**Catalytic Combustor for Fuel-Flexible Turbine
(DE-FC26-03NT41891)**

**Final Report Phase 2
October 2004 through October 2007**

for

**U.S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory
3610 Collins Ferry Road
Morgantown, West Virginia 26507-0880**

**Prepared by
W. R. Laster
E. Anoshkina**

**Siemens Power Generation, Inc.
4400 Alafaya Trail
Orlando, FL 32826-2399**

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ABSTRACT

Under the sponsorship of the U. S. Department of Energy's National Energy Technology Laboratory, Siemens Westinghouse has conducted a three-year program to develop an ultra low NO_x, fuel flexible catalytic combustor for gas turbine application in IGCC. The program is defined in three phases: Phase 1- Implementation Plan, Phase 2- Validation Testing and Phase 3 – Field Testing. Both Phase 1 and Phase 2 of the program have been completed.

In IGCC power plants, the gas turbine must be capable of operating on syngas as a primary fuel and an available back-up fuel such as natural gas. In this program the Rich Catalytic Lean (RCLTM) technology is being developed as an ultra low NO_x combustor. In this concept, ultra low NO_x is achieved by stabilizing a lean premix combustion process by using a catalytic reactor to oxidize a portion of the fuel, increasing the temperature of fuel/air mixture prior to the main combustion zone.

In Phase 1, the feasibility of the catalytic concept for syngas application has been evaluated and the key technology issues identified. In Phase II the technology necessary for the application of the catalytic concept to IGCC fuels was developed through detailed design and subscale testing. Phase III (currently not funded) will consist of full-scale combustor basket testing on natural gas and syngas.

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EXECUTIVE SUMMARY

In this program the Rich Catalytic Lean (RCL™) technology, Figure 1, is being developed as an ultra low NO_x gas turbine combustor for Integrated Gasification Combined Cycle (IGCC). In the RCL™ concept, ultra low NO_x is achieved by stabilizing a lean premix combustion process by using a catalytic reactor that produces a nominal gas temperature increase in the fuel/air mixture (by converting a portion of the fuel in the catalyst section). Operation of the catalytic reactor under fuel rich conditions provides for a more robust design with respect to variations in fuel and air flow rates.

Figure 1 Schematic of the RCL™ Catalytic Combustor

A key challenge in developing a fuel flexible catalytic combustor is the ability to provide one basic design that will accommodate the different process flow conditions that are indicative of different IGCC plant designs. Cold vs hot gas cleaning, degree that the gas turbine is integrated with the IGCC plant and how the plant might be optimized for efficiency vs power output all impact the process flows that must be managed within the combustor. In Phase 1, the feasibility of the concept for syngas applications was evaluated, benchmarked and a validation test program (Phase 2) was defined.

During Phase 2 the detailed design work necessary to adapt the RCL™ concept for IGCC applications a large industrial gas turbine engine was performed and the concepts were validated through subscale testing. The goal of this program was to produce a fuel flexible catalytic combustor applicable for syngas and natural gas in the SGT6-5000F engine. In addition an assessment of the technology for the high hydrogen fuels typical of an IGCC plant equipped with carbon sequestration technology was performed. In phase 2 catalyst materials were developed which can meet the required design criteria for gas turbine engines operating on natural gas, syngas and hydrogen. The basic catalytic reactor was redesigned to accommodate the changes in fuel flow necessary for IGCC applications. Subscale catalytic module testing was performed on a variety of fuels to validate the design concept. Initial design of the full scale fuel flexible catalytic basket was performed.

1. INTRODUCTION

The feasibility of the application of the RCL™ technology to the design of a fuel flexible catalytic combustion system was confirmed in phase 1 of the program. The SGT6-5000F engine is a typical large industrial gas turbine engine which can be applied to IGCC and was chosen as the design basis for the fuel flexible catalytic combustor. Considerable design work has already been performed on this engine and the adaptations required for IGCC application have been identified.^{1,2} Figure 2 gives the specifications for this engine.

SGT6-5000F

- Power: 180MW
- 16 Combustor Baskets
- Natural Gas/Oil
- Turbine Inlet Temperature: 2600F (1430C)
- Pressure Ratio: 16

Figure 2 SGT6-5000F Engine Conditions

Table 1 lists the combustor design requirements which must be met by the catalytic combustor design.

Table 1 – Combustor Requirements

Overall Requirements	Specification
Fuel Flexible	Operation on natural gas or syngas above 30% load. Engine will start on natural gas and must transfer to syngas at 30% load.
Engine: New and Retrofit	Developed components must fit within current engine casing.
Emissions over Load Range (70% to Full Load)	NOx 2ppm or less CO 10ppm or less
Turndown	100 to 50% (on syngas)
Dynamics	Meet current engine requirements.
Component Life	8000 hrs – Catalytic Elements 32,000 hrs – Other Combustor Components
Maintainable/Serviceable	8000 hrs, Inspection (annual)
Cost	Lower than SCR Back-End Cleanup

Much of the previous work on syngas capable combustion systems for the SGT6-5000F engine have focused on diffusion flame combustion systems. Although the operation of these systems has been proven for a wide variety of fuels including syngas and hydrogen, they require a substantial amount of dilution flow to meet current emission requirements and cannot achieve single digit NO_x emissions. To get low emissions without large amounts of dilution flows a premixed system is required. The lowest emissions possible from a combustion system can be obtained from a catalytically stabilized premixed system such as the RCL™ design. The feasibility of extending the operation of the rich catalytic design to syngas fuels was confirmed in Phase 1 of this program. In Phase 2 of the program, the technology necessary for the design of a fuel flexible catalytic combustion system for the SGT6-5000F engine is performed.

Considerable work has been performed on the rich catalytic design for natural gas applications and a basic design has been developed. The goal of this program was to extend this design to syngas and high hydrogen fuels. Figure 3 shows the basic building blocks of the RCL™ Catalytic combustor. The most basic building block of this design is the catalytic elements (a) which in the baseline design are tubes with catalytic coating on the outside diameter. These elements are formed together into the catalytic reactor (b) where the air flow is split into the main cooling air and into the rich combustion zone. The basic catalytic reactor design is used to develop the full scale catalytic module (c) which forms the main portion of the catalytic basket. The full scale catalytic basket (d) is created from 6 modules which surrounds a central pilot nozzle.

Figure 3 Basic Building Blocks for the Catalytic Combustor

Because of the modular nature of the rich catalytic design, validation testing can be performed through the use of subscale testing at the catalytic element, catalytic reactor, catalytic module and basket level. This procedure was successfully used to develop the natural gas version of the design and will be used to develop the modification necessary for operation on syngas and high hydrogen fuels. The major thrusts of this program include:

- Development of a fuel flexible catalytic coating for application to natural gas, syngas and high hydrogen fuels. Screening and performance testing of coatings is performed in the single tube catalytic rig. Durability testing is performed in the 60 tube subscale reactor rig.
- Design of the catalytic reactor for natural gas, syngas and high hydrogen fuels. The initial catalytic reactor design is performed in the 60 tube subscale rig using data from the single tube rig to obtain the optimal flow split between the rich catalytic air and the main cooling air.
- Design and verification of the catalytic module for natural gas, syngas and high hydrogen fuels. Testing at the module level is required to verify that the modification for syngas fuel do not impact the combustion performance of the design.
- Conceptual design of the combustion basket for natural gas and syngas. The final verification of the design in a full scale basket test is in phase 3 of the program.

2. FUEL FLEXIBLE CATALYTIC DEVELOPMENT

Development of catalyst for partial catalytic oxidation of fuel prior to combustion in fuel-flexible gas turbine faces several challenges, including: 1) the catalyst must become active or light-off at temperature of air supplied by the compressor (350 - 370°C for the SGT6-5000F); 2) the catalyst must efficiently oxidize multiple fuels: natural gas, syngas and hydrogen; 3) the catalyst must provide stable fuel conversion while maintaining catalyst temperatures below the design limit (20-30% based on fuel consumption, 40-70% - based on oxygen conversion for natural gas); 4) catalyst must display durability for a minimum of 8,000 hours and at least 800 start-up cycles. Catalyst performance must remain stable for the designed life time and number of cycles. Properties required for catalyst durability include sintering resistance, phase stability, excellent adhesion properties, and catalyst resistance against poisoning effects from the various compounds contained in the fuel or developed during fuel oxidation process.

Because the RCL combustion design does not have a preburner, light-off temperature is critical to successful operation. Light off is defined as the lowest temperature at which the catalyst surface initially becomes active. Once the catalyst is lit it will remain active even if the temperature is reduced below the initial light-off temperature. Testing in the combustor basket rig has shown that combustor dynamics can be an issue at loads in excess of 80% when the catalyst was not active. To insure sufficient margin, the target light off temperature was set to be 50% load on the SGT-6-5000F engine. Since the single tube rig has heat loss effects that are not present in the engine, light-off temperatures measured in this rig are higher than those of a full basket or a tube bundle. For an acceptable coating the goal is to obtain repeatable light-off at temperatures below 375 C. All catalyst coatings are initially screened for light off. Those with acceptable light-off characteristics then undergo further testing for durability. All coatings are compared to the baseline coating developed by Precision Combustion Inc. (PCI). The PCI coating light-off is consistently between 330 and 350 C in the single tube rig.

In addition to light-off properties, the reactivity of the catalyst at typical base load operating conditions must be known. The reactivity of the catalyst at base load conditions is measured by the amount of fuel and air that is converted in the catalyst region. Experimental

investigations have shown that the fuel conversion properties of the catalyst can be independent of the light-off temperature. The main purpose of the catalyst is to provide a partially reacted fuel mixture at increased temperature to the homogeneous burnout zone of the combustor. This partially reacted mixture at elevated temperatures provides increased stability to the main combustion zone. The goal of the catalyst zone is to provide the maximum fuel conversion and gas temperature rise possible without over heating the catalyst region. On natural gas the target conversion from the catalyst is 20-30% fuel conversion and 40-70% oxygen conversion with the design split of 15% of the air entering the rich combustion zone. This conversion rate must be repeatable and stable over time. On syngas and hydrogen fuel the reactivity of the catalyst is higher and the amount of air entering the rich catalytic zone must be reduced to maintain acceptable temperatures.

Durability of the catalyst is a significant parameter in the design of the catalytic combustor. The light-off and conversion properties must be stable over the full 8000 hour expected life of the catalyst. Most importantly the catalyst must remain attached to the substrate.

The main development focus for this program has been traditional coatings, ceramic washcoat with precious metal catalyst. The PCI coating is an example of a traditional catalytic coating. The catalyst is applied to a 0.1875 inch diameter Haynes 230 tube. Haynes 230 was chosen because of its resistance to oxidation. Oxidation is a concern because the tube wall thickness is only 0.010 in. The active metal catalyst can be platinum, palladium, rhodium or a mixture of these compounds. Preliminary testing has shown that pure platinum catalysts have a light off temperature of greater than 450 C and therefore do not satisfy the light off requirements for this program. Pure palladium catalysts display acceptable light-off characteristics initially but testing shows that the light-off temperature degrades with respect to time in part due to a poor resistance to coke formation. Development on this program has focused on catalysts with combinations of platinum, palladium and rhodium as the precious metal. Figure 4 shows the catalyst system for the traditional ceramic catalyst. In addition to the traditional ceramic coatings an internal Siemens ceramic metal coating as shown in Figure 5 was developed and tested.

The catalytic coating development on this program is pursued with the following industrial partners:

•Precisions Combustion Inc	Kevin Burns
ACS Advanced Catalyst Systems	Dr. Larry E. Campbell
•Engelhard	Dr. Tom Giroux, Dr. Bob Farrauto
•Guild Associates Inc.	Dr. Joseph Rossin
•Miratech	Don Newburry
•CFI/CTI Coatings for Industry/Coating Technologies Inc	Dr. Basil Mucha

The first 4 companies are involved in the production of traditional ceramic catalyst materials. CFI/CTI is involved in the design of the Siemens ceramic metal coating.

Figure 4 Traditional Ceramic Coating

Figure 5 Siemens Metal Ceramic Coating

2.1 TESTING OF CATALYSTS

The following criteria were set up for initial ranking of catalysts: 1) initial and final stabilized light-off temperature which is defined as the repeatable of light-off characteristics achieved after several tests (3-6); 2) original and final fuel and oxygen conversion rates; 3) coating adhesion and durability properties. For catalysts which demonstrate the acceptable screening properties, additional poisoning, adhesion, and durability studies were performed.

Screening of catalyst light-off properties and fuel conversion characteristics was conducted in the single tube rig at Casselberry labs. This rig was designed to duplicate the conditions (pressure, temperature, flow velocity) of a single catalytic element operating under SGT6-5000F conditions. Figure 6 shows a schematic of the single tube rig as well as the typical catalyst testing conditions for both natural gas and syngas. The main cooling air and the air to

the rich section of the catalyst were controlled independently in the rig so that the air split to the rich catalytic region could be varied. The high pressure air to the test section was provided an Atlas Copco compressor. The temperatures of the split air and the main air were controlled by tube furnaces. For natural gas testing the fuel was obtained from the pipe line, for syngas mixtures and hydrogen the fuel was supplied by bottled gasses. The single tube rig and instrumented test section used for screening catalysts are shown in Figures 7 and 8.

Figure 6 Testing Conditions in the Single Tube Rig (Casselberry Labs)

Figure 7 Single Test Rig

Figure 8 Instrumented Test Section of the Single Tube Rig

Because the light-off temperatures on syngas and hydrogen are significantly lower than those of natural gas, the initial coating screening tests were conducted on natural gas. As a rule, any catalyst which would light off on natural gas at the acceptable temperature range of 350 to 375°C, will light-off on syngas at temperatures below 300 °C (250°C -as average). Light-off temperatures on hydrogen are even lower. Once a coating has satisfied all of the requirements on natural gas, additional testing is performed on syngas and hydrogen.

Thermocouples were included to measure gas temperatures of the incoming main cooling air and the split air as well as the mixed gas temperature at the exit to the reactor. Three thermocouples were attached to the catalyst surface at the following sample locations: gas inlet, middle of catalyst area, gas outlet end. Catalyst light-off temperature was determined as the temperature at which the sudden increase of temperature off the catalyst surface by 200-300°C was observed. Three GC ports were installed at the rig to monitor the gas fractions: at the reactor inlet; at the catalyst outlet end, and at the reactor exhaust. Fuel conversion rates and/or oxygen conversion rates were calculated from the differences in gas compositions measured reactor inlet and the reactor outlet, which represented post-catalyst and pre-catalyst mixtures, respectively. The oxygen conversion for most of the tests was verified by both the gas chromatograph and the Ultramat Emissions Analyzer.

Figure 9 shows a typical light-off data obtained on natural gas. The light-off event is clearly visible from the sudden increase in temperature of all three surface temperatures on the catalyst surface. This figure shows data for multiple light-off and demonstrates the repeatability of the catalyst light-off.

Figure 9 Typical Catalyst Light-off Data

Precision Combustion Inc. (PCI) has developed the initial catalyst for use in the RCL catalytic combustor. The PCI catalyst demonstrated stable light-off properties (LOT) and fuel conversion rates in the acceptable ranges. All new catalyst formulations are compared to the PCI data. Newly developed catalysts were prepared by collaborative interactions with four companies: Advanced Catalyst Systems (ACS), Guild Associates Inc., Miratech Corporation, and Engelhard Corporation (now BASF). Approaches in the development of catalysts were undertaken in two directions: adjustment of washcoat composition in order to develop the high-surface-area and sintering resistant catalyst support; adjustment of catalyst combination and concentrations in order to find the best catalytic system. In addition to the traditional catalyst coatings the Siemens metal ceramic coating was tested. For the initial screen tests each catalyst was subjected to a minimum of 5 light-off events. Following the light-off the catalyst was brought to base load SGT6-5000F conditions and gas chromatograph measurements were taken to determine conversion. Five light-off attempts were chosen because it was determined that the catalyst light-off achieved a stable value after 5 attempts. After the testing was completed the catalyst surface was examined for any loss of coating or apparent damage. The initial screening results indicated that the following catalysts demonstrated the most promising results: Mirateck DOE 3 developed using a design of experiments approach, Guild Silica-Alumina catalyst with pre-stabilized washcoat, and the BASF COM7 catalyst. After reviewing the all the data a final down selection was made to concentrate on the BASF catalyst because it showed the best combination of durability and light-off characteristics.

Additional modifications were performed on the BASF catalyst to improve the light-off characteristics and the repeatability and reproducibility of the catalyst. Long term durability studies were initiated on this coating using both natural gas and syngas fuels. Additional work was performed on the BASF catalyst to improve light-off characteristics and an improved catalyst formulation, COM10 was developed. Figure 10 shows the light-off and conversion performance of several samples of COM7 and COM10. Not only does COM10 show improved initial light-off characteristics, the light-off of the catalyst improves with time. Figure 10 gives an indication of the repeatability and reproducibility of the catalyst samples. These results show the typical variation seen from different catalyst samples.

Figure 10 Repeatability Properties for BASF Catalysts

2.2 CATALYST DURABILITY STUDY – SYNGAS

It is not cost effective to perform durability studies on syngas using bottled gases. For durability studies on syngas fuel the small scale continuous fluid bed reactor (CFBR) gasification system at the Energy and Environmental Research Center (EERC) at the University of North Dakota was utilized. This system is illustrated in Figure 11. The goal for these tests was to produce a consistent, coal-fired fuel gas for testing in the Siemens catalyst test rig. A duplicate of the Siemens single tube rig was built at EERC with two independent catalyst test sections. With the two leg design it was possible to obtain durability data on two catalyst materials simultaneously. Gases used for fluidization in the CFBR are mixed in a gas manifold. Typically, the fluidizing gas for the CFBR is a mixture of air, nitrogen and steam; for these tests, product gas was used instead of nitrogen to achieve the desired fluidizing velocity in the reactor.

Figure 11 EERC CFBR system.

The pilot-scale gasification system was used to produce syngas using coal as the feedstock. Syngas flow into the reactor was measured along with conversion efficiency, tube temperature, and emissions. Pre- and post reactor gas compositions were obtained through the use of CEMs and a gas chromatograph for SO_2 , NO_x , CO , CO_2 , and O_2 .

The level of sulfur in the syngas was identified as a crucial parameter in the durability studies. To minimize the sulfur levels in the gas stream, a two-stage desulfurization process was employed for this test series. The first stage utilized a Zn-based regenerable sorbent useful for both H_2S and COS and can bring sulfur levels as low as 10 ppm. This was followed with a nonregenerable polishing sorbent which has been shown to be able to bring sulfur levels to less than 1 ppm. For these tests the sulfur levels entering the catalyst section were below the detectable limit.

The output from the EERC CFBR gasifier was used as fuel for the two different candidate catalytic coatings. The coatings used for this test period were the PCI coating and the BASF COM 7 coating. The composition of syngas from the EERC gasifier is shown in Table 2. Because the EERC CFBR gasifier is air blown rather than oxygen blown, as the design gasifier for the catalytic combustor development, the LHV of the gas is significantly reduced. To increase the LHV closer to the design target of the catalytic system, the gas was spiked with 20% hydrogen. Because of the lower LHV of this syngas composition, the temperatures of the catalyst surface were significantly below the design target when operated at the air split typical of syngas operation (10%). In order to obtain meaningful durability data the split was increased until catalyst surface temperatures in the range of 700°C were obtained. This occurred with an air split of 15% to the rich region. Testing was split into two separate periods, low sulfur testing and high sulfur testing. The first test period was with the sorbent system for sulfur removal operating. With this system in place the sulfur concentration in the

syngas was below the detectable limit (> 3ppm). Tests with the sorbent system were conducted for a period of 5 days and a total of 112 hours of fired catalyst time was obtained. At the conclusion of the first test period the existing tubes were removed and a new set of tubes was installed in the reactor and the rig was restarted. During the first hour of operation the bypass valve to the sulfur sorbent system was gradually opened until the base syngas with a sulfur content of 350 ppm was sent to the reactor. This total time for the high sulfur testing was of 19.5 hours.

	Syngas	Syngas + H ₂
O ₂	0.72	0.60
N ₂	55.4	46.21
CH ₄	1.85	1.54
CO	13.99	11.67
CO ₂	13.62	11.36
H ₂	13.51	28.62
LHV (BTU/lb)	1427	2216.00
LHV (BTU/scf)	98.7	129.80
MW	26.23	22.23

Table 2 Syngas Composition for the Durability Tests

The results of the durability testing can be clearly seen from the temperature rise of the gas through the catalyst. Figure 12 shows the temperature rise through the catalyst over time for both the a) low sulfur and b) high sulfur testing. During the entire period of the low sulfur tests, the temperature rise across the catalyst remained relatively constant, indicating that there was no degradation in the activity of the catalyst. For the high sulfur portion of the test, there was an initial decrease in the temperature rise across the catalytic section for both materials during the first two hours. After the first two hours the temperatures stabilized at roughly a 30% reduction in conversion. After the initial reduction the catalyst performance remained stable for both materials. At the conclusion of the test period all four of the tubes used in the syngas durability testing were sent to Casselberry Labs for examination and retesting on natural gas. Analysis of the coated tube did not reveal any coating degradation. During natural gas testing no significant change was observed in the light-off temperature of the conversion for any of the tubes. This indicated that the performance degradation observed during the high sulfur tests was reversible.

Figure 12 Syngas Durability Results for a) low Sulfur, b) high sulfur

2.3 CATALYST DURABILITY STUDIES – NATURAL GAS

Siemens has a subscale 60 tube catalytic reactor located in Casselberry, Florida which is designed for development and testing of catalytic reactor designs and catalytic coatings. The air to this rig is supplied by two Atlas Copco compressors capable of producing two pounds per second of air at 280 psia. Process air heaters are available to heat the inlet air to 800 F. Currently the facility operates on natural gas fuel from the pipeline but modifications have been performed to allow operation with the addition of hydrogen and nitrogen from fuel tanks. The catalytic reactor test rig is shown in Figure 13. In order to increase flexibility of this rig the upstream braze on the tubes and the downstream flare were eliminated and a downstream capture plate was employed to hold the tubes in place. In this design the catalytic elements are held in place by counter bores in two plates which are bolted together. By removing the bolts it is possible to inspect and remove individual elements from the catalyst assembly. The downstream plate is designed to enable the cooling and rich air streams to mix while minimizing the potential of flashback. Figure 14 shows the catalyst module ready for installation in the rig. Figure 15 shows the catalytic module during installation of the catalytic elements.

Figure 13 Subscale Catalytic Test Facility

Figure 14 Subscale Catalytic Module

Figure 15 Installation of the Catalytic Elements into the Reactor

The 60 tube Casselberry rig was used for a rainbow durability test on catalytic coatings. Total testing time was 111 hours of test with 30 start-up cycles. Total time of catalysts at base load (700 -750°C catalyst surface temperature) was 90 hours. The rainbow durability testing enabled durability data to be obtained on 6 different types of catalytic elements: BASF COM7,

BASF COM10, Miratech DOE, Guild, ACS, and PCI. The catalytic reactor module was composed of six elements each from Miratech, Guild, ACS and BASF COM7 and BASF COM10. The remaining elements in the reactor were the PCI design. Two PCI tubes were instrumented with thermocouples to measure light-off temperature and monitor the catalyst temperatures during testing.

Because the Casselberry rig is not designed for unmanned operation, it was necessary to start and stop the durability testing each day. At the beginning of the test, the air temperature was set to a value below the light-off temperature of the catalyst. Fuel was then introduced to the rig and an ignitor was used to create a downstream flame. After the downstream flame was established the air temperature was increased until catalyst light-off was achieved as evidenced by the catalyst surface temperatures and the module exit temperatures. Once catalyst light-off was achieved the air flow, pressure and temperature was set to simulate base load conditions.

After a period of 50 hours the rig was disassembled and all the tubes removed and inspected. Any tubes which showed significant signs of coating degradation were removed and replaced with PCI tubes. At the conclusion of the test, all the catalytic elements were removed from the rig and examined. After 30 cycles and 111 hours of operation the catalysts prepared by BASF and PCI demonstrated very acceptable adhesion properties. Figure 16 shows the BASF catalytic elements removed from the test rig.

Figure 16 BASF Catalytic Elements after Durability Testing in 60-Tube Rig

From Figure 16 it is clear that all elements, except one, exhibited no visible damage and the coating was still attached to the metal substrate; no spallation due to thermal shock was noticed. The one catalytic element which showed some coating loss had been used in the single tube test rig and the coating loss can be related to damage that occurred when the surface TCs were installed. Before the test, the coating was partially scraped from the tube for thermocouple installation. Additional damage to the catalyst was added when the thermocouples were removed from element after testing. After completion of cyclic durability test, several BASF and PCI elements were re-tested at the Single Tube rig and demonstrated the acceptable light-off temperatures and conversion. Based on the 60 tube durability testing and on the single tube light-off testing, the BASF and PCI catalysts were determined to have the best overall performance in terms of durability, light-off and fuel conversion.

2.4 POISONING TOLERANCE OF THE CATALYST

One concern with the operation of the catalytic combustion system on syngas is the higher levels of contaminants that may be present in the fuel. Natural gas does not possess the significant amounts of catalyst poisoning compounds; however, the same cannot be said for coal-derived syngas. In general coal derived syngas will consist of significant concentrations of sulfur containing compounds which may have a detrimental effect on the catalyst life. Studies of tolerance of catalytic coatings against sulfur poisoning effect were conducted at Siemens Corporate Technology.

Figure 17 shows a schematic of experimental setup constructed for Sulfur-poisoning studies. In these tests the catalyst material was coated to a Haynes 230 coupon placed into the gas stream. The temperature of the reaction zone was controlled with a tube furnace. Backside cooling was not modeled in these tests. The flows of main components through catalyst in experimental reactor were matched to the design parameters: flows of fuel-air mixture over catalyst, velocities of fuel-air mixture, fuel-air equivalence ratio, and residence time of fuel molecule on catalyst. H_2S gas was added at controlled quantities to the fuel mixture during S-poisoning experiments. Prior experimentation has shown that H_2S -gas provides more destructive influence on catalyst compared to SO_2 -gas; thus, hydrogen sulfide was chosen as a poisoning agent for conducting S-poisoning experiments. S-poisoning studies were conducted at a temperature of $\sim 700^\circ\text{C}$. Three thermocouples were used to monitor the temperatures in the coupon. Fuel conversion parameters were determined via gas analysis performed by means of FTIR and GC analyzers.

Figure 17 Experimental Setup Constructed for Catalyst Poisoning Study

The poisoning study was conducted for four types of catalyst: Miratech DOE, Guild, BASF COM7, and BASF COM10. Only the BASF COM7 and COM10 catalysts demonstrated reliable fuel conversion characteristics in environment with increased amounts of sulfur – up to 800 ppm. Additionally, both COM catalysts demonstrated excellent catalyst regeneration properties and did not show any visible destruction of coatings such color changes or visible stains and crack caused by influence of S-contaminants. On the other hand, catalysts developed together with Miratech and Guild companies demonstrated an irreversible loss of

performance during the S-poisoning tests. Examination of the Miratech and Guild catalysts after the sulfur testing showed visible damage to the coating.

Efficiency of fuel conversion on catalysts was determined by comparison of available moles of methane (main component of natural gas) measured before ($\dot{n}_{ed,CH_4}$) and after catalytic reaction ($\dot{n}_{pro,CH_4}$) and was calculated via the following formula:

$$X_{CH_4} = \frac{(\dot{n}_{ed,CH_4} - \dot{n}_{pro,CH_4})}{\dot{n}_{ed,CH_4}}$$

Figure 18 represents the efficiency of fuel conversion observed on COM10 catalyst under poisoning influence of sulfur. Conversion characteristics were established after 60 minutes of catalyst exposure to certain concentration of H₂S added to the fuel. The following concentrations of hydrogen sulfide were added to the fuel-air mixture during testing: 2; 4; 6; 8; 10; 15; 200; 800 ppm.

Figure 18 Methane Conversion in Contaminated State on COM10 Catalyst

It is obvious from the Figure 18 that even smallest concentration of H₂S (2 ppm) caused a measurable reduction in the efficiency of catalyst with methane conversion dropping from 52% to 39%. Increased concentrations of hydrogen sulfide proportionally decreased the catalyst activity with the conversion reduced to only 10% at high concentrations.

In Figure 19 the decrease of methane conversion due to the sulfur-contamination effect is presented as a function of time. The relative decrease of methane conversion under effect of S-poisoning compound was measured as a ratio of methane conversion on S-contaminated catalyst to the maximum possible conversion of methane on catalyst.

It is obvious from Figure 18, that for low concentrations of H₂S (≤ 8 ppm), only partial deactivation of catalyst takes place. After partial deactivation, the catalyst still demonstrated

reasonable fuel conversion properties. When concentrations of S-contained components were increased up to 200 and 800 ppm, deactivation of catalyst occurred in a matter of minutes and only a small amount of conversion was observed. The small percentage of remained activity still was higher than the percentage of blank activity of substrate-construction material (Haynes 230).

Figure 19 Decrease of Methane Conversions under S-Contamination on COM10 Catalyst

After the sulfur poisoning tests were completed the sample was operated on methane to determine if the performance degradation was permanent or if any catalyst regeneration was possible. Regeneration of catalyst was measured as the ratio of methane conversion on S-contaminated catalyst to the maximum conversion of methane on non-contaminated catalyst. Figure 20 represents the regeneration kinetics of the BASF COM10 catalyst as a function of time.

Figure 20 Methane Conversion during Regeneration on COM10 Catalyst

Figure 19 demonstrates that after exposure of catalyst to low doses of S-poisoning contaminants (≤ 8 ppm), the 90%-regeneration occurred after 10 minutes of regeneration, and full regeneration of catalyst occurred in 50 minutes of regeneration. When catalyst was exposed to high doses of S-contaminants (≥ 15 ppm), the 90%-catalytic regeneration occurred after 50 minutes of regeneration, and full regeneration has been achieved after 1000 minutes (17 hours) of regeneration. No exposure time dependency on regeneration kinetics of catalyst was observed.

Yields of produced gases during catalytic reaction in the presence of S-contaminants were determined through the ratio of moles of produced components to moles of methane available for reaction:

$$Y_{H_2} = \dot{n}_{pro,H_2} / \dot{n}_{ed,CH_4}$$

$$Y_{CO_2} = \dot{n}_{pro,CO_2} / \dot{n}_{ed,CH_4}$$

$$Y_{CO} = \dot{n}_{pro,CO} / \dot{n}_{ed,CH_4}$$

Figure 21 demonstrates the influence of S-contaminants on changes in yields of H₂, CO, and CO₂ gases. Significant drop in yield of hydrogen is already visible at 2 ppm of S-contaminates; and at doses of 200-800 ppm of S-poisoning agent – none hydrogen yield was determined at all. With increasing of S-contaminant doses, production of carbon monoxide was reduced, while production of carbon dioxide was slightly increased.

Figure 21 Yields of Gases on COM10 Catalyst under Influence of S-Contaminates

As a result of catalyst poisoning study, it was determined that even at low concentrations of sulfur contaminants (2 - 15 ppm) in fuel mixture, the activity of COM catalysts were

significantly reduced, from 52% to 39% and lower, depending on the contaminant concentration. However, the reduced level of catalytic activity has reached certain plateau and, after that, remained stable for a long period of time (up to 167 total hours of testing). It was possible completely regenerate the catalytic activity of catalysts exposed to low levels of contaminants after 50 minutes of regeneration time.

At higher concentrations of S-contaminates (200-800 ppm), quick and almost complete deactivation of catalyst was observed; however, the low level of residual activity of catalyst still remained visible for extended period of time. 90% regeneration level of highly-poisoned catalyst (at 200-800 ppm of H₂S) was achieved after 50 minutes of regeneration, and a complete regeneration of catalyst was achieved after 17 hours of regeneration.

A level of 4 ppm of H₂S-contaminants in the fuel mixture was found to be a maximum level that would not significantly effect the performance, durability, and life characteristics of COM catalysts.

2.5 CATALYST DEVELOPMENT SUMMARY AND CONCLUSIONS

Based on the testing performed in this program, two catalysts materials were identified which met the requirements for the fuel flexible catalyst. The baseline PCI catalyst and the BASF COM10 catalyst met the light-off requirements on natural gas and successful operation on both syngas and hydrogen was demonstrated. In addition to acceptable light-off these catalyst also demonstrated acceptable durability during a 111 hr and 30 cycle durability test on natural gas. In addition to natural gas both catalysts demonstrated acceptable performance during a 100 hour durability test on syngas in the EERC reactor.

Sulfur poisoning tests were performed on the COM 10 catalyst and the results showed that even low levels of sulfur (4-15 ppm) caused a reduction in the activity of the catalyst. At high levels of sulfur (200-800 ppm) a significant loss of catalyst activity was observed. It was possible to regenerate the catalyst by operating on natural gas. The BASF COM10 catalyst showed the best tolerance to sulfur of the catalysts tested. Based on these tests, it will be necessary to reduce the sulfur concentration in the syngas to less than 4 ppm before entering the catalytic combustor.

3. DEVELOPMENT OF THE CATALYTIC REACTOR

Once a catalyst has proven repeatable light-off characteristics on natural gas, additional work was performed on alternative fuels, including syngas and hydrogen. Although light-off is not an issue for syngas or hydrogen fuels, knowledge of the fuel and oxygen conversion as a function of the air split is necessary for optimal design a fuel flexible catalytic reactor. Syngas compositions vary considerably depending upon the type of fuel and the gasification process used. For these studies a syngas composition typical of petcoke operation was chosen for the design basis as given in Table 3. The petcoke case was chosen because it provides a lower hydrogen concentration and therefore should produce the worse case for catalyst light off and fuel conversion.

% vol (unless otherwise noted)		Petcoke	Coal
Ar		0.00%	0.00%
CH4		7.42%	3.34%
CO		59.83%	40.07%
CO2		7.89%	11.35%
H2		23.97%	27.35%
H2O		0.00%	0.00%
N2		0.89%	17.90%
Total		100.0%	100.0%
LHV(BTU/lb)		5565.00	3974.00
MW		22.15	22.32

Table 3 Representative Syngas Composition

Single tube testing has confirmed that syngas and pure hydrogen are considerably more reactive than natural gas. A typical lightoff on syngas will occur at roughly 50-100 C lower than natural gas on the same coating. Pure hydrogen is even more reactive with lightoff occurring at temperatures slightly above ambient. The higher reactivity of syngas is also evident from fuel and oxygen conversions as calculated from the GC data. Table 4 shows the measured fuel and oxygen conversions for natural gas, syngas and hydrogen. Natural gas data was obtained at the design air flow split of 15 %. When this split was applied to hydrogen and syngas, the conversion rates increased significantly, and catalyst temperatures exceeded the design limit. Typically at the design case on natural gas at the design split, 40-70 % of the available oxygen is reacted in the catalyst region. With syngas and hydrogen fuel, 100 % conversion of the available oxygen could be achieved. For the data presented in Table 4, the air split was reduced for hydrogen and syngas to the lowest split which would provide a temperature below the design limit and maximize the conversion of the available oxygen. This table shows that the optimal air split to the rich catalyst region is reduced when operating on natural gas and syngas. Figure 22 shows the effect of air split on the conversion of syngas. At higher air splits, more oxygen is available for the reaction and a greater percentage of the available fuel and oxygen is converted, resulting in the higher surface temperatures on the catalyst.

Fuel	Rich Air Split (%)	Fuel conversion (%)	O2 conversion (%)	Catalyst Temperature (deg C)
methane	15	14	45	630
syngas	12	CO - 21 H2 - 31	98	890
hydrogen	10	25	99	855

Table 4 Conversion as a Function of Fuel Type

Figure 21. Effect of Air Split Fraction on Syngas Conversion

Based on this data the catalytic reactor must operate on lower split fractions on syngas and hydrogen fuels. Optimal splits are roughly 10 % while operating on syngas and 7 % when operating on pure hydrogen. The goal of the fuel flexible combustor design is to develop a single design for the catalytic reactor which can operate on all three of the possible fuels. In the RCLTM catalytic combustor design the flow split between the cooling air and the rich combustion air is controlled by the geometry of the system. One way to adjust the splits in the reactor would be to add an adjustable valve to the design which could be used to modify the air splits during operation as a function of the fuel type. This would allow the reactor to always operate at the optimal air split for any fuel but provides a significant complication to the system.

Because the air split to the catalytic reactor is controlled by the geometry and the pressure drops through the system, it will automatically be adjusted when the fuel is changed. When operating on syngas fuel the fuel flow rate through the reactor is increased by a factor of four or more. The higher fuel flow rate on syngas results in a higher pressure drop through the catalyst region. This increase in pressure drop though the rich catalytic path forces more of the air through the backside air cooling path and therefore reduces the split. Typically the air split is reduced from 15 % to 7 % during syngas operation. By slightly increasing the split on natural gas operation it is possible to optimize the reactor for performance on both fuels with a single geometry. In order to operate the reactor on pure hydrogen fuel, it will be necessary to add dilution to the fuel with either nitrogen or steam to increase the fuel flow rate and achieve the desired split. This should not be an issue because this nitrogen or steam will most likely be needed for flashback control on high hydrogen fuel.

4. DEVELOPMENT OF THE CATALYTIC MODULE

4.1 MODULE TEST RESULTS

The Siemens catalytic combustor design consists of a central premixed pilot nozzle surrounded by a group of catalytic modules. The pilot is necessary for stability at part load operation, at high loads it is expected that the fuel to the pilot will be turned off. The goal for phase 2 of this program was to develop a module design which could be used for both natural gas and syngas. The validated module design would be used in phase 3 of the program for a full scale fuel flexible catalytic combustor basket. Because of the modular nature of the catalytic basket design, it is possible to reduce development costs by performing validation testing at the module level. Catalytic module testing is performed at the Siemens small industrial gas turbine facility in Lincoln, England. Figure 23 shows the module test rig. This facility has the capabilities to test a catalytic module at full SGT-6-5000F conditions on both natural gas and syngas fuels. Two designs for the catalytic module were investigated. The first design was the baseline flared tube module which was developed for natural gas operation. The second design was a module with an alternative catalyst module developed to reduce manufacturing costs and complexity.

Figure 23 Catalytic Module Test Rig

4.2 BASELINE MODULE DESIGN

The design of the baseline catalytic combustion module is shown in Figure 24. In these modules the catalyst section consists of an array of tubes with catalytic coating on the outside diameter. These tubes are brazed to a plate on the upstream end and flared on the downstream end. The air entering the module is split into two streams. One stream mixes with the fuel and reacts on the outside surface of the tubes at an equivalence ratio of greater than the flammability limit of the mixture. The other stream flows inside of the tubes and is

used to backside cool the catalyst. The fraction of the air that mixes with the fuel is called the split flow and is a critical parameter in the design of the catalytic reactor. This fraction is controlled by the component flow resistances and resulting pressure drops through the system. At the exit to the reactor, the two streams mix before entering the downstream burnout section of the reactor.

Figure 24 Baseline Catalytic Module Design

As part of this program a new fuel flexible module design, module 8 was created. Module 8 uses the basic flared tube design for the catalyst section with the fuel injection manifold redesigned to include the capability for both natural gas and syngas operation. Because of the lower heating value of syngas, the flow rate of syngas to the module is significantly higher than natural gas. To accommodate this change in fuel flow rates the fuel manifold was split into two independent sections, each manifold with a different fuel injection pattern. Figure 25 shows the dual fuel manifold design for the fuel flexible catalytic module. With the dual fuel manifold design each fuel path is independent and it is possible to optimize the mixing pattern for both natural gas and syngas. CFD analysis was used to optimize the fuel injection patterns for each fuel. The parameters adjusted during the design were the number of fuel injection holes, size of the holes and injection angle.

Figure 25 Dual Fuel Manifold Design

Initial testing on the fuel flexible baseline catalytic module was performed in September, 2005 on natural gas. The results were comparable to previous natural gas module designs which were tested at Solar Turbine test facility. In Figure 26 the NO_x emission results obtained during this round of testing was compared with previous data obtained during module testing at the Solar Turbines test facility. The data obtained at Solar Turbine test was scaled to 11 bar pressure because of facility limitations. At the Siemens Lincoln facility it was possible to run tests at full SGT6-5000F conditions. At the Lincoln facility data was obtained at reduced pressure for comparison with the previous data and at full pressure. No operational issues were encountered during the natural gas testing and the emissions and combustor dynamics were low.

Figure 26 NO_x Emission Data from the Catalytic Module

Figure 27 shows the NO_x emissions from the catalyst module compared with the perfectly premixed flame data from Leonard and Stegmaier³. The emissions measured during this test are slightly below those of the perfect premixed system. The main advantage of the catalytic combustor is it enables high pressure operation at perfectly premixed conditions without combustor dynamics limitations. At temperatures typical of the SGT-6-5000F engine the emissions were below 2 ppm NO_x and even at SGT-6-6000G conditions the emissions were still below 3 ppm NO_x. CO emissions were single digit and combustor dynamics were minimal except for near blow-off conditions. Blow-off of the flame was observed at flame temperatures of less than 1300° C. Due to rig issues, testing on syngas was postponed until April, 2006.

Figure 27 Catalytic Module Natural Gas Emissions

In April 2006 the dual fuel module design was tested using syngas fuel. For these tests the module was ignited and brought to base load on natural gas and then the fuel was transferred to syngas. The plan was to test two typical syngas compositions as listed in Table 5. The main difference between the two fuel compositions is the ratio of hydrogen to carbon monoxide in the fuel. The initial testing was performed on the petcoke composition. All testing was performed with undiluted syngas as the catalytic module is designed to produce low emissions without the need for dilution.

% vol (unless otherwise noted)		Petcoke	Coal
Ar		0.00%	0.00%
CH4		7.42%	3.34%
CO		59.83%	40.07%
CO2		7.89%	11.35%
H2		23.97%	27.35%
H2O		0.00%	0.00%
N2		0.89%	17.90%
Total		100.0%	100.0%
LHV(BTU/lb)		5565.00	3974.00
MW		22.15	22.32

Table 5 Syngas Composition by Volume

The results of the April test campaign are shown in Figure 28 compared with the natural gas data. While operating on syngas fuel the NO_x emissions increased over natural gas at a comparable firing temperature. As the temperature was increased a flashback event occurred in the downstream mixing zone and the module exit was damaged. The flashback event was contained to the downstream mixing section, no damage was found to the catalyst section. Figure 29 shows the damaged exit section of the module.

Figure 28 Syngas Testing Results

Figure 29 Flashback Damage to the Module Exit

An examination of the design indicated that the velocities in the downstream mixing section were too low and did not provide sufficient margin to prevent flashback when the hydrogen content of the fuel was increased. Figure 30 shows the calculated turbulent flame speeds for

natural gas and several different syngas mixtures. The laminar flame speeds were calculated using the GRI 3.0 Mechanism⁴ and the turbulent flame speeds were determined from the laminar flame speeds using Gulder's correlation⁵. For natural gas the flame speed is significantly less than the bulk velocities in the downstream mixing section (45 m/sec). Although the bulk velocity in the downstream mixing section exceeds the turbulent flame speed of syngas there is not sufficient margin to avoid flashback. To eliminate flashback in this region it is necessary to reduce the area in the downstream mixing section to increase the velocities in this region.

Figure 30 Calculated Turbulent Flame Speeds for Gas Mixtures

Another possible cause of the flashback and also the higher emissions during syngas operation could be less than optimal mixing in section where the syngas fuel and air mix prior to entering the catalyst. Mixing in this section is accomplished through fuel jets into the air channel created by angled holes in the bottom of the fuel manifold. The number of holes, sizes, locations and angles were optimized using CFD. The computation domain for the initial calculations did not include the syngas plenum and therefore the pressure boundary at each of the injection holes is assumed to be uniform. Examining the flow in the manifold this was not a good assumption. In the original design the area of the flow entering the plenum was too small and the inlet was not symmetrically located. When the plenum was included in the calculations the flow distributions was significantly altered and the fuel air mixing was no longer optimal.

To improve the fuel air mixing the module was redesigned to include two larger inlets to accommodate the high fuel flow rate of the syngas. These two inlets were placed to remove the asymmetry of the previous design. With the plenum included it was necessary to adjust the fuel injection hole pattern to obtain optimal mixing. Figure 31 shows the module before and after the design changes. This figure shows both the new inlet fuel piping to the manifold and the downstream mixing section redesigned to increase the velocities. Figure 32 shows the CFD calculations of the equivalence ratio at the entrance to the tube region. The equivalence ratio is significantly more uniform for the new design and the unmixedness (S) is reduced from 12% to 4%.

$$\text{Unmixedness } S = \sqrt{\frac{\frac{1}{\dot{m}_{gas}} \sum_i (Y_i - \bar{Y})^2 \Delta \dot{m}_i}{\bar{Y}^2}}$$

$$\text{where } \bar{Y} = \frac{1}{\dot{m}_{gas}} \sum_i Y_i \Delta \dot{m}_i$$

Figure 31 Redesign of the Catalytic Module (left)

Figure 32 Equivalence Ratio at the Tube Entrance for the Redesign (left) and Old Design (right)

Verification testing of the redesigned module was performed in November, 2006. Unfortunately facility problems prevented full verification of the module. As before, the module was ignited on natural gas and then the transfer to the syngas mixture was initiated. The natural gas was initially flowed through the syngas manifold for these tests. The emissions recorded on natural gas were similar to those of the April, 2006 test. It is expected that the

emission on natural gas injected through the syngas manifold would be high because this manifold is optimized for the higher flow rates of syngas and therefore the mixing is not optimal on natural gas. The testing was aborted during the transfer to syngas because of problems with flow measurement on the individual gas lines in the mixing station. Unfortunately the fuel lines were not purged properly prior to restart and pure undiluted hydrogen was sent through the module on light-off. It was not possible to shut down the module before catalyst damage occurred. The damage was confined to a few tubes located at on corner of the module as can be seen in Figure 33.

Figure 33 Catalyst Damage at Lightoff

Based on a borescope inspection a total of 6 tubes were damaged all in one section of the module. The tubes remained in place but significant burning occurred and the cooling air passages were blocked. Because pure hydrogen has much wider flammability limits than natural gas, it is more difficult to maintain a mixture above the rich flammability limit. The damage was most likely do to a small region of gas in the tube region below the rich flammability limit. This situation should not occur during normal operation. It is anticipated that the catalytic combustion system would be ignited on natural gas and then transferred to either hydrogen or syngas at roughly 30% load. It is also not anticipated that this module will operate on pure undiluted hydrogen, but that some nitrogen or steam dilution would be required for flashback control.

The current module design, flared tubes, brazed on the upstream end does not allow for repair of the module. Testing was attempted with the damaged module, the module was able to run with the damaged tubes but a significant nonuniformity in temperature gradient was observed at the module exit. Testing was terminated at this point.

4.3 ALTERNATIVE MODULE DESIGN

The baseline flared tube module design requires a large number of parts (over 2000 tubes per full scale SGT6-5000F combustor basket) and has significant costs. Several attempts have been made to reduce the cost of the design. Additionally this design does not provide any means to prevent tubes from going downstream through the engine. An alternative module design has been developed at Siemens to address the costs and part count of the catalytic

combustor design. The concept which has been down selected for testing is the corrugated plate concept. The basic idea of this concept is shown in Figure 34. In this concept the catalyst section a series of concentric cylinders with corrugations added for strength. The catalytic coating is applied to the outside surface of the corrugated cylinders. The cooling air flows through the corrugations and the rich air fuel mixture flows between the cylinders.

Figure 34 Corrugated Cylinder Concept

The detailed design work of this concept was completed and a full basket design was developed. In order to compare with the results of the baseline module, a 1/8 cylindrical section was been designed as a module for prototype testing. The goal of this design was to maintain the same catalyst surface area as the baseline flared tube concept. Figures 35 and 36 show the module used for the tests. Testing of the alternative module was performed in November 2006, following the test of the baseline flared tube module. After the flared tube module tests were completed the issues with the flow meters in the mixing station were resolved. All of the flow meters were correctly calibrated for the alternative module test.

Figure 35 Corrugated Cylinder Catalyst Section

Figure 36 Corrugated Cylinder Catalytic Module

All previous tube modules were tested with the PCI catalyst. For the alternative module the BASF COM 10 catalyst was applied to the cylindrical test sections. Additional development work was required to evaluate the manufacturing challenges associated with catalyst application to these cylindrical sections. These challenges were overcome and the coating was successfully applied to the cylindrical sections. Figure 37 shows the cylindrical sections with the COM 10 coating applied. For the alternative module the plan was to ignite the module on natural gas and then transfer to syngas.

Figure 37 COM10 Coating Applied to the Cylindrical Test Sections

Immediately after light-off the catalyst was shut down because of high catalyst surface temperatures. Two subsequent light-offs were performed with the same result. The module was disassembled and burning was evident on the fuel air mixing section feeding the catalyst section. The damaged mixing section after the test is shown in Figure 38. Burning was

confined to the first 3 catalyst channels. Although spare parts were available for the catalyst and mixing section it was determined that additional analysis should be performed to determine the root cause of the problem before further testing was performed.

Figure 38 Damage to Catalyst Mixing Section

The fuel air mixing section to the catalyst was designed using CFD analysis. This design was optimized for the baseload syngas fuel conditions. Separate passages were not included in the fuel nozzle for natural gas and syngas. Figure 39 shows the equivalence ratio in each of the catalyst channels as a function of radial position for syngas operation. Both radial and circumferential variations were examined but only radial profile is plotted because it had the greatest variation. The goal of this design was that the variation in equivalence ratio must be less than $\pm 20\%$. The chosen design met the design criteria.

Figure 39 Equivalence Ratio Distribution in the Catalyst Section for Syngas Operation

Since this module was designed for syngas operation, no work was done to optimize the mixing profile during natural gas operation. Since the problem occurred during light-off on

natural gas, CFD analysis was used to predict the module performance on natural gas during light off conditions. Because of the fuel flow difference between natural gas and syngas, there is a significant difference in the jet penetration at the fuel injector. Figure 40 shows the radial profiles of equivalence ratio in the slots for natural gas fuel on light-off. In this case the mixing is significantly worse than syngas and the design criteria is not met in all of the channels. In this case the mixture entering the catalyst is not maintained above the rich flammability limit. The first 2 channels where the burning occurred were operating with a near stoichiometric mixture. Clearly the fuel mixing section of this design needs to be redesigned to provide adequate operation on both natural gas and syngas fuel. This will require modification of the fuel injector to include separate passages with different fuel injection patterns for natural gas and syngas.

Figure 40 Equivalence Ratio Distribution in the Catalyst During Light-off on Natural Gas

4.4 CATALYTIC MODULE SUMMARY AND CONCLUSIONS

The baseline catalytic module testing confirmed the ability of the design to achieve the target conditions of less than 2 ppm NO_x at SGT-6-5000F conditions on natural gas. The catalytic module was stable for temperatures above 1300° C. Because at low load operation in a gas turbine engine temperatures are often encountered that are less than this value, it will be necessary to include a pilot in the basket design. The baseline catalytic module was redesigned for syngas operation and operation was confirmed on syngas fuel. Emissions on syngas fuel were higher than those obtained with natural gas. Additional design improvements were identified to improve flashback margin and improve the fuel air mixing. These changes were not verified.

An alternative module design using the corrugated plate concept was developed. The design work and manufacturing development for this concept was completed. A prototype 1/8 scale module was fabricated and initial testing was performed. The initial testing indicated problems with the fuel injection pattern on natural gas. The nozzle needs to be redesigned for dual fuel operation on both natural gas and syngas. Additional testing is necessary to verify this concept.

Down selection of the basket concept for Phase 3 cannot be performed until additional module testing is performed.

5. CATALYTIC BASKET DEVELOPMENT

5.1 BASELINE BASKET TESTING

Prior to the start of this program the baseline module was used to produce a full scale combustion basket for natural gas operation on the SGT6-3000E engine. In this program the natural gas basket design was modified for application to the SGT6-5000F engine. The catalytic basket design is shown in Figure 41. This basket design consists of 6 catalytic modules surrounding a central pilot nozzle. The pilot nozzle is required for stability at low load operation. In order to minimize the emissions the pilot nozzle is designed with two stages one for premixed operation and one for diffusion. Initial testing was performed on the natural gas module design to confirm operability of the design at SGT6-5000F conditions.

Figure 41 Catalytic Combustor Basket for the SGT6-5000F

Full scale basket testing was performed on the catalytic basket design in the Siemens test facility located at ENEL in Italy. This facility duplicates the engine geometry and is capable of simulating full pressure and flow conditions for the SGT6-5000F engine. Figure 42 shows the installation of the combustion system in the SGT6-5000F engine. This design can be implemented in the SGT6-5000F engine with no changes to the casing, tophat extension or transition. The instrumented basket used for testing is shown in Figure 43. This basket utilized the baseline flared tube catalytic module developed for natural gas. The full scale basket test results confirmed that with the addition of the pilot, the basket could be loaded from startup to baseload and that stable operation could be maintained throughout the load range. Catalyst light off was repeatably obtained at temperatures between 300 and 330 C.

Typical NO_x emissions results from the full scale basket tests are presented in Figure 44. All emission values are corrected to 15% O₂. The results are presented as a function of the air fuel ratio to the head end of the catalytic basket. The addition of the pilot resulted in a slight increase in NO_x emissions over the module test results. In addition, because of the shorter residence time in the engine, as compared to the module test rig, modifications to the burnout zone were necessary to maintain acceptable CO emissions when operating at the lower firing temperatures typical of the SGT6-3000E. It was necessary to add dilution air to the transition of these engines in order to increase the operating temperature of the combustor to achieve acceptable CO burnout. When testing was performed at SGT6-5000F conditions CO burnout was no longer a problem, dilution air was no longer required and the NO_x emissions were essentially the same as the SGT6-3000E. This is because the higher firing temperature provided additional stability to the catalytic burnout region enabling these engines to run at a significantly lower pilot fraction. Based on these tests emissions in the range of 3 ppm NO_x and 10 ppm CO are achievable at on natural gas for both SGT6-5000F and older SGT6-3000E engine with the baseline catalytic design.

Figure 42 Installation of the Catalytic Combustor in the SGT6-5000F Engine

Figure 43 Catalytic Combustor Basket for the SGT6-5000F

During normal operation the basket and module metal temperatures remained within design limits. To verify the robust nature of the rich catalytic design, an over firing test was performed by increasing the fuel flow to the combustor. Even through transition temperatures were 200 C above the design temperature limit during this event, the catalyst tube temperatures remained within limits throughout the entire test and no damage to the catalyst was observed. These tests confirmed the robust nature of the rich catalytic design with respect to variations in fuel flow to the combustor.

Figure 44 Full Scale Catalytic Basket Test Results

During phase 2, the conceptual design of the SGT6-5000F fuel flexible catalytic basket was performed and the design modifications necessary for syngas operation were identified. For syngas operation the same baseline module design was employed with the exception that additional fuel lines need to be added for the syngas stage. Because of the high fuel flow rate of the syngas fuel this becomes a significant issue and modifications to the engine are necessary. Figure 45 shows the fuel piping to the syngas manifold. The dual fuel syngas module requires two separate fuel feeds and the syngas line is substantially larger than the natural gas line. In Figure 46 the basket with the dual fuel syngas line is placed in the current SGT6-5000F engine tophat. Although the dual fuel basket design can theoretically fit into the existing top hat, the air flow to the combustor would be significantly restricted by the additional piping. This design work was performed with Module 8 which has only one syngas feed. For the redesigned syngas module with 2 syngas feeds per module, the space would be even more limited. To fit the design into the existing SGT6-5000F engine an expanded diameter tophat as shown in Figure 47 was developed. In the expanded tophat the diameter of the tophat is increased to make room for the additional fuel lines and the top hat is lengthened. To fit with the existing SGT6-5000F casing the diameter of the bolt circle on the tophat remains the same. With this design the modules are shifted back into the top hat allowing for a longer burnout zone. The longer burnout zone will be necessary for syngas fuel.

Figure 45 Fuel Piping for the Dual Fuel Module

Figure 46 Dual Fuel Catalytic Module Installed in Engine Tophat

Figure 47 Expanded Tophat for Fuel Flexible Catalytic Combustor

5.2 ALTERNATIVE BASKET DESIGN

The baseline catalytic design requires a significant number of parts; a full engine set of combustors for the SGT6-5000F engine would require 29,376 catalytic elements. Another issue with the design is that with the tubes brazed on the upstream end and flared at the downstream end there is nothing to prevent a tube from being liberated from the catalyst section into the engine. Liberation of a tube from the catalyst section has occurred during module testing.

Several alternative designs were investigated to improve the cost and address the tube liberation issue. The most promising alternative design was the corrugated plate design where the catalyst is composed of plate elements. In this design, corrugations were added to the air side of the catalyst to maintain spacing and strengthen the structure. One problem with the plate design is edge effects. Edge effects can be eliminated by using corrugated cylinders, as shown in Figure 48, instead of flat plates.

Figure 48 Corrugated Cylinder Catalyst

The conceptual design of an alternative catalytic basket was performed with the concentric cylinder catalyst. The catalyst was designed to maintain the same surface area as baseline catalyst with the flared tubes. It was found that the 1,836 tubes in a single basket could be replaced with 11 cylindrical catalyst elements. Figure 49 shows the conceptual design of a SGT6-5000F combustor using the alternative catalyst design. The combustion system was designed to fit into the engine casing and transition of the SGT6-5000F engine and use the same pilot nozzle as the existing basket. The alternative catalyst was slightly larger in diameter than the original catalyst but this increase could be accommodated within the existing engine tophat design.

Figure 49 Alternative Catalytic Basket Design

One of the main challenges of the cylindrical plate design is obtaining a well mixed even distribution of the mixture entering the rich catalytic region. In this design the main fuel to the modules enters through 8 fuel injectors. The fuel air premixing section entering the catalytic region is shown in Figure 50. Figure 51 shows view of the fuel distribution section. Figure 52 shows the area analyzed with CFD for the mixing optimization study. The air entering the mixing section is controlled with a baffle plate. The fuel flow distribution is controlled by the hole pattern in the fuel injection nozzle. For the CFD analysis performed under this program, only a single fuel channel with one set of injection holes was modelled. Based on the test results, it will be necessary to add a dual fuel nozzle with two separate passages and injection hole patterns.

Figure 50 Fuel Air Mixing Upstream of Catalyst

The mixture of fuel and air is delivered to the catalyst section using the fuel distribution section shown in Figure 51. This section is designed with channels to deliver the fuel evenly to the fuel rich sections of the catalyst. Baffles are added to the ends of the fuel channels to assure even fuel delivery all of the catalyst sections. The open area between the channels allows the cooling air to reach the corrugated sections of the catalyst.

Figure 51 Fuel Distribution Section for Catalyst

Figure 52 CFD Model of Fuel Injection to the Catalyst Section

Since the ability to deliver a well mixed even distribution of fuel and air to the rich catalytic region is critical to the performance of the catalytic combustor, considerable design work was performed in this area. The mixing region as shown in Figure 52 was analyzed using CFD. In this analysis the fuel air mixing to the individual catalytic channels was optimized based by adjusting the baffle plates, fuel injection pattern and the internal geometry of the passage. Figure 53 show a typical CFD result obtained during this process. The goal of the design was

to maintain the equivalence ratio at the entrance to the catalytic region within +/- 20% of the nominal value. This goal was accomplished for the base design when operating on syngas.

Figure 53 CFD Calculations in the Fuel Mixer

6. CONCLUSIONS

During this program considerable progress was made on the adaptation of the rich catalytic combustion technology to syngas fuels and the SGT6-5000F engine.

- Catalytic materials were identified which could be used for syngas and hydrogen containing fuels.
- Alternative catalytic coatings were identified which met all of the design requirements of the program.
- Durability testing was performed on catalyst materials for both natural gas and syngas.
- The impact of sulphur poisoning was determined on catalyst materials.
- The operational conditions for the catalytic reactor were identified for syngas and hydrogen fuel.
- Catalytic module tests were performed on natural gas and syngas proving stable operation and low emissions were achievable on both fuels.
- An alternative catalyst design was developed to reduce the cost and complexity of the current design. This design showed promise but additional work is necessary before this design can be implemented in a basket.
- Conceptual design work was performed on the fuel flexible catalytic basket. Basket designs were developed for both the baseline module design and the alternative module design. Both designs can be adapted to the SGT6-5000F engine with minimal changes to the casing and transition.

The RCL™ catalytic combustion design shows considerable promise for low emission operation as a fuel flexible combustor for IGCC applications. This design should enable low emissions operation on syngas fuels with minimal dilution flow. It is recommended that additional testing be performed at the module level before a down selection between the baseline module design and the alternative module design is completed.

REFERENCES

1. Gadde, S., Wu, J., Gulati, A., McQuiggan, G., Koestlin, B., Prade, B., "Syngas Capable Combustion Systems Developed for Advanced Gas Turbines", ASME Turbo Expo, Barcelona, Spain, 2006.
2. Wu, J., Brown, P., Diakunchak, I., Gulati, A., Lenze, M., Koestlin, B., "Advanced Gas Turbine development for High Hydrogen Fuels", ASME Turbo Expo, Montreal, Canada, 2007.
3. Leonard, G., Stegmaier, J., "Development of an Aeroderivative Gas Turbine Dry Low Emissions Combustion System", International Gas Turbine and Aero Engine Congress, Cincinnati, 1993.
4. Gregory P. Smith, David M. Golden, Michael Frenklach, Nigel W. Moriarty, Boris Eiteneer, Mikhail Goldenberg, C. Thomas Bowman, Ronald K. Hanson, Soonho Song,

William C. Gardiner, Jr., Vitali V. Lissianski, and Zhiwei Qin
http://www.me.berkeley.edu/gri_mech/

5. Gülder, O. (1990), Proc. Combust. Inst., **23**, pp. 743-750.