Cost-effective High-efficiency Advanced Reforming Module (CHARM™)

Final Technical Report

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Executive Summary

Background

Creation of a hydrogen infrastructure is an important prerequisite of widespread fuel cell commercialization, especially for the automotive market. Hydrogen is an attractive fuel since it offers an opportunity to replace petroleum-based fuels, but hydrogen occurs naturally only in chemical compounds like water or hydrocarbons that must be chemically converted to produce it. While an ultimate goal is to produce hydrogen through renewable energy sources, steam methane reforming (SMR) of natural gas is currently the most economical solution to initiate the transition to a hydrogen economy.

Centralized hydrogen generation using large industrial SMR plants is already in place to serve customers. Yet, because of the weight and size of cylinders needed to contain hydrogen gas or liquid, transportation of hydrogen is only economical for very short distances. Consequently, distributed natural gas reforming, which trades off the economies of scale of large plants for simplified delivery logistics, is an attractive alternative that could address immediate problems with the lack of hydrogen infrastructure.

CHARM Program Overview

Over the past 5 years, Nuvera Fuel Cells conducted a development program to advance fuel processing technology for distributed hydrogen generation. This work performed under a collaborative effort with the U.S. Department of Energy (DOE) is called CHARMTM (Cost-effective High-efficiency Advanced Reforming Module).

The CHARM program goals focused on the development and demonstration of an advanced fuel processor module for stationary applications and development of next-generation system concepts. The main drivers included addressing the special durability concerns of these frequently-cycled fuel processors while achieving efficient operation and the lowest life cycle cost (LCC) to the customer.

An extensive design effort started with a system definition and modeling effort. Nuvera then worked in an iterative manner with the mechanical design, materials selection, and catalyst selection to build and test a complete fuel processor. Several generations of fuel processors were used in the CHARM program and the latest design is the core enabling technology of Nuvera's PowerTapTM hydrogen generation system. While the primary focus of the PowerTap system (rated 57 kg H₂/day) is in material handling applications, Nuvera analysis indicate that it can support small automotive fleets of up to 76 fuel cell vehicles. The fuel processor was tested for many performance metrics including efficiency and durability, both independently and in collaboration with Argonne National Laboratory who audited the results.

Design Challenges

Although steam reforming is a well-proven technology, industrial reformers run continuously with constant hydrogen demand and undergo only a few shutdowns per year. In contrast, for small scale hydrogen generators in the early market introduction phase, constant hydrogen demand cannot be assured, necessitating a need for frequent start up - shut down cycles. Cycling the reformer metal and catalyst, sometimes daily, poses a serious durability threat due to the interaction between creep, corrosion and cyclic fatigue. It was a pre-eminent focus of the CHARM program to find a commercially acceptable balance between fuel processor capital cost, operating cost (i.e. efficiency), and maintenance cost (i.e. durability) in pursuit of a system with the lowest life cycle cost.

Results

In the CHARM program, Nuvera developed a fuel processor that is projected to meet the targets of 40,000 hours and 1,000 start/stop cycles. Unfortunately, the expected catalyst life is short of the target due to frequent cycling (catalyst attrition), and substantial collaborative effort with catalyst suppliers is ongoing to further improve catalyst durability. Within the test campaign of the CHARM program, a PowerTap fuel

processor ran for 6,000 hours and 250 cycles, while maintaining high system thermal efficiency of 75% (LHV), as confirmed by Argonne National Laboratory.

A robust control strategy, utilizing industrial control hardware, was developed to ensure safety and reliability of the hydrogen generator. Additionally, the burner subsystem was designed to achieve favorably low emissions – both NO_x and CO emission profiles indicated single digit parts per million (ppmv) values for typical reformer operating conditions tested.

Using lessons learned from the fuel processor testing, a next-generation design was conceived to further improve durability and allow scaling to larger sizes. Nuvera conducted extensive studies of the behavior and limitations of the tubular design used as a repeating unit in the fuel processor. Based on knowledge of a singular tube element, Nuvera developed a new fuel processor concept, fully modular and readily scalable, and used it to complete a preliminary design of a 500 kg/day hydrogen generator. The key advantage of the new design is its ability to effectively supply heat to the steam reforming reaction with reduced peak temperature and reaction equilibrium, thus further improving fuel processor life and reducing LCC.

Nuvera also developed system level concepts that will allow for further improvements in efficiency, cost and durability, especially at larger product scales, and offering economically viable hydrogen infrastructure solutions.

In Nuvera's assessment, a combination of the newly conceived fuel processor and advanced system concept will offer a life cycle cost appealing to the widest range of potential hydrogen consumers. Therefore in addition to plans for commercialization of the CHARM fuel processing technology in the material handling market, Nuvera is initiating efforts targeting the design and realization of a system for use in fuel cell vehicle (FCV) refueling applications.

Major Conclusions

- Fuel processor to date demonstrated durability of over 6,000 hours and 250 cycles
- FP durability is projected to meet targets of 40,000 hours and 1,000 startup-shutdown cycles
- FP efficiency of 75% (LHV) confirmed by Argonne National Laboratory
- Cost of compressed (350 bar) hydrogen at 57 kg/day scale range from \$7.84/kg (DOE H2A model under automotive assumptions) to \$5.24/kg (H2A model with material handling assumptions)
- New advanced FP concept and combined cycle system are expected to improve durability to 80,000 hrs and reduce hydrogen cost to below \$4.50 per kg for automotive refueling

1 Introduction

The development of a hydrogen economy and realization of its benefits requires widespread and affordable hydrogen generation technology. This report summarizes work of Nuvera Fuel Cells for the advancement of hydrogen-producing fuel processor technology. The work was conducted through a DOE-sponsored program referred to as CHARMTM (Cost-effective High-efficiency Advanced Reforming Module).

Nuvera Fuel Cells has been advancing hydrogen-producing fuel processor technology for over 15 years. Through evolution of multiple fuel cell and fuel processing systems for automotive and stationary applications, Nuvera has made significant progress and developed expertise in fuel processor design, integration and performance. Remaining challenges include cost reduction and durability improvements, which are required to evolve the commercialization of distributed hydrogen generation appliances and support increasing deployment of fuel cell systems. Accordingly, Nuvera has developed a modular fuel processor with a design emphasis on life cycle cost reduction via optimization of the burner-reformer assembly.

Nuvera has developed an advanced, stationary, and flexible fuel processor (FP) to produce hydrogen onsite for various applications. A new generation of low pressure steam reformer was produced to address the widest range of specifications with the lowest risk. The FP is designed for high efficiency and long life, low capital cost in accordance with Design for Manufacturing and Assembly (DFM&A) principles, and it respects emissions standards and affords scalability. Scalability is a central objective to defray development costs associated with new scales and applications conceived in the future. Due to economy of scale principles, the challenge to making a low cost FP increases as its size decreases. The intent is to develop a low-cost FP that is scalable from approximately 500 to 10,000 scfh (28 to 570 kg/day) hydrogen output to cover the needs of early markets (such as fuel cell forklifts) and medium term applications (such as the introduction of fuel cell passenger vehicles). A 1,000 scfh (57 kg/day) H₂ product flow FP was built and evaluated at Nuvera laboratories with Argonne National Laboratory oversight; lifetime confidence is achieved through a combination of endurance testing and thermal profiling studies.

2 Objectives

The primary design targets for the fuel processor used in the CHARM program are listed in Table 1. These include the production of hydrogen from natural gas (NG) and LPG with 75% thermal efficiency of the fuel processor. They also include a fuel processor lifetime of 40,000 hours with 1000 thermal cycles as a step toward commercialization targets of 80,000 hours with 4000 cycles.

CHARM Design Targets		
Fuels	NG, LPG	To afford fuel flexibility
Efficiency	>75% (LHV)	Thermal Efficiency: {H ₂ ,CO,CH ₄ } / {Total Fuel In}
Lifetime	40000 hours 1000 cold cycles	Ultimate goal = 80000 hours & 4000 cold cycles represents daily cycling

Table 1. CHARM design targets

The CHARM program objectives focused on the development and demonstration of an advanced fuel processor module for stationary applications:

- Develop a 1,000 scfh H₂ (57 kg H₂/day) fuel processor with low product life cycle cost. Minimize capital, operating and maintenance costs over a 40,000 hour life.
- Develop a scalable technology from 1,000 to 10,000 scfh (57 to 570 kg/day)

- Achieve a lowest life cycle cost, namely a cost-effective balance between efficiency and durability
- Perform a lifetime assessment through modeling of stresses and accelerated aging of the fuel processor
- Demonstrate fuel processor durability by achieving 5,000 hrs and 250 cycles
- Verify performance of a 1,000 scfh fuel processor by a third party: Argonne National Laboratory
- Apply DFMA principles to guide cost comparisons and the ultimate mechanical specification of the hardware

2.1 Technical Barriers

This project addressed the following technical barriers to developing a natural gas (NG) fuel processing system from the Fuel Cell, section 3.4 and Hydrogen Production, section 3.1 of the Hydrogen, Fuel Cells and Infrastructure Technologies (HFC&IT) Program Multi-Year Research, Development and Demonstration Plan [1].

Fuel Cells (Section 3.4):

- 1) Fuel Processor Durability

Hydrogen Production (Section 3.1):

- (A) Reformer Capital Costs
- (B) Reformer Manufacturing
- (C) Operation and Maintenance (O&M)
- (D) Greenhouse Gas Emissions
- (E) Control and Safety

2.2 Approach

The objective of the CHARM program was to develop a modular steam reformer while maintaining balance between cost, efficiency, durability, manufacturability and environmental standards. A low pressure steam reformer was designed to address the widest range of applications with the lowest risk. The reformer was designed for long life, low capital cost in accord with DFM&A principles, high efficiency and it respects strict emissions regulations. The intent was to develop a steam reformer technology that was scalable from 500 to 10,000 scfh of hydrogen.

The most significant stigma associated with small-scale reformers is durability. Although industrial scale reformers have been in use for decades, they rarely see more than a few thermal cycles per year. In order for a small-scale fuel processor to survive frequent thermal cycles (perhaps daily), the stresses must be reduced significantly and interaction between creep, corrosion and cyclic fatigue must be minimized.

The fuel processor design philosophy incorporated the functional requirements, design of the reforming process, inputs from CFD and FEA modeling and DFM&A principles to influence the mechanical design, a stress & failure mode analysis, material selection, and a life-cycle cost analysis to arrive at the final detailed design.

Simultaneous progress on performance, lifetime, and cost requires a dedicated development and optimization program targeting the reformer/burner assembly specifically. To accomplish this, Nuvera executed the following tasks as described in the following list and in Table 2.

Task 1 – System Definition. The formal specifications for the reforming module were developed in a system context. Process and subcomponent models were created and used to conduct performance, durability, and cost tradeoff analyses. A key objective was to clarify the operating conditions of all subsystems with which the FP will be interfaced, including other reaction zones, heat exchangers, and fluid prime movers. This allowed determination of the boundary conditions and fixed the FP requirements. In addition, novel system concepts with focus on improved efficiency and emissions reduction are being explored.

Task 2 – Design & Analysis. Generation and evaluation of FP concepts took place in this task, with scalability being a foremost priority. Scalability is a central objective to defray development costs associated with new scales and applications conceived in the future. In parallel with 1,000 scfh system development, the conceptual design of a 10,000 scfh system was performed. The key question to ask: *What are the tradeoffs of capital and production costs with efficiency and durability?* Thorough analyses, supported by concept prototyping and subscale testing, informed a decision regarding module geometry and sizing. Heat flux and temperature distribution, as predicted using CFD and actual thermal profiling, were important tools for designing for longevity. Furthermore, a concept for a novel SR/Burner architecture relying on highly effective heat exchange was developed to improve fuel processor longevity and cyclability. DFM&A principles were applied to guide cost comparisons and the ultimate mechanical specification of the hardware.

Task 3 – Prototyping & Testing. A test stand was built that replicated the boundary conditions of the FP, including the thermal context and material inputs (as derived from system considerations) to both the reformer and burner. Prototyping was done with the intent of validating DFM&A objectives, and producing a reproducible FP test article amenable to development of Quality Assurance protocols. Testing involved determination of temperature and heat flux profiles throughout the reformer bed, within the segregating metal surface between reformer and burner, and within the burner itself. Reformer product composition and burner emissions were measured to tune process conditions over a range of throughput, and an operating map for the FP was developed. Amendments to the original SOPO include system assessment and microreactor testing of the novel desulfurization method(s), as well as implementation of the monolith based high temperature shift (HTS) and industrial burner controls.

Task 4 – System Demonstration. The system context for the FP was refined as the program progressed, and used as the durability test bed with the goal of proving robustness in extended running and cycling modes. Off-design conditions associated with system-consistent startups, dynamics, variable ambient conditions, and shutdowns were characterized to develop projections for performance in the field. A formal demonstration of a test stand containing the newly developed 1,000 scfh FP was conducted at Nuvera by a third party: Argonne National Laboratory.

Project Task	Program Milestones
1. System Definition	Define specifications & operating conditions
2. Design & Analysis	Complete subscale testing
	1000scfh fuel processor design & analysis (1 st generation)
	Develop advanced system concept to reduce operating cost by 10% or more while maintaining or reducing emissions profile
	Develop SR concept with optimized heat flux profile
3. Prototyping & Testing	1000scfh fuel processor testing & validation (1 st generation)
	1000scfh fuel processor testing & material validation (2 nd generation)
	Validate scalability via 10,000scfh (560 kg/day) FP conceptual design
	Implement monolith based HTS for fast start, easy packaging, reduced LCC
	Implement industrial burner control
	Assess NG desulfurization method based on hydrodesulfurization technology
4. System Validation	1000scfh subsystem validation by Argonne National Laboratory (ANL)
	Durability achievement: 5000hrs, 250cycles
5. Project Management	Final report & presentation to DOE

Table 2. List of CHARM tasks and milestones

Achieving these milestones required simultaneous iterative development in the following areas: System definition and modeling, Fuel processor design, Material selection, Catalyst development, Testing, Validation and Conceptual design of advanced system and fuel processor options, as shown in Figure 1. A detailed description of these activities is presented in the forthcoming sections of the report.

Figure 1. CHARM program flow chart

3 Task 1 – Hydrogen Generator System Definition

Nuvera's Hydrogen generator, PowerTap, is a fully integrated system designed to generate and dispense hydrogen fuel on-site. The current scale is geared towards material handling applications. The PowerTap system, combined with a fuel cell power module for forklift trucks and other industrial vehicles provides the Total Power Solution (TPS™) for the material handling market, where fuel cells are competing successfully with batteries today.

Generating hydrogen on-site solves an infrastructure problem, allows reduction of operating cost of the fuel cells, and increases the overall value proposition.

The heart of the system is a fuel processor assembly (FPA), which consists of the fuel processor, high temperature shift, fuel system, steam system, burner air system, heat exchangers and steam generators as well as some balance of plant hardware. In addition to FPA, the system includes a reformat compressor, a pressure swing absorption system, an electrically driven hydrogen compressor, a scalable cascade storage system and a dispensing system.

The scope of the PowerTap encompasses everything from reforming to Hydrogen refueling. The requirement specification for the PowerTap™ system is shown in Table 3.

Hydrogen Production Capacity	28 Nm3/hr (1,000 SCFH, 56.6 kg/day)
Purity	99.995% H ₂ , <1ppm CO
Hydrogen Dispense	350 Bar (5,000 psig)
Fuel Requirement	Natural Gas
Fill Time	2.5 kg H ₂ in < 5 minutes
System Design Life	10 years
Burner Emissions	NOx < 15 ppmv, CO < 30 ppmv
Product Certification	CSA, CE (pending)
Ambient Temperature Rating	-20°C to +40°C (-4°F to +104°F)

Table 3. Requirements specification for PowerTap Hydrogen generator.

Since there may be applications that do not require compression or storage, the product has been divided into two systems: Hydrogen Generation and Hydrogen Storage. Each of the blocks included in the simplified process flow schematic in Figure 2 represents a major subsystem. The CHARM fuel processor is utilized with the “fuel processor” block represented below. A complete PowerTap system, consisting of Generation system, Compression, Hydrogen Storage and Dispense, is shown in Figure 3.

Figure 2. Schematic of PowerTap Hydrogen generator

Figure 3. PowerTap Hydrogen generator.

3.1 Generation System Architecture

The Fuel Processor subsystem utilizes a natural gas steam reformer and burner technology to produce a hydrogen syn-gas (or reformat) stream from purified water pressurized to 200 psig and low pressure natural gas (< 5" H₂O) for use in the PowerTap on-site hydrogen generator, nominally 50 kg/day H₂ production rate, 99.995% H₂ purity.

The endothermic steam reforming reaction is driven via combustion of a range of gasses from natural gas to hydrogen rich syn-gas in the burner which is co-located in the same vessel with the steam reformer. The process of syn-gas production involves the following functions:

- Fuel desulfurization
- Water supply train
- Steam reforming reaction zone
- Water-gas shift reaction zone
- Fuel combustion zone
- In-process steam generation
- Two-phase steam control & conditioning
- Natural gas pressurization via steam/fuel ejector
- Steam/fuel superheat (pre-heat to the steam reformer)
- Induced draft air supply via blower
- Mixing of burner fuel and air
- Burner ignition device & monitoring
- Exhaust cooling

A simplified process diagram of the hydrogen generation system which includes the PowerTap fuel processor is shown in Figure 4.

Figure 4. Process diagram of the CHARM FP-based Generation system

The NG feed is split into two streams – one going to the process side (into the steam reformer catalyst tubes) to produce hydrogen, while the other is combusted in the burner on the shell side of the fuel processor, to provide the heat for the endothermic steam reforming reaction. The NG feed to the steam reformer is mixed with steam at a controlled steam-to-fuel ratio before entering the catalyst tubes in the reformer. The reformat from the reformer is cooled in the superheater (SH) before it enters the catalytic high temperature shift reactor to convert some of the remaining CO to CO₂ and H₂. Reformat from the HTS makes steam in the steam generator (SG2), and then it is further cooled in an air-cooled heat exchanger HX1.

The reformat stream from the HTS is compressed and processed in the pressure swing adsorption (PSA) unit, where the hydrogen gas is purified to the required product level. The remaining tail gas (raffinate) from the PSA, containing residual hydrogen and the other SR by-products (primarily CO, CO₂, CH₄, and some H₂) is sent to the burner to supply heat for the steam reforming reaction.

Most of the steam for the reforming reaction is generated in the steam generator (SG1), using the sensible heat in the combustion products leaving the FP burner. Additional steam is generated in SG2 using the heat in the reformat gas from the HTS. The steam pressure is used to draw in the NG feed for the process side in an ejector, with the reactant mixture emerging at a pressure of ~22 psig (2.5 bara) and a molar steam-to-carbon ratio of about 3.

Air for the FP burner is supplied by an induction blower. Hot products from the combustion of raffinate gas from the PSA and some additional natural gas maintain the required temperatures within the catalyst-loaded tubes, where the endothermic steam reforming reaction occurs. Sensible heat remaining in the burner gases leaving the FP unit is recovered in the boiler SG1. Hot exhaust gas is further cooled in an air-cooled heat exchanger HX3, before being vented.

The fuel processor was evaluated on the fuel processor test stand (FPTS). For simplification purposes, the FPTS doesn't include every component of the Generation system shown in Figure 3. For instance the PSA, PSA exhaust surge tank, reformat compressor and HX2 were not included into the test stand. In addition, to simulate raffinate return to the burner a portion of reformat after HX1 is redirected back to the burner via a separate line with a control valve and a flow meter. Reformer temperature in this mode of operation is controlled by adjusting supplemental NG flow to the burner, which represents a small fraction of the total burner heating value.

Other test equipment utilized during CHARM program included burner test stand for rapid cycling of the fuel processor and a steam generator. Performance evaluation of different catalysts (new and used) was performed in a micro-reactor setup in Nuvera's Chemical laboratory.

4 Task 2 – Design and Analysis

4.1 Task 2.1 – Fuel Processor Design

4.1.1 Design Philosophy

Steam reforming is a strongly endothermic reaction, often requiring temperatures exceeding 900 – 1000°C on the reformer walls. Standard practice for design of large industrial systems is a tubular steam reformer with catalyst inside many tubes that are surrounded by multi-stage and often “impingement” style burner module. These reformers are designed with thick walls and run continuously with very infrequent cycling. The burner fuel – air mixture is fired directly onto the reformer tubes. That creates localized hot spots on the tube’s metal surface leading to formation of local high stress points. As a result, creep, which is a gradual increase in plastic strain with time at constant load, is a dominant failure mechanism.

Unfortunately, for smaller scale Hydrogen generators, such as PowerTap, a practical reality is that the H₂ consumption profile can be somewhat irregular, necessitating a need for more frequent cycling. Depending on the application (material handling, automotive, etc.), weekly or even daily start – stop cycling might be dictated by economical or practical considerations.

The design methodology shown in Figure 5 was employed in designing the CHARM steam reformer.

Figure 5. Design process for the CHARM fuel processor.

The process started with market analysis including Quality Function Deployment (QFD) and Voice of the Customers (VOC) analysis that turned customer requirements into functional specifications. The design effort focused on evaluation of several concepts and on subscale testing of the best two options. Based on preliminary modeling and on subscale testing results, the current fuel processor architecture was chosen. In order to achieve the stringent durability goals of the CHARM program, the fuel processor was designed as a low pressure steam reformer with unconstrained SR tubes. Nuvera's design seeks to minimize mechanical and thermal stress, both during operation as well as during transients. However, while phenomena of creep, corrosion and cyclic fatigue interaction have been mitigated, they have not been eliminated. When cycled, thermal stress due to local hot spots and resulting plastic deformation at operating temperatures will cause stress in metal when cooled off. Each heat cycle can result in a finite amount of plastic strain and consequent fatigue failure in relatively small number of cycles.

To address the problem, extensive analyses of temperature mapping of the metal tubes as well as detailed modeling of stresses were performed for several reformer design configurations. In tandem, various material options have been studied extensively with emphasis on life cycle cost minimization.

The schematic of the process and electrical interfaces for the fuel processor is presented in Figure 6.

Figure 6. Schematic of Fuel Processing Assembly Subsystem Process & Electrical Interface

4.1.2 Process Model

Aspen Plus™ process modeling software was used for design and optimization of the PowerTap fuel processor. Because the reformer design is flexible enough to afford operation in either co-flow or counter-flow configurations, two independent steady state Aspen process models were generated to model the inherent differences between two configurations for the PowerTap hydrogen generation system. Both models were later calibrated with the actual test data from two systems: a lab based fuel processor and a full hydrogen refueling station that supplies hydrogen for Nuvera fuel cell testing needs. A screenshot of the Aspen process model is shown in Figure 7.

Figure 7. Aspen process model of the CHARM fuel processor subsystem

Key process model assumptions are:

1. Burner: Gibbs reactor assuming complete combustion and perfect mixing.
2. Steam Reformer: Gibbs reactor to chemical equilibrium, with a design specification to vary burner fuel flow rate to achieve desired reaction conversion (calibrated with experimental data)
3. Burner - Steam Reformer heat exchange: heat transfer block with temperature approach specification
4. HTS: adiabatic equilibrium reactor
5. Heat exchangers: all fixed UA, other than steam generators, which use fixed temperature approach to the steam temperature, based on steam saturation pressure.

Fuel processor design started with optimization of global design parameters in the fuel processor, such as steam reformer operating pressure and selection of the flow configuration in the burner – SR heat exchanger.

4.1.3 SR Operating Pressure

Reformer pressure is an important optimization parameter for Hydrogen generator system design. Specification of the PSA unit used in the PowerTap system calls for 10 bara feed pressure. Upstream compression of SR feed gas minimizes parasitic power (compression of natural gas only, as steam pressure is maintained by the feed water pump) and consequently reduces operating cost. Unfortunately, SR operation at high pressure requires high reforming temperatures due to unfavorable steam reforming reaction equilibrium, resulting in added capital and/or maintenance costs. The alternative option of operating the steam reformer at low pressure requires subsequent compression of the reformat stream. The operating cost is increased due to high hydrogen content and high volumetric flow and consequently higher cost of reformat compression. Yet favorable SR reaction kinetics and equilibrium afford lower reaction temperatures and consequently results in the lower capital cost of the fuel processor.

A trade off analysis between capital and operating costs was performed by evaluating overall cost impact on the basis of maintaining constant stress levels in the reformer tubes at different reformer pressures and corresponding temperatures by varying reformer metal thickness. The analyses were performed at different pressures in the range from ambient to 10 bara, as required for the PSA. The normalized results of the study are shown in Figure 8.

Figure 8. Trade off analysis of the capital and operating costs for optimization of the FP operating pressure

As indicated by the analysis, a reduction of the operating cost at higher pressure is offset by the increase in material cost. The optimal operating pressure was found to be in the range of 2 – 3 bara. In addition, such range of operating pressures is suitable for the design of the fuel ejector, where steam pressure is used to draw natural gas in, thus eliminating a need for a fuel pump. As a result, a steam reformer operating pressure of 2.5 bara (~22 psig) was adopted, which should represent the lowest life cycle cost.

4.1.4 Flow Configuration Selection

The key difference between co-flow and counter-flow operation on the system level is that in co-flow operation burner exhaust temperature pinches to the SR outlet temperature, which must be relatively high for good fuel conversion. Alternatively in counter-flow operation, burner exhaust temperature pinches to a much cooler SR inlet temperature. Every other effect cascades from the difference in burner exhaust pinch temperature conditions.

In the original design configuration, shown in Figure 9, flow directions of the hot combustion gas and the SR flow in the catalyst bed are opposite, hence called “counter-flow”.

Figure 9. Flow direction in counter-flow reformer configuration.

In heat exchange terms, counter-flow is a preferred arrangement due to the most favorable temperature profile, where hot sides and cold sides of the two streams are aligned. Thus the amount of heat transferred into the reforming bed is maximized, resulting in the least amount of burner fuel required to drive the SR reaction. However, since the steam reforming reaction, a strong endothermic process, occurs throughout the catalyst bed, the SR fuel becomes depleted as it flows through the bed and approaches the cap. As a result, methane concentration is the lowest near the tube cap, and the SR reaction absorbs less heat exactly where the temperature is the highest due to the direct contact of the cap with flames and hot combustion gas as well as exposure to strong radiation from hot burner gas and hot surroundings. This creates an inefficient cooling environment for the SR tube/cap and thus may result in high metal temperature and a potential failure point.

In contrast, reversing the SR flow direction, as shown in Figure 10, produces a different methane profile in the catalyst bed, especially inside the cap. It is expected that the high methane concentration in the co-flow case would allow a more active reforming reaction inside the cap, potentially resulting in lower bed and metal temperature, albeit at expense of diminished overall heat transfer from the burner and system efficiency.

Figure 10. Flow direction in co-flow reformer configuration.

Furthermore, steam generation in the system is linked to burner exhaust temperature and burner exhaust flow. For a fixed steam flow (or Q into the steam), co-flow operation will always need less exhaust flow or will have higher steam production than counter flow operation because the burner exhaust gas temperature in the reformer outlet will always be greater in co-flow. An undesirable side effect of this is more exhaust energy is shifted into steam generation as opposed to supporting the steam reforming reaction, where it is needed most, typically resulting in an increased burner thermal input to compensate. Consequently it is expected that the main advantage of the counter-flow configuration is higher efficiency. However in theory, co-flow might offer lower peak temperature in the fuel processor because the highest burner temperature will correspond to the lowest SR bed temperature, thus resulting in more efficient heat dissipation (largest possible heat sink) in the hottest zone of the reformer.

CFD model results of the co-flow and counter-flow configurations are presented in Figure 11.

Figure 11. Peak metal temperatures for co-flow and counter-flow configurations as predicted by CFD modeling

These initial results were obtained assuming the exact same boundary conditions and flow specifications for two flow configurations. These assumptions are very conservative and assume the worst case scenario. Thus the model was expected to overpredict the actual peak temperatures. Given model assumptions co-flow operation was expected to reduce peak metal temperature by approximately 150 °C and therefore offset any efficiency penalties by significant increase of reformer life and consequent savings in maintenance cost.

4.2 Task 2.2 – Materials Selection

The CHARM fuel processor consists of steam reforming tubes, a burner or combustion chamber and the outer core assembly consisting of pre-heaters and outer weight bearing structure. The mechanical design philosophy was to keep stresses as low as possible in order to eliminate the need for expensive expansion joints and enable the use of commonly available materials. This was achieved by using relatively small diameter steam reforming tubes, for low hoop stress, in a free floating configuration that allows for unrestricted thermal expansion. The CHARM fuel processor specification calls for 40,000 hours and 1000 cycles design life.

Known failure modes for the fuel processor metals are outlined below:

Creep: is a gradual increase in plastic strain with time at constant load, and is the primary failure mode encountered in Industrial steam reforming plants. Steam reforming tubes are typically designed for 100,000 hour creep life, though many SR tubes last much longer than that.

Thermo-Mechanical Fatigue: is a series of progressive inelastic deformations due to cyclical thermal stresses. This mode is usually not a problem for industrial steam reforming tubes as they typically see only a couple of cycles a year or 20 to 50 cycles over their service life. This is in stark contrast to the daily cycling requirement of the CHARM fuel processor.

Creep-Fatigue Interaction: at elevated temperatures creep causes creation of voids or cracks in metal over time. Once the crack is initiated, thermal cycling quickly leads to fatigue failure. Thus, thermal cycles are more injurious to SR tube life after significant run time at elevated temp (once voids have formed). This interaction is not well understood and very limited material data is available on high temperature creep-fatigue interaction.

High temperature corrosion: the outer surface (burner side) of steam reforming tubes is exposed to an oxidizing environment while the inner surface (steam reforming side) is exposed to a reducing environment containing natural gas, hydrogen and CO. Corrosion is addressed by selecting material suitable for the operating environment and adding corrosion allowance on top of design thickness.

Hydrogen embrittlement: a form of environmentally assisted failure that results from the combined action of hydrogen and residual or applied stress. The pressure theory attributes hydrogen embrittlement to the diffusion of atomic hydrogen into metal and its accumulation at internal defects like voids etc. As the concentration of hydrogen increases at these micro structural discontinuities, a high internal pressure is created. This pressure added to the applied stress thus lowers the apparent fracture stress. The Hydrogen Enhanced Localized Plasticity (HELP) theory of hydrogen embrittlement proposes that atomic hydrogen enhances dislocation motion and the creation of dislocations at internal surfaces and crack tips, leading to softening of the material on a localized scale. High resolution electron microscopy of intergranular fracture surfaces reveals evidence of crack tip plasticity in support of this mechanism.

Several factors determine the degree of hydrogen embrittlement of various alloys, key among them are: material composition, microstructure, heat treatment, specific hydrogen environment, hydrogen pressure, purity, temperature, deformation rate, notch sensitivity and exposure time.

The first two proof-of-concept fuel processor prototypes were built entirely from 316SS. However due to refinement of initial models and early indication of high metal temperatures during first weeks of testing a need for more advanced materials became clear.

4.2.1 Design for Creep

Due to its low cost, good corrosion resistance, and strength at elevated temperatures, 310 stainless steel was chosen as the material of construction for SR tubes. 310 SS is the wrought equivalent of the cast alloy HK-40 typically used in industrial steam reforming tubes. The tube dimensions were chosen to keep the hoop stress below the 40,000 hour creep rupture stress. Fluent™ CFD models were created to generate the SR tube temperature profile for co-flow and counter flow burner operation. The CFD models predicted hot spots due to flame impingement near the SR tube caps. Due to its higher creep rupture strength, the relatively inexpensive super alloy Inconel 625 was chosen as the SR cap material. The ASME Sec VIII boiler and pressure vessel code rates Inconel 625 grade 2 up to 1600°F. The steam reformer cap dimensions were chosen to keep stresses significantly lower than the ASME allowable values.

The creep failure mode was addressed by keeping the principal stress (considered proprietary) due to pressure well below the stress value corresponding to 40,000 hour creep rupture. This was achieved by a combination of low operating pressure, SR tube dimensions and architecture and material selection.

In fact the design intent was to keep the principal stresses so low that there should be minimal creep occurring over the first 40,000 hours, thus eliminating possibility of void formation and creep-fatigue interaction.

Figure 12 and Figure 13 show the Larson Miller (LM) parameter for Inconel 625 and 310SS respectively. The Larson–Miller parameter (LMP) allows prediction of time to rupture under given temperature and stress levels.

The following graph enables determination of the mean stress resulting in fracture as a function of the Larson-Miller parameter. The parameter combines temperature and time in accordance with the formula $X = [20 + \log(t)] \times T/1000$.

Figure 12. Larson-Miller Parameter for Inconel 625 (SI units: T in Kelvin, t in hours) [17].

Larson-Miller parameter = $T/1000 (20 + \log t)$ where T is temperature in °R and t is time in h. All data taken from 1000-h tests.

Figure 13. Larson-Miller Parameter for 310 stainless steel. (British units) [13].

Two major conclusions of these charts are:

1. Achieving thousands of hours FP life will require very low stress design;
2. Material physical properties for expected PowerTap operating conditions such as high temperatures and uncharacteristically low stress (SR operating pressure is very low compared to a typical pressure in the industrial reformers) are not readily available.

Nuvera's design approach is somewhat unconventional as it is operating at only 2.5 bara (in contrast industrial reformers typically operate as high as 25 bar or higher [20]), resulting in significantly reduced stress levels in the reformer tubes. Consequently creep data for typical materials is not available at such low stress values, since such data was first generated for aircraft turbine applications and is currently used for the design of industrial plants, both having much higher hoop stress values, compared to the PowerTap reformer. Thus the biggest uncertainty in the fuel processor design for durability and consequent life assessment has to do with an interpretation of the available materials data and a need to extrapolate it for the expected design conditions. For the PowerTap fuel processor, operating at much lower level of hoop stress, compared to the published data, determination of the creep life requires extrapolation of the materials LM data.

Inconel 625 LM data in Figure 12 was used to make prediction of rupture time as a function of metal temperatures as shown in Table 4.

Operating Pressure Hoop Stress Larson-Miller Parameter		psia ksi	37 Proprietary 29
Temperature		Rupture Time	
°C	K	hours	
850	1123.0	666,325.7	
875	1148.0	182,525.7	
900	1173.0	52,836.3	
925	1198.0	16,106.9	
950	1223.0	5,154.5	
975	1248.0	1,726.6	
1000	1273.0	603.7	
1025	1298.0	219.8	
1050	1323.0	83.2	
1075	1348.0	32.6	
1100	1373.0	13.2	

Table 4. Estimate of Inconel 625 rupture time vs. temperature using Larson-Miller parameter

Although the highest value of the LM parameter for Inconel 625 in Figure 12 corresponds to a stress value of 20 MPa (2.9 ksi), which is significantly higher than the stress in the PowerTap's reformer tubes, it was used here to bracket the analysis. In this example, design with 20 MPa hoop stress value will fail due to creep after 52,836 hours of operation at 900°C.

The same LM method was used to obtain desired values of Larson-Miller parameter and peak metal temperature corresponding to 40,000 hours life of the PowerTap fuel processor. If the stress vs. LMP function in Figure 12 was extended it would be possible to find a new combination of the maximum metal temperatures and LM parameters resulting in a 40,000 hours creep life. Results of such analysis using extrapolated values of stress vs. LMP for Inconel 625 are presented in Figure 14.

Figure 14. Maximum metal temperatures vs. extrapolated LMP for Inconel 625 corresponding to a creep failure at 40,000 hours.

Exponential extrapolation of the Stress vs. LMP function shown in Figure 12 was used to generate the data. In this case of a constant $t = 40,000$ hours, any point on the line will satisfy a 40,000 hours life due to creep. In other words, for a given value of LM parameter, peak metal temperatures must not exceed the value given by the line in Figure 14. The current fuel processor design has such low hoop stress magnitude that any reasonable extrapolation of Inconel data shown in Figure 12 will predict creep life of well over 40,000 hours with metal temperatures possibly above 1000°C. Therefore during the initial design the team had good confidence that creep was not a problem for either co-flow or counter-flow configurations, despite expected high peak metal temperatures.

4.2.2 Design for Fatigue

While creep was determined to not cause a problem for a 40,000 hours FP life target, the fatigue is a different issue. The fatigue life is a function of the thermal stress amplitude in the SR tubes. The hot spots on SR caps due to flame impingement cause high thermal stresses. Frequent cycling along with very high thermal stress amplitude can cause inelastic deformations leading to failure within a few thermal cycles. There is limited material fatigue data available for metals at high temperatures (above 1600 °F) and steam reforming environments. Inconel 625 was chosen as SR Cap material due to its fatigue strength at elevated temperatures.

Life prediction based on fatigue and creep-fatigue interaction failure modes requires knowledge of thermal stresses and/or strains in the part that is being designed or analyzed. Coupling of CFD-FEA software packages has proven to be an extremely useful tool, especially for cycling operation. Nuvera worked closely with a manufacturer of FEA software to develop a coupling method. The approach was to transfer reformer tubes boundary conditions: loads, surface temperature, heat flux, pressure, etc., provided by CFD into an FEA model, as shown in Figure 15.

Figure 15. Coupled CFD – FEA model for fuel processor life prediction.

A detailed thermal stress investigation of the reformer tubes was performed using GEOSTARTM FEA package. The thermal profile for the FEA was imported from the FluentTM CFD analysis. High temperature excursions due to flame impingement resulted in elevated thermal stresses in the SR cap in both flow arrangements. However, compared to counter flow mode, the co-flow SR mode predicted 25% lower stresses due to lower peak metal temperatures by as much as 150°C, as shown in Figure 16.

Figure 16. Results of coupled FluentTM - GeoStarTM FEA for two flow arrangements.

Results of the FEA were compared against material property curves to ensure that stresses were below the creep rupture and fatigue stress limits. During the initial design effort thermal stress values for fatigue analysis were estimated at about 60 ksi for the counter-flow and 45 ksi for the co-flow operation. Given such stress levels at predicted temperatures, co-flow was expected to last for 1,000 cycles, while counter-flow fell just short of the target and will therefore require two SR core replacements (a total of three SR tube bundles) during 10 years or 80,000 hours of operation, compared to just one replacement with co-flow.

Ductility which is an extent to which materials can be deformed plastically without fracture is another important property that must be taken into consideration. Though Inconel 625 does undergo loss in ductility between 1100°F to 1500°F, it regains ductility above 1600°F, Figure 17.

Figure 17. Impact of long term exposure to elevated temperatures on Inconel 625 ductility [14].

The steady state SR cap operating temperatures are above 1600°F, thus no significant loss of metal ductility is anticipated for most of the fuel processor's operation time. Metal does go through this transition during start ups and shut downs, however only a long term exposure in this low ductility range is important for metal durability.

4.2.3 Oxidation Resistance

The material used for the SR tubes is 310 SS, and the SR caps are made of Inconel 625. Both 310SS and Inconel 625 have very good high temperature oxidation resistance and exhibit good resistance to reducing environments found inside the SR beds, as shown in Table 5 and Table 6.

According to data from Hynes International shown in Table 5, the expected metal thinning on the SR caps and tubes due to corrosion is approximately 18 micrometers (at 980°C) per 1000 hrs of exposure to an oxidizing environment (such as the burner). The total metal loss for the SR caps and tubes after 40,000 hours is then approximately 0.72 mm (0.028"). Such amount of metal loss indicates that 40,000 hours life should easily be achievable.

Material	Average Metal Affected**							
	1800°F (980°C)		2000°F (1095°C)		2100°F (1150°C)		2200°F (1205°C)	
	mils	µm	mils	µm	mils	µm	mils	µm
HAYNES 214 alloy	0.2	5	0.1	3	0.3	8	0.7	18
HAYNES 230 alloy	0.7	18	1.3	33	3.4	86	7.9	201
HASTELLOY alloy S	0.5	13	1.3	33	1.7	43	>31.7	>805
HAYNES alloy 188	0.6	15	1.3	33	8.0	203	>21.7	>551
Alloy 600	0.9	23	1.6	41	2.9	74	8.4	213
Alloy 617	1.3	33	1.8	46	3.4	86	12.5	318
Type 310 stainless	1.1	28	2.3	58	4.4	112	10.3	262
HAYNES 556 alloy	1.1	28	2.6	66	11.6	295	>150.0	>3810
Alloy 601	1.3	33	2.6	66	5.3	135	7.5*	191*
HASTELLOY alloy X	0.9	23	2.7	69	5.8	147	>35.4	>899
HAYNES alloy 150	1.0	25	3.8	97	>26.8	>681	>46.1	>1171
Alloy 625	0.7	18	4.8	122	18.2	462	>47.6	>1209
RA330 alloy	4.3	109	6.7	170	8.7	221	-	-
Alloy 800H	1.8	46	7.4	188	8.9	226	13.6	345
HAYNES HR-120 alloy	3.7	94	7.7	196	16.3	414	25.3	643
253MA* alloy	2.9	74	8.2	208	16.4	417	29.2	742
HAYNES alloy 25	0.7	18	10.2	259	19.2	488	>37.9	>963
HAYNES HR-160 alloy	5.9	150	10.3	262	13.0	330	24.2	615
MULTIMET alloy	1.3	33	11.6	295	>47.2	>1199	>146.4	>3719
800HT* alloy	3.8	97	12.0	305	18.8	478	>58.0	>1473
Type 446 stainless	2.3	58	14.5	368	>21.7	>551	>23.3	>592
Type 304 stainless	8.1	206	>27.1	>688	>23.6	>599	>63.0	>1727
Type 316 stainless	14.3	363	>68.4	>1737	>105.0	>2667	>140.4	>3566

Table 5. Oxidation in flowing air at elevated temperatures over 1008 hours. Samples were cycled to room temperature once a week [15].

Material	Carbon Absorption During Exposure (mg/cm ²)			
	1600°F (870°C) 215 Hours	1700°F (925°C) 215 Hours	1800°F (980°C) 55 Hours	2000°F (1095°C) 24 Hours
HAYNES® 214™ alloy	0.1	0.3	0.6	3.4
Alloy 800H	0.5	1.0	1.0	12.6
HAYNES 556™ alloy	0.4	1.0	1.3	14.0
HAYNES 6B alloy	0.2	0.8	1.5	-
Alloy 671	-	-	1.9	-
HASTELLOY® S alloy	0.3	1.6	2.1	10.6
HAYNES 230® alloy	0.4	2.0	2.5	10.3
HASTELLOY X alloy	0.5	1.8	2.5	10.6
HAYNES 188 alloy	0.5	1.1	2.7	8.6
Alloy 600	0.4	1.3	2.8	9.9
Type 310 Stainless	2.4	6.4	3.3	-
HAYNES 25 alloy	0.1	0.9	4.5	14.4
Alloy 601	-	1.8	4.8	11.5
Alloy 617	0.3	2.4	5.0	-
HAYNES 625 alloy	0.3	1.1	5.3	9.9
HASTELLOY N alloy	0.1	-	5.4	-
HAYNES 150 alloy	-	-	8.1	-

Table 6. Resistance of alloys exposed to mixture of hydrogen, methane and carbon monoxide gases [16].

4.2.4 Hydrogen Embrittlement

With respect to hydrogen embrittlement, Nuvera conducted an extensive literature search on hydrogen embrittlement of Inconel 625, references [8], [9], [10] and [11]. Unfortunately, almost no hydrogen embrittlement data under steam reforming conditions is available for either Inconel 625 or 310SS. In absence of material data, comparison of factors effecting hydrogen embrittlement to SR operating conditions indicates that Inconel 625 should not be significantly affected. The low operating pressure, high metal temperature, low purity hydrogen and presence of inhibitors like CO in the SR reformat are all unfavorable to hydrogen embrittlement. The issue was discussed with several metal experts at Inconel alloys manufacturing companies including Haynes International, VDM Krupp, and Nickel Institute. All the parties involved are of the opinion that Inconel 625 should not undergo hydrogen embrittlement under PowerTap operating conditions.

In order to address hydrogen embrittlement and other durability concerns, a steam reformer, FP1R, having a suite of various Inconel alloys was built and tested under the CHARM program. The data generated during PowerTap FP1R steam reformer durability testing is expected to contribute significantly in measuring impact of hydrogen embrittlement on various alloys and in SR tube material selection.

To summarize, the initial design and analysis of the FP concluded that the steam reformer tube bundle made of 310 stainless steel tubes and Inconel 625 caps:

- Will perform adequately with respect to all known failure mechanisms
- Fatigue and creep – fatigue interaction are key to the FP durability and life
- The design keeps hoop stress below the **40,000** hours creep life threshold in both flow configurations
- Co-flow FP is projected to meet a 1,000 cycles target, while counter-flow will require one extra replacement of the SR tubular core during 80,000 hours system life.

4.2.5 Fuel Processor Life Cycle Cost Analysis

Although extremely important, fuel processor durability alone does not guarantee the lowest cost of ownership to the customer. It is necessary to find a commercially acceptable balance between fuel processor capital cost, efficiency and operating cost, and durability and maintenance costs, in the development of a system with the best value proposition.

The life cycle cost analysis drove the fuel processor design optimization as it allowed evaluation of all of the above mentioned cost contributors in tandem.

The reformer Life Cycle Cost over a 10 year product life was defined as:

$$\text{\$/kg H}_2 \text{ Life Cycle Cost} = \text{\$/kg Capital Cost} + \text{\$/kg Operating Cost} + \text{\$/kg Maintenance}$$

Lower $\text{\$/kg H}_2$ life cycle cost represents a lower cost of ownership to the customer. Here the Life Cycle Cost, Capital and Maintenance costs refer to the cost of the FP metal only. Some aspects of the LCC trade off were considered during the initial design phase, while optimizing SR operating pressure, as described in Chapter 4. Therefore this study focused on the other system characteristics. Operating cost for the analysis took into account the difference in system efficiency for co-flow and counter-flow configurations at fixed operating pressure and also included the cost of hydrogen compression. Installation cost was not included in the reformer life cycle cost analysis, as installation cost is a function of the Hydrogen Generation system and is not affected by the reformer specifics. Maintenance cost included spare parts, labor, shipping and scrapping costs.

As followed from above, CFD analysis of the CHARM reformer indicated significantly lower metal temperatures in co-flow SR operation. Lower metal temperatures imply less stress and longer reformer life or in other words fewer reformer replacements over the 10 year product life. The study was conducted focusing primarily on impact of material selection (310 stainless steel vs. Inconel alloys) and operating mode (co-flow vs. counter-flow) on life cycle cost.

Table 7 below summarizes normalized values of lifecycle costs for different operating and tube cap material configurations. Inconel 600 alloy was also considered, but based on preliminary evaluation its LCC was expected to fall between 310 stainless steel and Inconel 625 and therefore it was not included into the detailed study.

Cap Material	Mode of Operation	SR Core Replacements	Normalized LCC
310SS	Co-Flow	3	1.14
310SS	Counter-Flow	5	1.26
Inconel 625	Co-Flow	1	1.00
Inconel 625	Counter-Flow	2	1.05

Table 7. Normalized Life Cycle Cost analysis results for various materials and flow configuration.

The analysis demonstrated that Inconel cap material for both SR operating modes in question had lower life cycle cost indicating that the overall value proposition was more strongly affected by reformer

durability due to lower maintenance and replacement cost. Efficiency or operating cost represented a secondary effect in the fuel processor cost of ownership.

Despite higher initial capital cost, a reformer with Inconel 625 caps required far fewer SR tube bundle replacements and consequently had better value proposition, compared to the all stainless steel option. Furthermore, co-flow configuration offered LCC advantages due to more manageable temperature and stress profiles. It was expected that Inconel 625 co-flow option would last 40,000 hours, while its counter-flow alternative fell just short of the target. Efficiency benefit of the counter-flow operation didn't fully offset additional cost of the extra SR core replacement. As a result, Inconel 625 in co-flow configuration was recommended for going forward.

In this analysis it was assumed that only replacements of the SR tubular core were needed, while keeping the same outer core assembly and the burner for the entire life of the system. Replacing the entire fuel processor would make the relative life cycle cost of stainless steel options even worse due to higher replacement frequency.

4.3 Task 2.3 – Catalyst Development

Large scale industrial steam reformers for H₂ generation usually have very few cycles of start-up and shutdown (2-4 times/years). When the start-ups and shutdowns are carried out, very conservative steps like small temperature ramp rates, reduction by H₂ and purging by nitrogen, are taken to enable long durability for both SR catalyst and SR tubes. However, the reformer design and requirements of the PowerTap system, are different from that of industrial steam reformers in some aspects like much smaller size of SR tubes, and frequent startup and shutdown cycles (sometimes daily). This combination of characteristics of the PowerTap reformer makes the operations with the desired durability very challenging. Through a series of literature searches and studies, consultations with experts in the field and internal R&D work, gradual technical improvements on catalysts, especially on SR catalyst *via* collaboration with catalyst suppliers, extensive testing at both micro-reactor systems and full scale PowerTap reformers, a cost effective suite of catalysts were adopted. The catalysts include steam reforming (SR), high temperature shift (HTS) and desulfurization materials (De-S). Despite the good progress seen in the catalyst development during the CHARM program, some problems still exist, especially with catalyst durability, as will be explained in the consequent sections of this report. The performance, current status, existing issues and the proposed solutions are discussed as follows.

4.3.1 Steam Reforming Catalyst

Because of limited space due to a small tube diameter, the large wagon wheel shaped SR catalyst widely used in large scale reformer, as shown in Figure 18(a), could not be used in the CHARM fuel processor. Only small size pellets were considered. During the CHARM program Nuvera went through three generations of steam reforming catalysts:

1. The first generation catalyst, referred to as **Catalyst 1** or SR1, despite having high SR activity, it had weak hydrothermal stability and low crush strength, due to an un-optimized catalyst/support combination.
2. **Catalyst 2** (SR2) was very similar in properties to Catalyst 1, but it had a spherical shape and smaller dimensions, more appropriate for PowerTap steam reformer architecture. Unfortunately, like the predecessor it had low hydrothermal stability and crush strength, resulting in easy catalyst cracking and dusting, as shown in Figure 18(b).
3. The newly developed SR catalyst, **Catalyst 3** (SR3), shown in Figure 18(c) not only maintains high SR activity but also improves in hydrothermal stability, anti-coking, crush strength and it is shaped as cylindrical tablets. According to the manufacturer, the promoter in Catalyst 3 increases the preferred calcium aluminate phase: Ca-6Al₂O₄ (Hibonite) resulting in improved mechanical strength and anti-coking properties.

Figure 18. Pictures of SR catalysts: (a) Wagon wheel shaped SR catalyst used for large scale industrial reformers; (b) Partially crushed spherical SR Catalyst 2; (c) Adopted SR Catalyst 3.

The comparison of the currently adopted and previous generations of SR catalysts in reforming activity, hydrothermal stability and Hibonite formation is shown in Figure 19, Figure 20 and Figure 21 respectively.

Figure 19. SR activity comparison for three generations of PowerTap steam reforming catalysts. (a): Methane conversion; (b) Product distribution.

Figure 20. Comparison of relative rates of methane steam reforming at 538 °C after continuous high temperature steaming for Catalyst 1 and Catalyst 3 tablets.

Figure 21. Comparison of Hibonite formation in three SR catalysts.

Even though most of the system operation time is spent in steady state mode, in Nuvera's experience most damage to the catalyst occurs during startup and shutdown. Thus there is room for improvement in terms of startup and shutdown procedures and some design changes of the reformer are needed to reduce the risk of SR catalyst crushing. Unfortunately powder formation cannot completely be avoided with the pellet based catalyst.

In order to eliminate the root cause of the powder formation and enhance SR performance, Nuvera has in parallel been advancing the technology of metallic heat exchanger-coated SR catalyst (MHXCSR) that can potentially be used in the future generations of the PowerTap reformer. A corrugated metallic foil washcoated catalyst with donut shape, as shown in Figure 22, is one potential candidate that could be used in future fuel processor designs.

Figure 22. Corrugated FeCrAlloy foil-washcoated catalyst concept.

The SR reactor based on the new MHXCSR technology might offer the following advantages over the conventional reactors:

- Minimal catalyst loading
- Smaller size
- Smaller pressure drop
- Faster dynamic response
- Better shock and vibration resistance
- Lower operating temperature
- Smaller local temperature gradient
- Longer life

Performance of a methane SR reactor based on metallic foil washcoated catalyst is shown in Figure 23, Excellent SR performance has been demonstrated at $WGHSV = 10,000 \text{ hr}^{-1}$ that is approximately five times that of space velocity currently used in PowerTap reformer. A more straightforward comparison between the MHXCSR catalyst and pellet/tablet catalyst is shown in Figure 24, which indicates that advantages of metallic substrate washcoated catalysts over pellet-based catalysts are obvious from a kinetic point of view, the catalyst bed volume of MHXCSR catalyst can be reduced to only 10% to 20% of pellet-based catalyst while retaining the same kinetic performance. After several hundred hours durability test at micro-reactors with about 30 start-up and shutdown cycles no peel-off catalyst loss from the substrate of washcoated SR catalyst was observed. However, such technology is still considered a high risk and further evaluation in full scale system is necessary before it could be implemented in the actual product offering.

Figure 23. Summary of methane SR at $10,000 \text{ h}^{-1}$ and $S/C = 4$ using MHXCSR catalysts

Figure 24. Comparison of SR performance between MHXCSR catalyst and pellet-based SR Catalyst 3

4.3.2 High Temperature Shift

The burner and steam reformer in the system are coupled in two ways. First, the burner supplies energy for a highly endothermic steam reforming reaction. Second, energy in the PSA exhaust (raffinate) containing mainly unutilized hydrogen, unreformed methane and CO is sent directly into the burner. If there is too much energy in the PSA raffinate sent to the burner (in other words more energy than is required for SR reaction), as is the case for poor reformer performance with high CH₄ or high CO, the system is not in energy balance, leading to loss of control and to higher than desired temperatures in the reformer.

The water-gas-shift (WGS) reactor, also called high temperature shift or HTS, mitigates both problems. By converting a large fraction of CO available in SR exit into CO₂ and Hydrogen, it reduces burner raffinate energy content. In addition, since the burner energy content is reduced, some burden is taken off the steam reformer by affording it to run with higher methane slip and consequently at lower temperature. The result: both system efficiency and durability are improved.

Three generations of HTS catalysts have been used for the PowerTap reformers. The first generation of HTS was HTS 1, a very mature commercial catalyst widely used by large scale industrial reformers. Later during the course of the program Nuvera adopted a different HTS2 catalyst, based on the catalyst supplier's claim of better durability. In addition, HTS 2 is superior to HTS 1 with respect to thermal cycling and pressure drop. Manufacturer's life time projection of HTS 1 vs. HTS 2 is shown in Figure 25.

Figure 25. Comparison of HTS performance between HTS1 and HTS2

For the first 1,100 hours the latest generation fuel processor was tested with HTS2 shift catalyst. However the primary weakness of the pelleted based HTS reactor is a large mass, volume and consequently a long start-up time. In order to overcome the problem, a third generation HTS3 was adopted by Nuvera. It is a precious metal (PM) based catalyst washcoated on ceramic monolith. This catalyst was validated in micro-reactor testing and it demonstrated excellent durability over 1,500 hours. No CO conversion decrease was observed, despite several unexpected test stand shutdowns. For the entire durability test duration the catalyst performance did not deteriorate and CO conversion at 380 °C followed water gas shift reaction equilibrium line, as shown in Figure 26.

Figure 26. Results of 1,500 hours micro-reactor durability testing of PM-based HTS3 catalyst washcoated on ceramic monolith.

The monolithic HTS3 catalyst reduces the catalyst volume and heating mass. Therefore, the heating time for HTS bed and the overall startup time for the reformer are significantly shortened. After 5,000 hours of testing, this catalyst is showing sign of deactivation, likely because of negative impact from the upstream of SR bed and some problems mentioned above.

4.3.3 Desulfurization of Natural Gas

The adsorption approach to desulfurization depends on the sulfur concentration and speciation in the natural gas. Natural gas composition varies by region and locality due to differences in natural gas source, processing and the choice of sulfur odorants. Before introduction to the natural gas pipeline, natural gas from the ground is processed to meet limits on hydrogen sulfide, water, hydrocarbon condensibles, energy content, and inert gases (carbon dioxide and nitrogen).

From a system stand point, the easiest for implementation sulfur removal approach for fuel processors would incorporate the use of ambient temperature adsorbents. Historically, both activated carbon and a wide variety of zeolites have been utilized to perform ambient temperature desulfurization. Unfortunately these products are limited in both overall sulfur capacity (capacity limitations lead to large beds and frequent change-outs) and specific sulfur species adsorption (not very selective). Activated carbon performs poorly with respect to inorganic sulfur compounds like H_2S and COS but easily trap higher hydrocarbons like benzene. Therefore, spent activated carbon can possibly be classified as “hazardous waste”.

The first generation of desulfurization material for PowerTap reformer was zeolite-based, which was abandoned due to drawbacks mentioned above. The current approach is to use a new set of materials based

on transition metal oxides. In comparison to the zeolite-based desulfurization, new method has the following characteristics:

- Base metal oxides-based
- High sulfur capacity
- Low maintenance
- Not sensitive to moisture
- Minimal HC's adsorption
- No adsorption/absorption of benzene and higher hydrocarbons (safer disposal)
- Recyclable and regenerable
- Visual indication when replacement needed

The main objectives for proposing a new desulfurization method were to:

- Enhance *chemisorption* of sulfur compounds on active centers of the adsorbent/catalyst
- Restrain *physisorption* of higher hydrocarbons on the surface of adsorbent/catalyst

The current desulfurization materials for NG consist of two materials. The first one, DESULF-1 is for removal of mercaptans, COS and H₂S and the second one, DESULF-2 is for removal of tetrahydrothiophene (THT), dimethyl sulfide (DMS) and other disulfides.

Figure 27 shows that compared to activated carbon and zeolites, both DESULF-1 and DESULF-2 have a much lower adsorption on higher hydrocarbons. DESULF-1 has a much higher sulfur removal capacity of tert-butyl mercaptane (t-BuSH). On the other hand, DESULF-2, especially DESULF-2/2, has a very good sulfur removal capacity of THT, according to catalyst manufacturer.

Figure 27. Comparison of DESULF-1 and DESULF-2 vs. activated carbon and zeolites on desulfurization of t-BuSH, THT and on adsorption of higher hydrocarbons

The influence of temperature on sulfur capacity of DESULF-1 is shown in Figure 28, which indicates that the sulfur removal capacity of DESULF-1 increases with increasing operating temperature. In contrast, the sulfur removal capacity for the desulfurization materials based on physisorption, like activated carbon, is decreased with increasing operating temperature.

Figure 28. Influence of temperature on sulfur capacity of DESULF-1

When DESULF-2 reaches its capacity, the spent material changes color, see Figure 29, which gives good visual indication when a replacement of desulfurization bed is needed. Therefore, a transparent window is added to the desulfurization bed of PowerTap fuel processor to monitor the desulfurizer.

Figure 29. Visual comparison of fresh and spent DESULF-1

In addition, the desulfurization material supplier also developed a proprietary simulator program, based on the properties of DESULF-1 and DESULF-2. This program was very helpful for the design of PowerTap desulfurization absorber as it allows:

- Determination of optimum bed volume for all sulfur species;
- Calculation of breakthrough characteristic;
- Quick, easy and accurate sizing of sulfur guard beds

The desulfurization materials work very well from performance point of view, however, the cost of current desulfurization materials is the highest maintenance cost of the entire PowerTap system, exceeding fuel processor replacement costs. In order to lower the cost, Nuvera has been searching for alternatives. The proposed approach is based on a combination of a hydrodesulfurization (HDS) reaction with a following adsorption bed by zinc oxide. The HDS reactions and H₂S removal reactions for the possible sulfur compounds in natural gas are summarized in Figure 30.

Step 1: HDS

$\text{R, R}' = \textit{methyl, ethyl, tert.}\text{-butyl, } i/n\text{-propyl, etc.}$

Step 2: H₂S Removal

Figure 30. Scheme of HDS reactions and H₂S removal reactions for possible sulfur compounds in natural gas

As shown above, this method is generally used to remove sulfur-containing compounds in natural gas including, mercaptans, THT (tetrahydrothiophene) and sulphides or disulfides. During the HDS reaction, the fuel passes over a catalyst where sulfur-containing compounds in the fuel react with H₂. Hydrogen for HDS reaction can be sourced from several places within PowerTap system including:

- Case 1: Pure hydrogen after PSA purification
- Case 2: H₂-rich reformat in SR outlet
- Case 3: HTS outlet reformat
- Case 4: Recycled PSA raffinate

Based on catalyst supplier recommendations, the optimal temperature range of the HDS reaction is between 300-400 °C. Therefore initial testing was performed at 350°C. If a pure H₂ is used, both typical HDS catalysts, CoMo/Al₂O₃ and NiMo/Al₂O₃, can be used. However, if either a H₂-rich reformat or a PSA raffinate are used, either NiMo/Al₂O₃ or precious metal-based HDS catalyst are better choices because steam has a significant negative impact on HDS performance with CoMo/Al₂O₃, but it only marginally affects functionality of NiMo/Al₂O₃ and precious metal-based HDS catalysts. The summary of subscale test results for HDS of the listed cases is presented below in Table 8.

For these proof of concept tests a combination of the HDS bed followed by ZnO H₂S removal bed, sized according to catalyst manufacturer recommendations was used in Nuvera's microreactor setup.

Case #	HDS Gas Composition ¹	WGHSV, hr ⁻¹	Reactor Temp., °C	Pressure, psig	[S], ppbv ²
1	2.5% H ₂	3,500	350	22.5	N.D.
2 and 3	H ₂ : 2.5% CO + CH ₄ : 0.8% CO ₂ : 0.8% H ₂ O: 1%	3,500	350	22.5	N.D.
4	H ₂ : 2.5% CO + CH ₄ : 0.8% CO ₂ : 3%	3,500	350	22.5	N.D.

¹ Feedstock: 1 ppmv isopropyl mercaptan and 3 ppmv tert-butyl mercaptan in methane; ² Detection limit of the Sulfur analyzer – 50 ppbv; N.D. – not detected

Table 8. Subscale test results of hydrodesulfurization of mercaptans in methane and the following ZnO-based H₂S removal.

Because the difference between SR outlet and HTS outlet compositions is small, cases 2 and 3 were combined and an average of SR and HTS compositions was used for testing.

Nuvera's feasibility studies for the four cases mentioned above indicate that sulfur can be removed from 4.0 ppmv to below the detection limit of Nuvera's sulfur analyzer, which is 50 ppbv. Test results concluded that there are multiple options available for HDS desulfurizer integration into the PowerTap reformer.

As explained earlier, due to the high cost of desulfurization materials and their low sulfur capacity (high replacement frequency), conventional physisorption and chemisorption methods are not economical, especially at larger system scales. Therefore evaluation of HDS desulfurization method will continue and in the future Nuvera is contemplating building a full scale HDS reactor and installing it into a FPTs for a full system validation. If successful, next generation larger scale PowerTap system will incorporate HDS technology and design modifications will also be considered at a current scale.

4.3.4 Catalyst Disposal

For a complete Life Cycle Cost analysis, all costs associated with catalyst exploitation, including disposal must be considered. Because the base configuration of the PowerTap fuel processor doesn't use any precious metal catalyst (PM-based HTS is in evaluation phase), catalyst recycling strategies were not considered. All spent catalysts are treated as hazardous materials. A one-time disposal cost of the entire suite of PowerTap catalysts is estimated at about \$980, including labor for catalyst extraction and hazmat disposal fees. This amount is not insignificant, especially when multiple catalyst replacements are required during the life of the system. Therefore addressing catalyst durability and increasing its life are critical for a value proposition of the PowerTap hydrogen generator.

5 Task 3 – Fuel Processor Testing

Using key findings from the design, materials selection and catalyst work described in previous sections Nuvera built and tested four FP design generations and a total of eight fuel processors, as described in Table 9.

Unit	Build Date	Vendor	Cap / Tube Material	Catalyst	Tested Configuration
FP1A	Nov-04	Nuvera	316 SS (short cap) / 316 SS	SR1, HTS1	counter-flow only
FP1B	Apr-05	Nuvera	316 SS (short cap) / 316 SS	SR2, HTS1	counter-flow only
FP1C1	Dec-05	Nuvera	310 SS (short cap) / 310 SS	SR2, HTS1	counter-flow only
FP1C2	Jul-06	Nuvera	In625 (short cap) / In625	SR2, HTS1	counter-flow only
Alpha1	Oct-06	Nuvera	In625 (long cap) / In625	SR3, HTS2	counter-flow only
FP1R	Nov-06	Nuvera	In625 & 600 (long) / 310SS	SR3, HTS2/HTS3	counter, co-flow
Alpha2	Sep-07	External	In625 (long drawn) / 310SS	SR3, HTS2	counter-flow only
Alpha3	Jan-09	External	In625 (long drawn) / 310SS	SR3, HTS2	not tested yet

Table 9. Log of the design differences in the fuel processors used during the CHARM program.
(Lab-based stand alone fuel processors – shaded yellow, full H₂ generation systems – white)

The first generation **FP1A** reformer was used as a proof-of-concept system. It was built in November 2004 with tubes and short caps (1” length), all made of 316 stainless steel. FP1A served its purpose by highlighting shortcomings in burner and reformer performance and was retired shortly thereafter.

The second all 316 stainless steel fuel processor **FP1B** underwent significant design modifications based on the new modeling results and on the learning from FP1A. It was built 6 months after its predecessor and was tested for nearly 1000 hours before one of the tube cap welds failed prompting the third generation FP1C-series design.

FP1C1 made with 310 stainless steel tubes and caps was installed on the burner test stand in December 2005 to endure frequent cycling of the FP (burner – reformer assembly) and SG1 heat exchanger. It accumulated over 1000 cycles on the main FP vessel and over 3000 cycles on the steam generator. FP1C1 later took part in high temperature high pressure (1000°C, 300 psig) cycling study for creep-fatigue evaluation, when it was finally retired due to a tube creep rupture.

The fourth and the most current generation **FP1R** fuel processor was built in December 2006 with SR tubes made of different materials including 310 stainless steel, Inconel 600 and Inconel 625 for materials evaluation. Lessons learned with previous generations reformers resulted in design of 6” long Inconel caps to further improve life of the fuel processor and consequently reduce maintenance and replacement cost.

As shown in Table 9, in addition to four laboratory-based integrated prototypes, Nuvera also manufactured two PowerTap Hydrogen generators with FP1C series fuel processors (**FP1C2** and **Alpha1**) and two more complete systems with fuel processors based on FP1R architecture (**Alpha 2** and **Alpha 3**). The FP1C2 based system is installed on a customer’s site since July 2006, while Alpha 1 and Alpha 2 are currently supplying hydrogen to Nuvera laboratories. The newest Alpha 3 based generator is the first outsourced system built by an independent system integrator. It just arrived to Nuvera and is currently being installed

on the hydrogen pad next to Alpha 1 and Alpha 2 systems. Collaboration with an outside company improved Nuvera's capabilities in product development and system packaging and also validated PowerTap's costing structure.

Most of the results reported here are obtained with the FP1R lab-based fuel processor. In few instances, results of the FP1B and FP1C1 units testing and product experience of Alpha 1 system will also be mentioned.

5.1 Control Strategy

In order to improve reliability and safety of the test stand, an industrial Burner Management Module (BMM) was incorporated into the control scheme. The BMM helps to control the start-up sequence and monitors the flame during steady state operation. A UV sensor works in conjunction with the BMM to control the system fuel shut off valve and to monitor proof of flame.

The burner in the CHARM fuel processor must be able to operate on different fuels ranging from:

1. Natural gas during start-up;
2. Mainly reformat during warm-up phase;
3. PSA raffinate during steady state operation

All these burner fuels have very different compositions, as shown in Table 10, and consequently different flame properties.

	H ₂ %	CH ₄ %	CO %	CO ₂ %	H ₂ O (g) %
Start up (100% NG)	NG composition varies regionally				
Reformat	70	4	2	17	7
PSA raffinate	42	10	5	40	3

Table 10. Fuel compositions handled by the burner in key control states.

The burner thermal input varies from approximately 8 – 65 kWth HHV, imposing additional constraints on the control system. Furthermore, the system must be able to go through a non trivial transition from one fuel to another, making design and optimization of the system, and burner especially, even more challenging.

Nuvera optimized the position of the UV sensor and performed extensive validation of the BMM unit. Test results on natural gas fuel are shown in Figure 31, while performance on simulated reformat and hydrogen / nitrogen mix is presented in Figure 32.

Figure 31. BMM testing on natural gas.

Figure 32. BMM testing on hydrogen containing fuels

In all cases the BMM performed reliably and identified the flame for all fuel compositions as indicated by a consistent and predictable voltage signal shown in Figure 31 and Figure 32 below. The unit is now incorporated in all operational Nuvera systems. As a side note, industrial BMM module adopted by Nuvera is UL and CSA certified.

To initiate a start-up of the system, warm up and maintain in steady state, a series of control states are used. To light the burner, the burner fuel proportional solenoid valve (PSV) and the air blower voltage are adjusted to set values. Once the BMM receives a true signal from the UV sensor that a flame is present, the control scheme continues with a start-up sequence.

A proprietary control sequence was developed to balance start-up time and reformer and catalyst durability. Once the system is in steady state, two main control parameters are used. The air blower voltage controls to the specified steam pressure, and the burner fuel PSV is controlled to a desired SR bulk exit temperature.

For smooth system operation it is important that these controllers respond to the dynamics of the system accurately and efficiently. A system identification study was carried out to facilitate the controller tuning. Step changes in air blower voltage, burner fuel PSV voltage and HX3 fan voltage respectively excited the dynamics of steam pressure, SR outlet temperature and HX3 outlet temperature are shown in Figure 33, Figure 34 and Figure 35.

Figure 33. System identification of steam pressure dynamics

Figure 34. System identification of SR outlet temperature dynamics

Figure 35. System identification of HX3 temperature dynamics

5.2 Test Results

A wide variety of test conditions were run on the FPTs system, shown below in Figure 36, while collecting a multitude of operating parameters including pressures, temperatures, flow rates, reformat composition and burner emissions data. The objective of the testing was to evaluate fuel processor performance within the possible window of operating parameters and also define a nominal mode of operation resulting in desired hydrogen production.

Figure 36. Photo of the Fuel Processor Test Stand (FPTS)

There are two main control knobs for reformer operation: the steam reformer bulk outlet temperature, representing reformat temperature in the exit of the reformer vessel; and steam pressure, characterizing steam production or steam-to-carbon ratio, since pressure is maintained by a fixed orifice upfront of the ejector. The SR bulk outlet temperature controller ultimately controls burner fuel flow rate to give a desired reforming conversion, and steam pressure control is managed by burner blower air flow. Full system performance mapping using a 3 x 3 matrix consisting of three SR outlet temperatures and three steam pressures representing a range of steam-to carbon ratios from approximately 2.7 – 3.4, was performed for two flow arrangements and is presented in this section.

As explained previously, different temperature constraints in co-flow and counter-flow configurations affect burner exhaust energy distribution available for the steam reforming reaction and for steam generation. Less heat is available for steam generation in counter-flow, thus the range of steam flows or steam pressures is lower in counter-flow compared to the co-flow mode.

For the same reason, due to the nature of burner/SR heat exchanger temperature pinch conditions and consequent heat exchange inside the return reformer path, SR bulk temperatures in the counter-flow are lower compared to the co-flow. Yet the appropriate control windows were chosen to cover as wide as possible ranges of operation from low SR conversion and therefore high durability cases to high conversion and consequently high efficiency cases.

A comparison of SR methane conversion versus measured peak temperatures for two modes of operation is shown in Figure 37. Full gas chromatograph (GC) results for the nominal co-flow and counter-flow test runs are presented in Figure 38 and Figure 39, respectively.

Figure 37. SR conversion vs. measured peak metal temperature in co-flow and counter-flow configurations

Figure 38. SR exit composition in a typical co-flow test run

Figure 39. SR exit composition in a typical counter-flow test run

As expected, the data indicated that it was much easier to obtain desired methane conversion in the counter-flow configuration. However, despite CFD models predicting substantially lower metal temperatures in co-flow due to more efficient tube cooling from the inside SR reaction, actual test data showed the opposite trend. For most tested conditions, regardless of SR reaction conversion, measured peak metal temperatures in co-flow were higher than in counter-flow. Upon further inquiry several original model assumptions were scrutinized.

First, the original model used the exact same burner boundary conditions (flow specification, composition, etc.) In practice, due to inherent constraints of co-flow temperature profile and associated temperature pinch conditions, as explained in the Fuel Processor Design section, the co-flow was forced to operate with higher burner fuel-air equivalence ratios (i.e. richer) than the counter-flow in order to maintain suitable reforming conversion and to have a thermally balanced system.

Second, lab data indicated that in both co-flow and counter-flow, the actual peak metal temperatures are closely linked to the burner gas temperature. This is indicative of the heat transfer within the SR bed being more limiting than on the burner side. The original CFD model underestimated the value of high heat flux on the burner side due to direct flame impingement and high temperature radiation. And perhaps the effect of metal cooling due to rapid reforming reaction inside the cap was overestimated.

Based on the test results, the co-flow configuration was abandoned in favor of the counter-flow arrangement, as a primary mode of the fuel processor operation due to penalties in both efficiency and peak metal temperatures and stresses.

5.3 Start up and Shut down

With frequent cycling of a small scale reformer and desire to maintain low stress levels on the reformer metal and catalyst, it is important to ensure smooth control during all modes of operation. In an effort to do so, the different run states, startup, steady state, and cool down, of the test stand were investigated closely. If the system is warming up or cooling down too quickly, the durability and lifetime of the fuel processor could be compromised.

The appropriate controls were implemented onto the test stand to maintain manageable temperatures in all states of the reformer operation. Below in Figure 40, a typical system startup is shown. The complete start-up of the system, defined as time to the full hydrogen production, is about 90 minutes. In the PowerTap system start-up is determined by the time it takes HTS reactor to heat up and reach nominal WGS reaction conversion. There are ways to heat up the fuel processor and HTS even faster. However, to extend the life of SR and HTS catalysts, a longer start-up time and/or more careful procedures are required.

Shutdown of the fuel processor is shown in Figure 41. Typical cool down duration is on the order of 3.5 hours, designed again to mitigate stresses on metal and catalyst.

Optimization of the system start-up and shutdown sequences has not been the focus of the CHARM program, yet they are critical for a PowerTap product offering.

Figure 40. Typical FPTS startup

Figure 41. FPTS steady state and shutdown

5.4 HTS Performance evaluation

As described previously in the catalyst development chapter of this report, the FPTs system was tested with two HTS catalyst types during the course of the program. Conventional pellet based HTS2 shift catalyst was used for the initial 1,100 hours. From that point on a new precious metal based monolithic HTS reactor has been used and it now has over 5,000 hours run time.

HTS2 is a well developed water-gas-shift catalyst used in the industry and it performed well on the FPTs and continues to perform well on the Alpha 1 FPA. A typical HTS performance of HTS2 in Alpha1 generator after 4,800 hours in operation is shown in Figure 42. After nearly 6,000 hours, the reactor's performance today, closely follows WGS reaction equilibrium.

Despite good performance, the biggest drawbacks of the HTS2 catalyst are large size, long warm-up and difficult plumbing and packaging. For that reason the team is evaluating alternative approach based on precious metal monolithic WGS catalyst HTS3. Performance of HTS3 catalyst after 2700 hours of operation is shown in Figure 43.

Figure 42. Typical product composition before and after HTS reactor from Alpha 1 system (HTS 2 catalyst after 4800 hours of operation)

Figure 43. Typical product composition before and after HTS reactor from FPTs system (HTS3 PM-based monolith after 2700 hours of operation)

When new, test data of HTS3 catalyst showed very similar conversions to that of HTS 2. However after about 2,000 hours the monolith performance started degrading, requiring an increase of operating temperatures to achieve WGS equilibrium. Today after about 5,000 hours HTS3 catalyst at nominal design conditions achieves only 50% conversion. Performance can be improved to about 70% conversion by raising HTS inlet temperature by 30 – 40°C. However, such temperature increase is already at the high end or possibly exceeding the range of recommended operating temperatures for HTS catalyst and will likely further affect catalyst durability.

Performance tracking of the HTS reactor on the FPTs throughout the program is shown in Table 11.

FPTS testing time, hr	CO conversion, %	Comments
0 - 1100	73-80 ¹	HTS 2 pellets testing (close to equilibrium conversion)
1100 - 3000	73-80 ¹	PM monolithic HTS installed at 1100 hrs Higher conversion required elevated temperatures
3000 - 4150	65-72	
4150 - 6000	50-70	

¹ Conversion near WGS equilibrium.

Table 11. Performance tracking of the HTS catalysts on FPTs.

Test data comparison of the normal runs for FPTs precious metal based monolith and Alpha 1 HTS2 pellets, including start-up and steady state operation is shown in Figure 44 and Figure 45 respectively. Despite the higher steady state operating temperature shown in the plots, monolithic HTS3 performs worse than its pelleted counterpart HTS2.

Figure 44. Start-up and steady state operation of the FPTs precious metal based monolithic HTS reactor

Figure 45. Start-up and steady state operation of the pellet based HTS reactor in the Alpha1 hydrogen generator

The advantages of the monolith HTS reactor include low mass and volume, fast startup and simplification of system packaging. Compared to conventional HTS employed in Alpha 1 system, the monolith shift reactor is about 12 times smaller in volume and offers a significant benefit in system start-up time. Using monolith resulted in 90 minutes startup or 40 minutes savings in time to full hydrogen production compared to conventional HTS, which corresponds to about 3% hydrogen production or system efficiency increase, assuming daily start – stop operation.

Cost wise, despite precious metal content and much higher per kilogram cost, the monolith-based shift reactor's small size offsets the cost differential with the conventional pellet-based reactor. Based on the current low volume quotations cost of the two options is very similar.

Both reactors have accumulated around 5,000 hours and conventional pellets seem to have durability advantage. However it is not clear how FPTs system upsets affected monolith HTS performance and its evaluation and performance monitoring will continue.

To summarize, monolithic HTS3 is still barely meeting performance targets, albeit at higher than nominal design temperatures. Yet the confidence in its durability is much lower than that of the conventional pellets. Durability evaluation will continue in 2009 and collaborative work with catalyst suppliers on improving catalyst durability is ongoing. Performance and durability of both types of HTS catalyst will be assessed based on catalyst lifetime specification of 20,000 hours.

5.5 Burner Emissions

As an enabling technology for fuel cells, the PowerTap hydrogen generator can help maintain “green” image associated with fuel cells by having a favorable emissions footprint. Therefore system emissions, particularly burner emissions, were a critical consideration for the design of the fuel processor. At the time of the design conception, there were no available emissions standards for hydrogen generation systems. As a result, Nuvera conducted an investigation of acceptable emissions levels for similar systems in California and found that South Coast Air Quality Management District (SCAQMD) had the most stringent requirements, when applied to a natural gas fired equipment. Working with SCAQMD and consulting with Canadian Standards Association (CSA), the most applicable process standards were determined to correspond to natural gas fired water heaters, boilers and process heaters, Rule 1146.2 [19]. By SCAQMD definition, based on the PowerTap burner throughput, the system falls into a category of units that have a rated heat input capacity of less than or equal to 2,000,000 Btu per hour. Furthermore this category has two sub-classes and PowerTap was classified as a Type 1 Unit with rated heat input capacity from 75,000 – 400,000 Btu/hr. Using SCAQMD requirements as a reference, Nuvera adopted a more stringent design specification that was later incorporated into a product spec.

A comparison of the SCAQMD Rule 1146.2 requirements, adopted Nuvera product specifications, and emissions measured on the FPTs is shown in Table 12.

	NO _x , ppm (at 3% O ₂ , dry)	CO, ppm (at 3% O ₂ , dry)
SCAQMD Rule 1146.2	55	400
PowerTap product specification	15	50
Measured peak FPTs emissions	9	8

Table 12. Summary of the measured FPTs emissions compared to PowerTap product specifications and to SCAQMD Rule 1146.2 requirements

To obtain burner emissions data, the FPTs system was running a steady state condition with approximately constant burner reformat and supplemental natural gas composition. The test was performed by varying burner air flow or air-to-fuel ratio. The emissions data for a wide range of possible operating conditions is shown below in Figure 46.

For all conditions the burner emissions showed both NO_x and CO parts per million emissions in single digits. Low NO_x emissions were achieved by thorough design of the burner fuel and air manifolds and arrangement of the combustion/mixing zone and SR-burner heat exchanger. Good CO emissions are attributed to mitigating effects of the high ratio of hydrogen in combustion mix, although it should also be noted that the current PowerTap fuel processor employs a small combustion catalyst zone designed for capturing unconverted hydrocarbons and CO.

Figure 46. Burner emissions data vs. burner air flow rate

5.6 Fuel Processor Durability Testing

Under the CHARM program Nuvera has developed a steam reformer that is expected to meet the 40,000 hours and 1,000 cycles design life. This was achieved using a low stress unconstrained SR tube design minimizing creep damage and stresses due to thermal expansion. The design details are covered in Chapter 4 of this report. Most of the data came from testing three fuel processors: FP1B, FP1C1 and FP1R.

A low cost fuel processor FP1B, was built using 316SS SR tubes and caps to verify heat exchanger performance and CFD predicted thermal profile. Multiple thermocouples were attached along the length of the SR tube to calibrate a Fluent[™] thermal profile with actual metal temperatures. Although CFD predicted higher peak metal temperatures especially in counter-flow operation, visual inspection of SR tube discoloration and oxidation scale patterns shown in Figure 47 suggested a close similarity in temperature gradients between the CFD model predictions & actual SR tube.

Figure 47. Close match between thermal Fluent predicted temperature distribution and thermal gradients observed on FP1B reformer.

The FP1B reformer failed after about 1000 hours of operation. The failure occurred at the weld between the SR tubes and caps. Failure investigation revealed poor weld quality (lack of full weld penetration) along with flame impingement along the weld as root cause for failure, as shown in Figure 48.

Figure 48. Weld failure between FP1B SR tube and cap.

Based on the results of the FP1B failure investigation, the SR cap was redesigned to move the weld beyond the direct flame region. Many manufacturing techniques including machining, casting, hydro-forming, spinning and forging were evaluated for making the long Inconel 625 caps. In all more than 15 vendors were contacted. In the end a deep drawing process in combination with heat treatment gave the best compromise between final part cost and quality. The FP1B failure happened when the FP1C1 reformer was already built with 310 stainless steel caps. However, all subsequent units starting with FP1C2 are manufactured with extended Inconel caps.

The main CHARM FP1R reformer was built with a suite of Inconel and stainless steel materials to evaluate long term material performance and potential for future cost savings by switching to a lower cost material. FP1R was also used to evaluate co-flow and counter flow SR operating modes. To date the FP1R fuel processor has more than 6,000 hours and over 250 cycles, as shown in Figure 49. Fuel processor testing was briefly suspended in the middle of 2007 during Nuvera facilities relocation from Cambridge, MA to the new headquarters location in Billerica, MA.

Figure 49. Durability achievements of the FP1R fuel processor

No changes were made to the fuel processor tubular core during the entire period. Despite several operational upsets reformer metal hardware withstood all the abuse and Nuvera now has high confidence in fuel processor metal hardware durability. However, the burner fuel manifold assembly and SR catalyst had to be replaced around 4,000 hour mark due to operational upsets related to test stand equipment failure.

The lab exhaust line became partially filled with condensate from the burner exhaust, causing offsets in blower air flow and burner mixing and distribution. Unfortunately the problem was not immediately recognized and for about 200 hours the system continued to operate in unintended unstable condition, until reformer performance degradation became very evident. As was determined by a subsequent inspection and failure investigation, due to decrease of burner air flow, some areas of the burner inlet manifold became exposed to very high temperatures leading to clogging of several fuel ports due to fuel coking and excessive corrosion, as shown in Figure 50, which skewed combustion uniformity even more.

Figure 50. Clogging of the burner fuel ports and corrosion of the fuel manifold.

Furthermore, a weld in the burner manifold assembly failed, as shown in Figure 51, causing one side of the reformer to run extremely hot at temperatures well above 1000°C. Fortunately, the reformer tubes survived, however significant sintering of SR catalyst in several of the tubes prompted complete SR catalyst replacement.

Figure 51. Weld failure in the burner manifold

To prevent from future reformer damage due to clogging and high temperature corrosion of the burner manifold, its material was changed from 304 to 310 stainless steel. Fuel manifold welds were redesigned and the combustion chamber insulation material was changed as a result of this failure. Though the extent of SR tube material damage is not known as this time, this operational upset could have shortened the life of SR tubes. Nuvera will continue durability testing of the FP1R reformer through 2009 and beyond to validate the 40,000 hour design expectation.

Performance of the steam reforming catalyst has been monitored during the course of the project. Before the burner manifold failure, which occurred around approximately 3900 hours mark, SR catalyst's performance was lower than that of the brand new catalyst, but still well within requirement specifications

of reactor performance easily meeting or exceeding $< 3 - 5\%$ dry methane slip target. However, considerable performance decline was observed in less than 200 hours after the failure occurred, when reformer CH_4 slip approached $10 - 12\%$. Upon subsequent inspection, substantial catalyst crushing and powder formation was discovered in some of the reformer tubes. Such catalyst crushing led to severe uneven flow distribution among SR tube bundle, as shown in Figure 52, prompting complete catalyst replacement.

Figure 52. Temperature profiles in FPTs SR tubes.

Catalyst samples from nearly all tubes were sent to the catalyst supplier for post mortem analysis. Furthermore internal evaluation of the spent SR catalyst performance was performed in Nuvera's micro-reactor setup.

The SR performance evaluation of the spent SR catalyst in the micro-reactor after 3900 hours of operation, shown in Figure 53, indicated that when the SR tubes like Tube C were under the normal operating temperature, the catalysts from the top, middle and bottom of Tube C performed well at $2,500 \text{ h}^{-1}$ space velocity (1.25 times the typical PowerTap operating space velocity). The post-mortem analysis indicates that surface area loss was approximately 25% compared to a fresh sample even though the catalyst underwent switches from counter-flow to co-flow and from co-flow to counter-flow and 160 cycles of startups and shutdowns.

Figure 53. SR performance analysis of spent SR catalyst from the normal SR tube.
 (a): Methane conversion; (b) Product distribution

The post mortem analysis of the SR catalyst from the top, middle and bottom of one of the “hot” tubes, as in case of tube J, showed that SR catalyst converted to significant powder near the cap, where the highest temperature was observed. Catalyst samples also suffered from significant surface area loss. Surface area losses for catalyst taken from top, middle and bottom of the reforming tubes were 75%, 87.5% and 84%, respectively, although the majority of the spent catalyst is still physically intact. Significant Ni crystallite growth was seen by XRD and large amount of carbon is deposited on the samples. The SR performance studies of the SR catalyst samples from tube J at micro-reactor is consistent with the post mortem analysis, presented in Figure 54. At $2,500 \text{ h}^{-1}$ space velocity, the catalyst on the top of Tube J is still within the safety factor, however, the SR catalysts from both middle and bottom, especially from the bottom, were greatly deactivated due to significant surface area loss and powder formation.

Figure 54. SR performance analysis of spent SR catalyst from tube J that was overtemperated during lab infrastructure failure.

The same SR catalyst is used in all Alpha systems. In contrast to the FPTs wide range of operating conditions, some of them being quite harsh, the Alpha systems are running in a milder mode for the catalyst. Alpha1 SR catalyst accumulated over 5,000 hours and catalyst performance is showing signs of slow deterioration. To meet hydrogen production capacity, the fuel processor is running hotter today than in the beginning. It is clear that catalyst durability must improve to meet the product requirements. The team will continue work in optimization of operating conditions and specifically start-up and shut down. In addition Nuvera is engaged in collaboration with catalyst suppliers.

In addition to FP1R testing, the earlier variant, FP1C1 reformer, made of 310 stainless steel tubes, was tested on a second test stand with an accelerated cyclic test protocol to evaluate thermal fatigue and creep-fatigue interaction.

The fatigue test procedure consisted of heating the SR tubes (with no SR flow) by firing the burner for twenty minutes followed by rapid cooling to 100°C. The test duration was designed to recreate the worst thermal stress conditions: direct flame impingement on cold SR tubes, seen by steam reforming tubes in actual operation. The FP1C1 reformer lasted more than 1000 fatigue cycles without failure.

After 1000 cycles, the test was modified to evaluate creep-fatigue interaction. The test goal was to induce creep in SR tubes by running at elevated pressures and evaluate impact of creep on fatigue life. The test protocol consisted of pressurizing the SR tubes and thereby running an accelerated fatigue test profile. The test stand was set up for unattended operation. Though each cycle lasted two hours, only 10 minutes per cycle were spent at high temperature. The remaining cycle time was used to cool the SR tubes to below 100°C. The reformer tubes were pressurized to produce a hoop stress of 3.0 ksi, which for 310 stainless steel corresponds to 1,000 hours creep rupture stress. Hydrogen gas was used to pressurize the SR tubes to create an environment similar to a steam reforming environment. The test profile was designed to lead to failure after thousands of cycles but the FP1C1 reformer failed after only 130 pressurized cycles.

Post-failure inspection of the FP1C1 reformer uncovered a 1" longitudinal crack in one of the SR tubes along with bulging in most of the other tubes, indicative of deformation just prior to pressure rupture, as shown in Figure 55.

Figure 55. FP1C1 reformer SR tube failure under accelerated cycling protocol.

This indicated the failure to be a creep rupture instead of fatigue or creep-fatigue interaction. Using the Larson Miller parameter, described earlier, evaluation of creep rupture time as a function of temperature was performed to confirm whether the failure occurred due to creep. Table 13 shows that for temperatures above 1050°C less than one hour creep rupture time is required to produce the observed failure.

Test Pressure		psia	300
Hoop Stress		ksi	3.0
Larson-Miller Parameter			48
Temperature		Rupture Time	
°C	°R	hours	
850	2021.67	5,530.3	
875	2066.67	1,681.8	
900	2111.67	538.1	
925	2156.67	180.5	
950	2201.67	63.3	
975	2246.67	23.2	
1000	2291.67	8.8	
1025	2336.67	3.5	
1050	2381.67	1.4	
1075	2426.67	0.6	
1100	2471.67	0.3	

Table 13. FP1C1 SR Tube Rupture Time Estimate Based on Larson-Miller Parameter

Review of the test data showed the control system, designed for unattended 24-hour operation, failed just prior to the last cycle. Temperatures in the burner reached as high as 1100°C before the safety system shut down the test. Also, the lethal cycle lasted for more than one hour instead of the typical 10 minute high temperature dwell period per cycle. The test data seems to confirm the suspected creep rupture failure mode. As such, creep failure invalidated the original intent of creep-fatigue interaction evaluation.

Despite creep-fatigue testing not reaching its objectives, Nuvera developed a valuable experience in understanding of the key parameters for evaluation of metal durability. As the failure occurred right at the end of the CHARM program, the team did not have time to complete a metallographic evaluation of the failed FP1C1 unit. The independent evaluation of the two fuel processors has been initiated with external recognized experts in the field of the fuel processing durability. As part of such study, metallographic evaluation of the failed FP1C1 fuel processor will be performed, as well as independent confirmation of Nuvera stress analyses and non-destructive inspection of FP1R reformer tubes for remaining life in the existing unit.

5.7 Fuel Processor Life Assessment

Catalyst issues aside, most of the infant mortality problems with the metal hardware, described in the previous section, occurred very early in the program and have since been resolved. The current design is much evolved and the FP1R hardware has accumulated over 6,000 hours and 250 cycles and shows no signs of degradation. This gives the team confidence in the overall design approach. However, there is a long way to go from 6,000 hours to the required 40,000 hours and a formal fuel processor life assessment must be done for confirmation of the projected life cycle cost and overall value proposition of the PowerTap product.

During the initial fuel processor design effort it was determined, that of all possible failure mechanisms only creep, fatigue and interaction between the two, are real threats to the reformer metal durability. At that time no actual operating data were available and the durability analysis were based on the very preliminary and often unrefined modeling results, since not all the design features of the fuel processor were finalized. By the end of the program with all the models greatly refined and calibrated with the actual test data, a comprehensive assessment of the fuel processor expected life was performed.

Creep-rupture evaluation

The determination of creep-rupture behavior under the conditions of intended service requires extrapolation and/or interpolation of raw data [21]. No single method for determination of properties exists; however, a variety of techniques have evolved for data handling of most materials and applications of engineering interest. These techniques include graphical methods, time-temperature parameters, and methods used for estimations when data are sparse or hard to obtain [21].

One such method was used for the original fuel processor design as described in the Analysis and Design section of this report. It includes evaluation of the Larson-Miller Parameter, which is related to temperature T in Kelvin and time to creep-rupture t in hours and defined as:

$$\text{LMP} = (20 + \log t) \cdot T / 1000$$

The convenience in using LMP is that for a particular material the relationship between stress, temperature and time to rupture falls on a single line as shown in Figure 12 in the case of Inconel625.

Unfortunately, Nuvera's low pressure design approach and resulting low stress fall outside of the range of most conventional applications and therefore the metal properties data is not readily available for PowerTap conditions. As suggested in literature [21], the team made an attempt at extrapolation of the existing data. Results of such extrapolation of Inconel 625 LMP data from Figure 12 are shown in Figure 56. Obviously, such approach introduces uncertainty and the results are highly dependent on the extrapolation method. Thus two different extrapolation methods were used. Exponential function seems a more logical extension of the data and this method was used earlier to predict maximum allowable metal temperatures corresponding to a 40,000 hours life, as shown in Figure 14. However, Polynomial extrapolation will give much more conservative results (predict shorter creep-rupture time) due to a sharp drop off of the Stress vs. LMP function.

Based on the conservative polynomial extrapolation of Inconel 625 LMP data, the allowable stress as a function of creep-rupture time at different temperatures is shown in Figure 57.

Figure 56. Larson-Miller Parameter for Inconel 625.

Figure 57. Allowable stress for a given lifetime – Inconel 625.
Polynomial Extrapolation used for stress below 20 MPa

For the analysis, the peak temperature of 975°C was selected, which represents the highest metal temperature achieved during counter-flow testing, see Figure 37. It should be noted that the system does not require SR reaction conversions corresponding to 975°C case. In fact, the normal fuel processor operating conditions correspond to the range of 900 – 950°C. Yet, to be conservative, the design space for a 40,000 hours life was defined based on 975°C metal temperature. Given the assumptions mentioned above, the stress levels below 4.7 MPa should result in over 40,000 hr life due to creep. Nuvera's design stress is safely below this threshold, therefore fuel processor metal is expected to achieve 5 years life target.

The weakest link in these analyses is the need to extrapolate the available properties data. Despite many conservative assumptions used, there is still some uncertainty. And Nuvera will continue work in trying to generate additional durability data closer to the intended operating conditions of the PowerTap fuel processor and will also involve independent experts in the field of fuel processor durability.

Cyclic fatigue evaluation

Fuel processor cycling capabilities were estimated using available material properties data for Inconel 625 [10], based on results of the CFD – FEA model. Based on testing results it became clear that new model with updated boundary conditions and with the latest generation burner predicted thermal stresses that are only 1/3 of the values used during the initial design process, reported in Chapter 4. Furthermore, test data in counter-flow configuration indicated that target Hydrogen production is satisfied with peak metal temperatures below 950°C, as shown in Figure 37. Based on the newly obtained data, the CFD – FEA coupled model was refined and recalibrated in the fuel processor. The expected range of maximum strain on the reformer tubes due to temperature gradients in the burner versus number of cycles to failure is shown in Figure 58.

Figure 58. Inconel 625 high temperature fatigue strength [10].

The analysis indicate the magnitudes of thermal stress amplitude and strain range obtained from the coupled FEA model are well above the 1000 cycle fatigue life for Inconel 625. Obtained stress and strain levels for Inconel 625 counter-flow arrangement indicate that the fuel processor hardware is expected to last over 40,000 hours and 1,000 cold cycles.

To summarize, a suite of modeling tools and testing methods enable the team to make a prediction of the fuel processor life and cycling capabilities. Detailed evaluation of temperature fields in the fuel processor and assessment of the possible failure modes coupled with a low pressure steam reformer operation and very low stress design of the SR tubes gives the team a high confidence in projecting that the current design architecture will satisfy product specifications of **40,000 hrs life** and **1,000 cold cycles**.

5.8 LPG Operation

Although LPG is not considered a strategic fuel for the commercial PowerTap H₂ Generator product line and scale of product, the terms of the CHARM contract require a design of a fuel flexible fuel processor. In addition to natural gas, it is expected to be capable of running on Liquefied Petroleum Gas (LPG).

LPG is produced through natural gas processing (55%) and crude oil refining (45%) routes. Most is produced domestically with only 10-15% being imported into the United States. The “LPG” term is often used interchangeably with liquid propane gas, but the composition can vary depending on the time of year/climate and supplier. Compositions of 50/50 – 60/40 propane/butane are common, although primary propane or butane supplies can also be sourced.

Propane is used by ~8% of the residential homes in the United States for heating or cooking purposes. And is typically prevalent in areas where local town gas (or natural gas) service is unavailable. Propane is distributed via 70,000-miles of interstate pipeline, but this is less than one-quarter of the available 302,000 miles of interstate pipeline network constructed for natural gas in the U.S. Due to its liquid nature at moderate pressure, the propane distribution network is supported by a fleet of liquid transport vehicles, including rail cars, highway bulk transport, and local delivery trucks.

Due to the bulk storage capability of LPG, this fuel is particularly useful for seasonal peak shaving of the NG supply, kick-starting new NG pipeline arteries, in serving developing countries and as emergency back-up supply.

Nuvera has extensive experience with alternative fuels and has designed and operated several fuel flexible systems for automotive and stationary applications. Fuel processor operation on LPG was verified on a companion SMR-based, residential combined heat & power (CHP) product, Avanti™, which is fundamentally very similar to PowerTap. The Avanti SMR is at 1/20th scale of the CHARM SMR and thereby affords easier implementation of propane supply to the Nuvera test facility and greater flexibility for experimentation. The experimental set-up is represented in Figure 59 below.

Figure 59. Avanti™ Reformer Test Stand Block Diagram

The Avanti™ residential 4.6kWeAC PEM fuel cell power system was designed for NG but in the above experimental set-up, was operated on LPG during a performance verification exercise. A portable 100-lb liquid propane tank was used as the fuel source to the Avanti™ reformer test stand. To generate the required fuel flow rate, a tank heater was employed to increase the LP gas vaporization rate. Propane fuel is then delivered to the tail-gas combustor (TGC, i.e. burner) and steam reformer (SR) through a carbon-desulfurizer (CDS) unit. The hydrogen rich syn-gas (or reformat) is further improved via a high and low temperature water-gas-shift reaction zones (HTS and LTS), and then purified by the Preferential-Oxidation unit (PROX) to reduce carbon monoxide (CO) to adequate concentration levels for the PEM fuel cell. A VOC trap, not shown in Figure 59, was placed before the PEM fuel cell to eliminate the potential for stack contamination before contamination sampling could be performed and any impurities verified.

All required steam is generated in-situ within the process hardware (i.e. no external steam or heat sources applied during test). For experimental simplicity, the unused portion of syn-gas from the fuel cell is then delivered to a laboratory afterburner as waste gas. The burner is therefore operated solely on propane fuel for this particular test protocol.

Table 14 below lists the three power levels tested and the corresponding steady state operating parameters. A maximum of 4.5kWeDC power from the fuel cell was achieved during these trial tests. It should be noted that low propane fuel pressure (caused by low outside temperatures) prevented the fuel processor from operating dependably at higher thermal inputs, despite the use of an auxiliary tank heater.

SR Power Input (kWth, LHV C3H8)	Burner Power Input (kWth, LHV C3H8)	H ₂ Product Post-PROX (kWth, LHV H ₂)	H ₂ Content (Dry %)	Fuel Processor Thermal Efficiency (%)	FC Power (kWeDC)	CO Content (ppmv)
7.0	5.0	7.9	65	65.8	3.5	23
10.0	5.7	11.0	64	70.0	3.9	45
12.0	6.6	13.0	64	69.9	4.5	20

Table 14. Avanti™ fuel processor and fuel cell operation parameters. All conditions at S/C=4.0

Table 14 shows the fuel processor thermal efficiency and hydrogen concentration over the range of thermal inputs operated. Thermal efficiency in this operating mode is defined as:

$$\eta_{TH} = \frac{kW_{th} H_2 (LHV, Post - Prox)}{kW_{th} C_3H_8 (LHV, SR and Burner)}$$

Thermal efficiencies of 70% were obtained between the 10-kWth and 14-kWth inputs to the SR. Reformate analyses were performed during the course of the demonstration. No trace amounts of ammonia in the reformate was found by FTIR analysis. General volatile organic compounds (VOC's) were detected by photo-ionization analysis to be ≤ 5 -ppmv at all conditions. A VOC trap would be required in such a power system for durable and stable operation of a PEMFC stack. In a system like PowerTap where a pressure swing adsorber (PSA) is employed versus a PROX unit, additional gas stream purification like a VOC trap could be eliminated.

Peak Shaving and Synthetic Natural Gas

LPG is combined with air to create a synthetic natural gas (SNG) suitable for NG service. To match the Wobbe Index for typical NG (~1280), a nominal 60/40 split of propane/air is used. This blending procedure enables the use of this gas with existing NG burner control hardware and to achieve similar combustion characteristics.

The Table 15 below shows the compositions that may be encountered by a SMR-based FC or H₂ generation system (fuel composition data collected from Western Europe/Germany region as part of a previous commercial contract work by Nuvera and is presented here as a reference). In addition, Nuvera/Boston gas (COM gas) and the “model” pure methane gases are included. Although Germany has a wide variance of gas types based on region, the use of H-type (high heating value range) and L-type (low heating value range) gases have been confirmed by 3rd party contacts in those areas.

The “peak” versions of the H&L-types are generally in two categories: spiked with propane or butane. Both peak gas styles were included in the modeling study.

Hysys process modeling was performed on Nuvera's Avanti™ PEMFC system for the variety of fuels listed in Table 15. The range of NetDC system efficiency is <1%-point loss compared to the model methane case, or alternatively, <3% reduction in model case efficiency.

Gas Type (Origin & Characteristics)	Name	Methane (vol%)	Ethane (vol%)	Propane (vol%)	Butane (vol%)	CO ₂ (vol%)	N ₂ (vol%)	O ₂ (vol%)	Lower Heating Value (kJ/kg)	Ave. MW
	German H-type Gas									
	Russia	98.3	0.5	0.2	0.1	0.1	0.8	0.0	49167	16.33
	North Sea I	88.6	8.4	1.7	0.7	0.0	0.6	0.0	48960	18.06
	North Sea II	83.0	11.6	3.1	0.5	0.3	1.5	0.0	47801	19.01
	Verbundgas	88.6	5.3	1.4	0.6	1.4	2.7	0.0	46094	18.11
	Russia/ Propane Peak	59.7	0.1	20.3	0.3	0.1	15.6	4.1	37000	24.38
	Russia/ Butane Peak	66.9	0.1	0.1	13.4	0.1	15.6	3.9	37032	24.23
	German L-type Gas									
	Holland I	81.3	2.8	0.4	0.3	1.0	14.2	0.0	38002	18.65
	Holland II	82.9	3.7	0.7	0.3	1.3	11.1	0.0	39873	18.58
	E. Hannover	79.5	1.1	0.1	0.0	0.7	18.6	0.0	35179	18.65
	Holland I/ Propane peak	47.1	1.6	19.2	0.2	0.6	26.5	4.9	30897	25.83
	Holland I/ Butane peak	53.6	1.8	0.3	12.4	0.7	26.6	4.7	30783	25.7
	Nuvera/Cambridge Gas									
	COM Gas	95.0	3.0	0.4	0.1	1.0	0.5	0.0	48267	16.95
	Model Gas									
	Methane	100.0	0.0	0.0	0.0	0.0	0.0	0.0	50047	16.04

Table 15. Gases used in the fuel study. The German gas specs are translated from Manual G260 from January 2000. Grayed-out gas mixtures were not included in the study due to repetition.

Figure 60. Effect of fuel composition on Avanti™ fuel cell system performance – Net System DC efficiency. All Cases run with identical LHV input (10kWth SR, 12kWth Total) and 75% FC Utilization assumed.

Ammonia Formation

The further deleterious effects of peak shave gases, especially ones with up to 20% by volume nitrogen, is the thermodynamic possibility of ammonia formation during steam reforming. Ammonia's detrimental effect on the PEMFC is well known in the industry; Nuvera requires <0.010ppmv NH₃ in the hydrogen feed stream.

Equilibrium would suggest higher ppmv level ammonia formation at lower temperatures. Likewise, higher N₂ levels in the feed stream also result in higher levels of ammonia. Of course, the model does not take into account any kinetics for the reaction. Included for comparison is an autothermal reformer (ATR) with a PHI=3.5. In general, the Gibbs solution would estimate somewhere between 20-100ppmv NH₃ over the 600-800°C operating range of the SMR and starts to approximate the ATR case at the elevated N₂ levels.

Figure 61. Ammonia Formation Equilibrium in SMR with varying N₂ Addition. SMR modeled as Gibbs using Hysys. Note, all cases assume S/C=4. Autothermal Reformer (ATR) at a PHI=3.5 provided as reference.

Since the Hysys simulations presented in Figure 61 do not account for the rate of ammonia formation, the Avanti™ SMR was used as the basis for the experimentation (depicted in the earlier Figure 1). Local Nuvera/Cambridge NG was used for the experiment, which contains negligible nitrogen levels. A nitrogen gas line supplied from the lab was installed at the SR fuel inlet line and controlled via a rotameter (0-5 SLPM). During steady state operation, varying nitrogen levels could be delivered into the SR by the rotameter and composition monitored by gas chromatograph/FTIR.

Gas samples were taken at the exit of the PrOx zone and analyzed by FTIR, GC and IR instrumentation. Reformate was chilled between 14-17°C by city water in a plate heat exchanger and the water collected by a separator/trap combination. Water samples were taken after at least 30-minutes at steady state to ensure sample integrity.

The baseline for the reformer operation was 11.8 kWth NG in the SMR and nearly 5.9 kWth NG in the TGC burner. The SMR exit temperatures vary circumferentially about 30°C, with an average of ~665°C. The baseline condition reports 3.7% N₂, which is a result of air addition to the PrOx reactor zone. The subsequent rows in Table 16 below show an increase in this N₂% value due to the direct addition of pure N₂ to the inlet of the SMR. At both the baseline condition and 1-SLPM N₂ conditions, ammonia is below detection limits. However, at the 4-SLPM condition, a slight amount is measured (0.4mg/L) through water analysis. The same 4-SLPM condition was run but with increased TGC fuel input to increase the operating temperature of the SMR zone. The average temperature of the SMR bed was increased to ~710°C in this manner. The detectable ammonia level in the reformate condensate increases nearly 7-fold with an increase in the bed temperature to 2.7mg/L, and a 10-fold increase to 4.0mg/L at an average SMR bed temperature of ~720°C. All samples corroborated with FTIR instrumentation and 3rd party water analysis.

							<i>Dry Composition (Post PROX unless otherwise noted)</i>						
N₂ Flow (slpm)	SMR Power (kWth, LHV NG)	Burner Power (kWth, LHV NG)	S/C Ratio	SMR Temp1 (Deg C)	SMR Temp2 (Deg C)	SMR Temp3 (Deg C)	H₂%	N₂%	O₂%	CO₂%	CH₄%	CO% (LTS)	NH₃ (mg/L)
0	11.8	5.9	3.3	651	678	681	70.40	3.73	0.05	21.40	2.12	0.72	<0.1
1	11.8	5.9	3.4	651	675	680	70.10	5.00	0.02	21.00	2.07	0.71	<0.1
4	11.8	5.9	3.3	650	674	680	67.50	8.32	0.03	20.10	2.01	0.68	0.4
4	11.8	7.0	4.3	690	713	727	69.20	8.02	0.01	20.40	0.90	0.55	2.7
5	11.8	7.0	4.4	702	725	739	68.40	10.40	0.01	19.80	0.78	0.48	4.0

Table 16. Operating Conditions and Resulting Ammonia Formation versus Nitrogen Addition to NG Fuel. NH₃ values obtained through water sampling (14°C) and subsequent analysis at Adirondack Environmental Services, Inc. Liquid samples obtained after the PrOx reactor zone.

These results are a primary concern for PEMFC systems using only a standard PrOx reformate conditioning configuration with no additional clean-up. In a system like PowerTap where a pressure swing adsorber is employed versus a PROX unit, hydrogen purity can be ensured.

To summarize, Avanti and PowerTap fuel processors' architecture is very similar and they use comparable catalysts. Thus based on Avanti fuel processor LPG experience it is concluded that PowerTap is a fuel flexible design which may require only minor modifications to run on LPG.

6 Task 4 – Performance Validation

By the terms of the contract, performance of the FP1R fuel processor was audited by the Argonne National Laboratory. In September 2008 Rajesh Ahluwalia and Shabbir Ahmed from ANL visited Nuvera to witness FPTs operation and acquire fuel processor performance data. Due to the abundance of the proprietary information that was shared by Nuvera, ANL performance verification memo [4] for the CHARM reformer that was presented to DOE was not made public. Thus the current chapter will consist mainly of excerpts and main findings and conclusions from the aforementioned ANL report.

For better precision in performance modeling and analytical calculations and to avoid any uncertainty in evaluation of the system energy balance, the CHARM fuel processor was operated exclusively on NG. In other words no raffinate/reformate were present in the burner.

Based on Nuvera's data shown in Table 17, ANL developed an analytical model of the CHARM fuel processor.

	Units	Run 4	Run 3	Run 1	Run 2	Mean
SR Fuel	g/s	2.08	2.25	2.56	2.58	2.37
Burner Fuel	g/s	1.12	1.13	1.17	1.14	1.14
SR Steam	g/s	7.9	8.0	8.2	8.0	8.0
SR Inlet P	bara	2.3	2.3	2.4	2.4	2.4
SR Outlet P	bara	2.2	2.2	2.3	2.3	2.2

Table 17. FPTs operating conditions (from ANL report [4])

Test data acquired by ANL included nominal condition (Run 3), as well as high efficiency cases (Runs 1 and 2) and improved durability case (Run 4).

ANL calculated “that for the conditions of Runs 1-4, the fuel processor test train has $78.7 \pm 0.7\%$ thermal efficiency (see Table 5) defined as the lower heating value (Δh) of CH_4 , H_2 and CO in the HTS outlet stream divided by the lower heating value of the NG fed to the unit (burner and steam reformer)” [4].

$$\eta_{th} = \frac{\sum_{HTS} \dot{N}_i \Delta h_i}{\sum_{NG} \dot{N}_i \Delta h_i}$$

	Units	Run 4	Run 3	Run 1	Run 2	Mean
NG to Burner and SR	g/s	3.20	3.38	3.73	3.72	3.51
FPS Thermal Efficiency - LHV	%	74.2	78.0	79.4	79.4	77.8
FPS Thermal Efficiency - HHV	%	77.5	82.0	83.3	83.2	81.5

Table 18. Performance of CHARM fuel processor (from ANL report [4])

“A thermal efficiency of $78.7 \pm 0.7\%$ implies that $21.3 \pm 0.7\%$ % of fuel heating value is unavailable due to the heat losses from the system, unrecoverable latent heat of water in the reformat stream, and the enthalpy of the combustion products exhausted to the ambient” [4].

ANL also “projected the performance of a distributed hydrogen production plant that employs the tested fuel processor for steam reforming of natural gas coupled to a PSA unit for hydrogen purification. In

projecting the performance, we have assumed that the PSA can be operated at a hydrogen recovery such that the heating value of H₂, CO and CH₄ in the tail gas is comparable to the heating value of the natural gas fed to the burner in the FP test train (balanced mode of operation). Field test on an integrated FP-PSA unit indicate that this may be a reasonable assumption under certain conditions and that the H₂ recovered in this operating mode can have ~99.995% purity with <1 ppm CO. We estimate that a hydrogen recovery of 74.3±7.2% is possible in the balanced mode of operation. The actual recovery is about 2 percentage-points higher than the mean value calculated for the balanced mode of operation. Table 19 indicates that the integrated unit operated in this mode can deliver 57.2±9 kg/day of hydrogen (79.4±12.4 kW_{th}-H₂) with 115.8±15.6 kW_{th}-NG input for an overall thermal efficiency (η_{H2}) of 68.4±1.7% defined on the bases of the lower heating values” [4].

$$\eta_{H_2} = \frac{\dot{N}_{H_2}^{PSA} \Delta h_{H_2}}{\dot{N}_{NG} \Delta h_{NG}}$$

	Units	Run 4	Run 3	Run 1	Run 2	Mean
Thermal Input	kWt	102.2	110.5	125.8	126.7	116.3
H ₂ Recovery in PSA	%	72.6	67.8	76.3	80.5	74.3
Pue H ₂ Production Rate	kg/day	44.3	53.2	63.3	64.0	56.2
Thermal Output of H ₂ - LHV	kWt	61.5	73.8	87.9	88.9	78.0
Thermal Efficiency - LHV	%	60.2	66.8	69.9	70.1	66.7
Thermal Efficiency - HHV	%	64.2	71.2	74.5	74.8	71.2

Table 19. Performance of CHARM fuel processor (from ANL report [4])

“Naturally, H₂ recovery would be smaller if the desired H₂ purity is higher than 99.995% (50-ppm total impurities). In this case, excess waste heat would be available in the PSA tail gas, which may be used to raise additional steam allowing the SR to operate at S/C higher than 2.9-3.3 and the overall thermal efficiency would be less than 68.4±1.7%. Conversely, H₂ recovery in PSA can be >74.3±7.2% if H₂ purity requirement is relaxed. In this case, supplemental NG would have to be fired in the burner and the overall thermal efficiency can be somewhat >68.4±1.7% (but always <78.7±0.7% with the fuel processor tested)” [4].

To summarize ANL findings, “the CHARM fuel processor can achieve 78.7±0.7% thermal efficiency defined as the ratio of the lower heating value of the reformat divided by the lower heating value of the natural gas supplied to the steam reformer and the burner. In the balanced mode of operation, the FPS can be integrated with a pressure swing adsorption unit to achieve 68.4±1.7% overall thermal efficiency defined as the ratio of the lower heating value of the high purity hydrogen produced to the lower heating value of the natural gas input to the fuel processor. At 100% duty, the integrated unit is capable of delivering 57.2±7.9% kg/day of high purity hydrogen in the balanced mode of operation. The projected capacity of the fuel processor integrated with a PSA unit capable of obtaining ~76% H₂ recovery is 63.3 kg-H₂/day at 69.9% thermal efficiency (LHV basis, 74.5% efficiency on HHV basis). The unit may need to be derated and the overall thermal efficiency would be lower if the H₂ purity standard is more stringent than what is achievable in the balanced operating mode in which the flammables in the PSA tail gas provide the thermal energy requirements of the steam reformer. The overall parasitic load with the compressors, blowers and pumps in use is about 7.8 kWe (2.9 kWh/kg-H₂), more than 50% of which is due to compression of the reformat to the working pressure (10 bara) of the PSA unit” [4].

7 Summary of Accomplishments of the PowerTap Fuel Processor Design

Although steam reforming is a well-proven technology, industrial reformers run continuously with constant hydrogen demand and undergo only a few thermal cycles per year. In contrast, for small scale hydrogen generators in early market introduction phase constant hydrogen demand cannot be assured, necessitating a need for frequent start up - shut down cycles. Cycling reformer metal and catalyst, sometimes daily, poses a serious durability threat due to the interaction between creep, corrosion and cyclic fatigue. It has been a pre-eminent focus of the CHARM program to find a commercially acceptable balance between fuel processor capital cost, efficiency and operating cost, and durability and maintenance costs, in pursuit of a system with the lowest life cycle cost (LCC) to the customer.

Nuvera now has high confidence in durability of the metal hardware of the fuel processor. It is expected with reason that it will last for 40,000 hours and 1,000 cold cycles. However, evidence of catalyst performance degradation, especially during cycling, suggests that catalyst durability is a weak link in life cycle cost of the hydrogen generator. More work will have to be done to either dramatically reduce number of cycles experienced by the system or significantly improve catalyst cycling capabilities or adopt alternative catalyst solutions.

Status versus the DOE technical targets for stationary fuel processors [1] is presented in Table 20. It should be noted that DOE Technical targets in Table 20 are designed specifically for fuel processors generating hydrogen containing reformat gas, unlike PowerTap, which supplies pure hydrogen. Inevitably, hydrogen purification step requires additional equipment, such as PSA and gas compression unit, and corresponding increase in capital cost of the system. As a result, two values for the cost per kWe in Table 20 represent two cases: 1) cost of the entire Hydrogen Generation System; 2) cost of the fuel processor excluding PSA and Reformate Compressor.

Technical Targets: Stationary Fuel Processors (equivalent to 5-250kW) to Generate Hydrogen-Containing Fuel Gas				
Characteristic	Units	2005 Status	2011 Target	CHARM Status
Cost	\$/kWe	1,000	220	2155 ¹ / 1432 ²
Cold start to rated power @ -20C ambient	min	<90	<30	93 ³
Transient response time (10 to 90% power)	min	<5	1	15
Durability	hours	20,000	40,000	Designed for 40,000
Survivability (min & max ambient temperature)	°C °C	-25 +40	-35 +40	-20 (managed by enclosure heater) +40 (verified)
CO content in product stream				Verified via 3rd Party Analysis
Steady State	ppm	10	1	<1 (product - 99.995% H ₂)
Transient	ppm	100	25	<6
H ₂ S content in product stream	ppbv (dry)	<10	<4	N.D. ⁴
NH ₃ content in product stream	ppm	<1	<0.1	N.D. ⁵

¹ Includes cost of the entire Generation System at 2,000 units production volume and assumes fuel cell efficiency of 53%;

² FP cost excluding PSA and Reformate Compressor; ³ Faster startup is possible but may be damaging for the catalyst;

⁴ Instrumentation detection level of 5.0 ppbv; ⁵ Instrumentation detection level of 1.0 ppm; N.D. - not detected.

Table 20. Status of CHARM fuel processor versus DOE HFC&IT Fuel Cell Program targets [1].

System cost at 2000 units production volume was estimated based on our current unit cost at low quantities using Wright method of learning curve (also known as progress functions) [22]. Wright's theory is based on repetitive production of airplane assemblies. "It is recognized that repetition of the same operation results in less time or effort expended on that operation. For the Wright learning curve, the underlying hypothesis is that the direct labor man-hours necessary to complete a unit of production will decrease by a constant percentage each time the production quantity is doubled. If the rate of improvement is 20% between doubled quantities, then the **learning percent** would be 80% ($100-20=80$). While the learning curve emphasizes time, it can be easily extended to cost as well." [22]

Very conservative learning percent value, more representative of repetitive electronics manufacturing, or repetitive machining or punch-press operations (both in 90-95% range) [22], was used for the analysis.

CHARM status versus DOE Hydrogen Production Program targets is shown in Table 21.

Select Technical Targets: Distributed Production of Hydrogen from Natural Gas				
Characteristic	Units	2010 Target	2015 Target	Application of CHARM
Production Energy Efficiency	% (LHV)	72.0	75.0	66.7 – 70.1% current system [4]; Novel high efficiency system concept is in design phase
Production Unit Capital Cost (Uninstalled)	\$	900K	580K	\$2.4M (@1550 kg/day) including ~\$1M H ₂ Storage
Total Hydrogen Cost	\$/gge H ₂	2.50	2.00	7.84 (automotive assumptions) 5.24 (material handling) [2]

Table 21. Status of CHARM FP versus DOE HFC&IT Hydrogen Production Program targets [1].

8 Advanced Concepts

8.1 New Modular Fuel Processor Concept

Despite rather high confidence that metal in the current fuel processor design will last for 40,000 hours, further mitigation of peak temperatures in the fuel processor might be required for other aspects of system durability, such as catalyst life, especially during cycling. While the current design is cycle-capable, there is work outstanding to reduce the start-up time to further improve economics, and this will require additional design effort. While it is important to have the temperature of the reformer tube sufficiently high to sustain a steam reforming reaction, it is also desirable to reduce the peak temperature in the reformer for improved durability. Harmful effects of direct flame impingement and radiation in high temperature reforming zone could further be alleviated, by designing a highly efficient burner – reformer heat exchanger relying on alternative means of energy transfer.

In addition, the current configuration of the fuel processor has a limited scaling capability. Being of an annular arrangement and as a result having unutilized volume imposes certain practical constraints on the number of tubes and tube sizes used. Even moderate scale increase will result in rapid increase of the annular fuel processor overall diameter, leading to significantly higher metal thicknesses and consequently higher cost as dictated by pressure vessel design considerations. Therefore significant scale-up of this technology might require a somewhat more modular configuration with close tube packaging and much more manageable footprint for a given throughput. To summarize, durability improvements, modularity/scalability and fuel processor cost considerations became the main drivers for looking into alternative reformer configurations.

Adhering to the present Nuvera practice of vertical, unconstrained, reversed internal reformat flow tubes, externally heated by hot gas combustion products, design goals included reduction of complexity particularly of assembly, and further improvement of the fuel processor life cycle demanding market applications. This study and design exercise has resulted in the continued use of the Nuvera tube format, albeit of larger diameter and much larger length, in looks not uncommon in industrial approach, but in a size and packaging appropriate for cycle-capable external heat transfer operation. Although our reforming experience has yielded confidence in the internals of this tube design for reforming performance, these cycling applications require much more uniform circumferential tube temperatures and minimized peak tube temperatures in order to realize favorable metal and catalyst life. Essentially Nuvera kept what works but generated a more benign external tube environment. Scaling is now anticipated by changing the number of set length, diameter tubes to meet applications of hydrogen output. Number of tubes has been substantially reduced. The deleterious effects of cycling have been addressed through tube external heat transfer rate control, radiation temperature reduction, and most importantly, cycling reduction and virtual elimination in the larger scale applications by incorporation of combining a prime mover power generator with the reforming process.

In the spirit of advocating an engineering change of design for more than one reason, the switch to fewer and much longer tubes allows the application of means of outer tube surface heat flux control. With removal of flame impingement and intimate association high temperature radiation heat fluxes, and the addition of hot gas flow convection controlled heat flux, the total tube surface now contributes to support of the reforming endotherm.

Unbridled high temperature radiation and flame impingement do provide maximum heat flux and even NO_x emission control thru flame quenching and are well used, making sense in commercial industrial reformers where cycling is avoided and thus local metal heating and temperature variations can be tolerated. Frequent cycling virtually eliminates such heat transfer luxury resulting in rapid metal fatigue.

Analysis of a single repeating tubular element in the new modular fuel processor concept and a comparison of temperature fields in the current and newly proposed fuel processor concepts are shown in Figure 62.

Figure 62. Comparison of CFD models predictions of temperature fields in the hottest zone of the a) current and b) newly proposed FP concepts

CFD model indicates much more uniform temperature profiles and a significant reduction of the peak metal temperatures compared to the current annular architecture. The recommended design removes the hot gas generation means from the heat transfer by locating the energy source burner or thermal reactor apart from the reactor such that essentially uniform hot low emissivity gas contacts the tubes. Radiation heat transfer in this vulnerable high metal temperature region is substantially reduced to manageable levels and convection heat transfer is low by virtue of lower Reynolds number and relatively large exhaust gas flow area. The key to maintaining this now uniform safe heat flux in the hottest zone of the reformer is by increasing heat flux in the downstream reduced burner gas temperature section of the tubes. It is achieved by installing inserts in the remaining half or two-thirds of the reformer. These inserts increase the exhaust gas turbulent heat transfer by factors, thus tending to maintain heat flux in this now lower temperature region where it is needed and can be easily tolerated by the lower metal temperatures. Tube metal temperatures as well as the catalyst are less stressed and more uniformly utilized over the full packed length.

Hot exhaust gas generation is done either by thermal reactor, or non-luminous flame combustion. A limited maximum uniform hot gas temperature is a necessary restriction from both a radiation control and NO_x emission control in the above approach. For the stand free burner case, a dilution of about 100% chemically correct ratio is added to the oxidation process, and even more in cases with burner preheats. Such operation with excess air, or cooled exhaust recirculation as diluent will allow excess steam generation which aids reforming process, but does impact slightly negative on the overall reforming efficiency. Such can be corrected through recirculation of the still warm burner products from the reformer exit. However, this complication is probably not worth the effort particularly on the smaller scale units. For the larger scale where perhaps energy consumption is more an issue, the combined cycle approach, the subject of one of the following chapters, addresses the energy efficiency of the total hydrogen reforming, pressure storage system and process.

8.2 500 kg/day Fuel Processor

In addition to plans for commercialization of PowerTap technology in the material handling market, Nuvera is considering developing a system for use in vehicular refueling applications. Introduction of the automotive hydrogen refueling technology is envisioned at 500 kg/day scale, a roughly 10X of magnitude increase over the present PowerTap output. The system is based on highly efficient heat flux controlled steam reformer concept described in the previous section.

For this reformer, the current evolved design designates an array of vertical tubes closely spaced, virtually contacting when at temperature, laid out as a rectangular FP assembly. Tubes are most likely constructed of standard 4 inch diameter, schedule 40 310 stainless steel pipe. The calculated outside total tube area required for heat transfer from the heat source under the conditions to be defined, stipulates a tube length of around 8.5 feet (2.6 m). This tube diameter is twice that of the present 50 kg/day functioning Nuvera product candidate; however, the proper sizing of the internal counter-flow reformat return tube yields an annulus catalyst packing similar enough to the present model and within the bench data generated in our laboratory. With similar space velocities preserved, the satisfactory performance of tube internals witnessed on the present unit is with reason anticipated.

The relatively long tube lengths support simplicity by reducing the number of tubes required, and thus construction costs such as welds. The squared vertical close tube spacing allows similar or even slightly smaller tube diameter manifolding of steam-methane input and reformat output, thus avoiding the extra required wall thickness of large diameter tubes for elevated temperatures/pressures. Hydrogen output

scaling is achieved thru variation of tube number at the given length in linear fashion. The heat transfer process, both inside and outside each tube remains relatively constant regardless of scaling except for secondary side effects.

As was mentioned previously, scaling up current annular FP architecture to 500 kg/day seems impractical. Therefore comparison of the footprints and volumes was performed at 50 kg/day scale. It is expected that the modular heat flux controlled reformer design will result in about 6 times footprint and volume reduction compared to the annular reformer configuration.

8.3 Advanced Combined Cycle System

The 500 kilogram H₂ per day fuel processing system described above is being developed for both materials handling and automotive refueling markets. In both of these cases, the larger scale and the nature of the convective heat transfer design allow for additional efficiency, cost and durability benefits that are not practical at current 50 kg/day scales. In particular, this fuel processing system enables a total system integration strategy in which a combustion engine generator set is used to produce electrical work from the PSA raffinate stream and where the engine exhaust is being used as a heat source for the reforming reaction. The electric power production from the generator is used to supply the parasitic loads of the hydrogen generation, compression and storage systems, and additional electric power can be available to offset the typical requirements of an automotive fueling station. The key enabling technology for this system integration strategy is the convective heat transfer design of the steam reformer, which allows for effective supply of heat to the reforming reaction without requiring the high temperatures associated with direct combustion on the hot side of the heat exchanger. This section provides a detailed description of this combined cycle system and an analysis of its operating cost and durability benefits.

8.3.1 Process Description

As shown in Figure 4 the current reference hydrogen generation system consists of a steam reformer, shift reactor, reformat conditioning and compression, and a pressure-swing adsorption purification step. The raffinate return from the PSA is combusted in the burner section of the steam reformer to provide heat for the reforming reaction, and the burner exhaust from the steam reformer, along with heat from cooling of the reformat stream, is used to generate steam for the process. A schematic of the proposed modification to this system integration is shown in Figure 63. In this case, a natural gas engine generator set, running in a fuel rich mode, is used to combust a portion of the raffinate stream. Given the dilute nature of the raffinate, which is primarily composed of hydrogen, methane, carbon monoxide, and carbon dioxide, the total volume flow through the engine is equivalent to lean operation on natural gas, even though the gas mixture is approximately 30 – 40 percent fuel rich. Additional air is added to the engine exhaust by an auxiliary blower, and the resulting mixture is passed through a thermal reactor in which the remainder of the fuel is combusted. The hot gas produced by the thermal reactor then provides the heat for the steam reforming reaction via primarily convective heat transfer in the steam reformer / heat exchanger vessel. The rest of the system is essentially identical to the current configuration, including high temperature shift, steam generators, reformat conditioning and compression, and pressure-swing adsorption.

Figure 63. Schematic process flow diagram of combined cycle hydrogen generator system. Ancillary equipment such as desulfurization beds, condensers, radiators and safety systems are not shown.

The engine generator set can be integrated into the system with minimal modification, as the raffinate mixture enters via the standard air intake manifold. In a 500 kg H₂/day system, the appropriate generator size to match the raffinate flow rate is approximately 200 kW electric, which produces sufficient power for all the electrical needs of hydrogen generation, compression, storage and delivery, with some excess available for additional fueling station power offset.

8.3.2 Process analysis methodology

To quantify the benefits of this system integration strategy, detailed process analysis has been conducted to compare the combined cycle system with the reference design at the 500 kilogram per day hydrogen production scale. The modeled systems included all reactors, balance of plant, and associated hardware for hydrogen production, compression, storage and delivery, assuming a storage pressure of 5000 psi, and delivery pressures from 5,000 – 10,000 psi, depending on the application. Each system configuration was modeled over a range of operating conditions, such as reactor temperatures and steam to carbon ratios.

Aspen Plus™ process modeling software was used to perform the calculations, with detailed modeling of each reactor, heat exchanger, and system component based on known hardware performance for standard BOP components, and detailed analytical models for reactors such as the convective steam reformer.

8.3.3 Process analysis results

Three system configurations were compared. The first is the existing system architecture, scaled to 500 kilograms per day of hydrogen production, and incorporating the convective steam reformer design. The second configuration incorporates the combined cycle using a standard natural gas generator, specifically the Caterpillar G3408 NA Natural Gas Generator Set [5], in a naturally aspirated configuration. The final configuration includes a modeled generator set incorporating near-term high efficiency technology. This generator set is based on Cummins Westport dual-fuel technology, which allows use of gas fuel in a diesel cycle via high pressure direct injection of a small quantity of diesel or natural gas for pilot ignition [6,7]. Key parameters for the generator sets are listed in Table 22.

Generator Type	Naturally Aspirated Spark Ignition Gas Generator Set	Turbocharged Pilot Injection Diesel Cycle Gas Generator Set
Reference Technology	Caterpillar G3408 NA [5]	Cummins-Westport HPDI [6]
Air Intake	Naturally Aspirated	Turbocharged
Compression Ratio	9.7:1	~14:1
Efficiency [AC, LHV basis, 100% load]	35%	42%
Exhaust Temperature	600 °C	500°C

Table 22. Assumed operating parameters of standard and high efficiency gas gensets for process model.

For each system configuration, the process model was run to determine fuel and electric consumption of all components, as well as electric generation in the case of the combined cycle configurations, for a total output of 500 kg / day of H₂ at a storage pressure of 5000 psi. The results are summarized with respect to operating cost of H₂ production in Figure 64. The operating costs were calculated using the 2010 – 2015 assumptions for natural gas and electric prices for distributed hydrogen production applications from the DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program plan [1]. For each case, two lines are shown on the plot: the total operating cost (solid line), which is the sum of natural gas and electric costs per kilogram of hydrogen produced and stored; and the natural gas operating cost (dashed line), which is the cost of all natural gas fuel used per kilogram of hydrogen produced and stored. The difference between these is the electricity cost contribution. Note that for the combined cycle cases, the electricity cost contribution is negative, as the generator produces more power than needed by the hydrogen production and compression systems. It is assumed that this power (on the order of 20 – 80 kW_e) could be used to offset the electrical needs of the fueling station. If this is not the case, the engine could be throttled to balance the electric output with the hydrogen generator and compressor consumption, which would result in a total operating cost very similar to the natural gas operating cost shown in the figure.

Figure 64. Operating cost of hydrogen production for convective steam reformer technology as a function of maximum reformer metal temperature in three configurations: standard system integration, combined cycle with low-efficiency (current technology) generator set, and combined cycle with high-efficiency (near-term technology) generator set. Natural gas and electricity prices are from the DOE HFC&IT Program Plan [1].

The first benefit of the combined cycle to be noted from Figure 64 is the significant reduction in operating cost for the combined cycle systems. Even without taking credit for the excess electric production, a 25% reduction in operating cost is achieved with the current technology generator set; this is primarily due to the use of the high-quality heat available from the PSA raffinate return to generate electricity before being used to supply heat of reaction for the steam reforming. If the excess electric generation is considered to be a direct offset of existing electric demand at the fueling station, the operating cost benefits are greater: 35% cost reduction for the current technology generator, and 48% reduction for the high efficiency generator. An additional benefit of the combined cycle systems is that the operating cost is insensitive to the reformer operating temperature over a relatively wide range. As reformer temperature is decreased, the steam reforming equilibrium shifts, resulting in lower hydrogen production, and more carbon monoxide and methane in the reformat. In the combined cycle systems, the CO and methane are used for electric generation, thus offsetting the effects of the less efficient hydrogen production. This allows for operation of the reformer at lower temperatures with little or no cost penalty, which can significantly increase the durability of the reformer hardware.

8.3.4 **Additional benefits of combined cycle hydrogen generation systems**

In addition to the direct operating cost benefits shown above, the combined cycle system integration has other advantages in a refueling application. Firstly, as noted in Figure 63, the system may be operated either in a hydrogen production mode or in an electric generation mode if there is no hydrogen demand. This prevents the need for on-off cycling of the hydrogen generator, and particularly thermal cycling of the reformer hardware, in cases where demand is lower than the generation capacity. This is very likely to be the case in automotive refueling applications, particularly during early marked introduction. The avoidance of excessive cycling eliminates one of the major durability challenges for the fuel processing hardware. The use of electric generation mode rather than on-off cycling also eliminates most of the startup and shutdown time for the hydrogen generator, providing a system that is more responsive to changes in demand.

A list of advantages of this NG fired total output system includes:

- high slip reformer operation with inherent life and stress advantage but no system efficiency penalty or compromise
- uniform primarily convection heating of reformer tubes by homogeneous hot gas
- improved FP metal and catalyst life through temperature reduction and substantial cycling reduction
- reforming energy cost savings by way of high efficiency gas fired electricity generation reduction or possible elimination of shift catalysts and associated apparatus
- potential 42% stand alone methane addition electricity generation efficiency with 2 to 3 year engine payback
- over 95% reformer efficiency since engine waste heat covers steam generation
- efficiency-favorable close-to-chemically correct system final exhaust at low temperature
- natural emissions control, NO_x in particular, with virtually total combustion air utilization , or nearly chemically correct exhaust
- option of adding compressed NG as a parallel customer product with same compressors
- freedom to use a variety of reformer designs

9 Life Cycle Cost Assessment

Overall product value proposition and life cycle cost or total cost of ownership depend on many parameters including capital cost, operating and maintenance cost and installation cost. Each cost category was scrutinized separately and also in combination with other variables as part of the cost tradeoff study.

The PowerTap reformer was designed for long life and low cost according to DFM&A principles. Based on CHARM fuel processor experience, the current third generation of reformer design has the same functionality, but is packaged much more efficiently.

Operating and maintenance costs were addressed in tandem, where a tradeoff between efficiency and durability drove optimization of reformer design and operation. It was concluded that the overall value proposition is more strongly affected by reformer durability and consequently high maintenance cost, while efficiency or operating cost represent a secondary effect in life cycle cost of the hydrogen generator. Therefore, normal fuel processor operation assumes running a reformer at lower temperatures, favoring durability over efficiency, yet still satisfying the efficiency target of the CHARM program. Such operating mode coupled with a very low stress design and marginal cost increase of using Inconel caps gave design team high confidence that reformer will last 40,000 hours and 1,000 cycles. However, expected catalyst durability is short of the 20,000 hours target. Catalyst durability validation is ongoing and will continue well into 2009 and beyond.

As was explained in the previous chapters, Nuvera is also working on a new concept for the reformer design and on the novel advanced combined cycle system concept. Both are still in conceptual design phase, however when complete, both concepts are expected to improve on durability and efficiency of the system as well as further mitigate the deleterious effects of start-stop cycling.

A comparison of the total H₂ cost for the current 50 kg/day system, a new modular concept at 500 kg/day scale and two advanced cycle options was performed using the DOE Hydrogen Analysis (H2A) Forecourt Production model, Version 2.1. The H2A model is intended to ensure transparent reporting and a consistent cost methodology. The H2A cost model for distributed hydrogen production uses a discounted cash flow technique to determine the cost of hydrogen needed to yield a prescribed internal rate of return (IRR).

The following is a list of key assumptions with notes whenever the H2A default values were not used:

- Plant Design Capacity: 57 kg of H₂/day
- Operating Capacity Factor: 70%
- Equity financing: 100%
- System life: 10 years (H2A default is 20 years)
- Depreciation schedule: 7 years
- Depreciation type: MACRS
- Decommissioning cost: 10% of depreciable capital investment
- Inflation rate: 1.9%
- After tax real IRR: 10%
- Income taxes: 35% Federal, 6% State
- Property taxes and Insurance: 2%
- Working Capital Rate: 15% of the annual charge in the total operating costs
- Natural gas and electricity prices by year obtained by using Annual Energy Outlook 2007 case. Commercial price rates are assumed.
- Compressed H₂ Storage: 87.5% of maximum daily
- Hydrogen Purity: 98% minimum; CO < 10ppm, sulfur < 10ppm
- Manufacturing volume: 500 systems annually

The summary of H2A model output is shown in Table 23.

System Option	Amortized H ₂ cost, \$/kg Automotive Refueling	Amortized H ₂ cost, \$/kg Stationary Applications
PowerTap-50 (57 kg/day)	\$7.84	5.24
PowerTap-500 (570 kg/day)	\$4.50	3.01
PowerTap-500 w/ SI engine	\$4.39	2.91
PowerTap-500 w/Diesel cycle engine	\$4.30	2.82

Table 23. Comparison of the hydrogen cost predicted by H2A model for several system options under automotive refueling and stationary applications assumptions.

H2A model's assumptions are designed specifically for the automotive refueling application. And unique requirements for a retail automotive refueling result in a significantly higher cost of hydrogen than what is anticipated for the material handling. The major cost add-ons for auto refueling compared to material handling market are:

- 70% generation utilization instead of up to 90%
- the use of commercial rates vs. industrial rates for natural gas & electricity
- federal and state taxes
- increased storage volume, which is not needed in material handling due to more uniform and more predictable consumption profile
- dispensing with data communications for composite automotive tanks (steel tanks on forklifts allow fast fill with no constraints on gas temperature inside)

Eliminating just these five requirements from the H2A model assumptions drops the cost of hydrogen to \$5.24 per kilogram for the current 57 kg/day system and to \$3/kg or lower for a 570 kg/day system. This makes the material handling sector a fantastic opportunity for early introduction of a cost effective distributed hydrogen infrastructure.

Hydrogen cost estimate for advanced system concepts was performed using very conservative low volume pricing for SI and Diesel cycle engines. The amortized hydrogen cost numbers in Table 23 assumed prices of \$35,000 and \$70,000 for SI and Diesel NG engines respectively with a maintenance contract of \$250,000 over 10 years. In any reasonable production volume of these currently custom engines the prices as well as maintenance cost should come down significantly, further improving cost of hydrogen and value proposition.

10 Conclusions and Future Direction

Nuvera successfully executed all program milestones, listed in Table 24.

Project Task	Program Milestones	Status
1. System Definition	Define specifications & operating conditions	Completed
2. Design & Analysis	Complete subscale testing	Completed
	1000scfh fuel processor design & analysis (FP1 series)	Completed
	Develop advanced system concept to reduce operating cost by 10% or more while maintaining or reducing emissions profile	Completed
	Develop SR concept with optimized heat flux profile	Completed
3. Prototyping & Testing	1000scfh fuel processor testing & validation (FP1)	Completed
	1000scfh fuel processor testing & material validation (FP2 series)	Completed
	Validate scalability via 10,000scfh (~560 kg/day) fuel processor conceptual design	Completed
	Implement monolith based HTS for fast start, easier packaging and reduced LCC	Completed
	Implement industrial burner control	Completed
	Assess novel NG desulfurization method based on hydrodesulfurization technology	Completed
4. System Demonstration	1000scfh subsystem demonstration at Nuvera Fuel Cells by Argonne National Laboratory (ANL)	Completed
	Durability achievement: 5000 hrs, 250 cycles	Completed
5. Project Management	Final report & presentation to DOE	Completed

Table 24. Status of CHARM program milestones.

A summary of major successes of the CHARM program follows.

Fuel processor design and performance validation:

- A 1,000 scfh (nominally 50 kg/day) fuel processor was developed
- Minimization of capital cost is achieved in accord with DFM&A principles.
- Actual cost was confirmed by a third party manufacturing house that is now in charge of the fuel processor manufacture.
- Trade off analysis between capital and operating and maintenance costs over a 40,000 hour life were performed, leading to optimization of the fuel processor design and operating conditions.
- A suite of catalyst technologies including steam reforming, water-gas-shift and desulfurization was developed and optimized for desired performance. However, expected catalyst life does not meet 20,000 hours target and substantial collaborative effort with catalyst suppliers is ongoing to further improve catalyst durability.
- Performance of a 1,000 scfh fuel processor was confirmed by Argonne National Laboratory. Fuel processor thermal efficiency of 75% defined in Table 1 was met or exceeded.

- Durability of the advanced FP with combined cycle system is projected at 80,000 hrs.

Fuel processor durability:

- Lifetime assessment was performed through modeling of stresses and through accelerated aging of the fuel processor.
- High confidence in fuel processor life of 40,000 hours and 1,000 cycles is achieved with internal analysis. Independent lifetime validation is planned for early 2009.
- Fuel processor durability of over 6,000 hrs and over 250 cycles was demonstrated

Hydrogen cost:

- Cost of hydrogen projected by DOE H2A model at 57 kg/day scale is \$7.84/kg (automotive assumptions) and \$5.24/kg (material handling).
- New advanced FP concept and combined cycle system are projected to reduce hydrogen cost to below \$4.50 per kg at 570 kg/day scale.

Advanced concepts:

- A scalable and modular convective fuel processor concept is developed, affording reduction of capital cost and improved durability.
- Advanced combined cycle concept is developed. A 25 – 48% reduction in operating cost is deemed possible based on DOE assumptions for electricity and NG rates [1].
- Preliminary designs of 500 kg/day fuel processor and of the entire generation system are completed.

Technology demonstration:

- First in Massachusetts hydrogen refueling station was unveiled at Nuvera headquarters in August 2008. Nuvera hosted a 2008 Hydrogen Road Tour. 10 fuel cell vehicles from 7 manufacturers were successfully refueled, as shown in Figure 65.
- Two complete PowerTap systems are now operational at Nuvera Billerica facility, supplying hydrogen for internal fuel cell testing needs, Figure 66. A third (Alpha 3) system has just been installed on Nuvera's hydrogen pad, Figure 67.

Figure 65. 2008 Hydrogen Road Tour hosted by Nuvera at Billerica headquarters.

Figure 66. Two PowerTap hydrogen generation systems (Alpha 1 and Alpha 2) are operational at Nuvera facility.

Figure 67. Alpha 3 system being installed at Nuvera hydrogen refueling facility.

In the future Nuvera will continue with development of a 50 kg/day PowerTap hydrogen generator. In 2009 the focus will be on product quality and delivery of actual systems into customers' hands. As part of a DOE solicitation for FY2009, Nuvera submitted six applications for installation of 50 kg/day PowerTap™ systems for material handling applications on actual customer sites.

In addition, a Federal Transportation Authority project at Boston Logan International Airport program will include a Nuvera fuel cell engine for a hydrogen fuel cell bus and a PowerTap hydrogen generation system.

Near term technology development activities will include:

- Metallographic evaluation of the failed FP1C1 fuel processor
- Non-destructive inspection of FP1R reformer tubes for remaining life
- Optimization of the start-up and shutdown procedures
- Assessment of catalyst cycling capabilities. An actual cycling test stand construction is planned that will allow durability assessment of different catalysts in start up and shut down conditions
- Further cost reduction of the fuel processor and the entire system
- Performance confirmation of the full scale HDS reactor in system context
- Detailed design of the heat flux controlled reformer
- Further evaluation of the advanced combined cycle concept

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Acronyms

BMM:	burner management module
CFD:	computational fluid dynamics
CHARM:	cost-effective high-efficiency advanced reforming module
DFM&A:	design for manufacturing and assembly
FEA:	finite element analysis
FC:	fuel cell
FCV:	fuel cell vehicle
FMEA:	failure mode and effects analysis
FPTS:	fuel processor test stand
H2A:	DOE Hydrogen Forecourt Production Model
HDS:	hydrogen desulfurization
HFC&IT:	Hydrogen, Fuel Cells and Infrastructure Technologies Program
HTS:	high temperature shift
HX:	heat exchanger
IRR:	internal rate of return
LCC:	life cycle cost
MHXCSR:	metallic heat exchanger-coated SR catalyst
PPM:	parts per million
PSA:	pressure swing adsorption purification sub-system
PSV:	proportional solenoid valve
QFD:	Quality Function Deployment
SCFH:	standard cubic feet per hour
SG:	steam generator
SMR:	steam methane reforming
SR:	steam reformer
TPS:	Total Power Solution™
VOC:	Voice of the Customer
WGS:	water-gas shift reactor

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