

# Rich-Catalytic Lean-burn combustion for fuel-flexible operation with ultra low emissions

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## Abstract

A Rich-Catalytic Lean-burn (RCL<sup>®</sup>) combustion system was developed for operation on natural gas, but also provides significant advantages for fuel-flexible operation on non-methane fuels. Most notably, fuel-rich operation limits the extent of catalyst-stage reaction based on available oxygen, regardless of the fuel's intrinsic reactivity on the catalyst. Thus, similar catalyst and reactor performance can be obtained for widely varying fuel types.

In addition, catalytic pre-reaction extends the combustor's lean flammability limit for all fuels, allowing low-temperature combustion of both conventional and low-heating-value fuels, with concomitant low NO<sub>x</sub> emissions.

This paper presents test results for RCL<sup>®</sup> combustion with various fuel types, including gaseous, pre-vaporized liquid, and simulated low-Btu fuels. Although these fuels have widely varying properties, a single type of catalytic reactor was successfully tested for all of these fuels by modifying only the fuel delivery system upstream of the reactor. Test results show similar reactor performance for all fuels tested.

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## 1. Introduction

Currently, gas turbines operating on natural gas offer the lowest achievable NO<sub>x</sub> emissions without exhaust-gas after treatment, as compared to other fuels. Commercially, this has been achieved through the use of lean-premixed combustion systems, allowing NO<sub>x</sub> emissions below 9 ppm (at 15% O<sub>2</sub>) to be guaranteed for natural gas operation, and emissions near 5 ppm to be demonstrated [1]. Catalytic combustion can provide even lower emissions (<3 ppm NO<sub>x</sub>) as demonstrated in recent natural gas engine tests [2,3], but a need still exists for similar low emissions operation with non-methane fuels. As reported here, recent high-pressure combustion tests have shown that fuel-rich catalytic combustion in particular can provide such low emissions on multiple fuels, while maintaining similar catalyst and combustor performance.

Fuel-rich catalytic combustion has been investigated by a number of researchers during the past decades [4–8], but has

only in recent years been successfully demonstrated as an ultra-low-NO<sub>x</sub> emissions technology for gas turbines [3,9,10]. In this recent work, a Rich-Catalytic Lean-burn (RCL<sup>®</sup>) combustion system was developed at Precision Combustion, Inc. (PCI) initially for use with natural gas fuel and subsequently tested with alternative fuels both liquid and gaseous, notably Diesel No. 2 (presented here) and simulated gasified coal or syngas [11]. For natural gas fuel the system has been demonstrated at full-scale and in-engine, delivering wide turndown with ultra-low NO<sub>x</sub> emissions below 3 ppm and CO emissions below 10 ppm [3].

Fuel-rich operation of the catalyst offers multiple advantages [3]. For methane or natural gas fuels, catalyst activity is significantly improved by operating the catalyst under fuel-rich conditions as compared to fuel-lean conditions, allowing a wider choice of catalyst materials [9]. Improved catalyst activity also enables the rich catalyst system to operate without a preburner, since compressor discharge temperatures are normally sufficient to provide the needed catalyst activity.

For both methane and non-methane fuels, another advantage of fuel-rich operation is important: fuel-rich operation starves the reaction of oxygen and thereby limits the extent of fuel oxidation and heat release regardless of the fuel's intrinsic

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reactivity on the catalyst. Thus, similar catalyst and reactor performance can be obtained for widely varying operating conditions and widely varying fuel types. This provides predictable, robust operation with well-controlled catalyst temperatures even in high-firing-temperature machines. Likewise, multi-fuel operation becomes possible, and the same basic reactor design, catalysts, and substrate metallurgy are applicable (and have been demonstrated) for both hydrocarbon and non-hydrocarbon fuels [11].

In fact, while early development of the RCL<sup>®</sup> combustion system was focused on the use of natural gas fuel [3,9], the system is equally well-suited to low-emissions combustion of alternative fuels, including liquid fuels, high-hydrogen fuels, and coal-derived syngas [11]. As with natural gas, combustion stability is improved (especially at low flame temperatures) by catalytic reaction of 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 NO<sub>x</sub> emissions by operating the combustor at lower allowable (stable) flame temperatures.

For low-Btu fuels, 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/ft<sup>3</sup> (e.g. blast furnace gas) have been successfully combusted at 10 atm pressure, with near-zero emissions of unburned fuel, CO, and NO<sub>x</sub>.

For any fuel type, 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 mass transfer to the catalyst under fuel-rich conditions, and not by fuel flow or fuel reactivity. Performances 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 (or similar) 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 pre-vaporization.

A schematic of the RCL<sup>®</sup> system is shown in Fig. 1. As shown, the combustion air stream is split into two parts upstream of the catalyst: one portion is mixed with all of the fuel, creating a fuel rich mixture, and contacted with a catalyst, while the second portion is used to backside cool the catalyst [12,13]. At the exit of the reactor, the catalyzed fuel-rich stream

and the cooling air are rapidly mixed to produce a fuel-lean, reactive mixture prior to final combustion.

By passing all of the fuel over the catalyst, the catalyst-cooling stream remains free of fuel, preventing failure by flashback or auto-ignition in the cooling stream. At the same time, 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, precluding flashback damage.

The fuel-rich catalyst system thus provides significant operational advantages for operation on multiple fuels. Most notably, the RCL<sup>®</sup> reactor requires no preburner at full to part-load gas turbine operating conditions, is immune to issues of auto-ignition and flashback, and provides long catalyst life (as a result of the non-oxidizing fuel-rich catalyst environment), all while providing ultra-low NO<sub>x</sub> performance.

## 2. Test conditions and hardware

### 2.1. Fuel types and corresponding catalytic reactors

A single sub-scale fuel-rich catalytic reactor was tested in the high-pressure combustion rig with three different fuels: methane, simulated landfill gas, and Diesel No. 2 (the first three listed in Table 1). No changes were made to the reactor or combustor for operation on these different fuels. For diesel fuel, however, a pre-vaporizer was added upstream of the reactor. Two different pre-vaporizers were used: initially we used a simple preheater to directly heat diesel fuel after adding less than 10 wt% N<sub>2</sub> to assist in atomization; later we improved pre-vaporization by mixing steam with the diesel fuel. The latter was considered ideal for co-generation applications with available steam.

Fuel-bound nitrogen content for the red-dyed Diesel No. 2 fuel was analyzed by an outside laboratory and measured as 188 ppm by weight. At this concentration, nearly complete conversion of fuel-bound N to NO<sub>x</sub> is expected [14]. Thus, based on fuel-bound nitrogen content, the diesel fuel would emit at least 8.1 ppmv NO<sub>x</sub> when burned, measured on a dry basis at 15% excess O<sub>2</sub>. Fuel-bound nitrogen for all other fuels was zero.

Methane and landfill gas fuels were tested at pressures of 9–10 atm, near the rig limit. The first diesel fuel pre-vaporizer was also able to operate near 9 atm pressure. Diesel fuel tests with steam-enhanced pre-vaporization were performed at about 6 atm pressure, however, based on limitations of the pre-vaporizer.

Prior to testing of the three fuels listed in Table 1, a separate fuel-rich catalytic reactor of similar design was tested with gasoline and natural gas fuels (for back-to-back comparison) at about 7 atm pressure. For these initial liquid fuel tests gasoline was chosen for its high volatility, simplifying pre-vaporizer design. Later, subsequent to testing of the three fuels listed in Table 1, non-hydrocarbon and low-Btu fuels such as simulated blast furnace gas (82 Btu/ft<sup>3</sup>) were tested in another similar fuel-rich catalytic reactor design, at pressures up to about

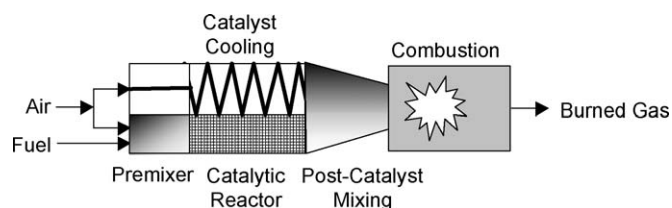


Fig. 1. Schematic of RCL<sup>®</sup> system. A fuel-rich fuel/air mixture contacts the catalyst, while heat is extracted into a cooling air stream. The cooling air stream and the catalytically reacted rich fuel/air mixture are rapidly mixed downstream of the catalyst, but prior to final combustion, to create a fuel-lean fuel/air mixture for low-NO<sub>x</sub> burnout.

Table 1  
Composition of six different fuel types tested

| Fuel tested       | Chemical formula                                                                               | C/H ratio (wt%) | Fuel-bound N (wt%) |
|-------------------|------------------------------------------------------------------------------------------------|-----------------|--------------------|
| Methane           | CH <sub>4</sub>                                                                                | 75/25           | 0                  |
| Landfill gas      | 65% CH <sub>4</sub> + 35% CO <sub>2</sub>                                                      | 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 | 70% CH <sub>4</sub> + 30% H <sub>2</sub>                                                       | 71.2/28.8       | 0                  |
| Blast furnace gas | 23% CO + 22% CO <sub>2</sub> + 1.4% H <sub>2</sub> + 0.6% CH <sub>4</sub> + 53% N <sub>2</sub> | 17.6/0.17       | 0                  |

10 atm. A simulated refinery fuel gas was also tested, containing a high percentage of H<sub>2</sub> in a hydrocarbon mixture, in this 10 atm reactor. All six of these fuels are listed in Table 1.

For all fuels tested, the basic fuel-rich catalytic reactor design was as shown schematically in Fig. 1. Thus, all reactors tested were air-cooled with primary combustion air, and all fuel contacted the catalyst. In all cases, the precious metal catalysts were applied to similar washcoated metal substrates.

## 2.2. Test facility and operating conditions

The catalytic combustion tests reported here were performed in a sub-scale combustion test rig, as pictured in Fig. 2. The gas-phase combustion section of this rig is nominally 5 cm (2 in.) in diameter and 46 cm (18 in.) in length, and is fabricated from high-temperature ceramic and housed in the steel pressure vessel seen in Fig. 2. The rig is capable of operation at pressures up to 10 atm, with pressure control by a water-cooled back-pressure valve at the combustor exit. Reactants enter the ceramic-lined combustor through an air-cooled fuel-rich catalytic reactor (see schematic representation of combustion system in Fig. 1) of nominally 1.9 cm (0.75 in.) diameter. Gas samples are extracted at 7.6 cm (3 in.) axial intervals along the 46 cm (18 in.) long combustor, as shown in Fig. 2, as well as from the catalytic reactor. Gas samples are analyzed by an emissions rack containing separate analyzers for NO<sub>x</sub>, CO, UHC, CO<sub>2</sub>, and

O<sub>2</sub>. A gas chromatograph is also used to analyze gas samples for major species (N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CO, H<sub>2</sub>, and low-order hydrocarbons), and to provide confirmation of overall fuel/air ratio in the combustor burnout zone. All combustion emissions reported below correspond to a gas sampling position at 30 ms residence time in the ceramic-lined combustor.

For the tests reported here, gaseous fuels and diluents were supplied from bottles or Dewar flasks at high pressure, and were pressure regulated to provide the proper delivery pressure to the rig. All gas flows (air, fuel, and diluent) were metered through electronic mass flow controllers. Liquid fuels were metered through positive displacement (constant flow volume) pumps. Each fuel component was separately metered and then mixed with the other components to provide the desired composition.

Each sub-scale reactor was installed in PCI's high-pressure combustion rig, as shown in Fig. 2. Two air supplies were provided, to enable metering of the catalyst cooling air independently of the air to be mixed with fuel (catalyst-bound air). Air was supplied at about 165 psia, allowing rig operation at pressures up to about 9 or 10 atm, after pressure loss through mass flow controllers and heaters. Cooling air and catalyst-bound air were both heated to simulate gas turbine compressor exit conditions, at temperatures from about 300–400 °C (depending upon the conditions selected). Fuel flow rate was varied to provide overall equivalence ratios from about 0.3–0.6 downstream of the catalyst, after mixing of the fuel-rich catalyst effluent with catalyst cooling air.

## 3. Results

For the two-stage catalytic combustion system tested (Fig. 1), the most relevant measures of performance are catalyst temperatures in the first stage (catalyst-stage) and combustor emissions from the second stage (gas-phase combustion stage). In this paper, we especially wish to compare these measures of performance for operation on various types of fuels.

### 3.1. Catalyst performance for hydrocarbon fuels

Initial tests were performed using methane, and diluted methane (landfill gas), to establish baseline performance. Catalyst temperatures and inlet gas temperatures are shown in Fig. 3 for both the methane and landfill gas fuels. For both fuels, the reactor was operated at 9.6 atm pressure, an inlet air temperature near 345 °C, and an overall equivalence ratio of 0.54–0.58. Similar performance was obtained for both fuels.

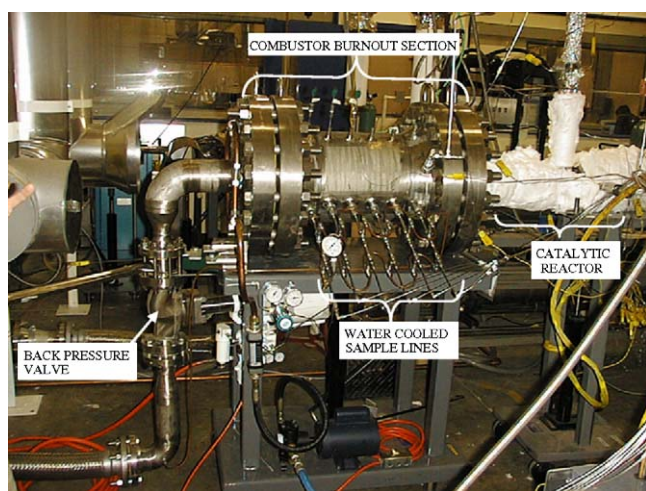


Fig. 2. Photograph of 10 atm sub-scale combustion test rig. Note that flow is from right to left in this photograph. The ceramic-lined combustor is housed in the steel pressure vessel, while the catalytic reactor is housed in a separate, smaller pressure vessel upstream of the combustor section, as shown.

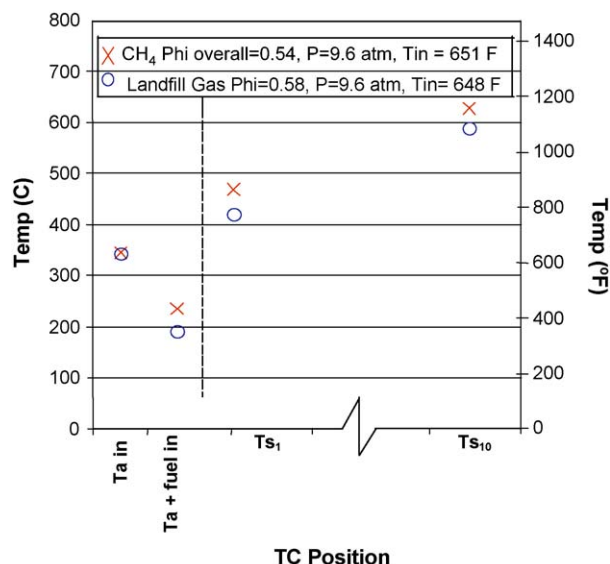


Fig. 3. Natural gas and landfill gas tests at 9.5 atm pressure and 345 °C inlet temperature.

Looking at Fig. 3, the abscissa (*x*-axis) shows thermocouple location from the inlet through the reactor. To the left of the first vertical line, the thermocouple labeled “Ta in” measured the air temperature entering the catalyst cooling channels, and the thermocouple labeled “Ta + fuel in” measured the temperature of the fuel-rich fuel/air mixture entering the catalyst bed. Note that heated air was mixed with unheated fuel (as expected in an engine), making the fuel/air mixture temperature significantly less than the cooling air temperature. As seen in Fig. 3, similar performance was obtained for natural gas and landfill gas fuels. The data show that the inlet and catalyst surface temperatures were very nearly the same for the two different fuels.

The first liquid fuel tests were performed with gasoline, and gave very similar results to tests performed with natural gas in the same catalytic reactor. Catalyst temperatures for operation on gasoline are compared to those for natural gas operation in Fig. 4, for operation at 7 atm pressure. As shown, catalyst operating temperatures (“*T<sub>surfaces</sub>*”) were both very similar for the two dissimilar fuels. Catalyst temperatures shown in Fig. 4

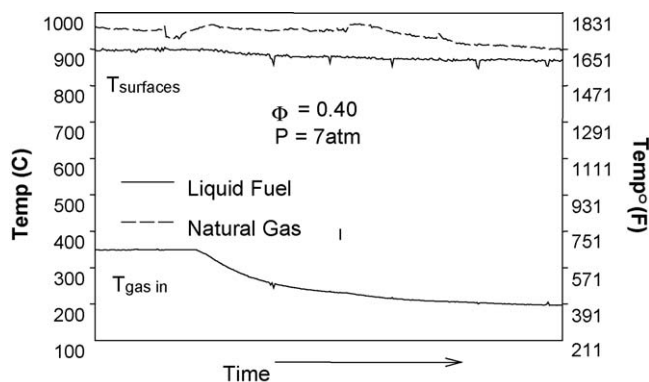


Fig. 4. Combined graph showing catalyst operation for both natural gas and liquid fuel (gasoline) at 7 atm pressure, as a function of time. For both fuels, the inlet gas temperature (“*T<sub>gas in</sub>*”) was initially held steady at about 350 °C, and then ramped down to about 200 °C without catalyst extinction.

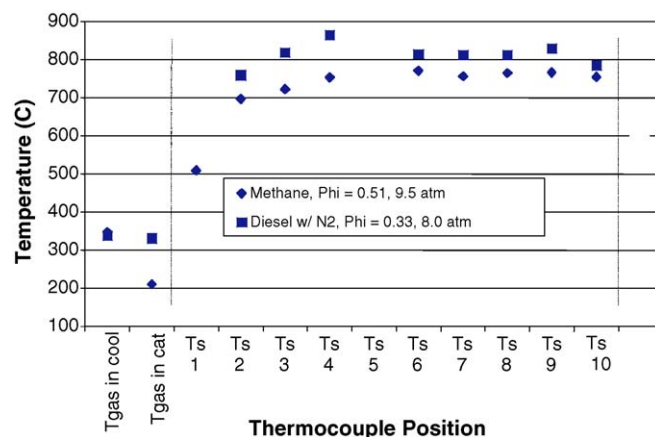


Fig. 5. Natural gas and diesel fuel tests at 8–9.5 atm pressure and 345 °C inlet temperature. Diesel fuel was pre-vaporized by PCI’s first laboratory pre-vaporizer, with ~8% N<sub>2</sub> addition but without steam.

are higher than those shown in Fig. 3, however, because Fig. 4 data were obtained on an earlier RCL reactor with less effective backside cooling of the catalyst.

Initial diesel fuel testing was performed using the first laboratory pre-vaporizer, without steam. Catalyst temperature data for this initial diesel operation are shown in Fig. 5, along with data from methane operation for comparison. For this data, diesel fuel was pre-vaporized while passing through a packed bed inside a 600 °C oven. Immediately, upstream of the packed bed (and inside the oven), the diesel fuel was sprayed into co-flowing N<sub>2</sub> (~8% mass ratio of N<sub>2</sub> to diesel fuel) to begin the process of droplet evaporation. At the packed bed exit a condensate collector showed no accumulation, confirming that all fuel was vaporized. After exiting the oven, the pre-vaporized fuel was injected into the catalyst-bound air stream, to form a fuel-rich fuel/air mixture.

As shown in Fig. 5, catalyst operation was similar on both methane and diesel fuel, with similar catalyst temperatures for both fuel types. Operating pressure was similar for both cases (8 atm for the diesel fuel case, as compared to 9.5 atm for the methane case), and inlet air temperature was the same (345 °C). Note, however, that the steam-free pre-vaporizer was only able to vaporize enough fuel to provide 0.33 overall equivalence ratio. Also note that the diesel fuel was heated in the pre-vaporizer, whereas methane fuel was un-heated (this is evident in the temperature reading at “*T<sub>gas in cat</sub>*” in Fig. 4). Because the fuel-rich equivalence ratio was lower for the diesel fuel case, and the fuel hotter, catalyst temperatures were approximately 50 °C higher for diesel fuel than for methane, as can be seen in Fig. 5. However, the same catalytic reactor was used for both fuels to provide a direct comparison, and to show the fuel flexibility of fuel-rich catalyst operation.

Catalyst lightoff and extinction temperatures for diesel fuel were tested at 6 atm pressure using the steam-free pre-vaporizer, as shown in Fig. 6. Pre-vaporized fuel temperature 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



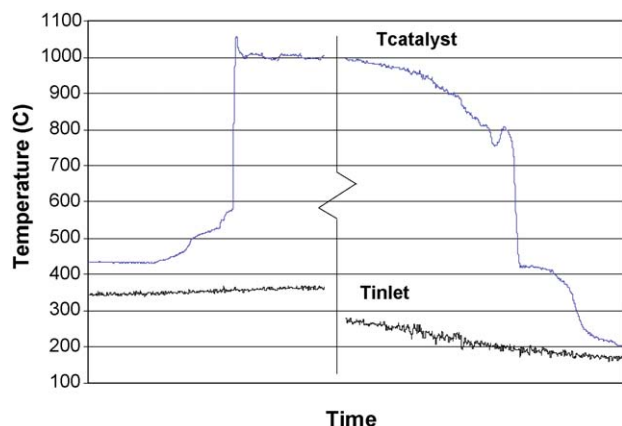


Fig. 6. Catalyst lightoff and extinction temperatures for diesel fuel. Tests were performed with the steam-free pre-vaporizer, at 6 atm pressure. “ $T_{\text{inlet}}$ ” represents air temperature entering the reactor, and “ $T_{\text{catalyst}}$ ” represents catalyst surface temperature.

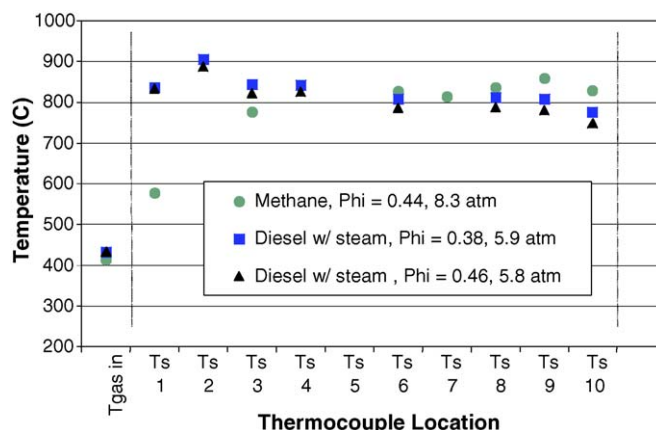


Fig. 7. Catalyst performance with diesel fuel, for steam-enhanced pre-vaporizer ( $\sim 5:1$  steam:fuel ratio by weight) operating at 6 atm pressure and 430 °C inlet air temperature. Compare to methane tests at 8 atm and 415 °C inlet temperature.

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 a period of steady-state operation, inlet air temperature was ramped down from about 280 °C until sudden loss of activity (extinction) occurred at about 200 °C inlet air temperature. Note that the catalyst extinction temperature (200 °C) was well below the catalyst lightoff temperature (360 °C). This was true for all fuel types tested under fuel-rich catalyst conditions.

For comparison, catalyst lightoff temperature was 370 °C for pure methane fuel and 450 °C for landfill gas fuel (methane with CO<sub>2</sub> diluent). Extinction temperatures were significantly lower (well below 300 °C), and in general we have observed stable reactor operation (continued catalyst activity) at inlet gas temperatures lower than lightoff temperature for all fuels tested under fuel-rich catalyst conditions. Such low extinction temperatures can be used advantageously in low pressure-ratio machines having combustor inlet temperatures below the catalyst lightoff temperature. In these cases, the catalyst can be lit off by an auxiliary means (such as a preburner) which can then be removed or shut off since the catalyst will remain active (once lit) at the available combustor inlet temperature.

In general, we find that for RCL combustion of hydrocarbon fuels, catalyst lightoff temperature shows little dependence on pressure, allowing a straightforward comparison of lightoff temperature for different fuels even if pressure is not held constant. Lightoff is of course dependent on heat removal rate versus heat release rate at the surface, and we therefore find higher lightoff temperatures for the case where significant heat-absorbing diluent is added, such as for the landfill gas fuel described above.

For diesel fuel testing at higher overall equivalence ratios and higher inlet temperatures an improved diesel fuel pre-vaporizer was required. For this purpose, a steam-enhanced pre-vaporizer was designed and fabricated, using superheated steam to pre-vaporize the diesel fuel. Positive-displacement pumps metered liquid water and liquid fuel. The water was

vaporized and superheated to about 200 °C at about 10 atm pressure. The liquid fuel was then sprayed into the superheated steam, and a heater raised the fuel/water mixture temperature to about 400 °C over a packed bed. The combined fuel/water vapor exited the packed bed and was injected into the preheated catalyst-bound air stream, to create a fuel-rich fuel/air mixture in contact with the catalyst. While some coking was observed in the steam-free pre-vaporizer, this was not an issue in the steam-enhanced pre-vaporizer. The steam-enhanced pre-vaporizer is an ideal situation for co-generation applications where high-pressure steam is available as part of the system.

Catalyst temperature data are shown in Fig. 7 for diesel fuel operation using the steam-enhanced pre-vaporizer. Data points between the two vertical dashed lines in Fig. 7 represent catalyst surface temperatures, while the left-most location (outside the dashed lines) represents inlet air temperature. Data were obtained at the pre-vaporizer's maximum operating pressure of 6 atm, and at 430 °C inlet temperature. Diesel fuel data are shown for two different equivalence ratios (0.38 and 0.46 overall), and are compared to catalyst temperature data for methane at similar operating conditions (overall equivalence ratio of 0.44 for 415 °C inlet temperature and 8 atm pressure). In general, very similar catalyst performance was obtained for both diesel and methane fuels, and with only small variation in catalyst temperature with length through the bed.

The comparison in Fig. 7 between two different fuels is not affected by the slightly different operating conditions (6 atm versus 8 atm) because we have found in general that catalyst temperatures are not sensitive to pressure or flow velocity, based on extensive methane testing of both sub-scale and full-scale RCL reactors. Catalyst temperature is insensitive to flow, and pressure, because both reaction and heat transfer are limited by turbulent transport, and therefore remain proportional to one another over the range of conditions associated with RCL operation in a gas turbine combustor. Slight variation of catalyst temperature with axial position can occur, however, as seen for example in Fig. 7. This is primarily a result of backside cooling of the catalyst, which reduces the reacting stream's enthalpy as

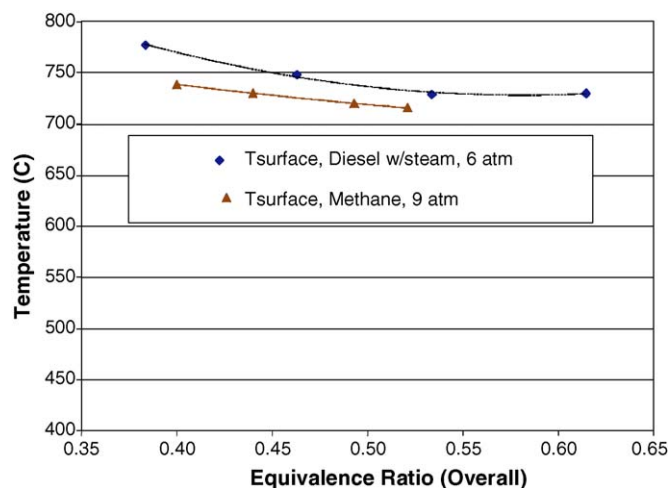


Fig. 8. Catalyst performance based on equivalence ratios with diesel fuel for steam-enhanced pre-vaporizer (~5:1 steam:fuel ratio by weight) operating at 6 atm pressure and 430 °C inlet air temperature compared to methane tests at 9 atm and 440 °C inlet temperature.

it moves downstream, and increases the cooling stream's enthalpy. Depending on the ratio of these streams, catalyst temperature may increase or decrease with axial distance. Also, at the upstream end, a small but finite distance is required to obtain catalyst lightoff. Both of these effects are present in the data shown in Fig. 7, where a peak in catalyst temperature occurs at the Ts2 position, after catalyst lightoff but before loss of enthalpy to the cooling stream.

Fig. 8 plots catalyst temperature, at a fixed downstream location in the reactor, as a function of overall equivalence ratio in the combustor. As shown in Fig. 8, catalyst temperature was insensitive to overall equivalence ratio for both methane and diesel fuels. This is because heat release per mole of reacted oxygen does not vary significantly with fuel type or with operating condition, since the selected catalysts were primarily selective to full oxidation products (CO<sub>2</sub> and H<sub>2</sub>O) over the range of fuel/air ratios tested, as also reported earlier for similar natural gas tests [3].

The insensitivity of catalyst temperature to operating condition in Fig. 8 is also a result of the small mass flow of fuel compared to total mass flow of air passing through the catalyst bed, such that the total flowing thermal mass (fuel plus air) does not change significantly with equivalence ratio. Note that airflow through the catalyst bed includes both backside-cooling air as well as air in contact with the catalyst itself. For all data points shown in Fig. 8, the reactor cooling airflow and catalyst-bound airflow were fixed at the same values. Thus, for constant catalyst-bound airflow, the oxygen available for reaction (the limiting reactant under fuel-rich conditions) is the same at all conditions. When cooling airflow is constant as well, the reactor's total thermal mass flow is also about the same at all conditions, and therefore heat release and temperature in the catalyst bed become insensitive to equivalence ratio, and are very similar for both methane and diesel fuels despite a wide difference in reactivity between these two fuels. This inherent behavior of fuel rich operation makes the concept a viable approach for fuel flexible gas turbine applications.

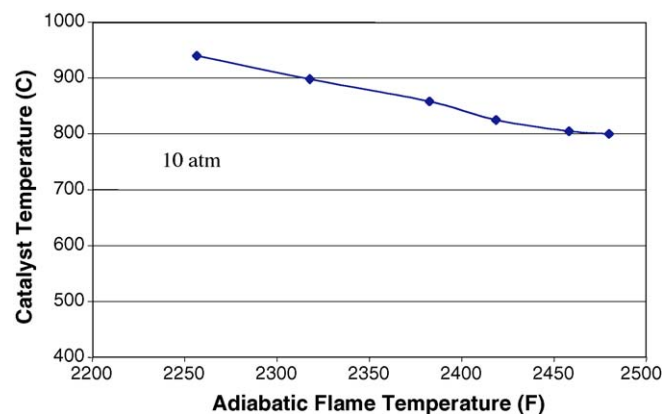


Fig. 9. Catalyst operating temperatures for low-Btu blast furnace gas fuel, for flame temperature from 2250 to 2480 F.

### 3.2. Catalyst performance for alternative fuels

A low-Btu simulated blast furnace gas, containing primarily CO as fuel, and a high-hydrogen content refinery fuel gas were also tested in the 10 atm sub-scale RCL combustor, and are listed in Table 1 for comparison to the hydrocarbon fuels tested.

Operation on these alternative fuels is described in greater detail under the section on emissions performance (below), but it is briefly noted here that, once again, catalyst performance was robust and well-controlled on both of these fuels.

Catalyst operating temperatures for the blast furnace gas tests are shown in Fig. 9 over the range of conditions tested, and are in all cases between about 800 and 950 °C as desired. Note that for this highly diluted (low-Btu) fuel the range of adiabatic flame temperatures downstream of the catalyst (after mixing with catalyst cooling air) is quite low, yet stable combustion was achieved at all of these conditions. Also observe that the high volume of diluent in this fuel leads to greater sensitivity of catalyst temperature to equivalence ratio than for typical hydrocarbon fuels. In fact, for the low-Btu fuel, unlike conventional hydrocarbon fuels, the mass flow of fuel is not small compared to the total mass flow of air through the reactor. Instead, for low-Btu fuel operation, total thermal mass flow through the reactor (including fuel, diluent, and air) changes noticeably with equivalence ratio. For constant catalyst-bound airflow, then, heat release rate is constant (based on available oxygen), but thermal mass flow increases with equivalence ratio so that catalyst temperature decreases with equivalence ratio. This effect is evident in Fig. 9, for the low-Btu fuel data. For other fuels such as methane or diesel, as shown in Fig. 8 for example, the effect of fuel flow on thermal mass is much smaller, but is present and measurable.

The flat temperature profile shown in Fig. 10 for the hydrogen-plus-hydrocarbon refinery fuel gas is also typical of hydrocarbon fuels, where the effect of fuel flow on thermal mass flow is much smaller than in the low-Btu fuel case. For the refinery fuel gas the important result from Fig. 10 is that catalyst temperatures are not adversely affected by the presence of high concentrations of hydrogen, and catalyst failure by flashback or auto-ignition does not occur because the catalyst

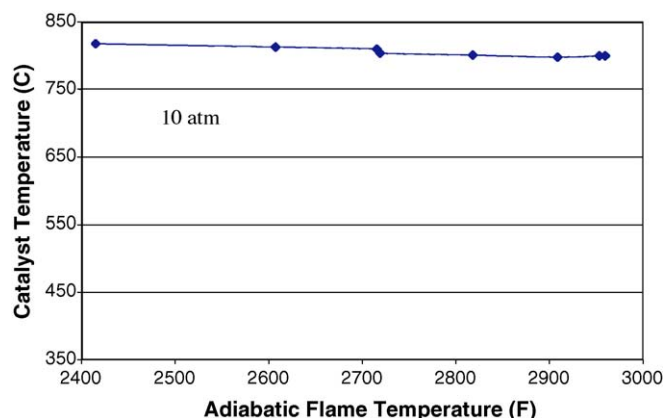


Fig. 10. Catalyst operating temperatures for refinery fuel gas operation, showing insensitivity of catalyst temperature even in the presence of high hydrogen concentrations.

operates fuel rich, with heat release limited by available oxygen.

### 3.3. Combustor emissions for hydrocarbon fuels

Measured  $\text{NO}_x$  emissions are shown in Fig. 11 for three representative hydrocarbon fuels tested: methane, bio-mass landfill gas, and Diesel No. 2 fuel. Here,  $\text{NO}_x$  emissions are measured on a dry basis and are corrected to 15% excess  $\text{O}_2$ .  $\text{NO}_x$  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.

For methane and bio-mass landfill gas fuels,  $\text{NO}_x$  emissions were below 3 ppm for measured flame temperatures below 2600 F. For diesel fuel,  $\text{NO}_x$  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, this leaves about 2 ppm  $\text{NO}_x$  that is likely formed by prompt (non-thermal)

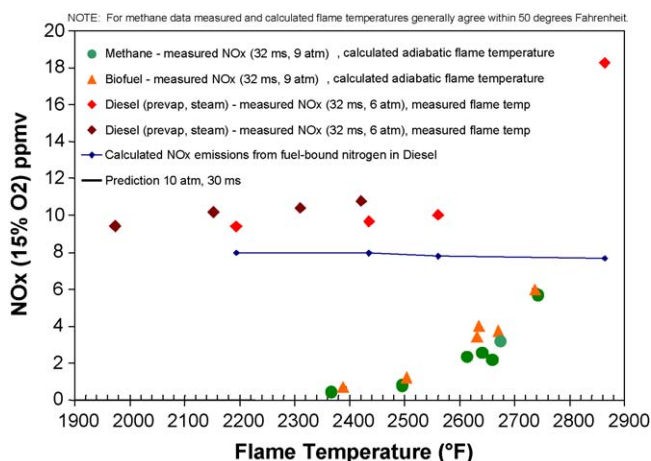


Fig. 11.  $\text{NO}_x$  emissions for all three fuel types (methane, biomass landfill gas, and Diesel No. 2 fuel). For all data points, CO/UHC emissions were less than 2 ppmv. For the Diesel No. 2 fuel, fuel analysis indicated that 8.1 ppmv  $\text{NO}_x$  would be emitted as a result of fuel-bound nitrogen alone.

mechanisms at low flame temperatures (below 2600 F). At higher flame temperatures,  $\text{NO}_x$  increased due to thermal formation mechanisms for all three fuels, as shown. The low  $\text{NO}_x$  levels at low flame temperatures indicate that well-mixed, fuel-lean combustion was achieved downstream of the catalyst for all three fuels: methane, bio-mass landfill gas, and Diesel No. 2.

### 3.4. Combustor emissions for blast furnace gas

For combustion tests of the low-Btu blast furnace gas, the fuel (complete with its diluent) entered the RCL reactor after being heated to about 446 F (230 °C). Combustion air (including catalyst-bound or catalyst-side air) entered the reactor at about 662 F (350 °C). Prior to catalyst lightoff, CO emissions for combustion of this fuel were extremely high at all fuel/air ratios, well beyond the range of the emissions analyzers, and combustion was difficult to sustain even at the highest possible equivalence ratios (near stoichiometric in the mixed stream downstream of the catalyst). Once the catalyst was lit off, however, combustion was well stabilized and CO emissions dropped to single-digit values for all data points shown in Fig. 12. Clearly the catalyst provided the needed stability to the flame for this low Btu fuel, and enabled stable gas-phase combustion following fuel-rich catalytic reaction, even at adiabatic flame temperatures as low as 2250 F (1232 °C).

Note that the high diluent fraction of this low-Btu fuel means that high fuel-lean equivalence ratios are needed in the combustor burnout zone to achieve the desired flame temperature for the turbine. Tests were performed over a range of adiabatic flame temperatures in the combustor burnout section, from about 2250 to 2500 F (1232–1371 °C) (representing maximum fuel flow capability of the rig for this blast furnace gas composition). For reference, the stoichiometric flame temperature for this blast furnace gas is only about 2700 F (1482 °C) for the inlet temperatures tested.

For RCL<sup>®</sup> combustion of blast furnace gas, ultra-low emissions of  $\text{NO}_x$  and CO were achieved for all conditions tested. Blast furnace gas  $\text{NO}_x$  emissions are plotted in Fig. 12, as measured by sample extraction from a cooled probe located

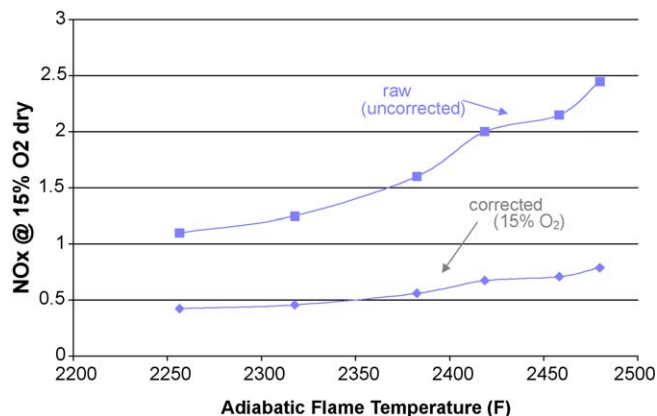


Fig. 12.  $\text{NO}_x$  emissions, uncorrected and corrected to 15%  $\text{O}_2$ , as a function of adiabatic flame temperature in the downstream combustion zone of the RCL reactor burning blast furnace gas (23% CO, 1.4%  $\text{H}_2$ , 0.6%  $\text{CH}_4$ , 22%  $\text{O}_2$ , and 53%  $\text{N}_2$ ).

15 in. downstream of the catalyst exit, corresponding to about 30 ms residence time in the gas-phase combustor. For all conditions tested,  $\text{NO}_x$  emissions were measured below 2.5 ppm on a raw basis (uncorrected) and below 1 ppm corrected to 15%  $\text{O}_2$  dry. CO emissions were near zero (<1 ppm) for all conditions shown.

Both raw and corrected  $\text{NO}_x$  emissions are plotted in Fig. 12 because measured oxygen concentrations following fuel-lean burnout were low as a result of the high level of diluent in the blast furnace gas. Oxygen concentration in the exhaust varied between about 2.5 and 5.5% for the conditions shown. Thus, the standard correction to 15%  $\text{O}_2$  may be misleading since oxygen levels would never reach 15% in an actual engine application. The raw  $\text{NO}_x$  data are probably as relevant as the corrected  $\text{NO}_x$  data, or perhaps more so. In either case,  $\text{NO}_x$  emissions were ultra-low as a result of the low blast furnace gas flame temperatures.

### 3.5. Combustor emissions for refinery fuel gas

Testing of refinery fuel gas was also conducted using the same hardware configuration as previous tests for blast furnace gas. Results showed  $\text{NO}_x$  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%  $\text{H}_2$  and 70%  $\text{CH}_4$ , 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 (1316–1649 °C) in the combustor burnout section, and at a pressure of about 10 atm.  $\text{NO}_x$  and CO emissions were measured at each condition, as well as  $\text{O}_2$  and  $\text{CO}_2$ .

$\text{NO}_x$  emissions for the RCL<sup>®</sup> combustion of refinery fuel gas are plotted in Fig. 13, as measured by the downstream emission probe corresponding to about 30 ms residence time.  $\text{NO}_x$  emissions were measured below 3 ppm for flame temperatures less than about 2800 F (1538 °C), indicating well-mixed fuel-lean combustion downstream of the catalyst. CO emissions were less than about 1 ppm for all conditions shown.

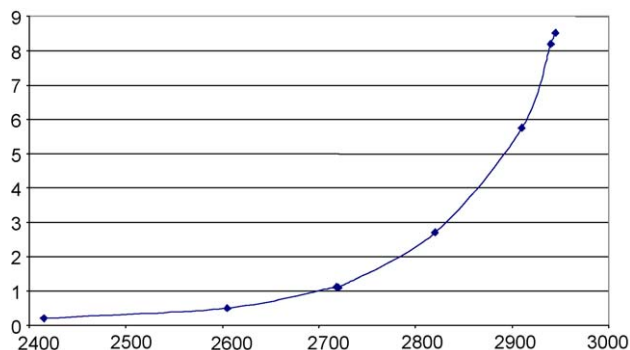


Fig. 13.  $\text{NO}_x$  emissions, corrected to 15%  $\text{O}_2$ , as a function of adiabatic flame temperature in the downstream combustion zone burning refinery fuel gas (30%  $\text{H}_2$  and 70%  $\text{CH}_4$ ).

## 4. Conclusions

A Rich-Catalytic Lean-burn combustion system has been tested at high-pressure and sub-scale with multiple alternative fuels, as listed in Table 1. For all fuels tested, catalyst temperatures were well-controlled and combustor emissions were maintained at low values over a wide turnaround 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 pre-vaporization of the fuel prior to fuel-rich catalytic reaction.

Overall, fuel-flexible operation was demonstrated for Rich-Catalytic Lean-burn combustion using six different fuels: natural gas, biomass landfill gas, gasoline, pre-vaporized Diesel No. 2, low-Btu blast furnace gas, and a refinery fuel gas. The similar catalyst performance and low emissions for all fuels tested indicates the insensitivity of the system to different fuels.

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## References

- [1] C.L. Vandervort. 9 ppm  $\text{NO}_x$ /CO Combustion System for 'F' Class Industrial Gas Turbines, ASME Paper No. 2000-GT-0086, ASME Turbo Expo, Munich, Germany May 8–11, 2000.
- [2] D.K. Yee, K. Lundberg, C.K. Weakley, Field demonstration of a 1.5 MW gas turbine with a low emissions catalytic combustion system, J. Eng. Gas Turbines Power 123 (2001) 550–556.
- [3] L.L. Smith, H. Karim, M.J. Castaldi, S. Etemad, W.C. Pfefferle, V.K. Khanna, K.O. Smith, Rich-Catalytic Lean-burn combustion for low-single-digit  $\text{NO}_x$  gas turbines, J. Eng. Gas Turbines Power 127 (2005) 27–35.
- [4] J.P. Kesselring, W.V. Krill, E.K. Chu, R.M. Kendall, in: Proceedings of New Fuels and Advances in Combustion Technologies Symposium, New Orleans, LA, March 26–30, 1979.
- [5] R.J. Rollbuhler. Fuel-rich, catalytic reaction experimental results, 27th Joint Propulsion Conference, Sacramento, CA, June 24–27, 1991 (NASA Technical Memorandum 104423, AIAA Paper No. 91-2463).
- [6] T.A. Brabbs, S.A. Merritt. Fuel-rich Catalytic Combustion of a High Density Fuel, NASA Technical Paper 3281, 1993.
- [7] M.B. Colket, A.S. Kesten, J.J. Sangiovanni, M.F. Zabielski, D.R. Pandey, D.J. Seery, 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, 1993.



- [8] G.O. Kraemer, Fuel-Rich Catalytically Stabilized Combustion for Aircraft Engine Applications, Ph.D. Thesis, Yale University, 1996.
- [9] M. Lyubovsky, L.L. Smith, M. Castaldi, H. Karim, B. Nentwick, S. Etemad, R. Lapierre, W.C. Pfefferle, Catalytic combustion over platinum group catalysts: fuel-lean versus fuel-rich operation, *Catal. Today* 83 (2003) 71–84.
- [10] H. Karim, K. Lyle, S. Etemad, L.L. Smith, W.C. Pfefferle, P. Dutta, K.O. Smith, Advanced catalytic pilot for low  $\text{NO}_x$  industrial gas turbines, *J. Eng. Gas Turbines Power* 125 (2003) 879–884.
- [11] L.L. Smith, H. Karim, S. Etemad, W.C. Pfefferle, Catalytic combustion of gasified coal for low-emissions gas turbines, in: 22nd Annual International Pittsburgh Coal Conference, September 12–17, 2007.
- [12] W.C. Pfefferle, L.L. Smith, M.J. Castaldi, U.S. Patent No. 6,358,040, 2002.
- [13] L.L. Smith, S. Etemad, M.J. Castaldi, H. Karim, W.C. Pfefferle, U.S. Patent No. 6,752,623, 2004.
- [14] C.T. Bowman, in: W. Bartok, A.F. Sarofim (Eds.), *Chemistry of Gaseous Pollutant Formation and Destruction. Fossil Fuel Combustion*, John Wiley & Sons Publication, New York, 1991.