3.2.2.1 Fuel-Rich Catalytic

Combustion



Dr. Lance Smith



Dr. Shahrokh Etemad



Dr. Hasan Karim



Dr. William C. Pfefferle

Gas Turbine Group, Precision Combustion, Inc. 410 Sackett Point Road, CT 06473

phone: (203) 287-3700 x217 email: setemad@precisioncombustion.com

3.2.2.1-1 Introduction

Currently, gas turbines operating on natural gas offer the lowest achievable NOx emissions without exhaust-gas aftertreatment, as compared to other fuels. Commercially, this has been achieved through the use of lean-premixed combustion systems, allowing NOx emissions below 9 ppm (at 15% O_2) to be guaranteed for natural gas operation, and emissions near 5 ppm to be demonstrated¹. Lower emissions are needed, however, and are possible through the use of catalytic combustion².

Because natural gas has historically offered the greatest potential for low emissions, catalytic combustor development has until recently focused largely on methane and natural gas operation. As a result, the unique properties of methane have led to a number of development issues and design strategies, generally related to the behavior of Pd-based catalysts used for methane oxidation.

In particular, for methane oxidation under fuel-lean conditions, only Pd-based catalysts among the PGM group are currently practical, because only they offer acceptable activity, lightoff temperature, and resistance to volatilization³. Unfortunately Pd-PdO catalyst morphology and its reactions with methane are complex, and lead to complex behaviors such as deactivation at high temperature (above about 750°C / 1380°F), hysteresis in reaction rate over heating and cooling cycles⁴, and oscillations in activity and temperature⁵. In addition, lightoff and extinction temperatures are well above 300°C (570°F) for fuel-lean reaction on Pd-based catalysts, thus requiring the use of a preburner in many engine applications⁶.

Fuel-rich operation of the catalyst circumvents many of these issues and provides significant catalyst advantages, including a wider choice of catalyst type (non-Pd catalysts are active to methane under fuel-rich conditions), improved catalyst durability (non-oxidizing catalyst environment), and low catalyst lightoff and extinction temperatures. Catalyst extinction temperature is particularly low, and is generally less than 200°C (400° F) for the precious-metal catalysts used in the work reported here (that is, once the catalyst has been lit off, the catalyst remains lit at inlet air temperatures less than 200°C / 400°F), and a preburner is generally not required. A more complete discussion of fuel-rich versus fuel-lean catalyst behavior for methane oxidation is given by Lyubovsky et al.⁷.

In addition to catalyst material challenges, commercial acceptance of catalytic combustion by gas turbine manufacturers and by power generators has been slowed by the need for durable substrate materials. Of particular concern is the need for catalyst substrates which are resistant to thermal gradients and thermal shock⁸. Metal substrates best fill this need, but their temperature must be limited to less than 950°C (1750°F) to assure sufficient material strength and long life. Downstream of the catalyst, combustion temperatures greater than about 1100°C (2000°F) are required for gas-phase reactions to complete the burnout of fuel and CO in a reasonable residence time (on the order of 10 ms). Thus, only a portion of the fuel can be reacted on the catalyst.

A major challenge, then, is to limit the extent of reaction within the catalyst bed such that excessive heat does not damage the catalyst or substrate, yet release sufficient heat that downstream gas-phase combustion is stabilized under ultra-low emission conditions. For systems which lean-premix fuel and air upstream of the catalyst, the degree of reaction can be limited by chemical reaction rate upon the catalyst, or by channeling within the reactor such that only a limited fraction of the fuel contacts the catalyst. In all cases, however, it is imperative that uncontrolled gas-phase reactions do not occur within the catalyst-bed, since this implies a loss of reaction limitation and ultimate over-temperature and failure of the catalyst bed. Preventing such gas-phase reactions is especially challenging in applications to advanced, high-firing temperature turbines, where fuel/air ratios in the catalyst-bed can be well within the flammability limits.

3.2.2.1-2 Fuel-Rich Catalyst Systems

Another approach to limiting the extent of reaction is to operate the catalyst fuel-rich. In this case, there is insufficient oxygen to fully oxidize all fuel in the catalyst bed, and the extent of reaction is therefore limited even if gas-phase reactions occur. To use a fuel-rich catalyst bed in a catalytic combustion system, additional air is introduced downstream of the catalyst so that combustion completion can occur fuel-lean. Based on this concept, fuel-rich catalytic reactors were tested by NASA and contractors for liquid fuel applications, and showed good soot-free performance⁹. An examination of fuel-rich catalysis on a variety of liquid fuels was also conducted at Yale University under support from NASA¹⁰. Like the NASA results, this work showed soot-free catalyst performance on a range of fuel types, including a surrogate jet fuel. United Technologies Research Center¹¹ also investigated fuel-rich catalytic reaction of liquid fuels, to reduce downstream thermal NOx generation by removing some heat of reaction prior to gas-phase combustion.

For these liquid hydrocarbon fuel applications, ultra-low NOx emissions (< 3 ppm) have not been considered feasible because of these fuels' propensity for autoignition during mixing with additional combustion air downstream of the catalyst. Even for natural gas fuel, previous systems have not permitted mixing of raw catalyst effluent with additional combustion air. For example, Acurex tested a two-stage natural gas combustion system having a fuel-rich catalyst stage followed by inter-stage heat extraction¹². Additional combustion air was introduced only after heat extraction, and prior to a final fuel-lean catalytic combustion stage.

Precision Combustion, Inc. (PCI), however, demonstrated that it is possible to directly mix catalyst effluent with additional combustion air without incurring autoignition¹³. This is possible because significant improvement in combustion stability is imparted to the downstream fuel-lean combustion process even at catalyst effluent temperatures well below the instantaneous autoignition temperature of the effluent. Thus, low-temperature low-emissions combustion requires only moderate catalyst temperatures, and autoignition can be avoided.

This improvement in combustion stability with only moderate heat release on the catalyst can be quantified most simply by modeling the gas-phase combustion process as a zero-dimensional stirred reactor, as shown in figure 1. A simple Perfectly-Stirred-Reactor (PSR) combustion model demonstrates that combustion stability is significantly improved when catalytic pre-reaction heats the combustor inlet gases from 400°C to 700°C, well below the instantaneous autoignition temperature. Details of the model are described by Smith <u>et al</u>. and model results for methane/air combustion are plotted here in figure 1 as flame temperature at incipient blowout (y-axis) versus combustor inlet temperature (x-axis)¹⁴. In this model, combustor inlet temperature is 400°C when there is no catalytic reaction. For the 400°C no-catalyst case lean blowout occurs at a flame temperature near 1305°C. With catalytic pre-reaction providing a 700°C inlet temperature to the combustor, however, the flame temperature at lean blowout drops by 55°C (100°F) to near 1250°C, a significant improvement.

This improvement is achieved without risk of autoignition. For a catalyst effluent temperature (combustor inlet temperature) of 700°C, the estimated autoignition delay time is about 25 ms. This autoignition delay time was calculated using the correlation of Spadaccini and Colket for a representative natural gas composition (94.9% CH₄, 3.1% C₂H₆, 0.65% C₃H₈, 0.3% C₄H₁₀, 0.1% C₅H₁₂, 0.1% C₆H₁₄, 0.05% C₇ and higher-order hydrocarbons, and 0.8% diluent)¹⁵. For this calculation, pressure was 15 atm, equivalence ratio was 0.5 and the effect of vitiation from catalytic pre-reaction was neglected.

Note that this 25 ms autoignition delay time at 700°C catalyst effluent temperature is far greater than the 2 to 5 ms residence time required to mix catalyst effluent with final combustion air, and is also greater than the typical 10-20 ms residence time of gas turbine combustors. Thus, complete mixing without autoignition is in fact possible downstream of the catalyst, yet combustion stability is markedly improved as a result of catalytic pre-reactions. The result is stable, low-temperature, ultra-low-NOx combustion.



Fig. 1. Gas temperature ("flame" temperature) within PSR reactor at imminent blowout, as a function of PSR inlet temperature (catalyst exit temperature).

3.2.2.1-3 Rich-Catalytic Lean-burn (RCL[®]) Combustion

Precision Combustion, Inc. (PCI) has developed a Rich-Catalytic Lean-burn combustion system (trademarked by PCI as RCL) based on this concept of stabilizing combustion of catalyst effluent having a temperature below the instantaneous autoignition temperature. The system catalytically reacts a portion of the fuel upstream of the combustor, thus preheating (and vitiating) the fuel/air mixture entering the combustor, and thereby improving combustion stability especially at low flame temperatures. NOx emissions are improved by operating at lower allowable (stable) flame temperatures, and turndown to low engine power can be improved by operating at still lower flame temperatures without excessive emissions of CO or unburned hydrocarbons.

A schematic of PCI's rich-catalytic combustion system is shown in figure 2. As shown, the combustion air stream is split into two parts upstream of the catalyst. One part is mixed with all of the fuel and contacts the catalyst, while the second part is used to backside cool the catalyst. At the exit of the catalytic reactor, the catalyzed fuel/air stream and the cooling air stream mix and then burn to completion to provide the final burner outlet temperature. As shown, combustion (fuel oxidation) occurs in two stages: a fuel-rich catalyst stage and an overall fuel-lean gas-phase combustion stage. Note that the catalyst is cooled only by primary combustion air, so that no heat is extracted from the system.

With this approach, the fuel-rich mixture contacting the catalyst has insufficient oxygen to completely oxidize all of the fuel, thus limiting the extent of catalyst-stage reaction and enabling limitation of the catalyst-stage operating temperature to a safe value.



Fig. 2. Schematic of Rich-Catalytic Lean-burn system, showing two-stage (rich-lean) combustion process.

3.2.2.1-4 Performance and Operating Characteristics of RCL[®] Combustion

PCI has tested the RCL[®] catalytic reactor at pressures from 1 to more than 15 atm, in both sub-scale and full-scale tests and for multiple fuel types, providing design data over a wide range of operating conditions. Key performance parameters for RCL[®] combustion are listed below, and measured values for these parameters are given in this section.

From *full*-scale full-pressure rig tests using natural gas fuel:

- Combustor emissions and turndown
- Combustor noise levels
- Combustion system pressure drop
- Catalyst operating temperatures

From sub-scale full-pressure rig tests to date:

- Catalyst lightoff and extinction temperatures
- Alternate (non-methane) hydrocarbon fuel capability
- Non-hydrocarbon fuel capability, e.g. syngas (discussed in later section)

In addition to these performance criteria, engine operational issues are also of interest, including method for engine start and catalyst lightoff, fuel staging needs, complexity of required controls, and transient capability such as load shifting and load rejection. To address these operational concerns, PCI and Solar Turbines have operated a modified Saturn engine using RCL[®] combustion; these results are also presented here.

3.2.2.1-5 Full-Scale Full-Pressure Test at Solar Turbines

Under DOE support and in cooperation with Solar Turbines, Inc., a full-scale fuel-rich catalytic reactor was fabricated and combustion tested to provide well-characterized experimental confirmation of the capabilities of Rich-Catalytic Lean-burn combustion for ultra-low-NOx power generation. The tests were performed in Solar Turbines' full-pressure single-injector combustion rig using natural gas fuel, and are described in detail by Smith et al.,and summarized here¹⁶.

A schematic of the catalytic combustor assembly, including premixer, catalytic reactor, and downstream combustor liner as tested in the rig is shown in figure 3. The catalytic reactor design is described generally in Smith et al. and includes backside cooling of the catalyst¹⁷. An annular reverse-flow premixer was fitted around the catalytic reactor, to provide a premixed fuel-rich mixture to the catalyst. Note that all fuel entered via this premixer, and all fuel contacted the catalyst. Catalyst cooling air bypassed the premixer, and entered from the left-hand side in figure 3. Downstream of the catalyst, but upstream of the combustor, the fuel-rich mixture and the catalyst cooling air were combined in a post-catalyst mixing duct ("post-mix" duct) to create a partially-reacted fuel-lean fuel/air mixture. The premixer, catalytic reactor, and post-mix duct together constitute what we call the "RCL-injector." Conceptually, the RCL-injector replaces a conventional Dry Low-NOx (DLN) premixer/swirler arrangement, such as Solar's SoLoNOx injector. For the tests reported here, a single Solar Turbines Taurus 70 SoLoNOx injector was replaced by an RCL-injector having a 3.0-inch diameter catalyst. An actual Taurus 70 engine would have 12 such injectors installed in its annular combustor.

In Solar's single-injector rig, the combustor liner was cylindrical, 8.0 inches in diameter, and backside-cooled. Four 0.5-inch diameter holes were located at the combustor's downstream end, to allow dilution air to enter the combustor after cooling it. Some leakage air also entered the combustor at the injector insertion seal (grommet seal), where the RCL-injector was inserted into the combustor's head end, or dome. A small amount of cooling air was also used to cool the combustor dome, and entered the combustor along the liner walls.

A flameholding cone was installed at the exit of the post-mix duct, as shown in figure 3. Recirculation of hot combustion gases in the cone's wake provided a flame anchor zone in the central part of the combustor. The expansion (dump) of the combustor liner's dome also served to anchor combustion. In general, the RCL-injector catalyst is intended to improve combustion stability and turndown at the flame anchor point, but is not necessarily intended to provide gas-phase ignition. Solar's torch igniter was used to ignite gas-phase combustion during rig testing.





Combustor Emissions and Turndown

Emissions performance and turndown were measured for the RCL[®] combustion system depicted in figure 3, at nominal Taurus 70 operating conditions (16-17 atm pressure and 4 pps total airflow to the single-injector combustor). Measured NOx and CO emissions are plotted in figure 4 as a function of adiabatic flame temperature at the emissions rake. For the tests reported here, the emissions rake was located just upstream of the combustor dilution air holes, corresponding to about 30 ms combustor residence time. NOx and CO emissions are reported after correction to 15% O_2 on a dry basis. UHC emissions are reported on a wet basis, corrected to 15% O_2 .

It is also worth noting that, as discussed earlier, some leakage and cooling air entered the combustor between the RCL-injector and the emissions rake. For this reason, fuel/air ratio as measured at the emissions rake gave an adiabatic flame temperature that was about 130°C (230°F) lower than that based on fuel/air ratio measured at the RCL-injector exit. Imperfect mixing of this leakage air with the injector's fuel/air mixture can increase NOx emissions to values slightly higher than expected for perfectly premixed combustion at the adiabatic flame temperatures measured at the emissions rake. In fact, the NOx emissions shown in figure 4 are about 1 ppm higher than expected at 1450°C (2650°F) based on perfectly premixed combustion.

As shown in figure 4, the RCL[®] combustion system achieved ultra-low emissions over a wide operating window of approximately 110°C (200°F) variation in flame temperature, with CO below 10 ppm and NOx below 3 ppm (and as low as 1 ppm). Unburned hydrocarbons (UHC) remained less than 2 ppm at all conditions shown in figure 4.

These high-pressure ultra-low-emissions results provide experimental confirmation of the ultra-low-NOx capability of the RCL[®] combustion concept. In particular, they demonstrate that it is possible to mix fuel-rich catalyst effluent with final combustion air, without inducing autoignition, yet imparting significant combustion stability to the downstream combustion process to allow low-temperature low-emissions combustion with wide turndown.



Fig. 4. NOx and CO emissions, as a function of adiabatic flame temperature at emissions rake. Data obtained at 16 atm pressure.

Combustor Noise Levels

Combustion-driven pressure oscillations (noise) were also monitored during full-scale combustion tests at Solar, and remained less than 2.4 kPa (0.35 psi) peak-to-peak (less than 0.15% peak-to-peak of mean combustor pressure) at all conditions tested, indicating quiet operation. Low levels of combustion noise are expected, since gas-phase energy release in the combustor (the driving force for combustion noise) is reduced when a portion of the fuel is catalytically reacted prior to gas-phase combustion.

Combustion System Pressure Drop

Pressure drop through the fuel-rich catalytic reactor is a primary determiner of RCL-injector size for any given application. For the 3-inch diameter reactor tested at Solar, pressure drop through the entire combustion system at simulated Taurus 70 full load conditions varied from about 3.5% to 5% of combustor inlet pressure, depending on hardware modifications made to redirect airflow during rig testing. This pressure drop includes both the losses through the fuel-rich catalytic reactor and losses in the downstream combustor (pressure drop across flameholder, dump loss at combustor inlet, fundamental combustion loss, etc.). We estimate that losses in the downstream combustor account for about 0.5% pressure drop, with the remaining best-case 3% attributable to the catalytic reactor in Solar's rig. Additional pressure loss data has been obtained for other full-scale RCL-injectors not tested in Solar's rig, but designed for reduced pressure drop. Data from other rigs indicate that at Solar rig conditions pressure drop would be about 2%.

Catalyst Operating Temperatures

Figure 5 shows steady-state catalyst surface temperatures plotted against adiabatic flame temperature at the full-scale RCL-injector exit, as tested at Solar. As shown in figure 5, catalyst surface temperature increases only slightly as fuel flow is reduced, and all catalyst surface temperature measurements remain below 780°C (1430°F) over the complete range of operating conditions tested (1440-1700°C / 2620-3090°F range in adiabatic flame temperature).

RCL catalyst temperatures do not vary significantly with fuel/air ratio because reaction rate (heat release) upon the catalyst surface is controlled by oxygen flow (air flow) under fuel-rich conditions, and because heat removal (heat transfer) from the catalyst is also determined primarily by air flow. Fuel flow has little effect on reaction rate and little effect on heat removal rate. This insensitivity of catalyst temperature to fuel/air ratio is advantageous in allowing combustor and turbine operation over a wide range of flame temperatures (including flame temperatures well above the low-NOx-emissions range), making the RCL[®] system suitable even for advanced high-firing-temperature machines.



Fig. 5. Catalyst surface temperature as a function of adiabatic flame temperature at RCL-injector exit.

3.2.2.1-6 Sub-Scale Test Data for Hydrocarbon Fuels

Catalyst testing under controlled conditions is best conducted at sub-scale, where smaller-size equipment allows for accurate metering and control of flow and temperature. Thus, accurate values for catalyst lightoff and extinction temperature are obtainable. Sub-scale testing is also useful for evaluating new concepts, such as use of alternative fuels.

Catalyst Lightoff and Extinction Temperatures

Catalyst lightoff and extinction tests have been performed under well-controlled experimental conditions at sub-scale for pressures from 9 to 15 atm. For natural gas fuel having one or two percent ethane, PCI's fuel-rich catalysts typically light off in the vicinity of 300°C. For natural gas fuel with greater than two percent ethane (or higher-order hydrocarbons) lightoff can occur at inlet temperatures below 280°C. This is shown in figure 6 below, which indicates a lightoff temperature between about 260 and 280°C for natural gas fuel, at 15 atm pressure. In figure 6, inlet gas temperature, catalyst surface temperature, and gas temperature exiting the module (following mixing of the catalytically reacted stream with the catalyst cooling air stream, but prior to gas-phase combustion) are plotted as a function of time in minutes. Lightoff occurs when the heat of reaction results in an increase in catalyst operating temperature and catalyst exit temperature as compared to the gas inlet temperature, as described in Section 3.2.2. of this Handbook



Fig. 6. Catalyst lightoff in a sub-scale high-pressure (15 atm) fuel-rich reactor operating on natural gas fuel. Inlet gas temperature ("T gas in"), catalyst surface temperature ("T catalyst"), and gas temperature exiting the module ("T gas out") are plotted as a function of time in minutes.



Fig. 7. Catalyst extinction does not occur until the fuel is shut off at an inlet air temperature less than 200 C. Data were obtained for the same sub-scale high-pressure (15 atm) fuel-rich reactor for which data were shown in Figure 6. Again, inlet gas temperature ("T gas in"), catalyst surface temperature ("T catalyst"), and gas temperature exiting the module ("T gas out") are plotted as a function of time in minutes.

Following catalyst lightoff, the inlet air temperature can be reduced well below the initial lightoff temperature without extinguishing the catalyst. Thus, once lit (active), the catalyst remains lit (active) down to inlet temperatures approaching ambient. Following the catalyst lightoff event depicted in figure 6, the inlet air temperature was reduced to less than 200°C, but catalyst activity was not diminished. This is shown below in figure 7, which plots the same parameters as figure 6, now after several hours of testing following the initial lightoff. Here, still at 15 atm pressure and with the same flow of natural gas fuel, catalyst activity was maintained until the fuel was shut off at an inlet air temperature less than 200°C.

Alternate Hydrocarbon Fuel Capability

Sub-scale fuel-rich catalyst tests have also been performed using alternative (non-natural-gas) hydrocarbon fuels. In particular, liquid fuels have been tested (gasoline and Diesel No. 2 fuel) with performance similar to that obtained using methane or natural gas, and a simulated landfill gas fuel has also been tested.



Fig. 8. Photograph of PCI's 10 atm sub-scale combustion rig, for testing fuelrich catalytic reactors with downstream combustion. Bulk flow is from right to left in this photograph.

Sub-scale tests with alternative fuels were performed in a 10 atm combustion test rig at PCI equipped for obtaining combustion emissions measurements, as shown in figure 8. The gas-phase combustion section of this rig is nominally 2 inches in diameter and 18 inches in length, and is fabricated from high-temperature ceramic and housed in a steel pressure vessel as shown in the photograph of figure 8. Reactants enter the ceramic-lined combustor through an air-cooled fuel-rich catalytic reactor of nominally 3/4-inch

diameter. Combustion emissions reported for the alternative-fuel tests were obtained from a water-cooled gas sampling probe location corresponding to 30 ms residence time in the ceramic-lined combustor downstream of the catalyst.

A single sub-scale fuel-rich catalytic reactor was tested in PCI's high-pressure combustion rig with three different fuels: methane, simulated landfill gas, and Diesel No. 2 (the first three listed in Table 3). No changes were made to the reactor or combustor for operation on these different fuels. For diesel fuel, however, a prevaporizer was added upstream of the reactor. Two different prevaporizers were used: initially we used a simple preheater to directly heat diesel fuel after adding less than 10% N₂ (by weight) to assist in atomization; later we improved prevaporization by mixing steam with the diesel fuel. The latter was considered ideal for co-generation applications. Note that liquid fuel tests were generally performed at 6-8 atm pressure, based on limitations of the fuel prevaporizers.

Prior to testing of the first three fuels listed in Table 3, a separate fuel-rich catalytic reactor of similar design was tested with gasoline and natural gas. For these initial liquid fuel tests gasoline was chosen for its high volatility, simplifying prevaporizer design.

For all fuels, the most relevant measures of performance for PCI's two-stage catalytic combustion system are catalyst temperatures in the first stage (catalyst-stage) and combustor emissions from the second stage (gas-phase combustion stage). We especially wish to compare these measures of performance for operation on various types of fuels.



Fig. 9 (left panel). Combined graph showing catalyst operation for both natural gas and liquid fuel (gasoline) at 7 atm pressure and 0.4 equivalence ratio (Φ), as a function of time. For both fuels, the inlet gas temperature ("T_{gas in}") was initially held steady at about 350 C, and then ramped down to about 200 C without catalyst extinction.

Fig. 10 (right panel). Catalyst surface temperatures, and lightoff and extinction temperatures, for diesel fuel operation. Tests were performed with non-steam prevaporizer, at 6 atm pressure and 0.33 overall equivalence ratio (Φ). "Tinlet" represents air temperature entering the reactor, and "Tcatalyst" represents catalyst surface temperature.

In figure 9, catalyst temperatures for 7 atm operation on gasoline are compared to those for natural gas. As shown, catalyst operating temperature (" $T_{surfaces}$ ") and catalyst lightoff temperature are both very similar for the two dissimilar fuels. Note that for both fuels the overall equivalence ratio was 0.4 downstream of the catalyst, after mixing of catalyst cooling air with fuel-rich catalyst effluent.

Catalyst lightoff and extinction temperatures for diesel fuel were tested using the first-generation prevaporizer at 6 atm pressure and 0.33 equivalence ratio, as shown in figure 10. For this test, temperature of the prevaporized fuel was between 350 and 380°C before mixing with air. For catalyst lightoff, inlet air temperature was ramped up from about 345°C until definitive lightoff occurred at about 360°C inlet air temperature, as indicated by a rapid increase in catalyst temperature. Prior to this event, some reaction occurred along the length of the reactor, as evidenced by catalyst temperatures nearly 75°C higher than the inlet temperature (e.g. 420°C versus 350°C). After lightoff, inlet air temperature was ramped down until sudden loss of activity (catalyst extinction) occurred at about 200°C inlet air temperature. Note that for all fuel types tested under fuel-rich conditions, catalyst extinction temperature was well below catalyst lightoff temperature. Also note the similar catalyst operating temperatures for diesel fuel as compared to gasoline and natural gas operating temperatures, as a result of fuel-rich operation of the catalyst.

Although successful operation on diesel fuel was obtained using the non-steam prevaporizer, it could only provide enough prevaporized fuel to establish an overall equivalence ratio of 0.33 downstream of the catalyst. A steam prevaporizer was therefore designed and used, allowing catalyst temperatures and combustion emissions to be measured over a wider range of equivalence ratios (flame temperatures), as shown in figures 11 and 12.

For diesel fuel operation using the second-generation prevaporizer, steady-state catalyst temperature data ("T surface") are shown as a function of the reactor's overall equivalence ratio in figure 11. Diesel fuel operating data were obtained at the prevaporizer's maximum operating pressure of 6 atm, and at 430°C inlet temperature. Average gas temperature exiting the reactor ("T gas out") is also shown. Note that "T gas out" and overall equivalence ratio are both defined after mixing of catalyst effluent with catalyst cooling air.



Fig. 11. Catalyst performance with diesel fuel versus methane, for second-generation prevaporizer (~5:1 steam:fuel ratio by weight) operating at 6 atm pressure and 430°C inlet air temperature. Compare to methane tests at 9 atm and 440°C inlet temperature.

As shown in figure 11, catalyst operating temperatures are insensitive to operating condition (overall equivalence ratio) for both methane and diesel fuels, and in general very similar catalyst performance was obtained for both fuels.

As stated earlier, catalyst temperatures do not vary significantly with fuel/air ratio because reaction rate (heat release) upon the catalyst surface is controlled by oxygen flow (air flow) under fuel-rich conditions. Thus, the oxygen available for reaction (the limiting reactant under fuel-rich conditions) is the same at all test conditions, with the result that heat release and temperatures in the catalyst bed are insensitive to equivalence ratio, and are very similar for both methane and diesel fuels despite a wide difference in reactivity between these two fuels.

NOx emissions from the fuel-lean combustion zone downstream of the fuel-rich catalyst were also measured for both liquid fuels and gaseous fuels, as shown in figure 12. Note that NOx emissions from the diesel fuel are primarily due to fuel-bound nitrogen, except at the highest flame temperature tested (near 2900°F). The Diesel fuel tested was red-dyed Diesel No. 2 fuel, and its nitrogen content was measured at 188 ppm by weight by an independent laboratory. At this concentration, nearly complete conversion of fuel-bound N to NOx is expected [4]. Thus, based on fuel-bound nitrogen content, the diesel fuel would emit at least 8.1 ppmv NOx (at 15% O₂) when burned. Fuel-bound nitrogen for all other fuels was zero.

NOx emissions are shown in figure 12 for three fuel types: methane, simulated bio-mass landfill gas (essentially diluted methane), and Diesel No. 2 fuel. Here, NOx emissions are measured on a dry basis and are corrected to 15% excess O_2 . NOx emissions are shown as a function of maximum measured flame temperature (via type S thermocouple) for each data point. For all data points obtained, CO and unburned hydrocarbon (UHC) emissions were less than 2 ppmv.



Fig. 12. NOx emissions for three fuel types (methane, biomass landfill gas, and Diesel No. 2 fuel). For all data points, CO/UHC emissions were less than 2 ppmv. For the Diesel No. 2 fuel, fuel analysis indicated that 8.1 ppmv NOx would be emitted as a result of fuel-bound nitrogen alone.

For methane and bio-mass landfill gas fuels, NOx emissions were below 3 ppm for measured flame temperatures below 2600°F. For diesel fuel, NOx emissions were about 10 ppm for measured flame temperatures below 2600°F, compared to the 8.1 ppm expected based on fuel-bound nitrogen alone. Thus, about 2 ppm NOx is likely formed by prompt (non-thermal) mechanisms at low flame temperatures (below 2600°F). At higher flame temperatures, NOx increases due to thermal formation mechanisms for all three fuels, as shown. The low NOx levels at low flame temperature indicates that well-mixed fuel-lean combustion was achieved downstream of the catalyst for all three fuels: methane, bio-mass landfill gas, and diesel.

3.2.2.1-7 Engine Test Results

Based on the successful full-scale single-injector rig tests at Solar Turbines, a "cluster" of four RCL-injectors was installed in a modified (single can combustor) Solar Turbines Saturn engine, to assess controls compatibility and transient operation in an engine environment, including engine start, acceleration, and load variation. In addition, steady-state operating data were obtained, including NOx and CO emissions at the engine exhaust. The engine test also provided a basis for evaluating fuel-rich reactor robustness in an engine environment, over a range of operating conditions and demands (including start, acceleration, and load).

Test Engine Specifications and Configuration

Combustor Housing Compressor Discharge Air Pipe Combustor Primary Zone Air Pipe Dilution Air Pipe Burner Outlet Pipe (to turbine)





Fig. 13. Side-mounted combustor configuration in modified Saturn engine, showing variable airflow control valves in primary zone air pipe and dilution air pipe.

Fig. 14. Photograph of four-RCL-injector assembly, prior to installation in Saturn engine.

The test engine was a modified version of a two-shaft recuperated Saturn T1200 engine, nominally rated at 750 kW (1000 hp) after modification. This engine was selected as a test bed because its external combustor configuration was amenable to modification. For catalytic combustor testing, the recuperator was removed, but the compressor discharge scroll and turbine inlet scroll were retained, allowing a single side-mounted combustor can to be installed.

The overall combustor configuration is shown in figure 13. Note that variable airflow butterfly valves were fitted in the combustor primary zone air pipe and the dilution air pipe, to allow combustor air to be varied for best emissions at any given fuel flow (engine load). Also note that a preburner was located in the combustor primary zone air pipe below the butterfly valve, to temporarily increase catalyst inlet air temperature to about 350°C (660°F) to ensure catalyst lightoff. The preburner was turned off after catalyst lightoff, and before engine emissions were measured.

All fuel and air entered the combustor through the four RCL-injectors (neglecting leakage air). The combustor liner was backside cooled with dilution air, before the dilution air entered the hot gas path 24 inches downstream of the combustor's upstream end (the round plate through which the post-mix ducts are inserted, visible in figure 14, forms the combustor's upstream end). The combustor liner itself was cylindrical and 15 inches in diameter. At full Saturn engine load, and assuming 1.3 pps airflow through each RCL-injector for ultra-low-emissions operation, combustor residence time was about 35 ms.

Engine Operating Procedure

Engine start-up data are shown in figure 15, with annotations, giving a graphical depiction of the start-up procedure. Note that there are three fuel circuits: a preburner fuel stage, which received about 25 kg/hr (55 pph) fuel during catalyst lightoff, and two RCL-injector fuel stages, which together received up to about 275 kg/hr (600 pph) fuel at load. RCL-injector fuel stage A supplied fuel to the top two injectors, while RCL-injector fuel stage B supplied fuel to the bottom two injectors.

At cold crank conditions (29% gas producer shaft speed, Ngp) the preburner was ignited and adjusted to 260°C (500°F) outlet temperature, below the catalyst lightoff temperature. As seen in figure 15, the small preburner fuel flow provided little motive power to the engine and negligible increase in engine speed. Next, while still at 29% Ngp, fuel was introduced to the RCL-injectors and combustion was ignited by a torch igniter in the main combustor. With the starter motor still engaged, fuel flow was ramped up as the engine accelerated to 65% Ngp. At 65% Ngp the starter motor was disengaged and the engine controller added fuel to maintain a constant idle speed of 65% Ngp (no load). Preburner outlet temperature remained at 260°C (500°F), and the catalysts remained inactive.



Fig. 15. Saturn engine start-up data, showing engine acceleration, catalyst activation by preburner (followed by preburner shutoff with continued catalyst activity), and operation at engine load by fuel supplied through four RCL-injectors.

Preburner temperature was then increased to about 350°C (660°F) to ensure catalyst lightoff. Engine speed was increased to 80% Ngp, the preburner was turned off, and the catalysts remained active. Engine speed was then increased to 90% and the variable airflow valves were adjusted to obtain optimum emissions. The valves served to vary the airflow to the RCL-injectors thus allowing control of NOx and CO emissions. Emissions data were taken as engine speed was reduced in increments of about 1% Ngp. The airflow valves were adjusted for best emissions at each speed.

Engine controls were based on a Saturn T1202R design and used a state of the art Allen-Bradley microprocessor console to run the logic. For the RCL[®] combustor engine tests, catalyst temperatures were not used in the fuel control algorithm. Instead, fuel control was performed according to standard DLN methods (primarily monitoring engine speed versus set point), with the addition of a preburner fuel control during initial start and catalyst lightoff. This was possible because catalyst temperature is insensitive to fuel/air ratio under fuel-rich conditions, as shown in figure 2.1.2 for the single-injector rig tests. In addition, the RCL[®] catalyst is air-cooled by a large fraction of the total combustion air, and reactions on the catalyst are limited by available oxygen (fuel-rich); thus, the catalyst is resistant to flashback, autoignition, and overheating damage, and can operate safely without active temperature control.

Engine Performance with RCL[®] Combustor

With RCL[®] combustion, Saturn engine NOx emissions averaged 2.1 ppm with less than 10 ppm CO over an achievable engine operating range (82% to 89% Ngp), as shown in figure 16. Over this engine operating range, UHC emissions remained below 3 ppm, and combustion-driven pressure oscillations (CDPO) remained less than 0.7 kPa (0.1 psi) peak-to-peak (less than 0.15% peak-to-peak of mean combustor pressure).

At 89% Ngp, combustor inlet air (compressor discharge air) was at 5.0 atm and 223°C (434°F). At 82% Ngp, combustor inlet air was at 3.9 atm and 191°C (376°F). For all data points shown in Figure 2.1.16 the preburner was turned off, the catalyst remained active at the available compressor discharge temperatures (as low as $191^{\circ}C / 376^{\circ}F$), and NOx emissions remained below 3 ppm.

Measured power output ranged from 237 kW (318 hp) to 453 kW (607 hp) over the 82% to 89% Ngp operating range, or about 32% to 61% load based on a 750 kW (1000 hp) nominal power rating for this modified engine. Engine load was delivered to a water dynamometer.

Engine operation was limited to the 82% to 89% speed range. At less than 82% Ngp the compressor was at its surge condition, and the compressor bleed valve was opened to prevent surge. This reduced the airflow to the RCL-injectors thus increasing NOx emissions. At speeds greater than 89% Ngp operation was limited by locally hot temperatures within the scroll ducting downstream of the combustor. This limitation was not attributable to the RCL[®] combustion technology but to inadequate mixing of combustor dilution air. Improving the test rig dilution mixing was deemed unnecessary to document the controllability of the RCL[®] system.

Table 1 summarizes the Saturn engine operating data at the low-end and high-end of the achievable operating range. In general, the results show good combustor performance (low emissions and low combustion-induced pressure oscillations, or CDPO) even at very low inlet temperatures. In addition, the Saturn engine operation shows the feasibility of engine start-up, acceleration, and operation at load using RCL combustion with simple engine controls. The engine was successfully started, accelerated, and powered at load by fuel injected through the four catalytic reactors, using conventional engine instrumentation and controls without instrumentation input from the catalyst.



Fig. 16. RCL combustor emissions during Saturn engine operation, showing ultra-low NOx and CO emissions over an achievable engine operating range of 82% to 89% speed.

Table 1	Saturn engine operating data at low-end and high-end of achievable operating range.	Note catalyst
	activity and ultra-low-emissions achieved at inlet temperatures as low as 191 C (376 F).

Engine Speed	82% Ngp	89% Ngp
NOx Emissions	2.2 ppm	2.2 ppm
CO Emissions	9.5 ppm	5.7 ppm
CDPO (noise)	< 0.7 kPa pk-pk	< 0.7 kPa pk-pk
Power Output	237 kW / 318 hp	453 kW / 607 hp
Nominal Load	32%	61%
Comb. Inlet Pressure	3.9 atm	5.0 atm
Comb. Inlet Temp.	191 C / 376 F	223 C / 434 F

3.2.2.1-8 Ultra-Low NOx Combustion of Coal-Derived Syngas and High-Hydrogen Fuels

While early development of PCI's Rich-Catalytic Lean-burn (RCL[®]) combustion system was focused on the use of natural gas fuel, fuel-rich operation of the catalyst is also advantageous for alternative fuels, including high-hydrogen fuels and coal-derived syngas. As with natural gas, combustion stability is improved (especially at low flame temperatures) by catalytically reacting a portion of the fuel upstream of the combustor, thus preheating (and vitiating) the fuel/air mixture entering the combustor. And, as with natural gas, this allows improved NOx emissions by operating the combustor at lower allowable (stable) flame temperatures.

For low-Btu fuels such as blast furnace gas, flame stability improvement by catalytic pre-reaction of a portion of the fuel is especially important since combustion may be otherwise unsustainable even at the highest possible flame temperatures. With catalytic pre-reaction and concomitant pre-heating, however, fuels having heating values as low as 82 Btu/ft³ have been successfully combusted at PCI, with near-zero emissions of unburned fuel, CO, and NOx.

For fuels with more moderate dilution levels, such as the syngas delivered from a coal gasifier, combustion of the raw fuel can occur without a catalyst, but low-emissions combustion is difficult as a result of the high levels of hydrogen. In particular, lean-premixed combustion for syngas fuels has not generally been considered feasible, because the high concentration of hydrogen leads to increased risk for flashback and flameholding in regions upstream of the combustor. Thus, syngas fuels are generally burned in a non-premixed mode, with NOx control accomplished by dilution of the fuel stream with water and/or nitrogen. This introduces combustion stability issues, however, such that low-single-digit NOx emissions have not yet been achieved in gas turbines burning coal-derived syngas.

One solution to this combustion stability problem is to catalytically react some portion of the syngas fuel prior to gas-phase combustion, effectively providing a higher inlet temperature to the combustor. This is exactly the role of a catalyst in a lean-premixed combustion system, and it can also be applied to combustion of syngas fuel, allowing greater dilution of the fuel and reduced NOx emissions.

For any fuel type, whether syngas, low-Btu gas, or hydrocarbon, fuel-rich catalytic reactor performance is insensitive to the fuel's reactivity, because reaction rate (heat release) upon the catalyst surface is controlled primarily by oxygen flow (air flow) under fuel-rich conditions, and not by fuel flow or reactivity. Performance on different type fuels will therefore be similar when heat release per atom of oxygen reacted is similar, and when the fuel's mass and thermal capacity is negligible in the fuel/air mixture. This is generally the case for hydrocarbon fuels, and the primary remaining issue for operation on heavy liquid fuels is prevaporization.

For coal-derived syngas fuel, heat release per atom of oxygen reacted is similar to hydrocarbon fuels, and additionally prevaporization is not an issue. However, unlike fuels consisting only of hydrocarbons, the large volume (low Btu value) of syngas fuels is not negligible, particularly when the syngas is highly diluted with steam or nitrogen for NOx control. Thus, while fuel-rich catalytic reactor performance for syngas fuels can be made similar to that obtained on hydrocarbon fuels (on the basis of heat release per atom of oxygen reacted), the reactor design must consider the large volume flow of fuel that it must pass, as well as the oxygen flow required for the desired level of pre-reaction or pre-heat.

3.2.2.1-9 Sub-Scale Test Data for Syngas Fuel

A sub-scale fuel-rich catalytic reactor was fabricated at PCI for testing with syngas fuel in PCI's high-pressure sub-scale combustion rig (pictured in figure 8). For the syngas tests, two independently controllable air supplies are provided, both heated and at high pressure. The larger air supply (entering from the right in figure 8) provides catalyst cooling air, which becomes primary zone combustion air in the gas-phase combustor, and the smaller air supply (entering from the vertical pipe at the top-right of figure 8) provides air to the fuel-rich fuel/air mixture. For operation with syngas fuel, two heaters are also provided (but not shown in Figure 8); one heater heats N, diluent just before it is mixed with fuel, and the second heater heats all other fuel components and CO₂.

Dry, oil-free, high-pressure air is supplied to the rig from compressors, at pressures up to about 145 psia entering the rig. At this flow rate, the rig inlet air can be heated to about 500°C. Fuel and diluent are supplied from bottles or Dewar flasks at high pressure, and are pressure regulated to the proper delivery pressure to the rig. All flows (air, fuel, and diluent) are metered with electronic mass flow controllers. Each fuel component is separately metered and then mixed with the other components to simulate the desired coal-derived syngas composition. Up to five fuel components can be introduced: H_2 , CO, CH_4 , CO₂, and N₂.

For syngas operation, combustion rig startup was accomplished by bringing the reactor to fuel-rich conditions using unheated methane fuel, with some diluent addition to ensure proper mixing. When necessary, a small amount of H_2 was temporarily added to the unheated methane to light off the reactor. Once the catalyst and combustor were lit and the rig was thermally stable, syngas fuel flow was ramped up while methane fuel flow was ramped down, holding catalyst equivalence ratio approximately constant. This startup procedure was economical and safe: it minimized the use of high-volume (costly) laboratory syngas fuel blend, and also avoided use of H_2 during transient and ignition events, where there was a concern that unburned H_2 might enter the exhaust stack and create an explosion hazard. This procedure is similar to syngas combustor startup in actual engine applications.

Catalyst Lightoff

Prior to high-pressure testing with syngas, atmospheric-pressure tests were performed to provide some initial experience in syngas fuel operation, and in catalyst and combustor behavior using syngas fuels. The results were used to help guide reactor design and test planning for the subsequent high-pressure tests. Catalyst lightoff tests were an important part of these early atmospheric pressure tests, and a lightoff temperature of 180°C was measured for fuel-rich reaction of syngas. This value was most carefully measured for a syngas mixture composed of 25% H₂ and 35% CO (remainder diluent), but it was found that lightoff temperature is relatively insensitive to syngas composition unless CO levels drop to very low values, leaving essentially a high-hydrogen fuel having significantly lower lightoff temperature. In all cases, the 180°C or lower lightoff temperature is well below compressor discharge temperatures of industrial and large-frame turbines, and the need for a preburner is thereby avoided in expected syngas applications.

High-Pressure Test Conditions

For the high-pressure sub-scale syngas tests, "baseline" operating conditions were scaled from those published for the IGCC plant at Tampa Electric's Polk Power Station. The Tampa Polk plant operates a GE 107FA combined cycle system on syngas generated from a Texaco oxygen-blown coal gasifier. Nitrogen injection reduces the effective heating value of the fuel, for NOx control.

Data from references by the U.S. DOE, GE Power Systems, and Brdar and Jones were used to establish a baseline syngas fuel composition representative of the Tampa Polk IGCC power plant fuel after dilution with nitrogen for NOx control, as well as a baseline full-load firing temperature¹⁸. This baseline syngas composition was used for most sub-scale high-pressure testing at PCI, and is tabulated in the first row of Table 2 as noted. The baseline full-load flame temperature was determined to be about 2550°F (1400°C), and represents a maximum in NOx emissions for an expected syngas application of fuel-rich catalytic combustion.

Additional tests were performed for a highly-diluted low-Btu syngas, to demonstrate the flame stability augmentation provided by the catalyst. The second row of Table 1 lists the composition of this low-Btu syngas mixture. Note that for all sub-scale tests at PCI, the nitrogen diluent was added to the syngas fuel prior to mixing with air, and well upstream of the catalyst.

Table 2 Syngas fuel compositions used for high-pressure sub-scale tests.								
Syngas Composition	H ₂	CO	$ CO_2 $	N ₂	LHV			
Syngas Composition	(%)	(%)	(%)	(%)	(Btu/ft^3)			
Baseline	20	20	10	50	117			
Low-Btu	15	15	10	60	88			

 Table 2
 Syngas fuel compositions used for high-pressure sub-scale tests.

Emissions measurements reported here were obtained from a water-cooled gas sample probe located 15 inches downstream of the catalyst, corresponding to about 50 ms residence time in the 2-inch inside-diameter ceramic-lined combustor. This represents the maximum residence time expected in a low-emissions gas turbine combustor, and therefore also represents the maximum expected NOx emissions for a given operating condition. Note that all emissions reported in ppm are parts per million by volume, and are corrected to $15\% O_2$ dry.

All measurements were made with a combustor inlet air temperature of 750° F (400°C) and a syngas fuel temperature of 570° F (300°C). Adiabatic flame temperatures were calculated based on fuel/air ratio as measured by the emissions analyzers (i.e. from gas samples extracted at the 15-inch gas sample probe location).

Combustor Emissions and Turndown

Figure 17 plots measured NOx and CO emissions as a function of adiabatic flame temperature at 10 atm pressure for the baseline syngas composition listed in row 1 of Table 2, having a Lower Heating Value (LHV) of 117 Btu/ft³. With this fuel composition, NOx emissions were 2.0 ppm (0.011 lbs/MMBtu) at the 2550°F (1400°C) flame temperature data point corresponding to baseline operation in the Tampa Polk IGCC plant at 100% load.

As the fuel/air ratio was decreased, CO emissions remained near zero for flame temperatures greater than about 2250° F (1230° C), permitting a 300°F (150° C) turndown in flame temperature from the 2550°F (1400° C) baseline point, allowing ultra low emissions operation over a wide range of loads. These results – CO near zero, and NOx equal to or less than 2 ppm (0.011 lbs/MMBtu) for full load and below – easily met PCI's emissions goals for these tests.



Fig. 17. Measured NOx and CO emissions for 10 atm baseline syngas tests, as a function of adiabatic flame temperature at the emissions probe.



Fig. 18. Measured NOx emissions for two different syngas compositions having LHVs of 88 and 117 Btu/ft³.

Subsequent to the baseline tests, the heating value of the diluted syngas fuel was reduced to determine operability and emissions for highly-diluted low-Btu syngas fuels. NOx emissions are shown in figure 18 for the low-Btu syngas composition listed in row 2 of table 2, as well as for the baseline syngas composition. It is important to note that the right-hand vertical axis in figure 18 (NOx values in ppm) is only applicable to the baseline syngas composition, as marked. For the fuel composition with the lower heating value (88 Btu/ft³), NOx emissions in ppm are slightly lower than shown (for the low-Btu fuel, 0.011 lbs/MMBtu is equivalent to 1.6 ppm).

It is worth noting that, as shown in figure 18, catalytic combustion allows stable operation with low emissions for the low Btu syngas case (88 Btu/ft³) even at flame temperatures as low as 2300°F (1260°C). CO emissions were less than 5 ppm in all cases, and were near zero for flame temperatures greater than 2200°F (1200°C).

3.2.2.1-10 Sub-Scale Test Data for High-Hydrogen and Low-Btu Fuels

In addition to syngas, other fuels containing non-hydrocarbon heating values are also of interest for power generation with low emissions. Industrial process and waste gases are particularly of interest, and PCI has therefore tested its fuel-rich catalytic combustion system with two such fuels: a low-Btu Blast Furnace Gas (BFG) and a high-hydrogen refinery fuel gas. Both gases were simulated in the laboratory by blending gases obtained from bottles or Dewars, using the same equipment that was used for the syngas fuel tests. Again, tests were performed in PCI's high-pressure sub-scale combustion test rig, pictured in figure 8.

Blast Furnace Gas

RCL[®] combustion of an 82 Btu/ft³ blast furnace gas was tested using a catalytic reactor that had previously been used for syngas testing. Results for the blast furnace gas show that combustion of this gas is extremely stable following fuel-rich catalytic reaction, even at adiabatic flame temperatures as low as 2250°F (1230°C). For these tests the simulated blast furnace gas comprised 23% CO, 22% CO_2 , 1.4% H_2 , 0.6% CH_4 , and 53% N_2 , and entered the reactor after being heated to about 450°F (230°C). Air entered the reactor and combustor at about 660°F (350°C).

Note that the high diluent fraction (low Btu value) of the blast furnace gas means that high fuel-lean equivalence ratios are needed in the combustor burnout zone to achieve the desired flame temperature. Therefore, tests were performed over a low range of adiabatic flame temperatures in the combustor burnout section, from about $2250^{\circ}F(1230^{\circ}C)$ to $2500^{\circ}F(1370^{\circ}C)$, representing maximum fuel flow capability of the rig for this blast furnace gas composition. For comparison, the stoichiometric flame temperature for this blast furnace gas is only about $2700^{\circ}F(1480^{\circ}C)$ for the inlet temperatures tested.

Because the catalyst was able to stabilize complete combustion at such low flame temperatures, NOx and CO emissions were ultra-low for all conditions tested. NOx emissions for blast furnace gas operation are plotted in figure 19, as measured by sample extraction from the cooled probe located 15 inches downstream of the catalyst exit. For all conditions tested, NOx emissions were measured below 2.5 ppm on a raw basis (uncorrected) and below 1 ppm corrected to 15% O_2 dry. CO emissions were near zero (< 1 ppm) for all conditions shown.

Because measured oxygen concentrations after fuel-lean burnout were very low, varying between about 2.5% and 5.5% for the conditions shown, the standard emissions reporting correction to 15% O, may be misleading. In fact, because of the high level of

diluent in the blast furnace gas, oxygen levels would never approach 15% in an actual engine application. Therefore, the raw NOx data are probably as relevant as the corrected NOx data, or perhaps more so, and both are therefore plotted in figure 19. In either case, NOx emissions were ultra-low as a result of the low blast furnace gas flame temperatures.



Fig. 19. NOx emissions, uncorrected and corrected to 15% O₂, as a function of adiabatic flame temperature in the downstream combustion zone of the RCL[®] combustor burning blast furnace gas (23% CO, 1.4% H₂, 0.6% CH₄, 22% O₂, and 53% N₂).

Refinery Fuel Gas

Testing of RCL[®] combustion of refinery fuel gas was also conducted using the same hardware configuration as previous tests for syngas and blast furnace gas. Results showed NOx emissions below 3 ppm for flame temperatures below 2800°F (1538°C).

For the refinery fuel gas tests, the simulated refinery fuel gas comprised 30% H₂ and 70% CH₄, and entered the reactor without passing through a fuel heater. However, some fuel heat was obtained from hot combustor rig components so that the fuel plenum gas temperature measured about 347° F (175° C). Combustion air entered the reactor at about 734° F (390° C).

Tests were performed over a range of adiabatic flame temperatures, from about 2400 to 3000° F (1315 to 1650°C) in the combustor burnout section, and at a pressure of about 10 atm. NOx and CO emissions were measured at each condition, as well as O₂ and CO₂.

NOx emissions for the RCL[®] combustion of refinery fuel gas are plotted in figure 20, as measured by sample extraction from the cooled probe located 15 inches downstream of the catalyst exit, corresponding to about 50 ms residence time. As shown, NOx emissions were measured below 3 ppm for flame temperatures less than about 2800°F (1540°C). CO emissions were less than about 1 ppm for all conditions shown.



Fig. 20. NOx emissions, corrected to 15% O_2 , as a function of adiabatic flame temperature in the downstream combustion zone burning refinery fuel gas (30% H_2 and 70% CH_4).

3.2.2.1-11 Technology Status and Outlook

For natural gas fuel, RCL combustion system has been demonstrated in engine testing of a modified Solar Turbines Saturn engine, and in full-scale full-pressure rig tests at Taurus 70 conditions and beyond, including F-engine type flame temperatures. The technology has been demonstrated viable in-engine, and the next step in technology maturity will be field demonstration for an extended period. Thus, the major challenges that lie ahead for natural gas applications will be durability demonstration and design integration for specific engine applications.

RCL combustion system has also been tested at sub-scale with multiple alternative fuels, as listed in table 3. For all fuels tested, catalyst temperatures were well controlled and combustor emissions were held to single-digit values over a wide turndown range, confirming the benefit of catalytic reactions in achieving low emissions for multiple types of fuels. The results also confirm that fuel-rich operation of the catalyst allows similar catalyst and reactor performance with widely varying fuel types.

For liquid fuel applications, the major outstanding development issue is prevaporization of the fuel prior to fuel-rich catalytic reaction. The primary concern here is autoignition and overheating of the premixer hardware. Likewise, the propensity for high-hydrogen fuels to autoignite is also problematic, as in syngas fuels. In both cases, the air-cooled catalyst structure is able to tolerate autoignition and gas-phase reactions, but conventional premixing devices located upstream of the catalyst may not. Therefore, advanced premixing concepts are to be developed for both liquid fuel and high-hydrogen fuel (e.g. syngas) applications.

Fuel Tested	Chemical Formula	C/H Ratio by Wt (%)	Fuel-Bound N by Wt (%)
Methane	CH ₄	75/25	0
Landfill Gas	$0.65 \text{ CH}_4 + 0.35 \text{ CO}_2$	46.5 / 10.1	0
Diesel No. 2	Multi component	87.6 / 13.0	0.0188
Gasoline	not analyzed	not analyzed	~0
Refinery Fuel Gas	$0.70 \text{ CH}_4 + 0.30 \text{ H}_2$	71.2 / 28.8	0
Syngas	20% H ₂ + 20% CO + 10% CO ₂ + 50% N ₂	14.75 / 1.64	0
Blast Furnace Gas	23%CO+22%CO ₂ +1.4%H ₂ +0.6%CH ₄ +53%N ₂	17.6 / 0.17	0

Table 3 Composition of seven different fuel types tested.

In addition, for IGCC applications with coal-derived syngas fuels, consideration must be given to the high volume flow of fuel that must pass through the catalytic reactor, to prevent excessive size or pressure drop penalties. Depending upon the application, this may require system level re-design and development of the catalyst and combustor.

Finally, it is also recognized that syngas fuels carry trace levels of catalyst contaminants that may affect long-term catalyst durability. This needs to be examined and remediated if problematic. Long-term durability tests are required, preferably in an actual syngas slipstream at an operating IGCC plant, where real contaminants will be present.

3.2.2.1-12 Conclusions

For natural gas operation, the Rich-Catalytic Lean-burn (RCL[®]) combustion concept has been tested at gas turbine conditions, first in a full-scale full-pressure single-injector rig, and second in a modified industrial gas turbine. These constitute two significant experimental milestones:

- 1. Experimental confirmation of the ultra-low-NOx capability of the RCL[®] combustion concept. In particular, we confirm the ability to mix fuel-rich catalyst effluent with primary combustion air, without inducing autoignition, yet imparting significant stability to the downstream combustion process.
- 2. Demonstration of RCL[®] combustion feasibility for gas turbine engine operation. In particular, we demonstrate engine start-up, acceleration, and robust operation at load by fuel injected only through RCL-injectors (effectively a single fuel stage, with all fuel contacting the catalyst), and with simple engine controls that do not monitor catalyst temperature.

In summary, the data presented show that fuel-rich catalytic reactions can stabilize fuel-lean premixed combustion to provide stable, quiet combustor operation with ultra-low NOx and CO emissions. In addition, the air-cooled fuel-rich catalyst system can operate safely without active temperature control because its temperature is insensitive to fuel/air ratio.

The RCL[®] system also provides significant operational advantages as compared to earlier catalytic combustion systems. Most notably, the RCL[®] reactor requires no preburner, is immune to issues of auto-ignition and flashback (and can therefore operate safely in high-firing-temperature machines such as F-class), and provides long catalyst life (as a result of the non-oxidizing fuel-rich catalyst environment).

Dr. Lance Smith, Dr. Hasan Karim, Dr. Shahrokh Etemad, Dr. William C. Pfefferle

Finally, fuel-rich operation of the catalyst allows operation on multiple types of fuels, as successfully demonstrated at sub-scale for gaseous and liquid hydrocarbon fuels, for low-Btu fuels and high-hydrogen fuels, and for simulated coal-derived syngas. For all of these fuels catalyst temperatures were well controlled, and ultra-low emissions were achieved.

3.2.2.1-13 Notes

- 1. C.L. Vandervort, "9 ppm NOx / CO Combustion System for 'F' Class Industrial Gas Turbines," ASME Paper No. 2000-GT-0086, ASME Turbo Expo May 8-11, 2000, Munich, Germany.
- D.K. Yee, K. Lundberg, and C.K. Weakley, "Field Demonstration of a 1.5 MW Gas Turbine with a Low Emissions Catalytic Combustion System," *Journal of Engineering for Gas Turbines and Power* 123 (2001): 550-556; L.L. Smith, H. Karim, M.J. Castaldi, S. Etemad, W.C. Pfefferle, V.K. Khanna, and K.O. Smith, "Rich-Catalytic Lean-Burn Combustion for Low-Single-Digit NOx Gas Turbines," *Journal of Engineering for Gas Turbines and Power* 127 (2005): 27-35.
- J.H. Lee and D.L. Trim, "Catalytic Combustion of Methane," *Fuel Processing Technology* 42 (1995): 339-359; R.A. Dalla Betta, "Catalytic Combustion Gas Turbine Systems: the Preferred Technology for Low Emissions Electric Power Production and Co-generation," *Catalysis Today* 35 (1997): 129-135; P. Forzatti and G. Groppi, "Catalytic Combustion for the Production of Energy," *Catalysis Today* 54 (1999): 165-180.
- 4. R.J. Farrauto, M.C. Hobson, T. Kennelly, and E.M. Waterman, "Catalytic Chemistry of Supported Palladium for Combustion of Methane," *Applied Catalysis A: General* 81 (1992): 227-237; R.J. Farrauto, J.K. Lampert, M.C. Hobson, and E.M. Waterman, "Thermal Decomposition and Reformation of PdO Catalysts; Support Effects," *Applied Catalysis B: Environmental* 6 (1995): 263-270; J.G. McCarty "Kinetics of PdO Combustion Catalysis," *Catalysis Today* 26 (1995): 283-293; N.M. Rodriguez, S.G. Oh, R.A. Dalla-Betta, and R.T.K. Baker, "*In Situ* Electron Microscopy Studies of Palladium Supported on Al₂O₂, SiO₂, and ZrO₂ in Oxygen," *J. Catalysis* 157 (1995): pp. 676-686.
- R.A. Dalla Betta, T. Shoji, K., Tsurumi, and N. Ezawa (1994). "Partial Combustion Process and a Catalyst Structure for Use in the Process," U.S. Patent No. 5,326,253; T. Furuya, K. Sasaki, Y. Hanakata, T. Ohhashi, M. Yamada, T. Tsuchiya, and Y. Furuse (1995). "Development of a Hybrid Catalytic Combustor for a 1300°C Class Gas Turbine," *Catalysis Today* 26 (1995): 345-350; Y. Ozawa, Y. Tochihara, N. Mori, I. Yuri, T. Kanazawa, and K. Sagimori, "High Pressure Test Results of a Catalytically Assisted Ceramic Combustor for a Gas Turbine," ASME Paper No. 98-GT-381, Stockholm, Sweden, 2-5 June 1998; R. Carroni, V. Schmidt, and T. Griffin, "Catalytic Combustion for Power Generation," *Catalysis Today* 75 (2002): 287-295.
- 6. S.T. Kolaczkowski, "Catalytic Stationary Gas Turbine Combustors: A Review of the Challenges Faced to Clear the Next Set of Hurdles," *Trans. I. Chem. E.* 73 Part A (1995): 168-190; D.B. Fant, G.S. Jackson, H. Karim, D.M. Newburry, P. Dutta, K.O. Smith, and R.W. Dibble, "Status of Catalytic Combustion R&D for the Department of Energy Advanced Turbine Systems Program," *Journal of Engineering for Gas Turbines and Power* 122 (2000): 293-300.
- M. Lyubovsky, L.L. Smith, M. Castaldi, H. Karim, B. Nentwick, S. Etemad, R. LaPierre, and W.C. Pfefferle, "Catalytic Combustion over Platinum Group Catalysts: Fuel-Lean versus Fuel-Rich Operation," *Catalysis Today* 83 (2003): 71-84.
- 8. R.E. Hayes and S.T. Kolaczkowski, *Introduction to Catalytic Combustion* (Amsterdam: Gordon and Breach Science Publishers, 1997); E.M. Johansson, D. Papadias, P.O. Thevenin, A.G. Ersson, R. Gabrielsson, P.G. Menon, P.H. Bjornbom and S.G. Jaras, "Catalytic Combustion for Gas Turbine Applications," *Catalysis* 14 (1999): 183-235; also see note 6 (Kolaczkowski).
- R.J. Rollbuhler, "Fuel-Rich, Catalytic Reaction Experimental Results," 27th Joint Propulsion Conference, Sacramento, CA, 24-27 June 1991, NASA Technical Memorandum 104423, AIAA Paper No. 91-2463; T.A. Brabbs and S.A. Merritt, "Fuel-Rich Catalytic Combustion of a High Density Fuel," NASA Technical Paper 3281 (1993).
- G.O. Kraemer, (1996). "Fuel-Rich Catalytically Stabilized Combustion for Aircraft Engine Applications," Ph.D. thesis, Yale University.
- M.B. Colket, A.S. Kesten, J.J. Sangiovanni, M.F. Zabielski, D.R. Pandy, and D.J. Seery (1993). "Method and System for Combusting Hydrocarbon Fuels with Low Pollutant Emissions by Controllably Extracting Heat from the Catalytic Oxidation Stage," U.S. Patent No. 5,235,804.
- 12. J.P. Kesselring, W.V. Krill, E.K. Chu, and R.M. Kendall. In proceedings of *New fuels and advances in combustion technologies* symposium, Mar. 26-30, 1979, New Orleans, LA.
- 13. W.C. Pfefferle, L.L. Smith, and M.J. Castaldi (2002). "Method and Apparatus for a Fuel-Rich Catalytic Reactor," U.S. Patent No. 6,358,040.
- 14. See note 2 (Smith).
- L.J. Spadaccini, and M.B. Colket, "Ignition Delay Characteristics of Methane Fuels," Prog. Energy Combust. Sci. 20 (1994): 431-460.

16. See note 2 (Smith).

- 17. L.L. Smith, S. Etemad, M.J. Castaldi, H. Karim, and W.C. Pfefferle (2002). "Method and Apparatus for a Fuel-Rich Catalytic Reactor," U.S. Patent No. 6,394,791.
- 18. United States Department of Energy (2000). Clean Coal Technology Topical Report Number 19, "Tampa Electric Integrated Gasification Combined-Cycle Project, An Update" July 2000; GE Power Systems (2002). "Gas Turbine and Combined Cycle Products," available at www.gepower.com/corporate/en_us/assets/gasturbines_heavy/prod/pdf/gasturbine_2002.pdf; R.D. Brdar and R.M. Jones (2000). "GE IGCC Technology and Experience with Advanced Gas Turbines," GE Power Systems Report No. GER-4207, October 2000.

BIOGRAPHY

3.2.2 Catalytic Combustion & 3.2.2.1 Fuel-Rich Catalytic Combustion



Dr. Lance L. Smith

Gas Turbine Group, Precision Combustion, Inc. 410 Sackett Point Road, North Haven, CT 06473

Dr. Lance L. Smith is a senior research & development engineer in the Gas Turbine Products group at Precision Combustion, Inc. (PCI), and a visiting assistant professor in the Engineering Department at Trinity College. Dr. Smith has 14 years experience in combustion research and combustor development, including work in turbulent non-premixed combustion, premixed combustion and premixing, aerodynamic design of combustor components, pulsed combustion, and catalytic combustion. His academic research has been primarily experimental, with a focus on laser-based measurements in flames, including work conducted as a visiting researcher at Sandia National Laboratories and as a post-doctoral researcher at UCLA. Dr. Smith is a principal engineer of, and holds multiple patents for, the RCLTM catalytic reactor. At PCI, he works with OEM gas turbine manufacturers to develop integrated catalytic combustion systems for ultra-low emissions gas turbines. A graduate of Brown University (B.S., 1986) and of University of California, Berkeley (M.S., 1990 and Ph.D., 1994), Dr. Smith is an elected member of the Tau Beta Pi and Sigma Xi honor societies, and a member of the Combustion Institute.





Dr. Shahrokh Etemad

Gas Turbine Group, Precision Combustion, Inc. 410 Sackett Point Road, North Haven, CT 06473

phone: (203) 287-3700 x217 email: setemad@precision-combustion.com

Dr. Shahrokh Etemad as Manager of Gas Turbine Products at Precision Combustion, Inc. (PCI) in North Haven, Connecticut, has full responsibility for technical and commercial development of two major products. He manages an advanced technology group to develop low-emissions combustion products in close collaboration with several OEM gas turbine engine manufacturers and the U.S. Department of Energy. Dr. Etemad is responsible for budgeting, funding opportunities, technology direction, proposal preparation and complete R&D operations including concept development, computational analysis, experimental testing, full-size performance demonstration and productionization. Prior to his present position at PCI, he worked for several years at Textron Lycoming and United Technologies, Carrier. Dr. Etemad has published 28 technical articles and holds 28 patents in the field of turbomachinery, combustion, and thermofluid systems. He earned bachelor's and master's degrees at Sussex University and University of London respectively, and received his Ph.D. from the University of Washington in 1984. He has been a member of ASME since 1995 and won the 2003 ASME Gas Turbine award.





Dr. Hasan Karim

Gas Turbine Group, Precision Combustion, Inc. 410 Sackett Point Road, North Haven, CT 06473

Dr. Hasan Karim is a senior research & development engineer at Precision Combustion, Inc. (PCI), where his responsibilities include design, development, analysis, numerical and computational fluid dynamics, and testing of catalytic combustors for natural gas, syngas, and liquid fuel. He is the principal investigator for the catalytic combustor development project for the U.S. Navy and lead engineer for the catalytic pilot and catalytic combustor for downhole combustion programs. After receiving a bachelor's degree from Indian Institute of Technology-Kharagpur in 1987, Dr. Karim earned his M.S. from New Jersey Institute of Technology in 1991, and his Ph.D. from Yale University in 1998. He is a co-inventor of air-cooled rich and lean reactor technology.





Dr. William C. Pfefferle

Gas Turbine Group, Precision Combustion, Inc. 410 Sackett Point Road, North Haven, CT 06473

Dr. William C. Pfefferle invented the original catalytic combustor for gas turbine engines in the early 1970s and now holds over 90 U.S. patents. In 1986, Dr. Pfefferle co-founded Precision Combustion, Inc. (PCI), a Connecticut-based company dedicated to developing clean and efficient technology for clean air. His research has led to important industrial advances such as the RCL catalytic combustor for ground power gas turbine engines, which is now in late-stage development and evaluation by several major gas turbine manufacturers, and the Microlith catalytic reaction system, which forms the basis for paradigm-shift, high heat mass transfer catalytic reactors for fast-lightoff automotive catalytic converters and fuel processor reactors. With a B.S. in Chemical Engineering from Drexel University (1944) and a Ph.D. in Physical Chemistry from the University of Pennsylvania (1952), Dr. Pfefferle is a member of the American Chemical Society (ACS), and received the ACS 31st Northeast Regional Industrial Innovation Award. He was inducted into the New Jersey Inventor's Hall of Fame in February 1990. He continues to work full-time to develop catalytic devices for clean and efficient energy.