NEW CATALYTIC COMBUSTION TECHNOLOGY FOR VERY LOW EMISSIONS GAS TURBINES

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ABSTRACT
A catalytic combustion system has been developed which feeds full fuel and air to the catalyst but avoids exposure of the catalyst to the high temperatures responsible for deactivation and thermal shock fracture of the supporting substrate. The combustion process is initiated by the catalyst and is completed by homogeneous combustion in the post catalyst region where the highest temperatures are obtained. This has been demonstrated in subscale test rigs at pressures up to 14 atmospheres and temperatures above 1300°C (2370°F). At pressures and gas linear velocities typical of gas turbine combustors, the measured emissions from the catalytic combustion system are NOx < 1 ppm, CO < 2 ppm and UHC < 2 ppm, demonstrating the capability to achieve ultra low NOx and at the same time low CO and UHC.

INTRODUCTION
The involvement of NOx in the photochemical reactions producing smog has resulted in increasingly stringent regulation to reduce emissions. A number of locations in the world limit the NOx emissions levels to less than 10 ppm, and in some locations the installation of a new gas turbine power generating facility requires NOx emissions levels below 5 ppm. The technology currently used to achieve this concentration is a combination of water or steam injection or lean premix combustion combined with post combustion treatment by selective catalytic reduction which uses NH3 to reduce the NOx over a selective catalyst. This process is very expensive.

Catalytic combustion of well premixed fuel air mixtures has been shown to produce very low emissions, typically in the range of 1 ppm NOx (Pfefferle and Pfefferle, 1987). However, this technology has not been commercialized due to poor performance of the catalyst systems at the high operating temperatures required by modern high efficiency gas turbines.

DESCRIPTION OF CATALYTIC REACTOR DESIGN
Traditional catalyst systems applied to catalytic combustion operate as shown in the schematic of Figure 1. The fuel/air mixture, with a composition to achieve the required combustor outlet temperature when combusted adiabatically, is fed to the catalyst. If the fuel/air mixture temperature is sufficiently high that catalytic reaction occurs, then the catalyst surface temperature rises rapidly until the catalyst surface reaction becomes diffusion limited. The catalyst substrate temperature will be close to the adiabatic combustion temperature of the fuel/air mixture. As shown in this schematic, the gas temperature rises due to heat transfer from the surface and at very high temperatures homogeneous combustion occurs inside the catalyst. For modern high efficiency gas turbines with turbine inlet temperatures of ~1250°C (2280°F), a combustor outlet temperature of 1300°C (2370°F) or higher is required. This would subject the catalyst to extreme abuse, causing problems such as:

- Thermal sintering of support surface area
- Thermal sintering and vaporization of active components such as noble metals
- Thermal shock fracturing of ceramic supports

In addition, this technology would be difficult to apply to the next generation of large power generation gas turbines since the higher turbine inlet temperatures, approximately 1400-1450°C (2550-2640°F), would require further development of ceramic supports and catalysts to withstand these higher temperature conditions.
A new approach to catalytic combustion is shown in the schematic of Figure 2. The full fuel air mixture to achieve the required combustor exit temperature is fed to the catalyst. Reaction on the catalyst results in a rise in the catalyst substrate temperature but the temperature rise is limited to a relatively low value. The gas temperature rises due to heat transfer from the hot catalyst substrate. Subsequent stages may be required with higher wall temperatures to achieve the required catalyst outlet temperatures. The partially combusted fuel air mixture then exits the catalyst and is combusted in a homogeneous gas phase reaction that causes the mixture to reach the full adiabatic combustion temperature. Several important aspects of the system design are:

**Inlet Stage**
- Designed to maintain a very low wall temperature
- Low substrate temperature makes possible a stable, very high catalytic activity necessary for catalyst operation at the compressor discharge temperature

**Outlet Stage**
- Can be designed with a higher substrate temperature to provide the required catalyst outlet gas temperature
- Lower catalyst activity is acceptable since a higher inlet gas temperature is provided by the inlet catalyst section

**Homogeneous Combustion Region**
- Localizes the high temperature after the catalyst
- Completes combustion of the fuel and burnout of CO and unburned hydrocarbons to the required levels
- Produces the required combustor outlet temperature

This system design can provide many advantages:
- Low catalyst temperatures can reduce or eliminate many of the deactivation mechanisms that could limit catalyst life
- Allows the use of a wider variety of substrate and catalyst materials
- Substantially reduces or eliminates the problems associated with thermal shock fracture of substrates during start up, shut down, or turbine trip type operations
- Technology can be adapted to higher combustor outlet temperatures without changes in catalyst materials

This system has been under development since 1989 and its operation will be described in the following section.

**DESCRIPTION OF TEST COMBUSTOR SYSTEMS**

Catalyst tests reported in this paper were performed in two high pressure reactor systems. One system was located at the Corporate Research and Development division of General Electric Corporation and has been described previously (Orenstein, et al., 1991). This facility uses a catalyst with a diameter of 76mm (3.0 in) and could provide non-vitiated air from a gas fired preheater or could use a natural gas fueled preburner to provide vitiated heated air to the catalyst. The fuel for the catalyst was injected into the heated air stream with a multiple venturi type fuel injector that produces a fuel/air mixture uniform to +/- 2%. This fuel injection system was developed for a full sized combustor and has been described previously (Beebe, et al., 1987).

The second high pressure catalyst test system is located at Catalytic, Inc. and is shown schematically in Figure 3. This reactor uses a 50mm (2.0 in) diameter catalyst and can operate over the range of conditions shown below.
Catalyst diameter up to 50mm (2.0 in)
Pressure 1 to 16 atm
(0 to 220psig)
Catalyst inlet temperature
  With electric preheater 25 to 550°C
  (77 to 1020°F)
  With preburner to 800°C
  (to 1470°F)
Air flow rate 200 to 10,000 std l/min
(0.009 to 0.471bs/s)
Maximum combustion temperature 1500°C (2730°F)

Air and fuel flows are controlled by electronic mass flow meters. The air is preheated with a 120kW electric heater and then flows through the preburner section where additional fuel is burned to achieve higher temperatures or simulate operation with a fired preburner upstream of the catalyst. The catalyst fuel is injected through a multiple port single tube then mixed with the air using a blade type static mixer (Sulzer model SMV). This system achieves a fuel/air uniformity of +/- 3% at the catalyst inlet.

Air supply
Static mixer
Catalyst
Thermocouples
Inlet gas
Outlet gas
Catalyst fuel
Gas sampling probe
Press control valve
Electric air heater
Figure 3. High pressure catalytic combustion test rig at Catalytica, Inc.

Both systems allow thermocouples to be located in the catalyst bed and downstream of the catalyst. In addition, a water cooled sampling probe is located downstream of the catalyst, 38cm (15in) from the catalyst exit. This gas sample passed through a heated sampling line to the analyzers. The analytical systems were similar for both reactors and can be summarized as follows:

a. The hydrocarbon analysis sample was taken directly from the heated sampling line into a heated analyzer. The analysis was done by flame ionization on a 0-10ppm scale.
b. The NOx analysis sample was taken after removing the water in a condenser operating at about 4°C. The analysis was by chemiluminescence on a 0-10ppm scale. The analyzer was typically operated with the sample gas passing through a NO2 to NO converter. However, the same results were obtained with the gas sample bypassing the converter.
c. The CO analysis sample was taken after removing the water as described for the NOx sample. The analysis was done by an NDIR analyzer operating on a 0-50 or 0-100ppm scale.

In all cases, the analyzers were calibrated with standard gases in the range of the measurements being made.

In both systems, the temperatures, pressures, gas flows and gas concentrations are monitored and recorded by computer data acquisition systems for subsequent analysis. The fuel used in both of these systems was pipeline natural gas as supplied by the local utility through the distribution network. Typical compositions were:

<table>
<thead>
<tr>
<th>Composition(mol %)</th>
<th>GE-CRD (Schenectady, NY)</th>
<th>Catalytica, Inc (Mtn View, CA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>96.1</td>
<td>95.9</td>
</tr>
<tr>
<td>Ethane</td>
<td>1.96</td>
<td>2.05</td>
</tr>
<tr>
<td>Propane</td>
<td>0.27</td>
<td>0.1</td>
</tr>
<tr>
<td>Butane</td>
<td>0.14</td>
<td>0.03</td>
</tr>
<tr>
<td>Pentane</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>C6 and heavier</td>
<td>0.03</td>
<td>---</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.87</td>
<td>1.42</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.59</td>
<td>0.48</td>
</tr>
</tbody>
</table>

PERFORMANCE TEST RESULTS
Substrate Temperature Limiting Demonstration
A demonstration of substrate temperature limiting is shown in Figure 4. In this test at 11 atmospheres pressure (150 psig) and a gas flow of 9300SLPM (standard liters per minute), the fuel/air ratio was fixed and the catalyst inlet temperature was increased. Thermocouples were embedded in the substrate wall to measure actual substrate temperature. At a catalyst inlet temperature of about 400°C (750°F) the catalyst ignited and the temperature of the substrate rose to about 800°C (1470°F) and remained at this temperature even as the inlet temperature

Figure 4. Ignition test results showing temperature limiting phenomenon.
was further increased. This fuel/air mixture would have an adiabatic combustion temperature of about 1300°C (2370°F), yet the catalyst temperature is limited to about 800°C (1470°F). The gas temperature rises to about 600°C (1100°F), controlled essentially by heat transfer from the hot catalyst substrate. These conditions, a pressure of 11 atmospheres and a gas linear velocity of 18 m/s at 400°C (750°F), are conditions typical of those present in a gas turbine combustor.

Homogeneous Combustion in the Post Catalyst Region

As the hot partially combusted fuel/air mixture exits the catalyst, the temperature must be sufficiently high to result in homogeneous combustion of the remaining fuel. This is a well known phenomenon analogous to spontaneous ignition. This process is theoretically modeled in Figure 5 where a combustion kinetics model is used to calculate the progress of the reaction. As the mixture of species exits the catalyst, the radical concentration builds until the remaining fuel begins to rapidly react. This particular example, at 12 atmospheres pressure and 925°C (1700°F), shows that most of the fuel is reacted within 2 to 3 milliseconds and the CO is below 10 ppm within 4 to 5 milliseconds. These results clearly show that the homogeneous combustion process is due to the high temperature of the fuel air mixture exiting the catalyst.

Figure 5. Results of kinetic model calculation showing fuel combustion and species population in hot post catalyst region.

System Operation

The operation of a complete catalyst system at gas turbine combustor conditions is shown in Figure 6. This test, done in the high pressure system at Catalytica, Inc., was at the following conditions:

- **Pressure**: 11 atm (150psig)
- **Catalyst inlet gas temperature**: 450°C (840°F)
- **Air flow**: 9300SLPM
- **Fuel/air ratio**: varied with time
- **Linear velocity at catalyst inlet**: 19 m/s at 450°C (842°F)

In this test run the catalyst inlet temperature was held constant and the fuel/air ratio increased in two steps. As the fuel/air ratio was increased to 0.026 vol/vol over time period 0.12 to 0.2 hrs, the catalyst outlet temperature at 2 cm downstream of the catalyst rose to about 650°C (1200°F). This temperature was not sufficient to initiate homogeneous combustion after the catalyst as is shown by the temperature of the gas 90 cm downstream. As the fuel/air ratio of the feed mixture was increased to 0.040 vol/vol over time period 0.26 to 0.4 hrs, the catalyst outlet temperature rose to about 820°C (1510°F) and homogeneous combustion occurred downstream of the catalyst as shown by the 90 cm temperature that is close to the adiabatic combustion temperature for this fuel/air mixture. The emissions measured during operation at this higher fuel/air ratio were:

- **CO**: <2 ppm
- **UHC**: <2 ppm
- **NOx**: <1 ppm

These are the emissions measured after water removal but without correction for oxygen.

Figure 6. Demonstration of catalytic combustion system operation showing post catalyst homogeneous combustion.

NOx Level Versus Combustor Outlet Temperature

The catalytic combustion system was operated at fuel to air mixtures that gave combustor outlet temperatures from 1300°C to about 1475°C (2370°F to 2687°F) and the NOx concentration at the end of the homogeneous combustion section was measured. The NOx levels formed in the post catalyst homogeneous combustion zone were calculated using the kinetic model of Miller and Bowman (1989) and the results are shown as the theoretical curve in Figure 7. These calculations included both prompt and thermal NOx generation mechanisms and assumed a reaction time of 20ms after...
reaching the full adiabatic combustion temperature, close to the reaction time present in the experimental test. The experimentally measured values were corrected to the actual “wet” composition present in the combustor exhaust. These data, presented in Figure 7, show experimental NOx levels from 0.2 ppm at 1300°C (2370°F) to 2 ppm at 1475°C (2687°F). Correcting these values to 15% O2 (dry) would give 0.13 ppm NOx at 1300°C (2370°F) and 1.2 ppm NOx at 1470°C (2680°F). This demonstrates the very low NOx levels that can be obtained by catalytic combustion, even at high combustor outlet temperatures. In addition, the UHC and CO levels were below 5 ppm.

![Theoretical calculation Experimental data](image)

**Figure 7.** NOx levels produced in the catalytic combustion system compared to theoretically calculated values. See text for details.

### Simulation of GE MS9001E GT Cycle Conditions

GE has developed full scale catalytic combustor system hardware for the E series gas turbines (Beebe, et al., 1987). This combustor has been shown to produce a fuel/air mixture with a uniform temperature and fuel/ratio at conditions representative of the GE MS9001E machine. In particular, fuel/air ratio uniformity was shown to be within the range of ±2-3%. A series of tests were performed at GE-Corporate Research and Development using the 3" diameter (76mm) facility described above at conditions that simulate the baseload conditions of the GE MS9001E gas turbine combined with the catalytic combustion hardware described above. The catalytic system used in these tests consisted of three catalyst sections making up a total length of 200 mm (8 in). The catalyst substrate was a metallic foil formed into a monolithic structure with the active catalyst deposited on the metal surface. The low substrate temperature afforded by this technology permits the use of metallic substrates. The monolith cell densities varied from approximately 200 cpsi (cells per square inch) to about 350 cpsi. This catalyst system was designed to produce the required outlet gas temperature at the conditions expected in this simulated gas turbine operating cycle.

The catalyst required an inlet temperature of 450°C (840°F). To simulate actual GT cycle conditions, a preburner was used to raise the simulated compressor discharge temperature to the required 450°C catalyst inlet temperature. This resulted in some NOx generation from the preburner. Selected test results are shown in Table 1. CO and UHC emissions are below 1ppm. NOx levels ranged from 25 to 4 ppm. However, analysis before and after the catalyst and tests without fuel to the preburner show that NOx emissions from the catalyst and post catalytic homogeneous combustion are generally <1 ppm. The NOx levels shown in Table 1 are produced predominately by the preburner.

### APPLICATION TO PRACTICAL GT SYSTEMS

The catalyst system tested here required inlet temperatures of 450°C. Under most cycle conditions of modern large power generation gas turbines, the compressor discharge temperature would be above 310°C (600°F), requiring a preburner temperature rise of ≤150°C (270°F). This temperature rise can be achieved with very low NOx production in the range of 2-3 ppm, using lean premix combustor design technology, especially since CO and UHC emissions will be controlled by the catalytic combustion system. In addition, recent catalyst designs have reduced the required inlet temperature, approaching the point where the catalyst can be operated at the compressor discharge temperature for some machines. These approaches will give a catalytic combustion system with NOx levels below 3-4 ppm and possibly below 1 ppm.

The fuel/air mixing systems used in the test rig at Catalytic and at GE produce a mixture with a uniformity of 1-3% as shown by measurement. This simulates the demonstrated uniformity that can be achieved in practical catalytic combustor systems and the level of catalyst performance shown here should be representative of larger systems. In addition, tests at fuel/air ratios near the full load condition show that this level of uniformity can be handled by the catalyst system. The use of metallic substrates should also substantially reduce the problems associated with some nonuniformity in catalyst temperature during start up. Rig test at simulated start up conditions show very uniform catalyst ignition for 50 mm and 76 mm (2 and 3 in) diameter catalysts.

### DEMONSTRATION OF CATALYST DURABILITY

Catalyst durability is an important aspect of a catalytic combustion system applied to gas turbines. A long term durability test was initiated under catalyst conditions similar to those described above, that is with natural gas fuel and an adiabatic combustion temperature of 1300°C (2370°F). The test system was similar to that shown in Figure 3 except that the reactor was not pressurized and was operated at 1 atmosphere pressure. Catalyst substrate temperature, catalyst
TABLE 1. SELECTED RESULTS AT SIMULATED GE MS9001E GAS TURBINE CONDITIONS

<table>
<thead>
<tr>
<th>Test point</th>
<th>Air flow</th>
<th>Pressure exit T</th>
<th>Preheater exit T</th>
<th>Preburner exit T</th>
<th>Combustor exit T</th>
<th>Catalyst AP</th>
<th>ISO NO\textsubscript{x} @15% O\textsubscript{2}</th>
<th>CO ppm</th>
<th>UHC ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preburner only fired</td>
<td>1</td>
<td>0.46</td>
<td>113</td>
<td>313/595</td>
<td>762/1404</td>
<td>715/1319</td>
<td>3.65</td>
<td>112</td>
<td>~2</td>
</tr>
<tr>
<td>Transition of fuel to catalyst</td>
<td>3</td>
<td>0.46</td>
<td>135</td>
<td>312/594</td>
<td>709/1308</td>
<td>894/1642</td>
<td>2.89</td>
<td>---</td>
<td>&gt;3000</td>
</tr>
<tr>
<td>Base load operation (with preburner to supply minimum 450°C catalyst inlet temperature)</td>
<td>6</td>
<td>0.45</td>
<td>147</td>
<td>306/582</td>
<td>567/1053</td>
<td>1166/2131</td>
<td>2.44</td>
<td>24.6</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>0.51</td>
<td>175</td>
<td>361/682</td>
<td>456/852</td>
<td>1198/2189</td>
<td>1.79</td>
<td>14.5</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.54</td>
<td>180</td>
<td>400/752</td>
<td>458/856</td>
<td>1196/2185</td>
<td>2.17</td>
<td>4.2</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Figure 8. Catalyst ignition temperature measurement results during long term durability test of a selected catalyst system.

FUTURE WORK

Work is continuing to develop this technology to meet the operating requirements of gas turbine engines. Specific work includes:

- Catalyst development to lower the required catalyst inlet temperature.
- System development to widen the operating windows including operation over wider fuel/air ratios.
- Adaptation of this technology to a full scale combustor and demonstration at full scale including an operating gas turbine.

ACKNOWLEDGEMENTS

The testing done at GE-CRD was funded by Tokyo Electric Power Company. The authors acknowledge the assistance of Kenneth Beebe, Robert Orenstein and Elizabeth Beaudoin of GE Power Generation Engineering and Steven Hung, Patrick Nestor and Nesim Abuaf of GE Corporate Research and Development.

REFERENCES


