction block is to combine all fluids before entering the mixing chamber. Vaporized fuel, air, and recycle are combined within the junction block. Fuel spray bars (see **Figure 5.3.2.4.1-2**) are implemented to promote mixing of all fluids within the junction block.

Figure 5.3.2.4.1-2: Gen 8T FDU – Cross sectional view

A perforated plate inside the FDU cavity divides the FDU volume in two parts. The volume upstream of the perforated plate is the mixing zone. The fluids are introduced in a tangential fashion creating a swirling flow pattern (see **Figure 5.3.2.4.1-3**). The swirling flow field together with the pressure drop generated through the perforated plate ensure near perfect mixing of all the fluids. The perforated plate has a second

function to straighten the flow field downstream of the perforated plate to minimize the risk of pre-combustion through flashback from the hot surface of the catalyst. The FDU is insulated to prevent the metal wall from heating up and becoming ignition sources for pre-mature combustion upstream of the catalyst. Second, the insulation prevents heat soaking to and overheating the cold zone of the fuel cell.

Figure 5.3.2.4.1-3 : Gen 8T FDU – Planar view

9.3.2.4.2 FEM Analysis of the heat transfer within the ICM, Reactor and the vaporization tubes

The objective was to conduct a Finite Element Analysis of the heat transfer occurring within the SPU1E reformer design contact vaporizer. Understanding the behavior of the SPU1E reformer would impact future designs. Progressive iterations were conducted to gain understanding of the method of heat transfer and the contribution by the exterior environment. **Figure 5.3.2.4.2-1** shows the components used in the analysis.

Figure 5.3.2.4.2-1: Model for Heat Transfer Study

Thermal temperatures of components were provided for the reformer exterior study. **Figure 5.3.2.4.2-2** shows the external temperature predictions of the ICM given a 1000°C internal temperature.

Figure 5.3.2.4.2-2: Thermal Study Results

The analysis did not contain estimations of the diesel vaporization at the conclusion of this testing. Empirical tests showed there were potential exothermic reactions within the fuel and air stream that could not be predicted by this model. **Figure 5.3.2.4.2-3** does show the propagation of heat along the tubes thus significantly increasing the zone for diesel vaporization beyond the confines of the vaporizer.

Figure 5.3.2.4.2-3: Analysis Results

The greatest heat predicted transfer was conduction between the ICM and fuel manifold block. These values were consistent with empirical testing despite the lack of vaporization and exothermic reaction contributions. Radiation effects were not included because the temperature difference between the heated element and non-connecting hot elements were relatively similar.

9.3.3 Develop Catalysts

9.3.3.1 Catalyst Formulation

A set of internally and externally developed catalysts were evaluated for durability to thermal cycling. The results are given in **Figure 5.3.3.1-1**. All of the catalysts are supported on 400 cells-per-square inch (cps) ceramic honeycomb substrates. The substrates are either zirconia-mullite in the case of the Delphi and Umicore catalysts or cordierite for the others. Prior testing has shown the choice of substrate does not impact performance in this test. The Umicore formulation is based on the Delphi internally developed formulation, but built on production-intent pilot equipment.

Figures 5.3.3.1-1: Performance of Delphi, Umicore, Süd-Chemie (SCI), and Johnson Matthey (JM) catalysts, supported on 2.5" diameter honeycomb substrates for natural gas partial oxidation, after 50 rapid screening cycles.

The catalysts were exposed to 50 rapid screening cycles prior to activity evaluation. The rapid screening cycles consist of operating on natural gas and air fuel, at an oxygen-to-carbon mole ratio (O/C) of 2.0, at 100,000/hr space velocity at 50 seconds, with a center catalyst temperature of about 1200°C. The flow is then adjusted to 50,000/hr space velocity, at an O/C of 1.3, for 15 seconds, followed by forced air cooling, until the temperature reaches 700°C. An additional 50 cycles were run for some of the catalysts and the results are summarized in **Figure 5.3.3.1-2**. The catalyst with the best initial activity, the most stable and best overall activity was the Delphi equivalent catalyst.

supplier	catalyst	activity at 900 °C (1/hr)		
		1 cycle	50 cycles	100 cycles
Delphi	RDRCA0-320:CB	280,000	76,600	45,900
Umicore	PZM323488	380,000	104,000	74,100
Süd-Chemie	POX2B	1,080,000*	47,400	43,700
Süd-Chemie	POX25	245,000	2,700	
JMI	R43	404,000	22,800	19,300
equilibrium at 98,000/hr space velocity		1,080,000		PS584C-45

*: Linear extrapolation of activity data, collected significantly below 900 °C, gives activity at 900 °C of 1,790,000/hr, which is beyond what equilibrium permits.

Figures 5.3.3.1-2: 900 °C activity of Delphi, Umicore, Süd-Chemie (SCI), and Johnson Matthey (JM) catalysts, supported on 2.5" diameter honeycomb substrates for natural gas partial oxidation, after up to 100 rapid screening cycles.

9.3.3.2 Substrate Development

The major activities in 2008 were: Evaluation of a variety of substrate candidates for stability in partial oxidation and recycle reforming operating modes, washcoat adhesion, and heat transport characteristics. The first two goals were evaluated simultaneously in a modification of the rapid screening test; while the third goal was evaluated in an apparatus specifically designed to measure overall heat transfer coefficient.

9.3.3.2.1 Substrate Stability

The modified rapid screening test consisted of a start-of-test activity measurement, 200 rapid screening cycles, and an end-of-test activity measurement. The activity was measured with natural gas and air mixtures operated at 100,400/hr space velocity and a 1.3 O/C mole ratio. Activity, k , was measured at 950°C by extrapolation or interpolation of the linear portion of the data. Data was collected by measuring overall conversion of carbon, contained in hydrocarbons, as an external temperature was applied from 700 to 1000°C, in 50° increments. A typical response is shown in **Figure 5.3.3.2-1**. The slope of the curves is the overall activation energy of the reaction, E_A , in units of kilocalories per mole (kcal/mol), while the intercept is k_0 , which is proportional to the number of active sites participating in the reaction. For the case illustrated, there was no change in rate limiting step, which would be reflected in a change in activation energy, E_A , or slope, while the number of active sites retained was about 88%.

Figure 5.3.3.2-1: Start- and end-of-test activity of a zirconia-mullite supported catalyst, after 200 modified rapid screening cycles.

The previously developed rapid screening test protocol was modified for use in 1 inch diameter reactor tube. A cycle consists of a 120 second reforming phase, at 17.6 standard liters per mole (SLPM) air and 5.0 SLPM natural gas, for a 1.47 O/C, followed by a nitrogen-only phase at 5.0 SLPM, for 600 seconds. Target temperature responses are given in **Figure 5.3.3.2-2**. This test results in rapid temperature swings in the catalyst, from approximately 400 to 1100°C. The maximum temperature is typical of what should occur during system warm-up mode in the DPS3000 design and thermal cycling has the most impact on catalyst aging. The number of cycles selected, 200, is typical of the number of cold-starts planned for the DPS3000 system.

Figure 5.3.3.2-2: Flow rates and target catalyst center temperatures for the modified 1" diameter rapid screening test.

The reproducibility of this modified rapid screening test was demonstrated using 600 cpsi cordierite substrates, as shown in **Figure 5.3.3.2-3**. End-of-test activity, measured at 950°C, varied by less than 5% for the five catalysts tested.

Figure 5.3.3.2-3: Performance of five tests before and after 200 modified rapid screening cycles, using catalysts supported on 600 cpsi cordierite honeycomb substrates.

Figure 5.3.3.2-4 lists the evaluated substrates, their start- and end-of-test activities, age factors, number of test startups, and an activity ranking. Age factor, the activity remaining after aging, is the end-of-test activity divided by the start-of-test activity. The corresponding performances are plotted in **Figure 5.3.3.2-5**. The ceramic honeycomb substrates had significantly higher end-of-test activities. While the cordierite substrate is more active than the zirconia-mullite honeycomb, the zirconia-mullite has a significantly higher age factor, indicating that it is the substrate most resistant to thermal aging.

substrate	SOT / (rank)	EOT / (rank)	age factor / (rank)	number of repeats	activity rating / (rank)
<u>honeycombs</u>					
zirconia-mullite 400 cpsi	351,000 (4)	309,000 (2)	0.88 ± 0.07 (1)	2	8 (2)
cordierite 600 cpsi	658,000 (1)	347,000 (1)	0.53 ± 0.02 (3)	5	3 (1)
aluchrom 300 cpsi	248,000 (6)	92,000 (6)	0.37 ± 0.14 (5)	3	180 (7)
aluchrom 600 cpsi	267,000 (5)	97,000 (5)	0.36 ± 0.07 (6)	3	150 (5)
aluchrom 1000 cpsi	444,000 (3)	74,000 (7)	0.17 (8)	1	168 (6)
<u>foams</u>					
ZTA	187,000 (8)	114,000 (4)	0.61 ± 0.14 (2)	3	64 (4)
FeCrAlY	237,000 (7)	62,000 (8)	0.26 ± 0.07 (7)	2	392 (8)

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Figure 5.3.3.2-4: Start- and end-of-test activities, age factors, and activity rankings for substrates evaluated with 200 modified rapid screening cycles.

Figure 5.3.3.2-5: End-of-test activities for substrates evaluated with 200 modified rapid screening cycles.

The visual appearances of the substrates, before and after the rapid screening tests, are given in **Figure 5.3.3.2-6**, **Figure 5.3.3.2-7**, and **Figure 5.3.3.2-8**. The washcoat appeared intact for all of the substrates indicating that washcoat adhesion was not a factor in changes to activity. There was no visible change in the appearance of the ceramic substrates. A Loss of activity in foam substrates was attributed to less than ideal washcoat distribution and a corresponding shift in rate limiting step to that of one with higher activation energy. This indicates that the reaction became more dependent on a certain type of active site. The same pattern was observed on the FeCrAlY foam substrate resulting in carbon deposits on the material and a higher E_A . Substrate material distortion and carbon deposits were noted for the Aluchrom parts. Because the activation energy was not shifted, Delphi believes the failure mode is due to site blocking caused by reduced accessibility of the active sites.

Figure 5.3.3.2-6: Start- (top) and end-of-test (bottom) appearances of the front face of ceramic honeycomb 1" diameter substrates before and after 200 modified rapid screening cycles.

Figure 5.3.3.2-7: Start- (top) and end-of-test (bottom) appearances of the front face of foam 1" diameter substrates before and after 200 modified rapid screening cycles.

Figure 5.3.3.2-8: Start- (top) and end-of-test (bottom) appearances of the front face of Aluchrom 1" diameter substrates before and after 200 modified rapid screening cycles.

9.3.3.2.2 Substrate Heat Transfer Characterization

Delphi evaluated substrates for heat transfer coefficients by using a flow tube apparatus held inside of a furnace. This was able to pre-heat the air entering the tube as shown in **Figure 5.3.3.2.2-1**. Metallic and ceramic substrates with lengths of 4, 5 or 6 inches were placed inside of a tube. The metallic substrates were brazed into the tube, while the ceramic substrates were held in place with alumina foam material. Incoming air flowing between 15 to 50 SLPM was preheated from 400 to 800°C. The furnace was either off (ambient operating conditions) or operated from 400 to 800°C. Substrate radial center front face ($T_{\text{heater center}}$) and radial center back face ($T_{\text{exhaust center}}$), and

furnace temperatures ($T_{\text{amb furnace}}$) were measured. Substrate wall temperatures at the front and back faces, T5 and T1 were recorded.

Figure 5.3.3.2-1: Diagram of Apparatus Employed to Measure Overall Heat Transfer Coefficients of Substrates

Air flow rates corresponded to space velocities of 14,000, 23,300, 32,600, and 46,600/hr. Space velocities of 14,000 and 23,300/hr are similar to the reformer operation, while 32,600 and 46,600/hr are similar to the combustor operation. Reynolds numbers measured at average fluid temperature in the flow tube for all sets of conditions and flow rates were less than 50 indicating well established laminar flow.

The heat transfer coefficient is a strong function of material properties, material configuration (e.g. porosity, relative density, cross-sectional areas), boundary conditions including inlet temperature, axial and radial temperature gradients, and superficial velocity. The contributions of conductive, convective, and radiative heat transfer are lumped by this approach. Each type may have significant contributions depending on the flow rates and temperatures at which the measurements take place.

Heat loss to the surroundings, Q , is related to change in heat according to:

$$Q = UA\Delta T_{lm} = -\Delta H$$

Where U is overall heat transfer coefficient, A is surface area for heat transfer (e.g. surface area of that portion of the tube containing the substrate), and H is enthalpy. H is equivalent to the expression mc_pT and is evaluated at mass flow rates (m), heat capacity (c_p) and temperature (T) of the fluid at the inlet and outlet boundaries of the substrate. ΔT_{lm} is the log-mean temperature driving force for heat transfer and is given by:

$$\Delta T_{lm} = \frac{\Delta T_{out} - \Delta T_{in}}{\ln(\Delta T_{out} / \Delta T_{in})}$$

Where:

$$\Delta T_{out \text{ or } in} = \text{average}(T_{\text{fluid-side}}, T_{\text{fluid-center}}) - T_{\text{tube}}$$

T_{tube} is the ambient temperature as controlled by the furnace and $T_{fluid-side}$ and $T_{fluid-center}$ are evaluated at either the substrate front or back faces.

Averaged overall heat transfer coefficients for most of the materials studied are listed in **Figure 5.3.3.2.2-2**. These were calculated by averaging individual values of U over all air flow rates and air inlet temperatures for cases in which the furnace was not in operation. These numbers are for transfer of heat out of the flow tubes to the ambient exterior. The ambient temperature was allowed to float, depending on the heat load, reaching from 83 to 580°C depending on substrate and boundary conditions. The averaged values of U reported are taken over a wide range of driving forces and represent values that frequently have a non-linear response to the independent variables.

Material	Overall Heat Transfer Coefficient (W/m ² ·K)
Aluchrom 1000 cpsi (6")	133
FeCrAlY foam (6")	100
FeCrAlY foam (5")	99
Aluchrom 1000 cpsi (4")	56
Aluchrom 600 cpsi (4")	52
Aluchrom 300 cpsi (4")	34
zirconia-mullite 400 cpsi (4")	31
G-mat FeCrAlY mat material (5")	26

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Figure 5.3.3.2.2-2: Overall heat transfer coefficients averaged over all air inlet temperatures and flow rates, with no external heat input, with substrates of differing length.

Based on **Figure 5.3.3.2.2-2**, the longer and denser metallic substrates have higher heat transfer coefficients than shorter, less dense, or non-metallic parts. A different analysis using a constant driving force of nearly isothermal and consistent 800°C ambient temperature, 400°C air inlet temperature, and 15 SLPM air is given in **Figure 5.3.3.2.2-3**. While the substrate rankings from the two methods are slightly different, the same conclusion remains valid: metallic parts have higher values of U as compared to ceramic parts.

Figure 5.3.3.2.2-3: Overall heat transfer coefficients measured at 800 °C external temperature, 400 °C inlet temperature, and 15 SLPM air, for a variety of substrates.

There is a sufficient driving force that longer parts have lower values of U under the conditions shown in **Figure 5.3.3.2.2-3**. Length is a factor in the calculation of U, and in the case of the Aluchrom 1000 cpsi substrate, adding an additional 2" of length did not impact exhaust temperatures enough to show an improvement, so the overall heat transfer coefficient decreases with increasing length. The variation in U with respect to air flow rate is given in **Figure 5.3.3.2.2-4**. Behaviors ranged from almost no response to a strong response in U with flow. Little to no response indicated that the rate limiting step is heat transport by conduction from tube wall to substrate. For materials with a large internal surface area, such as Aluchrom 1000, increasing flow increases U as convective heat transfer increases with flow rate. Other materials behave in an intermediate fashion.

Figure 5.3.3.2.2-4: Change in overall heat transfer coefficient with air flow rate, at 800 °C external temperature and 400 °C inlet temperature, for a variety of substrates.

9.3.3.2.3 Aluchrom Substrate Durability

Based on performance testing, only ceramic substrates are suitable for catalyst washcoat supports. But based on heat transfer studies, the best substrates are higher cell density Aluchrom metallic honeycombs. Several studies were conducted to determine the usability limits of Aluchrom substrates. In the first test, a Aluchrom 600 cpsi 1inch diameter substrate was operated on a typical drive mode durability cycle consisting of one hour at system start up partial oxidation mode, one hour at minimum power mode with added recycle, fifteen hours of normal operation conditions aging with added recycle, and one hour of no flow (dwell). The results of this test are presented in **Figure 5.3.3.2.3-1**. Significant degradation in efficiency was observed during the normal operation mode after approximately five cycles (less than 100 hours) and the test was halted. For comparison, zirconia-toughened alumina foam tested at the same conditions showed no significant degradation for over 1500 hours of testing.

Figure 5.3.3.2.3-1: Results of testing Aluchrom 600 cpsi and zirconia-toughened alumina (ZTA) foam 1" diameter substrates with a typical drive mode cycle.

Two additional tests on the Aluchrom 600 cpsi substrate in steady no flow variation operating modes were run to determine if the thermal cycling was a factor in aging. The first was with natural gas partial oxidation at an O/C of 1.30 and a space velocity of 100,000/hr (see **Figure 5.3.3.2.3-2**). Rapid and unacceptable rates of degradation occurred in less than 100 hours of testing. Previously reported testing on ceramic substrates have found little to no degradation for 500 hours at temperatures up to 1200°C and over 2500 hours at lower temperatures. The second test was conducted with recycle at a total O/C of 1.30 in the normal operating mode and a space velocity of 25,000/hr (see **Figure 5.3.3.2.3-3**). This test has run for over 150 hours with only minimal degradation.

Figure 5.3.3.2.3-2: Results of testing Aluchrom 600 cpsi 1" diameter substrate at steady partial oxidation conditions, O/C 1.30, 100,000/hr space velocity, at start-of-test catalyst temperature of 950 °C.

Figure 5.3.3.2.3-3: Results of testing Aluchrom 600 cpsi 1" diameter substrate at normal operating conditions, with simulated recycle, at an overall O/C of 1.30, 25,000/hr space velocity, at start-of-test catalyst temperature of 850 °C.

The Aluchrom substrate is susceptible to damage during exposure to partial oxidation conditions but appeared to be stable during operating modes employing recycle. This material is not suitable for use in DPS-3000 units because the operating strategy calls for a significant number of partial-oxidation cold-start operation modes. A typical post-test cross section image of an Aluchrom 600 cpsi substrate taken after the steady partial oxidation testing is given in **Figure 5.3.3.2.3-4**. Significant features in the image include: Presence of good adhering washcoat with no evidence of washcoat spallation in all channels from front to back; minor distortion and warping of the honeycomb structure; minor carbon deposition throughout; and a convex band with respect to flow

of significant material disintegration, carbonization, and carbon deposits with a maximum extent axially centered from 3 to 8 mm from the front face of the substrate. The washcoat is intact in the region of severe degradation.

Figure 5.3.3.2.3-4: Image of a front to back cross-section through a washcoated Aluchrom 600 cpsi substrate after testing for 130 hours in partial oxidation steady operating mode. Approximate width of channels is 1.0 mm.

This region of maximum degradation corresponds to the maximum temperatures observed during partial oxidation reactions. Delphi developed a strategy based on these observations to place a thermally stable ceramic substrate, zirconia-mullite 400 cpsi, in the first 0.5 inch of catalyst length with the Aluchrom 600 cpsi in the remaining 0.5 inch. This concept should enable the thermal benefit of ceramic, where thermal stability is required, while having the heat transfer ability of metallic, where endothermic reactions predominate. In a full scale reformer in which 4-6 inches of catalyst length are deployed, the first 1 inch could be ceramic, while the balance of the catalyst length would be metallic.

The results of testing this 0.5 inch/0.5 inch stacked concept for the 200 rapid screening tests are given in **Figure 5.3.3.2.3-5**. The benefit of this approach is seen in the fresh activity as the stacked configuration has significantly better activity than either of the two substrates individually. The aged activity of the stacked configuration is between the aged activities of the individual substrates after 200 rapid screening cycles. An age factor of 0.48 ± 0.03 was measured as compared to age factors of 0.88 for zirconia-mullite and 0.36 for Aluchrom 600. The post aging appearance of the front faces of the substrates is given in **Figure 5.3.3.2.3-6**. Little to no distortion of the Aluchrom material was observed and the cross-sectional appearances of the substrates are given in **Figure 5.3.3.2.3-7**. A significant degree of carbon deposition was noted on the ceramic zirconia-mullite honeycomb substrate, visually increasing toward the back face of the substrate. Minor amounts of carbon were observed on the Aluchrom honeycomb substrate. Carbon has not been observed previously on the ceramic honeycomb substrates exposed to this aging procedure. The significant loss in activity can be explained by carbon deposition, perhaps arising from the presence of the Aluchrom material. Considering that the reaction conditions are well in the laminar regime, upstream diffusion of carbonaceous materials from Aluchrom to ceramic is feasible.

While this stacked substrate approach has merit, additional work will be required to determine usability.

Figure 5.3.3.2.3-5: Performance comparison of fresh and 200 cycles rapid screening test aged stacked 0.5"/0.5" zirconia-mullite/Aluchrom substrate with 1" of either substrate

Figure 5.3.3.2.3-6: Front face appearance of stacked substrates, zirconia-mullite 400 cpsi honeycomb (top) and Aluchrom 600 cpsi honeycomb (bottom) after 200 rapid screening cycles.

Figure 5.3.3.2.3-7: Cross-section appearance of stacked substrates, zirconia-mullite 400 cpsi honeycomb (top) and Aluchrom 600 cpsi honeycomb (bottom) after 200 rapid screening cycles.

9.3.3.3 Catalyst Testing

9.3.3.3.1 Degreening Behavior

A degreening phenomenon was observed during cold start of a fresh reforming catalyst in the reformer or systems test labs, in which two to three hours are required for a catalyst to reach steady activity; this initial period is characterized by increasing amounts of hydrogen and decreasing methane content in the reformat product (see **Figure 5.3.3.3.1-1** and **Figure 5.3.3.3.1-2**). This behavior was due to the inability of the full-scale reformer to adequately heat the catalyst to the required temperature in a short amount of time. The inability of the reformer to heat the catalyst is due to either the large heat losses in these devices or insufficient or non-uniform initial heat input.

Figure 5.3.3.3.1-1: Reformate product compositions measured during diesel fuel partial oxidation cold start on full scale reformer.

Figure 5.3.3.3.1-2: Catalyst back face temperatures measured during diesel fuel partial oxidation cold start on full scale reformer.

9.3.3.4 Catalyst Characterization

9.3.3.4.1 Carbon Deposits

The two types of carbon deposits, amorphous and/or graphitic, occur on aged reforming catalysts. The amorphous type forms from gas phase reactions, has a relatively minor surface concentration, and does not impact on catalyst performance. Amorphous deposits typically have a dull to silvery visual appearance. The graphitic carbon deposits also form from the gas phase, may be fuel-derived from only partially reformed hydrocarbons, and is a significant source of catalyst degradation. The degradation is either from blocking of active sites, restricting flow passages, or extracting rhodium particles off of the catalyst surface. Graphitic carbon deposits have visually deep black resinous appearance. Two samples of catalysts retrieved from reformer or system level testing were examined to determine causes of observed high pressure drops.

The first carbon deposit example, shown in **Figure 5.3.3.4.1-1** and **Figure 5.3.3.4.1-2**, is a zirconia-mullite 400 cpsi honeycomb ceramic catalyst removed from a Gen 4.2T diesel fuel reformer partial oxidation test. This particular reformer was configured with an open volume between the flame arrestor and the catalyst resulting in a region of high-temperature gas-phase reactions. Thermal cracking, aromatization, and condensation of hydrocarbons to carbon via loss of hydrogen resulted in the formation of both amorphous and graphitic appearing carbon deposits. This material rapidly collected on the catalyst front face resulting in significant catalyst plugging and the rapid increase in pressure drop.

Figure 5.3.3.4.1-1: Front, left, and back, right, face visual appearances of a 1.81" diameter catalyst removed from diesel fuel reforming testing.

Figure 5.3.3.4.1-2: Cross-sectional view of a catalyst, from leading edge, removed from diesel fuel reforming testing. Approximate width of channels is 0.05".

The second carbon deposit example is illustrated in **Figures 5.3.3.4.1-2**, and **5.3.3.4.1-3**. This catalyst was tested in the reformer lab in partial oxidation mode, then in the systems lab in both partial oxidation and recycle modes, and finally in the reformer lab in recycle mode. The catalyst was reported to have excessive pressure drop and slow cold start behavior. Visual examination shows that carbon deposits occur from the front face to the back face of the catalyst. There is a continuous film of amorphous carbon throughout with extensive deposits of graphitic carbon closer to the front face but still present through at least half of the catalyst. The flame arrestor material was also found to have graphitic appearing carbon deposits. Both increase in pressure drop and slow start behavior can be attributed to the graphitic deposits. The absence of carbon deposits in the first few millimeters of the support may be attributable to operation in recycle mode during which carbon was removed in the region where oxygen and steam are present.

Figure 5.3.3.4.1-3: Portions of the front (top) and back (bottom) faces of a catalyst, with remnant adhering flame arrestor material, retrieved from a series of reformer and stack diesel fuel partial oxidation and recycle reforming tests. Cells are about 0.05" square.

Figure 5.3.3.4.1-4: Cross-sectional views of a catalyst, from leading to trailing edge, retrieved from a series of reformer and stack diesel fuel partial oxidation and recycle reforming tests. Channels are about 0.05" in diameter.

Figure 5.3.3.4.1-5: Close-up cross-sectional views of a catalyst, taken at the leading (top) and trailing (bottom) edges, retrieved from a series of reformer and stack diesel fuel partial oxidation and recycle reforming tests. Channels are about 0.05" in diameter.

9.3.3.4.2 Electron Microscopy of Washcoated Metallic Substrates

A series of washcoated metallic substrates, Haines 214 plate, Haines 230 plate, and FeCrAlY foam were characterized by scanning electron microscopy, operated in backscattered electron (BSE) imaging mode, and coupled with energy dispersive spectrographic (EDS) analysis. In all cases, the catalyst washcoat could be clearly distinguished from oxide scale formed on the metal and oxide scale can be clearly distinguished from bare metal. Yttria-stabilized zirconia pre-coat could be distinguished when present. Examples of BSE images are given in **Figures 5.3.3.4.2-1 through 5.3.3.4.2-4.**

Figure 5.3.3.4.2-1: BSE image of washcoat, yttria-stabilized (YSZ) pre-coat, and scale for a washcoated Haines 214 coupon. Darkest grey area, with cracking, is the washcoat. Lighter contrast, mottled areas is YSZ, with areas of grey metal oxide scale intermixed. Insets indicated elements detected by EDS.

Figure 5.3.3.4.2-2: BSE image of washcoat, yttria-stabilized (YSZ) pre-coat, and scale for a washcoated Haines 230 coupon. Darkest grey area, with cracking, is the washcoat. Lighter contrast, mottled areas is YSZ, with areas of grey metal oxide scale intermixed. Insets indicated elements detected by EDS.

Figure 5.3.3.4.2-3: BSE image of washcoat and scale for a washcoated Haines 214 coupon. Darkest grey area, with cracking, is the washcoat. Lighter contrast areas are metal oxide scale. Insets indicated elements detected by EDS.

Figure 5.3.3.4.2-4: BSE image of washcoat and scale for a washcoated FeCrAlY foam. Darkest grey area, with cracking, is the washcoat. Lighter contrast areas are metal oxide scale. Insets indicated elements detected by EDS.

9.4 Task 4: BOP Component Development

9.4.1 Process Air Subsystem

PAM S/N 1 ran for over 2,300 hours before a bearing failure. The bearings were replaced and the unit reinstalled in a SOFC system. PAM S/N 6 ran for over 700 hours without a bearing failure.

The first PAB was installed and run on the new test stand. The performance mapping confirmed that it exceeded Delphi's design requirements, see **Figure 6.3.3-1**. During the initial operation, the blower was operated outside the designated speed / load range during an attempt to measure maximum pressure. This caused pressure pulsations that damaged the bearings.

Figure 6.3.1-1: Process Air Blower Compressor Map

9.4.2 DPS3000D PAM Plenum

Figure 6.3.2-1 shows the CFD analysis of the PAM plenum design and **Figure 6.3.2-2** shows the prototype part.

Figure 6.3.2-1: PAM Plenum/CFD Analysis

Figure 6.3.2-2: PAM Plenum-Rapid Prototype

9.4.3 DPS3000D Integrated Component Manifolds

The solid models for the DPS3000D are near complete. A design which could be cast from a variety of materials was developed to accommodate manufacturing in high volumes. See Figures 6.3.3-1 and 6.3.3-2.

Figure 6.3.3-1: DPS3000D ICM

Figure 6.3.3-2: DPS3000D ICM/CFD Analysis

Delphi met with several suppliers to discuss materials that may have the ability to replace the high nickel content alloys. A few possible choices were identified as a result of these meetings. The design of the Integrated Component Manifold was made so that Delphi could manufacture prototypes from high nickel content alloys using traditional prototype manufacturing methods. The design then would be transitioned to the productive manufacturing material and production manufacturing process for fabrication. **Figure 6.3.3-3** lists the ICM material candidates and their respective composition based on SEM analysis.

SEM analysis	Grede Cast Iron	Wecast FSS 7224-6C	Wecast normal nodular (spheroidal) graphite SiMo iron	Wecast vermicular (compacted) graphite structure SiMo Iron	Wecast SiMo w/ Cr
C	11.63	11.48	11.86	10.52	0
O	7.38	4.27	6.52	5.39	0
Al	0	0.42	0	0	0
Si	2.6	1.12	3.88	3.19	4.6
S	0	0.54	0	0	0
Cl	0	0.35	0	0	0
Cr	0	17.83	0	0	1.19
Mn	0	0	0	0	0
Fe	78.39	63.99	77.75	80.91	93.13
Mo	0	0	0	0	1.08
sum	100	100	100.01	100.01	100

Figure 6.3.3-3: Material Candidates

9.4.4 DPS3000D Heat Exchangers

The larger size plate design is shown in **Figure 6.3.4-1**. It incorporates additional features to facilitate manufacturability. Peripheral joints were revised to be flange lap joints rather than crimp joints. A formed cup at the cold side inlet and outlet ports

eliminates the need for a spacer ring. Formability of Inconel 625 was demonstrated. An initial batch of plates has been received.

Figure 6.3.4-1: Revised plate design

The first nickel brazed formed plate heat exchanger, shown in **Figure 6.3.4-2**, was fabricated with the smaller plate design. This was later used to determine the effects of thermal stresses and to help validate mathematical models until a unit with the larger plates can be fabricated.

Figure 6.3.4-2: Formed Plate Heat Exchanger Prototype

Modeling indicated that the area in the hot flow passage behind the cold port obstruction was an area of concern due to lack of flow. **Figure 6.3.4-3**, shows a “half-section” of a hot side passage. FEA modeling of this area indicated that thermal stresses in the flow/no-flow boundary could be a problem in a severe start-up transient. **Figure 6.3.4-4**, illustrates the elevated stress levels in a heat exchanger plate in this location.

Figure 6.3.4-3: Flow Distribution Model

Figure 6.3.4-4: Stress Distribution Model

9.4.5 Liquid Diesel Fuel De-Sulfurization

9.4.5.1 Test Conducted by Delphi

Figure 6.3.6.1-1 shows the results of the sulfur in the effluent plotted as a function of volume of desulfurized fuel per gram of sorbent; The test conditions for two cases are (a) The original TDA benchmark data, tested using a locally purchased ULSD, and (b) Delphi's test data using Delphi's ULSD test fuel.

Figure 6.3.6.1-1: TDA “D1” Sorbent Performance- Delphi’ Test Data Compared with Original TDA Test Data

Based on Delphi’s test data, all the samples including the 2-h sample showed sulfur concentration levels higher than the targeted 3 ppmw. TDA sorbent did not effectively remove sulfur from Delphi’s ULSD fuel under the tested conditions. The total sulfur level in the ULSD feed was 14.1 ppmw. In contrast to TDA’s original benchmark data, two observations were made on Delphi’s test data: (1) The first data collected at two hours showed the leakage concentration to be 4.9 ppmw. This is two orders-of-magnitude higher than the 40 ppbw reported by TDA, and (2) the last data collected at 40 hours showed a concentration of 7.4 ppmw. This is about one order-of-magnitude higher than the 0.8 ppmw reported by TDA.

9.4.5.2 Test Conducted by TDA- Fuel Variability

It is possible that the fuel variability was responsible for the D1 sorbent performance differences observed between Delphi and TDA test results. In order to verify this assumption, TDA initiated a test using their sorbent and Delphi’s ULSD fuel. **Figure 6.3.6.2-1** shows the side-by-side comparison of performance data obtained using two different ULSD sources: (1) Pump fuel from TDA’s fuel source, and (2) Delphi’s drum fuel. Changing ULSD fuel source from the locally pumped fuel to Delphi’s test fuel had a negative impact; the leakage concentration increased from sub-ppm to 10 ppm.

**Figure 6.3.6.2-1: TDA “D1” Sorbent Performance Using Two Different ULSD Fuels
(based on TDA test data)**

Noted that 2-ring and 3-ring aromatics present in Delphi's ULSD at 9.2 wt% is higher than that in the local pump fuel at 7.6 wt%. It is possible that the higher concentrations of these aromatics, with structures similar to the sulfur-containing dibenzothiophene species, can reduce the sulfur removal efficiency of the sorbent.

In **Figure 6.3.6.2-2**, parallel testing of TDA sorbent using Delphi's ULSD performed at both Delphi and TDA sites respectively showed comparable performance. It should be noted that TDA used a different method for the total sulfur analysis. Their method was the ASTM D5623 method using GC/SCD (gas chromatography and sulfur chemiluminescence detector). The overall trend of both sets of data was very similar, with the highest concentration achieved being ~ 8 ppmw by Delphi vs. ~9.5 ppmw by TDA. The slight difference in results may be accounted for by the use of the different sulfur analysis methods. The good agreement in the above data increases the high confidence of the validity of test results reported by TDA.

**Figure 6.3.6.2-2: TDA Sorbent Performance Using Delphi's ULSD
Conducted at Two Sites.**

9.4.5.3 Effect of Operating Condition on D1 Sorbent Performance

It was not clear whether the poor performance of D1 - TDA sorbent when using Delphi's ULSD was caused by the non-optimized process conditions or whether it was caused by the actual sorbent chemistry. It was decided to (1) Continue using D1 sorbent and focus the investigation on understanding the effects of operating condition; and (2) examine sorbents of other chemistry. The initial plan for investigating the operating conditions was to increase temperature and pressure; and to decrease liquid hourly space velocity.

The effect of temperature in the range of 120°C to 200°C is shown in **Figure 6.3.6.3-1**. This temperature range displayed a profound effect on sorbent capacity. The best example of this can be seen at a concentration of 3 ppmw. Drawing an "imaginary" line starting with the 3 ppm sulfur point from left to right will generate cross points with various curves. These cross points are the amount of desulfurized fuel/gram of sorbent at various temperatures at a leakage concentration of 3 ppmw. There is between 2 and 20 ml of desulfurized fuel/gram of sorbent for the 120°C (pink curve) and the 200°C (green curve), respectively. This represents a large capacity increase for a temperature increase of 80°C. However, the improved performance at 200°C is still worse than TDA's original benchmark data obtained using the locally pumped fuel. This data suggests that a higher temperature is favorable and that an optimum temperature can be defined.

Figure 6.3.6.3-1: Temperature Effect on TDA Sorbent (D1) Performance with Delphi

The preliminary data from the 200°C run and the corresponding decrease in the LHSV from 1.6/h to 0.28/h appeared to exert a beneficial effect. This is also shown in **Figure 6.3.6.3-1** and warrants further study. Based on the liquid diesel desulfurizer requirements, the maximum LHSV of our device could be ~0.5/h. Therefore, 0.5/h SV condition will be used in future tests.

In addition to the temperature effect, the effects of pressure will also be investigated. Note that the fuel supply pressure target for the liquid diesel desulfurizer is in the range of 36.3 to 72.5 psig with a nominal pressure of 43.5 psig.

9.4.6 Hot Reformate De-Sulfurization

Small scale sorbent testing focused on determining the sorbent performance from ambient conditions up to 800°C and testing the sorbent's interaction with air. The sorbent's capacity was stable at about 5 mg sulfur captured per gram of sorbent from 200 to 800°C. However, below 200°C the sorbent did not have the ability to capture sulfur - see **Figure 6.3.7-1**.

Figure 6.3.7-1: Sorbent Capacity at Various Temperatures / Sorbent Test Data

Delphi learned the sorbent did not readily reduce at lower temperatures, **Figure 6.3.7-2**. It is important to perform initial reduction at the maximum anticipated sorbent operating temperature. Otherwise, as the operating temperature increases above the temperature at which the sorbent was reduced, sulfur that had been captured at low temperatures will be released at high temperatures.

Figure 6.3.7-2: Reduction Time at Various Temperatures / Sorbent Reduction Data

Because it is possible for air to enter from the system into the sorbent bed during sudden system shut down, it was important to determine the sorbent's response to air while at operating temperatures.

It was found that the sorbent reacts to oxidizers in air. This resulted in a rapid increase in sorbent temperature. **See Figure 6.3.7-3.** The amount of oxygen that would react with the sorbent varied based on the sorbent temperature - **see Figure 6.3.7-4.**

Figure 6.3.7-3: Sorbent Oxidation and Effects on Temperature / Sorbent Oxidation

Figure 6.3.7-4: Oxygen in Air Captured by the Sorbent / Oxidation and Temperature Data

A three liter bed shown in **Figure 6.3.7-5** was installed into the test stand and supplied with reformat from a natural gas reformer. The test stand can be seen in **Figure 6.3.7-6**. Reformat was flowed through the bed at an SOFC maximum power, flow rate of 100 splm. In order to control the sulfur input to the bed, the normal utility line natural gas feed to the reformer was de-sulfurized. This assured that testing initiated with 0 ppm sulfur into the test stand. H₂S was then metered into the reformat flow at 7 ppm. It was found that the bed is capable of reducing sulfur to the target value of 10 ppbv or less. However the sorbent capacity in the large bed was lower than the small scale

tests. For this sorbent generation and bed configuration we had expected 3 mg sulfur captured per gram of sorbent. Instead we achieved 0.3 mg/gram of sorbent.

Figure 6.3.7-5: 3.0 L Hot Reformate Desulfurizer

Figure 6.3.7-6: 3.0 L Bed Test Stand / Test Stand

The test data indicated that this lower than expected capacity is most likely due to the reformate gas not being homogenously distributed through the bed. The bed was mounted horizontally on the test stand. Sorbent settling and shrinkage could create open areas in the bed. This would allow gas to flow through preferentially, causing some percentage of the gas stream to not come into contact with sorbent. This phenomenon in packed reactors is commonly referred to as “channeling”. There are many common design solutions for channeling. Delphi will incorporate a suitable change to the bed design for eliminating the “channeling” phenomenon.

9.4.7 Hot Zone Igniter

9.4.7.1 Build

Analysis of the Norton igniter showed that the electro-ceramic igniter tip withstood the temperature of the application. Therefore, a process to recover the electro-ceramic tip of the Norton igniter was developed. A new material set for the remainder of the parts of the igniter needed to be developed. A new braze alloy was developed and new materials for the wiring and metal clip were specified. Cusil (Ag-Cu) brazes used to connect the igniter tip to the interior, metal clip to the interior, and metal clip to the copper wiring all decomposed catastrophically in the actual application. Delphi chose a high temperature capable wire material called 80/20 Ni-chrome, which contains 80% Ni, 20% Cr and can resist oxidation up to 900°C. 80/20 Ni-chrome wire has performed admirably in the SOFC product to date and is easily obtainable with an electro-ceramic Nextel braid as an insulating coating, which can resist temperatures up to 1400°C. The nickel-based alloys: Inconel 625, Inconel 600, Inconel 718, Haynes 230, Haynes 214 and the Fe-based alloys: 430SS, Crofer 22 and 316SS were chosen as material candidates for the interior metal clip.

The Ag-Cu braze alloy used in the Norton igniter was replaced with a braze capable of making the bond to the ceramic (SiC-AlN-MoSi_2) composite; igniter tip and survive operation at 850°C with periodic bursts to 1000°C. A literature search revealed that pure noble metals like Ag, Au, Pt, Pd, etc. can make a bond with SiC and AlN but the cost of these alloys is prohibitive or in the case of Ag has too low a melting temperature to be considered. There are reports of a braze alloy of $\text{CoNi}(\text{Si, B})\text{-Cr-Ti}$ making a bond with pure SiC. However, this braze alloy failed to make a lasting bond with the composite electro-ceramic of the igniter. On the assumption that it was the AlN in the composite that was causing the adhesion and wetting issues with this braze alloy. It was decided that an addition of a small amount of a noble metal like Pd might solve the issue. A small Pd addition should be economically possible because of the small size of the braze joint. Using the table of commercially available braze alloys shown in **Figure 6.3.8.1-1**, the braze alloys Palniro-4, Palniro-7, Palni and Palco were chosen for candidates for investigation. The Ni-based, braze alloy, BNi-9 was also chosen for its Cr, Ni and B content.

Brazing Alloy Name	Solidus Temperature (°C)	Max Use Temp in air (°C)	Cost of braze joint	Liquidus Temperature (°C)	Composition	Notable features
Palniro -1	1102	1002	0.12	1121	Au-50, Ni-25, Pd-25	similar to Palniro-4
Palniro -4	1135	1035	0.12	1169	Au-30, Ni-36, Pd-34	High strength, oxidation resistance for superalloys
Palniro -7	1005	905	0.12	1097	Au-70, Ni-22, Pd-8	High ductility, strength for superalloys and SS
Palni	1238	1138	0.12	1238	Ni-40, Pd-60	High strength. Wets superalloys, W, Ni and SS. Eutectic.
Palnicurom -10	970	870		1013	Au-25, Cu-37, Ni-10, Pd-15, Mn-13	brazes superalloys and WC tungsten carbide (one of the hardest materials to wet).
Palnicusil	910	810		1179	Ag-48.5, Cu-19, Ni-10, Pd-22.5	ductile alloy for wide gap brazing of SS
Niuro	955	855		955	Au-82, Ni-18	
Niuro-Ti	960	850		945	Au-81.25, Ni-18, Ti-0.75	
Palco	1219	1069	0.08	1219	Pd-65, Co-35	low penetration of substrate metals.
Paloro	1200	1150	0.30	1270	Au-92, Pd-8	Wets Mo, W, Ta and superalloys. Ductile, non-oxidizable.

Figure 6.3.8.1-1: Choice of Brazing Alloys

Studies investigating the brazing abilities and characteristics of the brazing alloys to wet and braze the electro-ceramic igniter tip were undertaken. The results of those studies showed that the Palniro-4 was too aggressive and decomposed the electro-ceramic tip and all the alloys under consideration for the material of the interior metal clip. **Figure 6.3.8.1-2** shows the interior metal clip, material candidate Haynes 230, after an attempt at brazing the electro-ceramic tip to the alloy with Palniro-4.

Haynes 230
with Palniro-4

Figure 6.3.8.1-2 Decomposition of Metal Substrate

The braze consumed the metal at the point of contact. All the Fe-based alloys and the Inconel 718 alloy reacts, similarly to that shown in **Figure 6.3.8.1-2** with all the Pd-containing brazes and were removed from further testing. Only the alloys, Inconel 625, 600 and Haynes 230 were successfully used with the Pd-brazes. The alloy Haynes 214 did not successfully braze to the electro-ceramic tip and was also removed from further study. During this initial brazing work, it was observed that the electro-ceramic igniter

tip was also decomposing in the brazing furnace leaving a bluish white substance as shown in **Figure 6.3.8.1-3**.

- Igniter A – oxidized in air furnace at 1200°C. Painted with braze Palco.
- Igniter B – painted with braze. Palco.
- Both igniters were brazed in the same furnace right next to each other. Brazed in hydrogen at 1100°C for 30 min. Heated up at 10°/min to 600°C, 5°/min to 1090°C, 15 min soak, then 5°/min to 1100°C.

Figure 6.3.8.1-3 Decomposed Electroceramic Igniter Tip with Si Pool which Developed During Brazing Process at 1125°C

This decomposition process occurred in both, a hydrogen and a vacuum brazing furnace. The Pd-containing and Ni-based brazing alloys require brazing temperatures in the 1125 to 1225°C range. SEM and EDAX analysis showed the pooled substance to be composed primarily of Si. Either the SiC and/or the MoSi₂ were decomposing under the brazing conditions.

Based on coating processes where a native oxide must be removed prior to the coating application (like organo-metallic chemical vapor deposition (OM-CVD) and others) an approach to solving this problem was devised. The amount of native oxide on some substrates used in these coating processes is merely and not completely removed. When the sample is placed in the reactor for coating, the reactor environment decomposes the remaining native oxide before depositing the coating. If the native oxide is too thin then the reactor environment will start to decompose the substrate itself. So, the idea of using an oxide scale formed in air on the surface of the electro-ceramic to act as a sacrificial layer, which would decompose just before the braze flows and the braze joint is established. Using this basic idea, literature was searched for information on the oxide scale phases that form on a SiC-AlN-MoSi₂ electro-ceramic and the vaporization kinetics of these oxide phases under high temperature and or brazing conditions. G. Honstein, et al., found the vapor pressure of SiC to be greater than the vapor pressure of SiO₂. Hence, a thin layer of SiO₂ should give protection to the electro-ceramic during the brazing process. The thickness composition and microstructure of the protective oxide layer will effect the brazing. Krnel, et., al. determined that the oxide phases on an AlN-SiC-MoSi₂ electro-conductive electro-ceramic composite below 1000°C was the result of MoSi₂ oxidation. Above 1000°C the electro-ceramics gained weight due to the formation of a mullite layer at the surface of the electro-ceramic. The oxidation kinetics of this electro-ceramic increase significantly between 800 and 1200°C then even more significantly increased between 1200 and 1400°C. Hence, the protective oxide scale formation should be studied between 800

and 1200°C. Meyer, et. al. showed that crystalline coatings of Al₂O₃ layers on Si or SiO₂ substrates formed polymorphs of Al₂SiO₅ and when the oxidation temperature was above 1000°C, mullitization of the polymorphs was observed. Meyer, et. al. further found that the oxide scale formed could have several different layers or a single layer. The layers of oxide scale could have different microstructures and different densities at varying oxidation temperatures. The oxidation temperatures tested by Meyer were 725, 750, 1075 and 1100°C. Meyer found that a lower density oxide layer formed under a higher density layer at temperatures from 725 to 1075°C. At 1100°C, a thick, dense mullite layer formed on the substrate. An L36 full factorial design of experiment was performed using varying oxidation temperatures in air, varying oxidation times, three different metal clips, material candidates and three different braze alloy compositions. The experiment is shown in **Figure 6.3.8.1-4**.

L36 Design of Experiment (DOE)									
All igniter tips were cleaned in ethanol for 30 minutes prior to surface preparation conditions.				Tip Decomposition	Resistance	Wetting	Flowing	weighted sum	
				0 = None	(ohms)	0 = Good	0 = no stipples; good flow		
				1 = non-Metal nodules		1 = Bad	1 = no stipples but more flow needed		
				2 = Nodules & minor Crervices			2 = melty stipples		
				3 = severe, large deep crervices;fracture			3 = stipples		
Sample No.	Oxidation Temp for 4 hrs	Surface Prep Prior to Brazing	Hydrogen Brazing Temperature @ 1125°C for 30 minutes						
23	975	palco	palco	0	0.5	1	2	8.5	
34	1100	none	combo	1	0.3	1	2	10.3	
6	725	combo	palco	1	0.5	1	2	10.5	
5	725	palco	palco	0	0.5	1	3	11.5	
17	850	palco	combo	3	0.5	1	1	11.5	
24	975	combo	palco	0	0.7	1	3	11.7	
33	1100	combo	palco	0	0.8	1	3	11.8	
22	975	none	palco	0	0.95	1	3	11.95	
31	1100	none	palco	0	1.0	1	3	12	
27	975	combo	combo	2	0.2	1	2	12.2	
26	975	palco	combo	2	0.4	1	2	12.4	
8	725	palco	combo	2	0.5	1	2	12.5	
25	975	none	combo	2	0.5	1	2	12.5	
35	1100	palco	combo	2	0.5	1	2	12.5	
16	850	none	combo	0	5	1	2	13	
7	725	none	combo	3	0.5	1	2	14.5	
9	725	combo	combo	3	0.5	1	2	14.5	
36	1100	combo	combo	3	0.5	1	2	14.5	
18	850	combo	combo	3	0.6	1	2	14.6	
15	850	combo	palco	0	10	1	2	18	
32	1100	palco	palco	0	10	1	2	18	
4	725	none	Palco	0	10	1	3	21	
13	850	none	palco	0	10	1	3	21	
14	850	palco	palco	0	10	1	3	21	
extra sample 1	975	none	combo	0	0.1	0	1	3.1	TIH mixed in the braze & coated on the tip surface.
extra sample 2	975	none	combo	1	10	1	2	20	TIH added as a thick layer only
extra sample 3	975	none	combo	2	10	1	2	22	TIH added as a thin layer only

Figure 6.3.8.1-4: L36 Designed Experiment

The decomposition of the electro-ceramic tip; the wetting ability of the brazes on the substrates; and the flow of the braze on the substrates, were evaluated for each electro-ceramic tip/braze alloy/metal clip material sample. The resistance of each sample was also measured. The results of the experiment are shown in **Figure 6.3.8.1-5**. **Figure 6.3.8.1-6** shows two braze joints, one where the electro-ceramic was protected with the oxide scale layer and one where the electro-ceramic was not. The unprotected electro-ceramic igniter tip shows the decomposition with the Si pooling and the other tip does not. The oxide scale did successfully protect the Delphi braze allowing the bonding of the electro-ceramic tip to the metal clip.

- **Means Plots**

975°C Best Temp.

Combo braze slightly better than Palco

Figure 6.3.8.1-5: Designed Experiment results

- Igniter A – oxidized in air furnace at 1200°C. Painted with braze Palco.
- Igniter B – painted with braze. Palco.
- Both igniters were brazed in the same furnace right next to each other. Brazed in hydrogen at 1100°C for 30 min. Heated up at 10°/min to 600°C, 5°/min to 1090°C, 15 min soak, then 5°/min to 1100°C.

Figure 6.3.8.1-6: Two electroceramic tips after brazing one protected with an oxide scale layer and the other without

During these initial brazing studies, a large amount of material was found to be securely attached to one of the electro-ceramic igniter tips. The material was analyzed with EDAX and found to have the following composition: Pd ~ 35%, Co ~ 3%, Cr ~ 6%, Ni ~ bal. Using this composition as a starting point, the composition of the Delphi braze was altered until the current braze composition was achieved. It was also found that the wetting of the Delphi's brazing alloy needed to be improved. TiH₂ and ZrH₂ are often used in brazing to improve wetting of braze alloys on ceramics. A literature search found reference to the addition of Ti to braze alloys to improve wetting of AlN ceramic brazing. The addition of a thin layer of TiH₂ to the electro-ceramic surface prior to the braze application improved the wetting of the Delphi braze dramatically. A Formica electrical insulation barrier was also added between the metal clips as a braze break to insure that the braze does not electrically short the igniter tip. The wire insulation was changed to a woven alumina. The potting compound was changed to Zirconia-based adhesive. This material system consisting of high temperature oxidation resistant alloys, brazes, and wires resulted in a high temperature capable igniter.

9.4.7.2 Igniter Brazing Procedure

The igniter tips used in this study were extracted from a commercially available Norton igniter. The igniter tips were extracted from the alumina body and metal clip using a diamond saw, hydrofluoric acid and forceps. The igniters were then rinsed in water followed by three one hour water baths to remove any remnant of acid from the tip. After the water baths, the igniter tip was then soaked in dehydrated ethanol for one hour. The igniter tips were then placed in a high temperature air furnace at 975°C for four hours. This step put a silicon dioxide layer on the igniter tip. The wiring used to connect the igniter is a Fe-Ni-Cr alloy. The 80/20 Nichrome 20 gauge wire is electrically insulated with an alumina woven fabric. The procedure for making the Delphi igniter tip is shown in **Figure 6.3.8.2-1**.

Figure 6.3.8.2-1: Igniter Fabrication Process

The brazing furnace procedure is as follows. Utilizing a hydrogen or vacuum furnace per the following procedure:

1. Ramp to 600°C at 10°C /minute.
2. Ramp to 1115°C at 5°C /minute, dwell at 1115°C for 15 minutes.
3. Ramp to 1125°C at 5°C /minute, dwell at 1125°C for 30 minutes.
4. Ramp to 0°C at 5°C /minute.

The H₂ furnace runs an initial 30 minute N₂ purge and a final 30 minute N₂ purge.

9.4.7.3 Testing Procedures for the igniter tips

Delphi's developed igniters were compared against the commercially available igniters, at 800 and 850°C. **Figure 6.3.8.3-1** shows a comparison of Delphi's developed igniter with a Norton and a LeMark igniter.

Figure 6.3.8.3-1: Igniter Comparison at 800°C Hot Soak in air

The Delphi igniters, ALM-003, DME-011, were hot soaked in air for sixteen hours then cooled and ignited. Each thermal cycle is identified. Delphi igniter, DME-006 was only thermally cycled. This was done to compare testing methods. The Delphi developed igniters have successfully met the aggressive requirements of the SOFC application. None of the commercial igniters met the requirements. **Figure 6.3.8.3-2** shows the igniters that were tested at 850°C.

Figure 6.3.8.3-2: Igniter Comparison at 850°C Hot Soak in air

9.5 Task 6: Hybrid System Evaluation

9.5.1 System Modeling and Control Design

UTRC conducted SOFC system modeling and conceptual design of a 400 kW SOFC power systems operating on natural gas. The goal for 2008 was to: 1) Establish conceptual system layout for system footprint, volume, and weight estimation; 2) update heat loss and pipe pressure drop model based on the conceptual system layout; and 3) perform preliminary control design.

9.5.1.1 Conceptual System Layout

The purpose to establish a conceptual system component layout was to understand potential packaging challenges and system gravimetric power density. Based on component dimensions from the conceptual design, the components are arranged so that system volume and connection pipe length are minimized while accessibility has been taken into consideration for installation and maintenance. The 3-D illustration of the 400 kW SOFC system is shown in **Figure 8.2.1-1**.

Figure 8.2.1-1: 3-D illustration of a 400 kW SOFC system

The weight calculation considers component weight, weight of insulation and accessories such as pipes and system frame. **Table 8.2.1-1** shows the component weight breakdown. Stack and the electric system module (ESM) account for 41% and 21% of the system weight, respectively. Total system weight is approximately 20,000 lbs and system power density is 44 W/kg.

Components	Weight (Lb)
SOFC stacks	8269
Reformer	648
HDS	2150
Air preheater	1057
Pre-anode HEX	229
Pre-reformer HEX	43
Catalytic burner	48
Startup burner	50
Fuel compressor	82
Air blower	859
Anode recycle blower	70
ESM	5200
System enclosure	647
Pipes	780
Total	20131

Table 8.2.1-1: Component weight estimates for 400 kW SOFC system

In the abovementioned configuration, each component is insulated individually. A hot box design concept was also considered, with which several high temperature components including the stack, the air preheater and the reformer are arranged in a hot box. A potential advantage of the hot box approach is that the overall heat loss could be smaller and less insulation material is needed. However, these components vary greatly in size and operation temperature. Thermal management within the hot box would be challenging. On the other hand, insulating the component individually likely does not increase heat loss substantially.

9.5.1.2 Model Update with Revised Heat Loss and Pipe Pressure Drop

The conceptual system layout shown in **Figure 8.2-1 above** enables the design of component insulation and an estimate of component heat loss, as well as pressure drop along connecting pipes.

Given component dimensions and operating temperatures; types of insulation materials and insulation thickness were chosen after discussion with insulation material vendors. Heat loss was calculated from the insulation material thermal conductivity thickness and the temperature gradient across the insulation material. For the 400 kW SOFC system considered, the overall heat loss to the ambient was 16.6 kW, or 2.3% of the fuel heat input (low heating value). This is close to the heat loss of 22 kW assumed before. The revised system heat loss leads to 0.1% of system electric efficiency change, which is considered insignificant.

Pipe pressure drop was also updated in the system model. Based on the system layout, pipe diameter and length was determined for each connecting pipe. The principle for selecting pipe diameter is that the length of pipe diameter should be large enough so that the flow velocity is below 15 m/s to avoid large pipe pressure drop. Compared to the original assumption, the revised overall pressure drop is slightly lower in both the main anode and the cathode loop, while the pressure drop in the anode recycle loop has a 10% increase. The overall impact to system efficiency is a negligible 0.2% increase.

9.5.1.3 Preliminary Control Design

The purpose of this effort is to gain a preliminary understanding of the system control at an early stage for any important potential design considerations. The preliminary control design includes identifying control requirements, determining major control hardware, and performance of preliminary dynamic modeling.

In general, there are two types of control depending on the control action timing: the continuous control and the sequential control, the latter usually being the startup and shutdown process. For continuous control, it is necessary to determine what system variables to control and how to implement those controls. For example, the stack temperature can be a variable to control or maintain. However, it cannot be controlled directly, but indirectly through controlling the cathode air flow rate with a given fuel flow rate. Some parameters, such as the hydrodesulphurizer (HDS) inlet temperature, need to be within a range as a reaction constraint. If during part load performance, the parameter is within the constraint range, no control device is needed. Otherwise, control hardware needs to be added. **Figure 8.2.3-1** shows the procedure in identifying the hardware for the continuous control.

Figure 8.2.3-1: Procedure determining control variables and needed actuators

The goal of the startup design was to establish a logical procedure to bring the system from idle or cold state to the hot state within material and functional constraints, e.g., avoiding large temperature gradient within the stack. Stack is heated up via a startup burner using natural gas. Various concepts for heating up the HDS and the reformer were considered. Electric heating was chosen as the optimal solution because of technology maturity and acceptable electricity consumption. A startup sequence including purge, component pre-heat and ramp up of electric load was designed. Finally, a similar sequence is also established for system shutdown, which mainly includes load ramp-down, load disconnect, cool-off and purge.

A dynamic system model is developed for the 400kW SOFC plant startup based on dynamic component models previously developed at UTRC. It is used to validate transient performance against the requirements and to assist architecture and algorithm design. Currently the dynamic model incorporates thermal mass of major components such as the stack and the reformer, but not the chemical reaction dynamics. The model predicts temperature response with a given startup procedure as shown in **Figure 8.2.3-2**, and demonstrated capability for control design and optimization for future detailed system design.

Figure 8.2.3-2: Dynamic modeling results for system startup

9.5.2 Large Foot-Print Stack Design

This section documents the design work performed for the creation of a solid oxide fuel cell repeat unit that utilizes large footprint cells. Similar basic components were also used in a laboratory-scale short stack to assess component behavior as well as large-footprint cell performance.

9.5.2.1 Stack Designs for Laboratory Demonstration

Testing of large single Delphi cells had previously been performed in a module that held the cell by clamping its edges between two thick frames. However, a number of cell fractures were observed with this design, and it was decided to move towards a brazed cell-frame assembly, as shown in the expanded view of 1-cell stack (**Figure 8.3.1-1**) in order to reduce stresses applied to the ceramic cell. The cell-frame assembly is based on Delphi's large footprint 16x27 cm cell (14x25 cm active area) and Delphi's braze material and technology. The cell is joined to a 0.30 mm thick sheet of Crofer-22 with a braze joint that runs around the perimeter of the top surface (electrolyte surface) of the cell. By attaching the cell to this thin metal sheet, a degree of compliance is provided. This approach is expected to minimize the stresses transferred to the cell due to any tolerance variations or misalignment in the thicker air and fuel frames. Delphi has developed the process for joining cells to Crofer-22 sheets of this thickness with a silver-based braze alloy. The electrochemical performance of the large footprint brazed cell is reported in **Section 8.4** of this report.

Figure 8.3.1-1: Exploded view of large footprint of 1-cell stack for lab demonstration

A variety of repeat unit concepts were evaluated for the next design phase. The goal was a configuration with a short fabrication lead time and which, while not deviating radically from UTRC's stack experience, incorporated the features desired in a repeat unit to gain knowledge for future iterations. The most promising options were those based upon layering stock-gauge flat metal sheets that employ through-thickness cuts for as many of the machining operations as possible. This allows for fabrication of multiple frames at once by cutting through a stack of plates with a method such as water jet, laser, or wire EDM. **Figure 8.3.1-2** shows the 3-cell stack which was built and tested.

Figure 8.3.1-2: Solid model of 3-cell stack for lab demonstration

9.5.2.2 Conceptual Window-Frame Cell Stack Design

Stack and stack module for MW scale power plant needs to meet stringent system criteria including efficiency, durability at steady state, robustness under thermal cycling, parasitic losses, and cost. These parameters, collective experience, and judgment

points to the need to produce power of about 1000 W per layer in a large stack in order to reduce part count, minimize manifolding and associated pressure drops and sealing issues. It is also well known that single ceramic planar cell footprints are of limited size and limit power generation to the 100's W, significantly lower than the desired 1000 W. One possible solution around this existing limitation of thin ceramic sheet manufacturing is to resort to what has been referred to as the Window Frame design. The window frame requires some level of compliance in at least one of the metallic interconnects in order to mitigate tolerance variations from fabrication. The compliance requirement is being met by UTRC's demonstrated compliant, creep resistant, and oxidation resistant interconnect materials and designs, which is considered as the enabling technology for large footprint, cost-effective, and large power SOFC cell stacks.

9.5.2.2.1 Repeat Unit Design

Figure 8.3.2.1-1 shows an expanded view of the cell stack components that are used to assemble a window frame cassette comprised of three planar cells in a repeat unit layer. This concept is referred to the 1x3 (one row, three columns in matrix notation) cell window frame design. In this concept, three ceramic cells are peripherally encapsulated by cell frame. On the anode side, a flat wire mesh is used as the current collector and is bonded onto one side of the separator sheet. On the cathode side, the compliant interconnect is used to facilitate footprint scale up. The present window frame cassette provides for internal, hermetically sealed fuel gas stream, while the air gas stream is managed without the need for layer-to-layer hard seals, essentially a seal-less air stream management that significantly reduces sealing complexity and the associated cost. In **Figure 8.3.2.1-1**, the primary fuel manifolds are shown to have a mostly rectangular geometry, which provides for reduction in sheet metal footprint and associated cost, at the potential cost of some difficulty with the shape of the metal rings that is needed to create the up-the-stack primary fuel manifold. These rings could be of any form, C-ring, V-ring, e-seal, etc., and bridge the gap between contiguous layers, which is approximately equal to the height of the compliant interconnect on the air side as shown in **Figure 8.3.2.1-2**.

Figure 8.3.2.1-1: 1x3 Cell Window Frame Cassette Concept

Fuel inlet and outlet streams flow into plane, and over the anode from left to right

Figure 8.3.2.1-2: Cross Sectional View of 1x3 Cell Window Frame Cassette

Figure 8.3.2.1-2 above is a cross section of the cassette along the length of the cell, showing the part lay up, the means of achieving hermetic sealing of the fuel gas stream at one layer and the formation of the secondary fuel manifolds (the cavities at the left and right ends of the figure, having the “fuel” arrows). Note that the cell frame is peripherally welded to the separator plate, thus creating a seal line of high robustness. The fuel and gas streams flow in parallel, co- or counter-flow, configuration.

For MW scale power systems, the stack module will consist of multiple stack building blocks. **Figure 8.3.2.1-3** illustrates a 100-layer (repeat unit) stack building block as an example. Each repeat unit is made of 1x3 cell window frame cassettes with the fuel manifolds properly sized for uniform distribution across each layer and over the stack height. The design and sizing of the manifolds is discussed in the next section. The window frame cassette shown here has cylindrical primary fuel manifolds, the preferred option from the sealing point of view.

Figure 8.3.2.1-3: 100-layer Stack Building Block as an Example

9.5.2.2.2 Conceptual Gas Stream Manifolds and Flow Distributions

For the large footprint stack discussed above, the fuel, or anode, gas steam is internally manifolded, while the air, or cathode, gas stream is managed by a “duct”-like enclosure (**see Figure 8.3.2.2-1**), which is essentially a seal-less manifold requiring only compliant ceramic fiber matting to control flow distribution. This manifold design enables air and fuel streams to be in a parallel flow arrangement. It is anticipated that the system will operate at high fuel utilization, and, as a result, it is necessary that each cell in a stack receive the same amount of fuel and evenly distributed along the width of the cell. The internal fuel manifold design concept is shown in **Figure 8.3.2.2-2**. Fuel flows vertically in two of the large passages, one on each end of the window frame, and anode products exhaust vertically through the other two large passages. These large passages are termed the primary fuel manifolds. The fuel enters or leaves the anode cavities through the secondary fuel manifolds. To ensure fuel flow uniformity, properly designed manifolds require that pressure drop in the anode cavity be large relative to that of the secondary fuel manifolds, which in turn must be large relative to the primary manifold pressure drop. In the current design, the anode-side interconnect is a woven mesh, which has a relatively large pressure drop. Therefore, design efforts were focused on the manifolds.

Figure 8.3.2.2-1: External “duct” Air Manifold Design

NOTE: Rectangular Primary Manifold is for Illustration only

Figure 8.3.2.2-2: Fuel Internal Manifold Design

CFD analysis was conducted to understand the effect of size and shape of the feed tube, size of the primary fuel manifold, and height and width of the secondary fuel manifold. The anode-side interconnect was modeled as a porous medium, with a pressure drop functionality derived from detailed CFD analysis of the anode gas channel and the associated flat wire weave interconnect.

Size of the fuel feed tube effects flow variation from layer to layer along the height of the stack. A stack with 400 anode cell layers was assumed for the CFD analysis. In this case, uniform flow requires that 0.25 percent of the flow enter each window frame unit, i.e., stack repeat unit or layer. In **Figure 8.3.2.2-3**, two results are shown.

Figure 8.3.2.2-3: Effect of the Fuel Feed Tube on Flow Variation from Layer to Layer along Stack Height

Uniform flow is obtained if the duct feeding the anode primary manifold is large, thereby reducing the jet velocity entering the primary manifold. In this case, the feed duct was assumed to be the same size as the primary fuel manifold. If a much smaller feed duct is used (an 18 mm-diameter duct versus a 112 mm-diameter duct), the flow is non-uniform for the first 50 layers.

The secondary fuel manifold presents a design challenge because its pressure drop must be intermediate to that of the anode passage and the primary manifold. CFD simulations were used to determine the appropriate width and height of the secondary manifold. When the secondary manifold is performing properly, the flow entering the anode cavity is uniform along the width of the window frame from each primary manifold toward the center. Equivalently, the total amount of fuel distributed to the anode cavities in a window frame varies linearly from 0 to 100 percent, except where there are frames between cells, as shown in **Figure 8.3.2.2-4**.

Figure 8.3.2.2-4: Fuel Internal Manifold Design for Flow Uniformity

The cathode passages contain no metering orifices into and out of each layer and only the manifold can provide uniform airflow. Although it is not necessary to have as strict a requirement for cell-to-cell uniformity on the cathode side as on the anode side because

there is excess air for thermal management, it is prudent to design for as uniform a flow distribution as possible to prevent additional thermal stresses. Various geometry and feed tube arrangements were considered for the cathode manifold design. It was found very uniform flow can be achieved above the first 50 cells or so for a 400-layer stack. Views of some streamlines of the best cases are shown in **Figure 8.3.2.2-5**.

Figure 8.3.2.2-5: Air Distribution – Example Streamlines for Best Case #14

9.5.3 Cell Evaluation and Stack Material Optimization

UTRC made progress in validating short stacks with the large footprint cells. One-cell and three-cell stacks were built and tested using large footprint Delphi cells with a metal frame. For the development of material solution to the long term durability of stacks, a new coating for cathode interconnects was examined via the electrochemical testing. New glass seal material was validated via single cell stack tests and introduced in the large footprint stack assembly.

9.5.3.1 Large Footprint Cell Development

Efforts continued on the development of a large footprint solid oxide fuel cell along with corresponding cell-to-picture frame assembly and cassette assembly. A cooperative effort amongst the commercial supplier of tape cast film, the Delphi materials development group, and the Delphi advanced manufacturing engineering team led to improved materials, lamination processes, and firing processes that allowed for the fabrication of the large cells with a high process yield. Some of the specific key additions and changes to the process are listed below:

- A large area screen printer has been installed
- Large area screens have been received and implemented
- A large vacuum bagger has been implemented to seal the larger footprint cells
- Setters / saggars have been purchased to accommodate the larger footprint cells

New alumina sheets used in creep flattening of the larger footprint cells
Currently in the process of procuring a laser scribe with a large x-y table
Laser program developed to scribe cell dimensions in single or multiple passes
Larger periodic and belt furnaces will be operational by October 2008
Validation of the process using Delphi manufacturing and quality systems

9.5.3.2 Evaluation of One-Cell and Three-Cell Stacks with Brazed Large Footprint Cells

As a step leading towards demonstration of stacks with higher power output, large footprint (16 cm x 27 cm) cells brazed to a metal frame were built into one-cell and three-cell short stacks and evaluated. The cell has an active area of 350 cm² (14 cm x 25 cm). In order to minimize mechanical load applied directly on the ceramic cell itself and to prevent cell fracture, cells with a metal frame were used in these tests. The metal frame was attached to the cell via established air brazing process by Delphi.

Figure 8.4.2-1 compares the initial V-I performance of the brazed cell (LF-D-02) and a non-brazed ceramic cell (LF-D-01). The brazed cell exhibited a slightly lower performance than the ceramic cell without a metal frame brazed onto.

Figure 8.4.2-1: Performance of brazed and non-brazed large footprint cells at 750°C

The large footprint brazed cell was held at 0.44 A/cm² and 750 °C for steady state performance evaluation. The cell delivered 0.35 W/cm² at roughly 0.8 V and exhibited a degradation rate of 14.6%/1000 h during the testing period of 297 h, which is significantly higher than that of the ceramic cell aforementioned (5.2%/1000 h). As shown in **Figure 8.4.2-2**, the iR-corrected cell voltage of the one-cell stack showed a degradation of 7.7%/1000h, whereas the ceramic cell showed a lower iR-corrected voltage degradation of 3.3%/1000h. The ohmic resistance revealed by the iR measurement is believed to partially contribute to the faster cell performance degradation. Although the exact cause for the poor durability of the large footprint brazed cells are not clear, post test observation did reveal cross over leakage and local combustion due to the presence of pin-holes in the electrolyte and openings in the cell frame braze joint, as shown in **Figure 8.4.2-3**. In addition, delamination and spallation

of cathode material is frequently observed in this batch of cells. These could have contributed to the higher degradation rate. Cell quality issues are not surprising since this was the first batch of large cells fabricated by Delphi. Process optimization is underway and better performance is expected in the near future.

Figure 8.4.2-2: Constant Load Test of Brazed Large Rectangular Cell at 0.44A/cm² and 750°C

Figure 8.4.2-3: Post-test Observations of Large Footprint Brazed Cell in a One-Cell Stack Assembly

During the reporting period, effort was also devoted to building a stack with multiple cells. A three-cell stack was built using the brazed cells. While negligible external leak was detected, a large cross-over leakage was observed after initial stack heat up and reduction. Initial performance of the stack is shown in **Figure 8.4.2-4**. The cells exhibited lower OCV than those in the single cell stack, suggesting cell fracture. The stack was tested for a short period of time (73h). The test was then terminated and the stack was disassembled for post-test analysis. It was found that the middle and bottom cell were fractured. Root cause analysis revealed that interconnect dimensional variation was largely responsible for non-uniform stress distribution and cell fracture. Changes in the fabrication process are required to improve the interconnect dimensional tolerance for future stack assembly and tests.

Figure 8.4.2-4: Initial Performance (V-I characteristics) of Three-Cell Stack at 750°C

9.5.3.3 Benchmarking of 2008 Batch Round Cells

A batch of round cells was fabricated by Delphi in early 2008 and provided to UTRC in April 2008. Compared to the previous batch of cells, cathode of this new batch exhibited a different appearance. As shown in **Figure 8.4.3-1**, the previous cell cathode had a smooth appearance and is relatively crack-free, while the new batch cell cathode has numerous mudflat cracks and spallation of cathode material in some areas. RM-D-10 was built with the same parameters as RM-D-9 and tested for benchmarking purposes. The cell from the April 2008 batch showed a lower activity than its baseline from the October 2006 batch, as shown in **Figure 8.4.3-2**). The difference amounts to 30 mV lower cell voltage at 0.4A/cm². In addition, the 2008 batch cell showed a higher degradation rate (5.6%/1000h) than the 2006 batch (<2.1%/1000h) during the 242-hour test. Comparison of RM-D-10 and RM-D-9 during the constant load test is shown in **Figures 8.4.3-3 and 8.4.3-4**.

Radial cell received
10/2006

Radial cell received
4/2008

Figure 8.4.3-1: Photographs of Radial Cells Received in 2006 and 2008

Figure 8.4.3-2: Polarization Curves of a 2008 Batch Cell (RM-D-10) and a 2006 Batch Cell (RM-D-9) at 750°C

750°C, fixed flow rates, U%=20%

Figure 8.4.3-3: Cell Degradation of RM-D-09 (2006 batch) During Constant Load Test at 750°C

Figure 8.4.3-4: Cell Degradation of RM-D-10 (2008 batch) During Constant Load Test at 750°C

9.5.3.4 Validation of New Stack Components

Glass seal material was validated in a square module using a third party cell. An electrochemical test was conducted at $0.3\text{A}/\text{cm}^2$ and 700°C to evaluate possible effects of the glass seal on cell durability. The module exhibited no measurable degradation of cell voltage during the 372-hour test, as shown in **Figure 8.4.3-1**.

Figure 8.4.4-1: Constant Load Test of a Square Cell with Glass Seals at 750°C

Another effort during this reporting period was the evaluation of a new cathode interconnect coating. The new coating was validated via radial module electrochemical testing (RM-D-11). Initial performance of this module was identical to the baseline module (RM-D-9). Although degradation rate was $1.8\%/1000\text{h}$ during 530h test at $0.438\text{A}/\text{cm}^2$, only slightly lower than the baseline ($2.1\%/1000\text{h}$ as observed in RM-D-9), post-test analysis revealed significantly less amounts of chromium on cell surfaces, indicating that the new coating was more effective on cells containing chromium from the interconnect.

10 2009 TECHNICAL PROGRESS AND ACHIEVEMENTS

10.1 Task 1: System Development

SECA Phase II is a continuation of the core hardware development activities begun in Phase I. The systems efforts in Phase II are more application-driven as Delphi moves this technology closer to pilot and production releases. The Phase II program supports and addresses two markets that Delphi selected to pursue with the SOFC technology it has been developing with the assistance of the DOE. The stationary market and the transportation market have unique demands, and the development tasks must address the specific values that are the economic drivers of the design and application.

Two power system products are the focus for SECA Phase II:

- Stationary: Small Residential Combined Heat and Power (CHP)
- Transportation: Heavy-Duty Commercial Vehicle Auxiliary Power Unit

Stationary power systems will be referred to as Stationary Power Units (SPU) and are the general product classification that applies to a power generation device that is permanent and fixed in a location with a structure that provides primary or back-up power to an occupant. The intended market would have the device installed and operation would be nearly continuous with few thermal cycles over the expected lifetime at that structure of nearly 10 years or about 80,000 operating hours.

Power systems for the Transportation Market will be referred as Auxiliary Power Units (APUs) and are the general product classification that applies to a power generation device that is not fixed in location but can be mounted to a vehicle or transported to a site for temporary power. The intended market would have the device mounted on a vehicle or portable frame and operate for short periods or cyclic, based on the usage time profile. The expected lifetime would be nearly 5 years or about 22,000 operating hours.

In the period between July and December 2009, no progress was recorded due to the program being put on hold.

10.2 Task 2: Stack Development

Delphi upgraded the existing stack test stand capability to test the simulated coal gas reformat compositions with Gen 3.2 30-cell stacks. Delphi successfully completed the tests with the Gen 3.2 30-cell stack in co-flow configuration. The testing included performance evaluation of the stack as a function of different fuel compositions, different inlet temperatures and different utilizations. Electrochemical performance, temperature distribution in the plane of the repeating unit and within the height of the stack and other stack outputs were mapped.

10.2.1 Test 30-cell Generation 3.2 stack

The major subtasks in this task include the following subsections.

10.2.1.1 Build.

Two 30-cell Gen 3.2 stacks were fabricated successfully. Initial characterization was completed. Stack # 833 (**Figure 4.2.1-1**) produced 1477 Watts at a power density of 469 mW/cm² at 570 mA/cm² (average voltage of 0.82 Volts, 750°C, 48.5% H₂, 3% N₂, rest H₂O fuel).

Stack # 834 produced 1512 Watts of power at a power density of 480 mW/cm² @ 570 mA/cm² (average voltage of 0.84 Volts, 750°C, 48.5% H₂, 3% N₂, rest H₂O fuel). Both the stacks have good sealing and will be used for further evaluation with simulated coal gas reformat.

Figure 4.2.1-1: Stack # 833: IV curve

Figure 4.2.1-2: Stack # 834: IV curve

A schematic of the stack with the three thermocoupled dummy cassettes is shown in **Figure 4.2.1-3**

Figure 4.2.1-3: Stacks with “thermocoupled dummy” cassettes: Thermal cassettes were located between cells 7-8, 14-15, and 21-22, with seven thermocouples located in each thermal cassette

10.2.1.2 Upgrade stand for the test

The stands were successfully upgraded to allow for testing of all the different fuel compositions. The stand was optimized to be able to test the high steam content in the fuels as stated in the fuel compositions. A dummy stack was used to debug the stand. The following simulated reformat compositions are being tested.

Blend	Fuel Composition					
	H ₂	CH ₄	CO	CO ₂	N ₂	H ₂ O
Delphi Standard	48.5%				48.5%	3.0%
SECA CBS 1	63.5%				14.4%	22.1%
SECA CBS 2	12.5%	17.0%	5.0%	21.5%	4.9%	39.1%
SECA CBS 3	12.9%	9.0%	7.1%	39.8%	0.6%	30.6%
SECA CBS 4	17.0%	2.0%	24.0%	9.0%	1.0%	47.0%

Figure 4.2.2-1 shows the stand that was developed to carry out this test.

[Hot / Cold Control \(complete\)](#)

Added capability to vary cathode and anode inlet temperature, allowing for greater stack temperature control during max power sweeps.

[I/O Upgrade \(complete\)](#)

Increased Thermocouple Channels to handle additional TC Dummy readings

[Co-Flow and Counter Flow Manifold \(complete\)](#)

Modified test manifold pre-heating tubes to enable simultaneous testing with co-flow and counter flow conditions

[Dual Water MFC's \(complete\)](#)

Increased overall turndown by installing low flow and high flow water meters. Added capability to humidify 30 cell flows up to 50% water

[High Capacity Vaporizer \(complete\)](#)

Increased vaporization capacity to handle water flow rates for 50% humidification levels.

[Test Stand Software \(complete\)](#)

Various upgrades to match hardware changes

Figure 4.2.2-1: Test Stand Improvements

10.2.1.3 Testing of Stack

Stack testing remained ongoing. With stack at operating temperature (700 – 800 °C inlet temp), load was applied to get constant utilization polarization curves. For each reformat composition multiple constant fuel utilization polarization curves were measured. Each operating point was held for achieving steady state operation. The tests are terminated when an individual voltage of a cell reached a limiting condition (0.6 V) or reach a max temperature (840°C). Stacks were tested in co-flow configuration and in counter-flow mode. Data collected included polarization curves at given utilization (Individual cell voltages versus current density), temperature profiles throughout the test and pressure (inlet, outlet).

Figures 4.2.3-1 through 4.2.3-21 shows data from the series of co-flow tests with the simulated reformat compositions. The trends observed demonstrate the impact of internal reforming in the reformat compositions with methane due to endothermic

reforming. Having a higher inlet temperature with these reformates was beneficial for maintaining higher voltage. The high steam compositions impacted OCV and therefore the voltages at 30 Amps (286 mA/cm²) and 60 Amps (570 mA/cm²) compared to the standard blends. The maximum limit for testing was 840°C max temperature and 0.6 Volts. Some of the runs with high inlet temps were not completed as the test reached the max limit and did not have enough cooling capacity. Overall, the tests gave Delphi an understanding of performance and temperature distribution within the stack and more importantly within the plane of the repeating unit.

Fuel Iteration	Utilization Set Point	Inlet anode temp
DelphiStandard A	30%	725 °C
DelphiStandard B	50%	725 °C
DelphiStandard C	70%	725 °C
SECA CBS 1 A	30%	700 °C
SECA CBS 1 B	30%	725 °C
SECA CBS 1 C	30%	750 °C
SECA CBS 1 D	50%	700 °C
SECA CBS 1 E	50%	725 °C
SECA CBS 1 F	50%	750 °C
SECA CBS 1 G	70%	700 °C
SECA CBS 1 H	70%	725 °C
SECA CBS 1 I	70%	750 °C
DelphiStandard B	50%	725 °C
SECA CBS 2 A	30%	750 °C
SECA CBS 2 B	30%	800 °C
SECA CBS 2 C	50%	750 °C
SECA CBS 2 D	50%	800 °C
SECA CBS 2 E	70%	750 °C
SECA CBS 2 F	70%	800 °C
SECA CBS 2 G	70%	820 °C
DelphiStandard B	50%	725 °C
SECA CBS 3 A	30%	750 °C
SECA CBS 3 B	30%	800 °C
SECA CBS 3 C	50%	750 °C
SECA CBS 3 D	50%	800 °C
SECA CBS 3 E	70%	750 °C
SECA CBS 3 F	70%	800 °C
SECA CBS 3 G	70%	820 °C
DelphiStandard B	50%	725 °C
SECA CBS 4 A	30%	750 °C
SECA CBS 4 B	30%	800 °C
SECA CBS 4 C	50%	750 °C
SECA CBS 4 D	50%	800 °C
SECA CBS 4 E	70%	750 °C
SECA CBS 4 F	70%	800 °C
SECA CBS 4 G	70%	820 °C
DelphiStandard B	50%	725 °C

Blend	Fuel Composition					
	H ₂	CH ₄	CO	CO ₂	N ₂	H ₂ O
Delphi Standard	48.5%				48.5%	3.0%
SECA CBS 1	63.5%				14.4%	22.1%
SECA CBS 2	12.5%	17.0%	5.0%	21.5%	4.9%	39.1%
SECA CBS 3	12.9%	9.0%	7.1%	39.8%	0.6%	30.6%
SECA CBS 4	17.0%	2.0%	24.0%	9.0%	1.0%	47.0%

Figure 4.2.3-1: Test Matrix

Figure 4.2.3-2: SECA Delphi Standard – Temperature Data at 30 Amps (286 mA/cm²)

Figure 4.2.3-3: SECA CBS 1 – Temperature Data at 30 Amps (286 mA/cm²)

Figure 4.2.3-4: SECA CBS 2 – Temperature Data at 30 Amps (286 mA/cm²)

Figure 4.2.3-5: SECA CBS 3 – Temperature Data at 30 Amps (286 mA per cm²)

Figure 4.2.3-6: SECA CBS 4 – Temperature Data at 30 Amps (286 mA/cm²)

Figure 4.2.3-7: 30% Constant Fuel Utilization_30 Amps (286 mA/cm²)

Figure 4.2.3-8: 50% Constant Fuel Utilization_30 Amps (286mA/cm²)

Figure 4.2.3-9: 70% Constant Fuel Utilization_30 Amps (286 mA/cm²)

Figure 4.2.3-10: Power Density Summary (286 mA/cm²)

Figure 4.2.3-11: Cell Voltage Summary (286 mA/cm²)

Figure 4.2.3-12: SECA Delphi Standard – Temperature Data at 60 Amps (570 mA/cm²)

Figure 4.2.3-13: SECA CBS 1 – Temperature Data at 60 Amps (570 mA/cm²)

Figure 4.2.3-14: SECA CBS 2 – Temperature Data at 60 Amps (570 mA/cm²)

Figure 4.2.3-15: SECA CBS 3 – Temperature Data at 60 Amps (570 mA/cm²)

Figure 4.2.3-16: SECA CBS 4 – Temperature Data at 60 Amps (570 mA/cm²)

Figure 4.2.3-17: 30% Constant Fuel Utilization_60 Amps (570 mA/cm²)

Figure 4.2.3-18: 50% Constant Fuel Utilization_60 Amps (570 mA/cm²)

Figure 4.2.3-19: 70% Constant Fuel Utilization_60 Amps (570 mA/cm²)

Figure 4.2.3-20: Power Density Summary (570 mA/cm²)

Figure 4.2.3-21: Cell Voltage Summary (570 mA/cm²)

11 2010 TECHNICAL PROGRESS AND ACHIEVEMENTS

11.1 Task 2: Stack Development

Delphi completed performance mapping tests with simulated coal gas reformat compositions with Gen 3.2 30-cell stacks. Delphi successfully completed the tests with the Gen 3.2 30-cell stack in co-flow and counterflow configuration. The testing included performance evaluation of the stack as a function of different fuel compositions, different inlet temperatures and different utilizations. Electrochemical performance, temperature distribution in the plane of the repeating unit and within the height of the stack and other stack outputs were mapped. The results give us valuable understanding of the performance of the stack with coal gas reformat compositions.

Two 30-cell Gen 3 stacks and a CPOx reformer were successfully fabricated and characterized in-house before being shipped to the customer as per DOE's requirement. Testing is ongoing at the customer site with encouraging results.

11.1.1 Test Results

Figures 4.2.-1 through **4.2-17** shows data from the series of counter-flow tests with the simulated reformat compositions. The trends observed demonstrates the impact of internal reforming in the reformat compositions with methane due to endothermic reforming. The effect of counterflow air and reformat is observed in thermal mapping. Again, having a higher inlet temperature with these reformates is beneficial for maintaining higher voltage. The maximum limit for testing was 840oC max temperature and 0.6 Volts.

Figure 4.2-1: Counter-Flow configuration in stack

Figure 4.2-2: SECA Delphi Standard – Temperature Data at 30 Amps (0.285 A/cm²)

Figure 4.2-3: SECA CBS 1 – Temperature Data at 30 Amps (0.285 A/cm²)

Figure 4.2-4: SECA CBS 2 – Temperature Data at 30 Amps (0.285 A/cm²)

Figure 4.2-5: SECA CBS 3 – Temperature Data at 30 Amps (0.285 A/cm²)

Figure 4.2-6: SECA CBS 4 – Temperature Data at 30 Amps (0.285 A/cm²)

Figure 4.2-7: 70% Constant Fuel Utilization_30 Amps (0.285 A/cm²)

Figure 4.2-8: Power Density Summary (0.285 A/cm²)

Figure 4.2-9: Average Cell Voltage Summary (0.285 A/cm²)

Figure 4.2-10: SECA Delphi Standard – Temperature Data at 60 Amps (0.570 A/cm²)

Figure 4.2-11: SECA CBS 1 – Temperature Data at 60 Amps (0.570 A/cm²)

Figure 4.2-12: SECA CBS 2 – Temperature Data at 60 Amps (0.570 A/cm²)

Figure 4.2-13: SECA CBS 3 – Temperature Data at 60 Amps (0.570 A/cm²)

Figure 4.2-14: SECA CBS 4 – Temperature Data at 60 Amps (0.570 A/cm²)

Figure 4.2-15: 70% Constant Utilization_60 Amps (0.570 A/cm²)

Figure 4.2-16: Power Density Summary (0.570 A/cm²)

Figure 4.2-17: Average Cell Voltage Summary (0.570 A/cm²)

11.1.2 Data collection and report

All the data was collected and analyzed. The mapping allowed for valuable understanding of performance with the coal gas fuel. **Figures 4.3-1** through **4.3-2** compare data between co-flow and counterflow at a given current density and with the same reformate compositions.

Figure 4.3-1: Comparison of co-flow and counter-flow CBS2 at 0.570 A/cm² and 70% fuel utilization

Figure 4.3-2: Comparison of co-flow and counter-flow CBS3 at 0.570 A/cm² and 70% fuel utilization

Figure 4.3-3: Comparison of co-flow and counter-flow Power Density at 0.570 A/cm² and 70% fuel utilization

In summary, Delphi successfully fabricated stacks with additional thermocoupled cassettes and was able to map performance of 30-cell Gen 3.2 stacks with various reformate compositions.

11.1.3 Stack Summary Results

Two 30-cell Gen 3.2 stacks were fabricated for NASA (stack 883 and 884). Stack 883 produced 1477 Watts at a power density of 468 mW/cm² with 48.5% H₂, 3% H₂O, rest N₂ (**Figure 4.2-1**). The average voltage was 0.82 Volts. Utilization evaluation at 570 mA per cm² also demonstrated very encouraging results (**Figure 4.2-2**). The stack showed minimal lowering of power going from low utilizations to 80% + fuel utilization.

Figure 4.2-1: IV curve for stack 883

Figure 4.2-2: Power density and voltage versus fuel utilization

The second NASA stack (884) produced 1499Watts at a power density of 476 mW/cm² with 48.5% H₂, 3% H₂O, rest N₂ (**Figure 4.2-3**). The average voltage was 0.83 Volts. The stack also showed minimal lowering of power going from low utilization to 80 % + fuel utilization (**Figure 4.2-4**).

Figure 4.2-3: IV curve for stack 884

Figure 4.2-4: Power density and voltage versus fuel utilization

Both the stacks were shipped to NUWC for testing for NASA (changed address of delivery to NUWC as per discussions with NASA and DOE). A CPOx Reformer was also assembled, characterized and delivered for NASA testing.

12 2011 TECHNICAL PROGRESS AND ACHIEVEMENTS

No work was completed in 2011 on this SECA project.

13 PROGRAM CONCLUSIONS

Over the years of its SOFC development, Delphi has moved the technology from proof of technology, to proof of concept, to near commercial applications. Early systems did not generate enough power to support their own parasitic requirements. Today, we are investigating the opportunities of providing single kW-scale, diesel fueled APUs to heavy duty commercial trucks to power hotel loads during periods of driver downtime; multi-100 kW-scale, natural gas fueled stationary power units for moderate commercial needs; and multi-MW-scale, coal fueled power plants for regional power generation from clean coal.

Delphi has worked through technical development challenges and is now able to engage prospective customers in detailed conversations about how a SOFC power system can meet the need for clean, efficient, environmentally friendly power. Delphi has been able to demonstrate significant advances in power density, thermal and load cycling, mechanical robustness to shock and vibration, and continuous durability. Based upon current discussions, Delphi is building its business case to bring the technology to market.

Delphi has been able to develop the stack and supporting BOP components to be fuel flexible. To date, the team has proven that SOFC technology is compatible with gasoline, natural gas, hydrogen, and diesel fuel. Future work will continue to expand this flexibility. Near term evaluation is planned for bio-diesel and bio-mass/waste fuels.

These gains would not have been possible without the financial and technical support provided by the US Department of Energy. The support provided by DOE during this period is greatly appreciated.

PROGRAM RECOMMENDATIONS

The SECA project has been very successful in developing Solid Oxide Fuel Cell capability in the United States. However, technical and business challenges still remain to be able to supply market-ready power systems. Durability and cost are areas which require continued focus. Therefore, it is recommended that the SECA program be continued to take advantage of the achievements to date and support the transition to market-ready systems. Technical focus needs to continue on cell and stack development in the near term, but should also include system integration activities, so that there is a path to market. The shift in emphasis in the end applications to allow for natural gas systems of moderate size (multi-100 kW) is a very positive step on the way to large coal-based systems, and that emphasis should be continued.

14 LIST OF ACRONYMS AND ABBREVIATIONS

A	
AE	Application Enclosure
AIM	Application Interface Module
APU	Auxiliary Power Unit
ASR	Area Specific Resistance
Atm	Atmosphere
AT%	Atomic Weight %
B	
BOP	Balance Of Plant
BEC	Bussed Electrical Center
C	
CAN	Controller Area Network
CARB	California Air Resources Board
CCP	CAN Communication Protocol
CFD	Computational Fluid Dynamics
CH ₄	Methane
CHEX	Cathode Heat Exchanger
CNG	Compressed Natural Gas
CPOx	Catalytic Partial Oxidation
Cr	Chromium
CTE	Coefficient of Thermal Expansion
D	
DC	Direct Current
Demo	Demonstration
DFMEA	Design Failure Mode and Effects Analysis
DMA	Dynamic Mechanical Analysis

DOE	Department of Energy
E	
ECU	Engine Control Units
EDU	Engineering Development Unit
EPAct	Energy Policy Act
E-Stop	Emergency Stop
F	
FCPP	Fuel Cell Power Plant
FDU	Feedstream Delivery Unit
FEA	Finite Element Analysis
FMEA	Failure Mode and Effects Analysis
FMM	Fuel Metering Manifold
G	
GC	Gas Chromatography
Gen	Generation
GHSV	Gas Hourly Space Velocity
GPC	Gas Phase Combustor
GPCM	Gas Phase Combustor Module
H	
HEX	Heat Exchanger
HIL	Hardware in the Loop
HSC	High-Shear Compaction
HZM	Hot Zone Module
I	
ICM	Integrated Component Manifold
I/O	Input / Output
IRU	Interconnect Resistance Unit
L	

LCD	Liquid Crystal Display
LED	Light Emitting Diodes
LHV	Lower Heating Values
LIR	Light Internal Reforming
LNF	Lanthanum (L _a) Nickle (Ni) Ferrite (F _e)
LSCF	Lanthanum (L _a) Strontium (S _r) Cobalt (C _o) Ferrite (F _e)
M	
MAF	Mass Air Flow
MRF	Mass Recycle Flow
MSE	Measurement System Evaluation
N	
NETL	National Energy Technology Laboratory
NG	Natural Gas
NOC	Nominal Operating Condition
O	
OP	Open Porosity
O/C	Oxygen to Carbon
P	
PAM	Process Air Module
PFD	Process Flow Diagram
PNNL	Pacific Northwest National Laboratory
PO	Pre-Oxidized
POx	Partial Oxidation
PSM	Plant Support Module
R	
Rh	Rhodium
RPN	Risk Priority Number
RTI	Ragen Technologies, Inc.

S	
SECA	Solid State Energy Conversion Alliance
SEM	Scanning Electron Microscope
S&D	Safety & Diagnostics
SOFC	Solid Oxide Fuel Cell
SPU	Stationary Power Unit
SVM	System Verification Manager
T	
TGR	Tail Gas Recycle
V	
Vol %	Volume %
X	
XRD	X-Ray Diffraction
Z	
ZTA	Zirconia Toughened Alumina

-
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