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Project Summary

Proceedings: Fifth Workshop on Catalytic Combustion (San Antonio, Texas, September 1981)

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Serving as a forum to stimulate the transfer of catalytic combustion technology, the Fifth Workshop on Catalytic Combustion was held in San Antonio, Texas, in September 1981. Results of recent research in the areas of catalyst performance, use of heavy fuels in catalytic combustion, and applications of catalytic combustion were presented to industrial, university, and government representatives. Catalytic combustion is under investigation as a candidate system for pollution control and performance improvement. Applications include firetube and watertube boilers, stationary and mobile gas turbines, and diesel engine exhaust systems.

Previous workshops were held in May 1976, June 1977, October 1978, and May 1980. Summaries of the first and second workshops and the proceedings of the third workshop appear in EPA-600/7-79-038 (NTIS No. PB 293336). The proceedings of the fourth workshop are in EPA-600/9-80-035 (NTIS No. PB 81-176067).

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

Catalyst Performance

Recent developments in catalyst performance were described by seven authors. These studies focused on the measurement of fundamental parameters at the combustion surface and an evaluation of their effects on overall combustor performance through modeling. The effects of various catalyst parameters on pressure drop and fuel nitrogen conversion were also evaluated, and the development of high durability catalyst materials was addressed.

C. Bruno of Princeton University presented a paper, "High Temperature Catalytic Reactions of $CO/O_2/H_2$, A, He, CO_2/H_2O Mixtures on Platinum," comparing experimental measurements and computations of monolith substrate temperature, CO, CO_2, and O_2 exhaust concentrations, and pressure drop. Tests were conducted at 600 to 700K inlet temperatures, 0.013 to 0.56 equivalence ratios, 110 kPa pressure, and 11 to 13 m/s inlet velocities. The computational tool was a two-dimensional steady-state model including axial and radial convection and diffusion of mass, momentum and energy, and homogeneous and heterogeneous, single-step irreversible reactions. The model equations were the complete, two-dimensional laminar-flow conservation equations for the flow in the monolith channels, solved by a numerical technique. The model required the measured substrate wall temperature as input. Comparisons of computed and measured quantities were adequate to satisfactory over the entire range of parameters investigated. It was concluded that, under the conditions tested, oxidation of CO proceeds mostly in a diffusion-controlled regime and that homogeneous reactions are important only for the lowest velocities and highest equivalence ratios. Indications were found that water significantly increases the rate of high temperature catalytic oxidation of CO.

A paper by G.C. Snow of Acurex Corporation, "Mechanisms and Kinetics in Catalytic Combustion," discussed unique experiments to isolate the heterogeneous portion of catalytic combustion and determine kinetic reaction rate constants. Platinum-coated alumina cylinders held in a cross-flow configuration were used. Under O_2-rich conditions, CO_2 was shown to be the dominant product of methane surface combustion. Adding small percentages of H_2 in the reactant mixture provided precise control of the catalyst surface temperature to extend the ranges in which methane and propane heterogeneous kinetics could be quantified. By eliminating the effects of reactant diffusion, activation energies were experimentally determined to be 7.70×10^7 J/kg-mole for methane and 6.95×10^7 J/kg-mole for propane.

A third paper, "Catalytic Combustion in a Shear Flow" by C.K. Law of Northwestern University, focused on the stagnation point flow region of a catalytic surface. The gas-phase ignition, steady burning, extinction, and heat transfer characteristics of a combustible premixture were investigated both theoretically and experimentally. A theoretical explicit ignition criterion as a function of all system parameters was derived for an isothermal surface, showing that gas-phase ignition is hindered in the presence of surface catalytic reactions. The model also implied that the surface catalyst has no effect on the steady burning characteristics of a flow with the Lewis number greater than 1, but may extend the extinction limit when the Lewis number is less than 1. The evaluation of prior experimental results substantiated these derived theoretical concepts.

The phenomenon of catalytic ignition was investigated further in a paper by E.G. Seebauer of the University of Illinois. "Ignition Instabilities in Catalytic Combustion" presents a mathematical model for oscillations in temperature which were observed in prior experiments and postulated to be a result of protrusions on the surface of the catalyst. The model predicted these oscillations with qualitative agreement to the experiments.

As an extension of prior catalyst development work at the State University of New York at Buffalo, a chromium and cobalt oxides pellet bed catalyst was tested to determine its ability to minimize fuel nitrogen conversion to NO_x. The paper, "Minimizing Fuel NO_x Using a Transitional Metal Oxide Catalytic Combustor" by L.A. Kennedy, describes tests for a wide range of conditions. The results showed that under fuel lean operation, the sole product of fuel-N conversion was NO_x, while in fuel-rich operation, HCN and unconverted NH_3 were also detected. The conversion to HCN and NH_3 increased (but the conversion to NO_x decreased) as the operation became more fuel rich. The concentration of HCN increased (but those of NH_3 and NO_x decreased) as the inlet temperature increased. The sum of the fixed nitrogen species showed a minimum at an equivalence ratio of about 1.43. These results suggested that, at sufficiently high inlet temperatures (873-913K), the total emission levels of fixed nitrogen compounds (NO_x, NH_3, and HCN combined) can be reduced to very low levels (5-20 percent of the fuel-N present at the combustor inlet) in both fuel-lean and fuel-rich regions.

In a paper by W.B. Retallick, "Minimum Pressure Drop for Cleaning Up Large Gas Flows," the energy consumed by pressure drop in various monolith configurations was investigated. The results showed that, when mass transfer of the pollutant is the rate limiting step, there is a theoretical minimum pressure drop for a given fractional cleanup and inlet velocity. This minimum pressure drop for a ceramic honeycomb, a metal honeycomb, and a packed bed has been calculated. It was found to be lowest for the metal honeycomb and prohibitively high for the packed bed.

The final paper in the catalyst performance section, "High Temperature Durable Catalyst Development" by G.C. Snow of Acurex Corporation, discussed an experimental program to define a catalytic reactor system with a high probability of successful integration into an advanced automotive gas turbine engine. The evaluation of laboratory furnace thermal aging was used as a cost effective catalytic reactor screening test, and a 1000-hour demonstration of catalyst combustion durability at representative conditions was conducted. The durability reactor consisted of a graded-cell honeycomb support with a combination of noble metal and metal oxide catalyst coatings. At a 740K air preheat temperature and a propane-fuel/air ratio of 0.028 by mass ($\phi_{FA} = 0.44$), the adiabatic flame temperature was held at 1700K. Measured NO_x levels remained below 5 ppm, unburned hydrocarbon concentrations registered near zero, and CO levels were nominally below 20 ppm. The durability test included several parametric turndown studies and ended with a series of on/off cycling tests to further characterize reactor performance. At the completion of testing, the reactor remained catalytically active and structurally sound.

Heavy Fuels Use in Catalytic Combustion

The second session of the workshop focused on the combustion of residual fuel oils for applications where clean fuels or high levels of preheat are not available. Tests were conducted that identified preferred operating conditions to achieve stable combustion with high fuel conversion efficiency while minimizing fuel handling and fouling problems. The following three papers presented the described experimental results.

The first paper of the session was "Investigation of Partially-Vaporized Residual Oil Catalytic Combustion" by T.J. Rosfjord of United Technologies Research Center. In this program, No. 6 oil and blends of residual fuel (No. 6 oil or shale residual oil) and No. 2 oil were tested on a graded-cell reactor with zirconia spinel substrate and noble metal catalyst. Operating conditions included inlet pressures of 0.3 to 0.6 MPa, inlet temperatures of 600 to 895K, and reference velocities of 10 to 40 m/s. Tests with incompletely vaporized No. 6 oil did not result in stable combustor operation, and streams of luminous particles were observed exiting the reactor, presumably the result of fuel deposition and carbonization on the substrate. A similar phenomenon was observed in tests with blends of No. 6 and No. 2 oil. Blends of shale residual oil and No. 2 oil were identified which resulted in stable operation. Tests with shale oil blends indicated that the combustor performance degraded with reduced degree of fuel vaporization. A similar effect was observed in tests with No. 2 oil.

A paper by W.J. Dodds of General Electric Company, "Demonstration of Catalytic Combustion with Residual Fuel," described tests of three catalytic reactors, including a baseline configuration and two backup configurations based on baseline test results, all operated on No. 6 fuel oil. All reactors were multi-element configurations consisting of ceramic honeycomb catalyzed with palladium on stabilized alumina. Stable operation on residual oil was demonstrated with the baseline configuration at a reactor inlet temperature of about 825K. At lower inlet temperatures, operation was prevented by apparent plugging of the catalytic reactor with residual oil. Reduced plugging tendency was demonstrated in the backup reactors by increasing the size of the catalyst channels at the reactor inlet; but plugging still occurred at inlet temperatures below 725K. Operation at the original design inlet temperature of 589K could not be demonstrated. Combustion efficiency above 99.5 percent was obtained with less than 5 percent reactor pressure drop. Thermally formed NO_x levels were very low (less than 0.5 g NO_2/kg fuel); but nearly 100 percent conversion of fuel-bound nitrogen to NO_x was observed.

The third paper, by D.L. Bulzan of NASA's Lewis Research Center, "Catalytic Combustion of Residual Fuels," describes tests of a noble metal catalytic reactor with two residual fuels at inlet air temperatures from 700 to 960K, pressures of 3×10^5 Pa and 6×10^5 Pa, and reference velocities of 10, 15, and 20 m/s. Combustion efficiencies greater than 99.5 percent were obtained for both residual fuels. Steady-state operation of the catalytic reactor required inlet air temperatures of at least 800K for both fuels. At lower inlet air temperatures, upstream burning in the pre-mixing zone occurred, probably caused by fuel deposition and accumulation on the premixing zone walls. Increasing the inlet air temperature to 800K prevented this occurrence. Both residual fuels contained about 0.5 percent nitrogen by weight. NO_x emissions ranged from 50 to 110 ppm by volume at 15 percent excess O_2. Conversion of fuel-bound nitrogen to NO_x ranged from 25 to 50 percent.

These programs have identified appropriate operating conditions and potential problems for burning heavy fuels in catalytic combustors. The application of catalysts to actual power systems was described in seven papers during the final session of the workshop.

Applications of Catalytic Combustion

The application of catalytic combustion to laboratory systems has advanced significantly since the fourth workshop on catalytic combustion in May 1980. The seven papers presented described a variety of applications including primary burners and combustors for residential and commercial appliances, firetube and watertube boilers, and stationary gas turbines. The final papers also addressed secondary power applications by the combustion of diesel engine exhaust and flue gases from enhanced underground recovery operations. The results of these studies are summarized below.

A paper, by W.V. Krill of Acurex Corporation, discussed results of a study to apply catalytic and infrared (IR) burners to appliances. The paper, "Assessment of Infrared and Catalytic Burner Gas Appliances," characterized the design features and operating conditions of major conventional gas appliances in the residential and commercial sectors. These aspects of The Gas Research Institute-sponsored program showed the development of most major appliances with IR burners to be technically feasible and, in many cases, desirable from the standpoints of economics, fuel efficiency, and emissions. The appliances considered for use with IR burners included four types of cooking appliances — rangetops, ovens, broilers, and deep fat fryers — as well as water heaters, room heaters, and central furnaces. Two IR burner types — the refractory tile and high temperature fiber matrix — were found to have the appropriate characteristics to improve appliance efficiency and emissions. An increase in efficiency of 10 to 20 percent is anticipated for most appliance designs. NO_x and CO emission reductions of up to 90 percent appear to be possible. Four of the appliances — the IR rangetop, deep fat fryer, water heater, and warm air furnace — also exhibit economic benefits on comparison of commercial size units, with payback periods of 3 years of less.

Two papers were presented on boiler systems that were developed under EPA Contract 68-02-3122 at Acurex Corporation. The first presentation, by E.B. Merrick, "Development of a Low NO_x Combustor for Gas-Fired Firetube Boilers," described the use of a fiber burner in a demonstration firetube boiler. The burner is a matrix of ceramic fibers vacuum-formed to a capped cylindrical screen. During operation, premixed natural gas and air pass through the fiber matrix and are ignited, burning only on the outer surface. The surface radiates energy to the firetube wall, controlling the combustion temperature to levels well below the NO_x formation temperature. The burner fits into the first pass of the firetube boiler with approximately the same volume as the conventional flame. Preliminary data from fiber burner tests in a York-Shipley 25 hp firetube boiler show a 90 percent reduction in NO_x from the conventional burner. The program will continue with a 1000-hour durability test. Earlier subscale test results and these preliminary full-scale boiler results indicate that NO_x emissions from gas-fired firetube boilers can be substantially reduced (while maintaining low CO and unburned hydrocarbon emissions) when retrofit with fiber burners.

The second presentation, by M.A. Friedman, "Development of a Catalytic/Radiative Watertube Boiler," discussed applying catalytic combustion to watertube boilers. Several small scale systems (2.64×10^8 J/hr) were designed and tested to establish the combustor radiant section geometry. Scaleup to a prototype small industrial sized boiler (1.055×10^9 J/hr) with steam generation was subsequently conducted.

Early tests with a nonconcentric watertube/catalyst arrangement resulted in extremely low NO_x emissions (less than 2 ppmv) and a combustion efficiency of 37 percent. By eliminating cold exposed watertube surfaces with a concentric watertube/catalyst arrangement, the combustion efficiency was improved to 93 percent. However, increases in combustor operating temperature caused fracturing of the ceramic catalyst tubes. This problem was resolved by using high strength, high thermal conductivity silicon carbide tubes. Several combustor section tube geometries were tested for combustion efficiency and thermal NO_x emissions. A close packed tube arrangement resulted in NO_x emissions less than 20 ppmv at 110 percent theoretical air and 2.64×10^8 J/hr (250,000 Btu/hr) heat release rate. Combustion efficiencies greater than 99.9 percent were achieved with a 50 percent energy removal efficiency in the radiant section watertubes. The final energy removal would be accomplished in a conventional convective heat transfer section of the boiler.

A scaleup to 1.055×10^9 J/hr (10^6 Btu/hr) was performed using a similar close-packed concentric watertube/catalyst tube arrangement. The system incorporated an all-welded watertube and steam drum for generation of low pressure steam in a naturally circulating cycle. A downstream adiabatic combustor with secondary air injection allows for staged combustion with distillate fuels. Initial testing with natural gas at 8.44×10^8 J/hr (800,000 Btu/hr) indicated a high combustion efficiency (greater than 99.9 percent) and thermal NO_x emissions of 30 ppmv at near stoichiometric conditions. Values of 10 ppmv or less were expected at 115 percent theoretical air.

Two papers described programs to apply catalytic combustion to stationary gas turbines, one in the U.S. and one in Japan. The U.S. program was conducted for the Electric Power Research Institute by Westinghouse Electric Corporation and Engelhard Corporation. In the paper, "Full Scale, Full Pressure Tests of Catalytic Burners for Combustion Turbines," P.W. Pillsbury of Westinghouse described rig tests at the Concordville, Pennsylvania, laboratories of the Combustion Turbine Systems Division of Westinghouse Electric Corporation during 1980 and 1981. The 0.36 m (14 in.) diameter catalytic elements employed were designed and prepared by Engelhard Corporation. Concept feasibility was demonstrated by steady-state operation. Extremely low NO_x emissions were noted with No. 2 oil as fuel. Additional development tests were found to be required to improve fuel/air distribution approaching the catalyst. Work remaining included demonstration of start-up and transient operation, improving performance, and durability verification.

The Japanese paper, "Catalytic Combustion for Gas Turbines" by H. Fukuzawa of the Central Research Institute of Electric Power Industry, discussed the development and evaluation of catalysts, a determination of optimum operating conditions for combustibility and flue gas composition, and development of a model catalytic combustor. The last stage of the program is to develop a prototype low NO_x catalytic combustor for a high temperature gas turbine.

The characteristics of catalytic combustion under both atmospheric pressure and pressurized conditions were investigated using in-house manufactured catalysts. A part of the catalytic combustion tests under pressurized conditions was sponsored by the Agency of Industrial Science and Technology of the Ministry of International Trade and Industry.

Results of the test program showed that thermal NO_x formation was reduced to less than 20 ppm at 1273-1773K at 0.101-0.808 MPa pressure, and complete catalytic combustion was achieved at 1373-1773K at 0.101-0.808 MPa pressure. The volumetric heat release rate increased as the combustion temperature, fuel flow rate, and combustion pressure were raised, and more than 1300×10^6 kcal/hr-m^3-cat was obtained at 1773K at 0.808 MPa.

These five papers have focused on the use of catalytic combustion for direct power applications in appliances, boilers, and gas turbines. The first of two papers on catalytic combustion related to secondary energy recovery was presented by M. Durilla of Engelhard Industries Division of Engelhard Corporation. In a program for Sandia National Laboratories, "Catathermal® Combustion of Diesel Exhaust to Produce an Inert Gas," the exhaust gas of an 84.3 kW (113 hp) engine was combusted with fuel oil, essentially eliminating O_2 and NO_x. This method of generating an inert gas can be useful to overall operating process economics where there is the need for operating diesel engines to do work. Areas of application include tertiary oil recovery from depleted oil wells, blanketing operations in petroleum tanker reservoirs, and providing noncorrosive drilling environments for geothermal drilling operations. Diesel engine exhaust gas concentrations of greater than 1000 ppm NO_x and 7 to 10 percent oxygen were reduced to less than 2 and 10 ppm, respectively. Durability of the 0.22 m diameter CATCOM® catalyst was demonstrated up to 200 hours of operation with numerous system start-ups and combustion temperatures of 1533K. Optimum system operation was at, or just slightly rich of, stoichiometric.

The final paper was "Development of a System to Utilize Flue Gas from Enhanced Recovery Underground Combustion Projects" by S.E. Kaye of Gulf Research and Development Company. Gulf has developed a process to utilize flue gas from underground-combustion-enhanced oil recovery projects to provide some of the energy necessary for air compression while incinerating air pollutants. Flue gas enters a two-stage catalytic combustor at elevated temperature, where it is burned at a controlled rate and expanded through a power turbine which drives an air compressor. Both the chemical energy and the potential energy of the pressurized gas are used to maximize the useful work extracted. Despite the low heat value of the flue gas, no supplemental fuel is required for catalytic combustion.

Data from small-scale high-pressure combustor tests using flue gas from an active combustion project illustrated the anticipated system performance in the prototype turbine. It was found that substoichiometric catalytic combustion fulfills the constant heat release and constant mass flow requirements of a gas turbine. Unburned hydrocarbon emissions from substoichiometric combustion were determined according to a combustion heirarchy with methane, an acceptable emission, the least likely to be totally burned. CO emissions can be controlled with proprietary catalyst formulations. NO_x emissions ranged from 2 to 10 ppm.

Conclusions

The papers presented at the Fifth Workshop on Catalytic Combustion represent all current major activities in the field. It was apparent from the results of the programs presented that significant advances have been made. The evaluation of catalyst performance continues to advance from early phenomenological measurements of catalyst performance to the development of models that will ultimately be used as catalyst selection tools for system applications. The required operating parameters and early identification of controls for successful combustion of heavy fuels have been performed and have identified additional system problems to be addressed. The actual use of catalytic combustors in system hardware has shown the variety of applications that are possible and are advancing toward prototype demonstration.

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The complete report, entitled "Proceedings: Fifth Workshop on Catalytic Combustion (San Antonio, Texas, September 1981)," (Order No. PB 84-145 580; Cost: $32.50, subject to change) will be available only from:
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