United States
Environmental Protection
Agency

Research and Development

Air and Energy Engineering
Research Laboratory
Research Triangle Park NC 27711

EPA/600/S7-86/021 Aug. 1986

EPA

Project Summary

Catalytic Combustion Component and System Prototype Development

J. P. Kesselring and W. V. Krill

The report gives results of a project to develop the components required for catalytic combustion system operation and evaluation. The systems investigated (firetube boiler, watertube boiler, and gas turbine), when integrated with the catalytic combustor, have potential for both significant reductions in NO_x emissions and increases in system thermal efficiency. The model gas turbine combustor incorporated a multiple spray nozzle fuel injector, an opposed jet igniter, and optical pyrometer for temperature control, and a graded cell catalytic combustor. The firetube boiler burner used a matrix of ceramic fibers vacuum-formed into a cylinder, and was successfully retrofitted into a 25-hp boiler. The radiative catalyst/watertube boiler was tested as a prototype for small industrial boilers with the catalyst tube either concentric with and surrounding the watertube, or surrounded by external watertubes. Significant reductions in NO_x emissions were noted in all three systems. Additional work included both catalyst and substrate development for increased durability in reactors, as well as completion of a successful 1000-hour catalytic combustor test under lean combustion conditions comparable to gas turbine combustor operation.

This Project Summary was developed by EPA's Air and Energy Engineering Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The U.S. EPA has sponsored research and development work in the area of catalytic combustion for over 8 years. This work has focused on the development of catalytic combustion technology by developing a thorough understanding of the operation of catalytic combustors, screening many catalyst and substrate materials to determine performance limitations, and then combining the basic understanding of the catalytic combustor with catalyst performance data and heat transfer considerations to design practical combustion systems. These systems have the potential benefits of lowered emissions of NO_x and CO and increased thermal efficiency. Composite systems tested and described here include a model gas turbine combustor, a fiber burner installed for retrofit or new firetube boiler applications, and a model watertube boiler. The testing of these systems was accompanied by durability testing of the burners.

Catalyst Development

Catalyst development is one of the keys to the commercial acceptability of the catalytic combustor. Prior to the development of the catalytic combustor there was little need for catalysts capable of operation at temperatures above 1400K for extended periods of time, and little information was available on the composition of high temperature catalysts or on suitable substrate carriers for the catalysts. A total of 12 noble metal and 20 metal oxide catalysts were tested to determine catalyst lightoff temperature, preheat temperature required for sustained catalyst operation, maximum throughput for the combustor without extinguishing the catalysts, and emissions performance of the combustors. The typical test time for each catalyst was 50 hours, and all of the noble metal catalysts tested showed significant decreases in activity during this period. However, high heat release rates were still achievable at the end of the test period.

Two of the noble metal catalysts were tested to evaluate the performance of the graded cell catalytic combustor concept, developed here and described in U.S. Patent 4,154,568. As predicted, the graded cell reactor was able to sustain stable combustion at volumetric heat release rates 2.7 times greater than those achieved with a single cell reactor. In addition, the graded cell reactor had a much more uniform axial temperature profile through the honeycomb monolith than the single cell reactor.

While metal oxide catalysts generally have lower activity than noble metal catalysts at temperatures of 1400K, they should have greater durability than nobile metals and good activity at temperatures above 1600K. In fact, at high enough temperatures uncoated ceramic monoliths should have catalytic properties. Test times for the oxide catalysts investigated were again on the order of 50 hours, and high heat release rates were generally obtained at test conditions of 1700K bed temperature. However, interactions between the coated metal oxide catalysts and the substrate ceramic materials usually led to poor thermal shock characteristics and fracture of the substrate material. Since the weakened substrate was a result of catalyst/substrate interaction, it appeared that testing of substrate materials with an active component as an integral part of the substrate would be of interest. Eight of these "active monolith" materials were prepared as either bundled tubes or drilled disks and combustion tested. All test specimens showed acceptable catalytic activity, with combustion data similar to the coated oxide systems tested. Thermostructural promise was also shown by these materials, but better fabrication techniques (such as extrusion) are required before futher testing should be done.

Fundamental Studies

Fundamental studies were initiated under this program to provide greater understanding of the chemical processes of catalytic combustion. Development of this information increases the ability to predict combustor performance and allows analyses leading to system optimization. The phenomena studied here include a determination of heterogeneous hydrocarbon and nitrogen oxidation rates, a comparison of the extent of reaction with predicted mass transfer rates, and a determination of heterogeneous oxidation rate constants.

In order to isolate surface reaction events from the simultaneous gas-phase reactions that occur in practical high-temperature catalytic combustors, the test setup incorporated catalyst-coated cylinders in crossflow. Exhaust gas was analyzed with continuous analyzers for CO, CO_2, O_2, NO_x, and HC. Tests were run over a range of stoichiometries from fuel-rich to fuel-lean.

Test results showed that the use of cylinders in crossflow was an effective technique for studying the heterogeneous portion of catalytic combustion. In the higher temperature ranges of operation (near stoichiometric), the surface reaction rate on the cylinder in crossflow configuration is limited by lean reactant diffusion. In this regime, the combustion of methane was promoted to completion by the catalyst with CO_2 as the major product. These data are most useful for understanding normal, steady state operation encountered in honeycomb monolith catalysts. They will allow further optimization in the amount of surface area required for a specific energy release rate.

The measured conversion rates were significantly underpredicted by calculated lean reactant mass transfer limitations. This may be due to the use of a mass transfer coefficient which does not fully account for freestream turbulence levels or high surface temperatures. Regions of flow stagnation or recirculation, possibly attached to the cylinders, may also promote higher conversion rates. However, other data, including CO formation behavior, do not clearly support this concept.

Small amounts of hydrogen in the reactant flow gave precise catalyst surface temperature control over ranges in which methane and propane heterogeneous kinetics could be quantified. The experimentally measured activation energies were 7.54×10^7 J/kg-mole for methane and 7.42×10^7 J/kg-mole for propane. These values compare favorably with those reported by others. Also, the relative magnitudes agree with experience in which propane ignition occurs earlier and at a lower temperature and is more difficult to blow out than methane on a given catalyst. This surface reaction rate information is required for efficient design of catalyst entry regions. The Nusselt number (Sherwood number for mass transfer) is large in these or other zones where flow stagnation may occur, giving high mass transfer rates. Additionally, kinetic information is necessry to predict lightoff characteristics and maximum throughput capabilities before catalyst blowout.

Gas Turbine Combustor

The model gas turbine combustor incorporated a multiple spray nozzle fuel injector for No. 2 diesel fuel, an opposed jet igniter, an optical pyrometer for temperature control, and a graded cell honeycomb catalytic combustor. The system was successfully tested at pressures from 1×10^5 to 5×10^5 Pa (1 to 5 atm), a combustor outlet temperature of 1700K, combustor inlet temperatures of 589 to 672K, and a maximum heat release rate of 4.78×10^5 J/hr. NO_x emissions obtained with this system were typically less than 15 ppm and resulted primarily from the nearly 100 percent conversion of the small amount of nitrogen in the liquid fuel. Combustion efficiencies above 99.985 percent were obtained at all test conditions.

Separate durability testing of a terbium-cerium-thorium (TCT) honeycomb catalyst which used a noble metal entrance segment for low temperature lightoff on propane showed successful performance for over 1000 hours at a pressure of 10^5 Pa (1 atm) and an inlet velocity of 13.4 m/sec. Emissions at the end of the test period were 2 ppm NO_x, 17 ppm CO, and < 1 ppm HC. The test was concluded with five successful on/off cycling tests.

Firetube Boiler Burner

A 1055-MJ/hr fiber burner was installed in a York-Shipley 245 kW (25 hp) firetube boiler. The fiber burner, a matrix of ceramic fibers vacuum-formed into a cylinder, radiates flamelessly to the firetube wall during operation. Following preliminary tests of the boiler with conventional burner and parametric tests of the fiber burner, the system was operated for over 1000 hours at 100 percent load and 15 percent excess air. At these conditions, emissions were 13 ppm NO_x, 29 ppm CO, and 10 ppm HC. This represents a decrease in NO_x emissions of almost 80 percent and is coupled with an efficiency increase of nearly 2 percent. In addition, because the fiber burner operates at lower excess air than the conventional burner and is capable of more uniform radiant energy transfer, the boiler with fiber burner could be successfully operated at 120 percent of load and operated in an extremely quiet manner.

Radiative Watertube Boiler

A radiative catalyst/watertube boiler was developed and tested as a prototype for small industrial boilers. Systems, both with the catalyst tube concentric with and surrounding the watertube, and surrounded by external nonconcentric watertubes, were tested. The catalyst tube consisted of a catalyst-coated ceramic cylinder, while the watertube was a concentric cylinder arrangement that operated on natural circulation of the water and steam.

The most successful system tested used concentric catalyst and watertubes and was capable of operation to 1319 MJ/hr with thermal NO_x emissions less than 20 ppm at excess air levels greater than 25 percent. A problem arose when both concentric and nonconcentric systems had ceramic tube fractures after several hours of operation. Further work to minimize this problem will be required.

Conclusions

The results of this program as described above, including a large body of data on individual catalyst performance and fundamental behavior of catalytic combustors, have brought the commercial application of catalytic combustors to certain systems much closer. The use of ceramic fiber burners in gas-fired equipment with a water-backed heat receiver, as for domestic water heaters and firetube boilers, appears to require only successful field demonstration before full-scale commercialization efforts can begin. Further laboratory demonstration of honeycomb catalysts used in gas turbine systems is required, but major advances have been made under the current program. The use of catalytic combustors in watertube boilers requires significant effort to eliminate ceramic tube failure and flameholding problems prior to field demonstration.

J. P. Kesselring and W. V. Krill (both presently with Alzeta Corp.) were with Acurex Corp., Mountain View, CA 94042.
***Jon E. Haebig** is the EPA Project Officer (see below).*
The complete report, entitled "Catalytic Combustion Component and System Prototype Development," (Order No. PB 86-211 380/AS; Cost: $28.95, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Air and Energy Engineering Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Official Business
Penalty for Private Use $300

EPA/600/S7-86/021