NASA TM-81748

DOE/NASA/51040-23
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Under Interagency Agreement DE-AI01-77CS51040

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EXPERIMENTAL EVALUATION OF CATALYTIC COMBUSTION WITH HEAT REMOVAL AT NEAR STOICHIOMETRIC CONDITIONS

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ABSTRACT

Two concentric tube configurations were tested to evaluate catalytic combustion with heat removal at near stoichiometric conditions. Tests were conducted at an inlet pressure of 1.5×10^5 Pa, inlet fuel-air mixture temperatures from 780 to 960 K, combustion air flow rates from 0.78 to 1.5 g/s, equivalence ratios up to 0.90, and a range of cooling air flow rates. Propane and propylene fuels were used. Both configurations used air flowing through the center tube for cooling and combustion in the annulus on the catalytic surface. One configuration had the catalyst applied to the outside surface of the inner tube. Conversion of the fuel was very low for this configuration. At an inlet fuel-air mixture temperature of 960 K, a combustion air flow rate of 1.5 g/s, an inlet velocity of 11 m/s, and a propylene fuel flow rate of 6.0×10^{-2} g/s, 34 percent of the heat available from the fuel was transferred to the cooling air in the center tube using a platinum catalyst. The other configuration had the catalyst applied to the inside surface of the outer tube. Conversion of the fuel was considerably better in this configuration. At an inlet mixture temperature of 925 K, a combustion air flow rate of 1.0 g/s, an inlet velocity of 22 m/s, and propylene fuel flow rate of 6.0×10^{-2} g/s, 58 percent of the heat available from the fuel was transferred to the cooling air in the inner tube using a platinum/rhodium catalyst. At equivalence ratios as high as 0.87, NO_x emissions less than 0.2 g NO_2/kg fuel were obtained. Combustion efficiencies greater than 99.5 percent were measured for certain operating conditions with this configuration.

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INTRODUCTION

An experimental study was conducted to evaluate catalytic combustion with heat removal at near stoichiometric conditions. This is part of a DOE/NASA project studying improvements to the Stirling engine for the Stirling Engine Highway Vehicle Systems Project. NASA Lewis Research Center is evaluating catalytic combustion as a concept for reducing emissions and improving the efficiency of the Stirling engine.

In a typical automotive Stirling engine heater head (fig. 1; from ref. 1), fuel is injected through an air-assist fuel injector, mixed with air flowing through a swirler, and burned in the primary zone at near stoichiometric conditions. The hot combustion gases pass over the heater tubes transferring heat to the working fluid flowing inside the tubes and then flow through a preheater to warm the incoming air. Because of the high flame temperatures produced in the primary zone, large amounts of exhaust-gas recirculation (EGR) are required to keep NO_x emission levels within acceptable limits (refs. 2 to 4). Advanced engines require higher working fluid temperatures for increased thermodynamic cycle efficiency. The in-

creased flame temperature required to increase the working fluid temperature may necessitate greater EGR levels over present engines to meet the NO_x emission limit. The combustion air blower required would have to be sized larger to provide the additional flow. This would result in an increased parasitic loss on engine efficiency.

An alternative that shows potential for providing acceptable NO_x emissions is catalytic combustion with integral heat removal. Catalytic combustion can efficiently react fuel-air mixtures at lower peak temperatures than would otherwise be possible (refs. 5 and 6). With heat removal to keep peak temperatures within acceptable limits from both a materials and an emissions standpoint, catalytic combustion can theoretically be used at any fuel-air ratio. Catalytic combustion with integral heat removal has been successfully tested for application to watertube boilers (ref. 7).

Two possible approaches which could be used to apply catalytic combustion to the Stirling engine are considered in this report. The first approach would use convection heat transfer from the catalytic surface to the working fluid. The outside surface of the heater tubes could be coated with a catalyst allowing reactions to take place on the surface of the heater tube with heat removal by convection to the working fluid inside the tubes. The second approach would use radiative energy transfer from a hot catalytic reactor to the working fluid. The catalytic surface could be located such that it effectively radiates energy from its hot surface to the heater tubes containing the working fluid.

To determine the feasibility of these concepts, two concentric tube configurations were tested. Both configurations used air flowing through the inner tube for cooling and combustion of the fuel-air mixture in the annulus on the catalytic surface. To simulate the convectively cooled catalytic concept, the outside surface of the inner tube was catalyzed for a length of 56 cm. The inside diameter of the outside tube was 2.21 cm, and the outside diameter of the inner tube was 1.27 cm. To simulate the radiation-cooled concept, the inside surface of the outer tube was catalyzed for 56 cm. The diameters of the tubes for this case were 1.39 and 0.95 cm, respectively. Tests were conducted at a pressure of 1.5×10^5 Pa, inlet fuel-air mixture temperatures from 780 to 960 K, combustion air flow rates from 0.78 to 1.5 g/s, and a range of cooling air flow rates. Propane and propylene fuels were used with most of the testing utilizing propylene. Temperatures, heat transfer to the coolant, and emissions of CO, CO_2, unburned hydrocarbons, and NO_x were measured for both configurations.

EXPERIMENTAL DETAILS

The convectively cooled test configuration is described in figure 2. It consisted of two concentric tubes with the outside surface of the inner tube catalyzed for a length of 56 cm. The outside diameter of the inner tube was 1.27 cm (0.08-cm wall thickness), and the inside diameter of the outer tube was 2.21 cm (0.165-cm wall thickness). Both 1 part platinum/1 part rhodium and all platinum catalysts were tested. They were applied to Kanthal tubes with an alumina washcoat. Catalytic tube wall temperatures were measured with Chromel-Alumel thermocouples at four axial locations. Air flowing inside the catalytic tube provided convective cooling of the catalytic surface.

The radiation-cooled test configuration is described in figure 3. It also consisted of two concentric tubes. For this configuration, the inside surface of the outer tube was catalyzed for a length of 56 cm. The outside

diameter of the inner tube was 0.95 cm (0.089-cm wall thickness) and the inside diameter of the outer tube was 1.39 cm (0.099-cm wall thickness). The only catalyst tested was platinum/rhodium. It was also applied to a Kanthal tube with an alumina washcoat. Catalytic tube wall temperatures were measured at four axial locations with Chromel-Alumel thermocouples attached to the outside surface of the tube. Inner tube wall and cooling-air temperatures were measured at three axial locations. Air flowed through the inner tube for cooling. The catalytic tube transferred heat by radiation to the inner tube and also by convection to the combustion gas in the annulus.

For both the convective and radiative cooled configurations, the inlet combustion air was indirectly preheated to temperatures up to 1000 K and mixed with either gaseous propane or propylene fuel. Combustion and cooling air flow rates were measured with 0.254-cm-diam calibrated orifices, and the fuel flow rate was measured with a calibrated 0.030-cm-diam orifice. Inlet and exit temperatures were measured at the locations shown in figures 2 and 3. All temperatures were measured with Chromel-Alumel thermocouples. Both configurations were externally insulated with 5-cm-outside-diameter Fiberfrax tube insulation, which was wrapped with an additional 5-cm thickness of blanket type insulation. Rig pressure was measured with strain gage pressure transducers at the locations shown in figures 2 and 3.

Exhaust gas emissions were measured by withdrawing samples through a 0.140-cm-inside diameter, stainless-steel, water-cooled gas-sample probe. The sample line was electrically heated to keep the unburned hydrocarbons from condensing. Concentrations of CO and CO_2 were measured with nondispersive infrared analyzers, unburned hydrocarbons with a flame ionization detector, and nitrogen oxides (total NO + NO_2) with a chemiluminescent analyzer.

MEASUREMENTS AND COMPUTATIONS

The reported inlet velocity was calculated using the measured inlet conditions and annulus cross-sectional area. Emissions were measured in ppm by volume and converted to emission indexes using the expressions in reference 8. The equivalence ratio is the fuel-air ratio divided by the stoichiometric fuel-air ratio. Fuel-air ratios were computed both from the measured flow rates of fuel and air and from a carbon balance on the measured emissions. The two values generally agreed within ±15 percent except for the very poor combustion efficiency conditions when the unburned hydrocarbons were extremely high and the analyzer measurements were invalid. The reported equivalence ratios were obtained from the carbon balance except for the extremely poor combustion efficiency cases. All reported equivalence ratios for the convectively cooled case are based on the flow measurements. All reported equivalence ratios for the radiation-cooled case are based on the carbon balance.

Combustion efficiency was computed from the expression,

$$EFF = 100-0.1[(EI)_{HC} - (EI)_{HC,eq}] - 0.1 \frac{(HV)_{CO}}{(HV)_{fuel}} [(EI)_{CO}) - (EI)_{CO,eq}]$$

where

EFF combustion efficiency, percent
$(HV)_x$ net heating value of specie x, J/kg
$(EI)_x$ emission index of specie x, g X/kg fuel

Equilibrium values $(EI)_{x,eq}$ at the measured exit temperature were calculated using the computer program of reference 9. Equilibrium values of unburned hydrocarbons were essentially zero and values of CO were very small.

RESULTS AND DISCUSSION

Convectively Cooled Catalytic Tube Configuration

The heat flux to the cooling air, based on the outside surface area of the catalytic tube is presented as a function of the fuel flow rate in figure 4. The heat flux available from the fuel is also shown. A platinum catalytic tube gave the best performance. At a fuel flow rate of $6x10^{-2}$ g/s, 34 percent of the heat available from the fuel was transferred to the cooling air using propylene fuel. A platinum/rhodium catalytic tube gave poorer performance. At the same propylene fuel flow rate, 15 percent of the heat available from the fuel was transferred to the cooling air. Even though the cooling airflow was almost three times as high for the platinum catalyst as the platinum/rhodium catalyst, catalytic tube wall temperatures were almost identical for both. This indicates increased activity of the platinum catalyst over the platinum/rhodium catalyst. A platinum/rhodium catalyst, operated on propane fuel transferred 10 percent of the heat available from the fuel to the cooling air. When operated on propane, a significant loss of activity was found after the platinum catalytic tube was run for about 2 hours. No significant loss of activity was observed when the catalytic tubes were operated on proplyene fuel. Heat losses to the environment were estimated to be less than 10 percent of the heat available from the fuel.

The convectively cooled catalytic tube was effectively cooled by the inner cooling air such that the combustion gas in the annulus was not heated sufficiently by the catalytic tube to initiate appreciable gas-phase reactions. The temperature of the combustion gas only increased slightly from the inlet to the exit. Since only surface reactions were probably occurring, conversion of the fuel remained low. Since the combustion gas temperature remained fairly constant, an estimate of the conversion can be obtained by comparing the heat flux to the cooling air with that available from the fuel. Since both heat flux and combustion efficiency were relatively low for this configuration, only minimal testing of it was performed.

Radiation-Cooled Catalytic Tube Configuration

Heat flux to the cooling air, based on the cooling tube outside surface area, as a function of the fuel flow rate is shown in figure 5 for the radiation-cooled configuration. At a fuel flow rate of $6x10^{-2}$ g/s, 58 percent of the heat available from the fuel was transferred to the cooling air. Data are presented for three combustion air flow rates with a combustion efficiency of 99.5 percent. Heat losses to the environment were greater for this configuration, since the catalytic tube was the outside tube and it also operated at higher temperatures. Based on the heat avail-

able from the fuel, heat losses were approximately 30 percent at a combustion airflow of 1 g/s.

The NO_x emission index (sum of NO + NO_2) expressed as g NO_2/kg fuel is presented in figure 6 for a combustion airflow of 1 g/s at equivalence ratios up to 0.87. A NO_x emission index goal of 1.6 g NO_2/kg fuel from reference 5 is shown for comparison. The NO_x emissions were at least an order of magnitude lower than the goal. Any trends shown are not considered significant since most of the NO_x emissions obtained were less than 1 ppm. The data only illustrate the extremely low values obtained.

The effect of the combustion products exit temperature on combustion efficiency for a combustion airflow of 1 g/s is presented in figure 7. Data for inlet mixture temperatures of 780 and 925 K are shown. Exit temperature was varied by changing the cooling air flow rate at a constant fuel-air ratio. Even though the inlet velocity is slightly higher for the 925 K inlet and the residence time is reduced, the 925 K inlet mixture temperature data generally required slightly lower exit temperatures than the 780 K inlet temperature data for the same combustion efficiency. At an inlet mixture temperature of 780 K, the data show an effect of equivalence ratio. An equivalence ratio of 0.85 required a higher exit temperature than equivalence ratios of 0.65 and 0.73 for the same combustion efficiency. An inlet mixture temperature of 925 K showed no effect of equivalence ratio for values of 0.65 to 0.87 within the scatter of the experimental data.

The effect of the combustion products exit temperature on CO emissions is shown in figure 8 for a combustion airflow of 1 g/s at inlet mixture temperatures of 780 and 925 K. CO emissions decreased sharply at exit temperatures above 1200 K. Even though the inlet velocity is slightly higher and the residence time is reduced for the 925 K inlet mixture temperature data, slightly lower exit temperatures are required at 925 K for the same CO emission index than at an inlet mixture temperature of 780 K at higher levels of the emission index. Little difference is evident at lower CO emission levels. Data at an inlet mixture temperature of 780 K show an effect of equivalence ratio on the CO emission index. Data at an inlet mixture temperature of 925 K do not.

The effect of the combustion products exit temperature on the unburned hydrocarbons emission index is shown in figure 9 for a combustion airflow of 1 g/s at inlet mixture temperatures of 780 and 925 K. The results show the same trends as previously seen for the CO emission index.

Axial temperature profiles for the radiation-cooled catalytic configuration are shown in figure 10 for two combustion efficiencies, 99.8 and 88 percent. At a combustion airflow of 1 g/s and an inlet mixture temperature of 925 K, temperatures are shown as a function of axial position for the platinum/rhodium catalytic tube, cooling tube, and cooling airflow. Combustion mixture inlet and exit temperatures are also given. The only difference between the two combustion efficiencies was the cooling air flow rate. For both combustion efficiencies, the catalytic tube wall temperature decreased with length as the fuel was consumed and the fuel-air ratio decreased. For the 88 percent combustion efficiency case, the cooling-tube wall temperature decreased from the point 29 cm from the inlet to the last measured cooling-tube wall temperature. For the 99 percent combustion efficiency case, the cooling-tube wall temperature increased from the 29 cm point to the last measured axial position where the cooling-tube temperature reached the temperature of the catalytic tube. The increase in temperature indicates that considerably more gas-phase reaction was taking place for this case, which increased the conversion of the fuel.

The effect of cooling-tube wall temperature on combustion efficiency is shown in figure 11 for a combustion airflow of 1 g/s at inlet mixture temperatures of 780 and 925 K. This cooling tube temperature was measured at the last axial position, 53 cm from the inlet tube center. The trends shown are similar to those previously shown for exit temperature of the combustion products. Even though the inlet velocity is lower and the residence time is increased for an inlet mixture temperature of 780 K, data at 780 K required a higher wall temperature than an inlet mixture temperature of 925 K for a given combustion efficiency. No effect of equivalence ratio is shown for either inlet temperature.

This configuration was able to release and transfer considerably more of the heat available from the fuel than the convectively cooled configuration. Compared to the convectively cooled configuration, the catalytic surface area was increased for this configuration. The catalyst was able to operate at a higher temperature which increased the catalytic surface reactions, and it also heated the fuel-air mixture sufficiently to initiate gas-phase reactions which then completed the conversion of the fuel to products.

The platinum/rhodium catalyst was operated for about 40 hours on propylene fuel. A slight loss of catalytic activity was initially observed, however, after the initial loss, the activity remained essentially constant for the duration of the testing.

CONCLUDING REMARKS

This study has demonstrated that catalytic combustion with heat removal is capable of high efficiency, low thermal NO_x operation at fuel-air ratios approaching stoichiometric. With heat removal to keep temperatures within limits from both a materials and an emissions standpoint, catalytic combustion can be used to efficiently react fuel-air mixtures with an otherwise high adiabatic reaction temperature. A concept utilizing radiation cooling of the catalytic surface was able to transfer and release considerably more of the heat available than a convectively cooled concept.

This study has demonstrated the feasibility of the concept. Considerably more effort is necessary to develop a configuration that could be integrated into an actual Stirling engine. A more realistic size and geometry is needed. Temperatures and flow rates must be matched to an engine. Better heat transfer and combustion performance may be obtained with other types of catalysts. Therefore, this effort is only a first step in applying catalytic combustion with heat removal to a Stirling engine.

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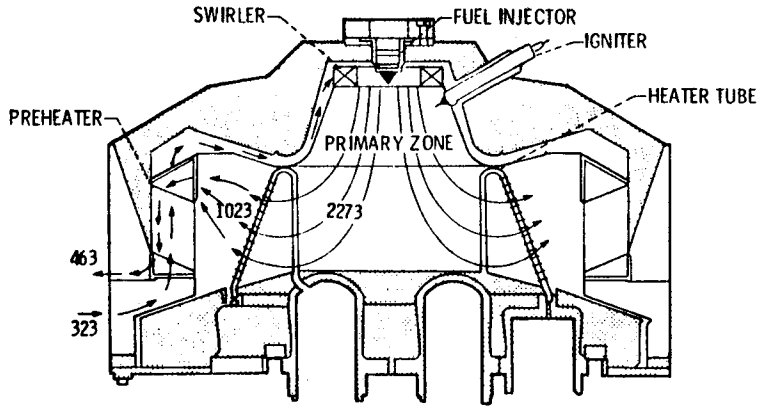

Figure 1. - Typical Stirling engine heater head gas temperatures, K.

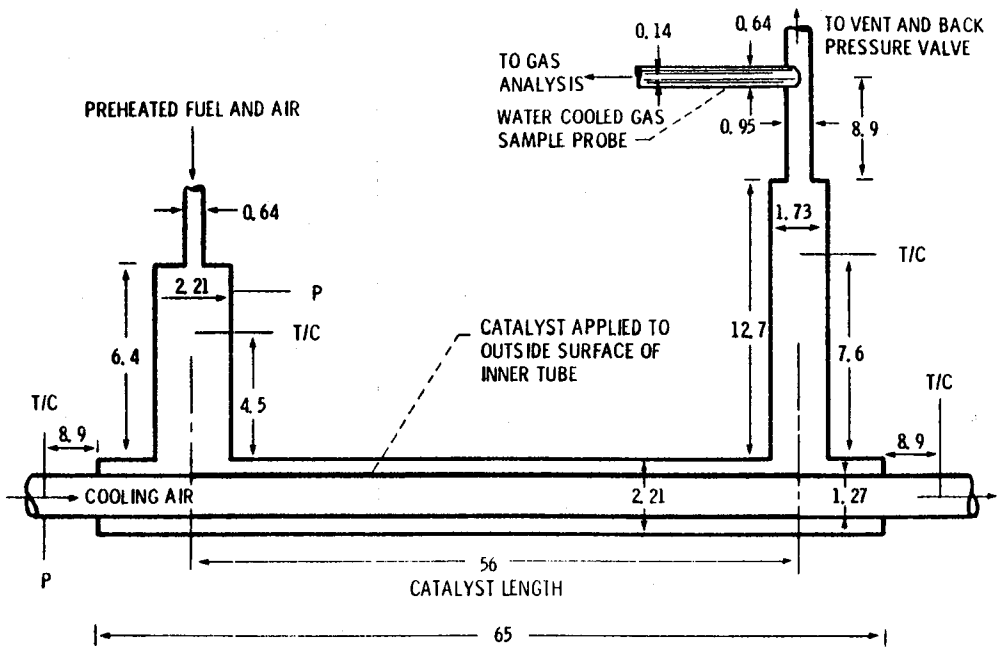

Figure 2. - Schematic diagram of convectively cooled configuration. (Dimensions in cm; insulation not shown.)

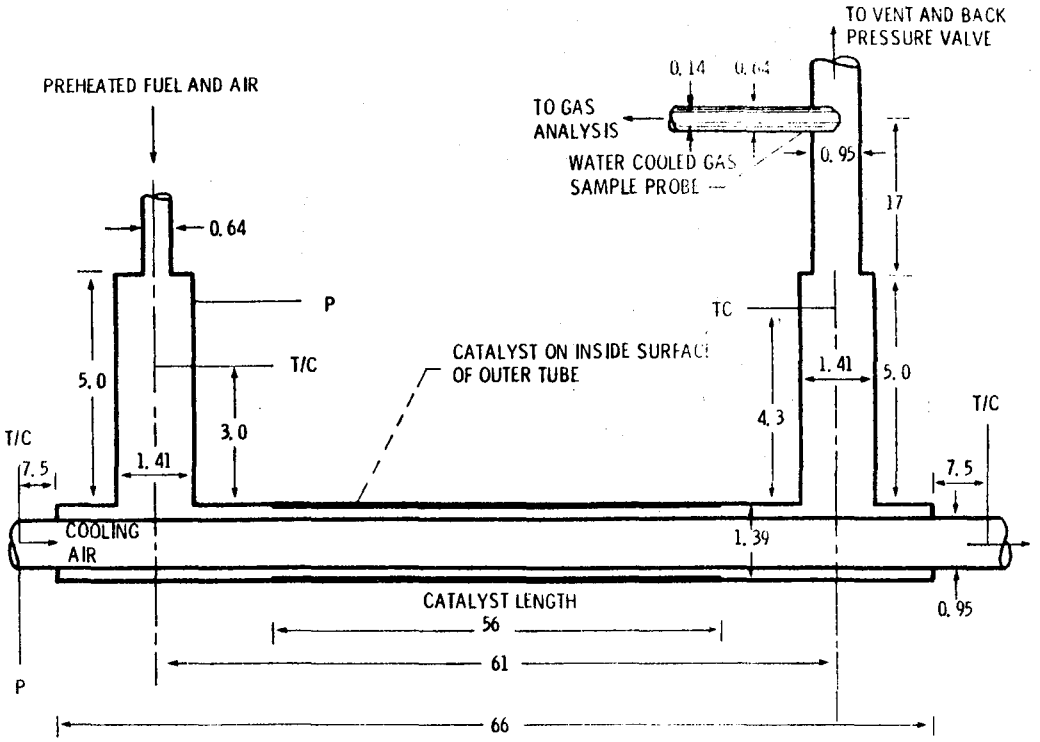

Figure 3. - Schematic diagram of radiation-cooled configuration. (Dimensions in cm; insulation not shown.)

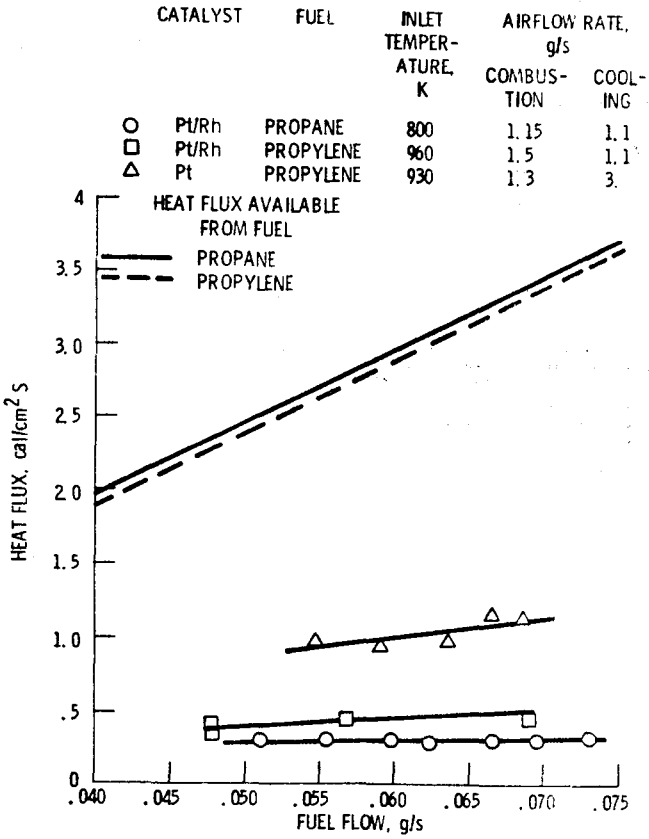

Figure 4. - Heat flux to cooling air versus fuel flow, convectively cooled configuration; pressure, 1.5×10^5 Pa.

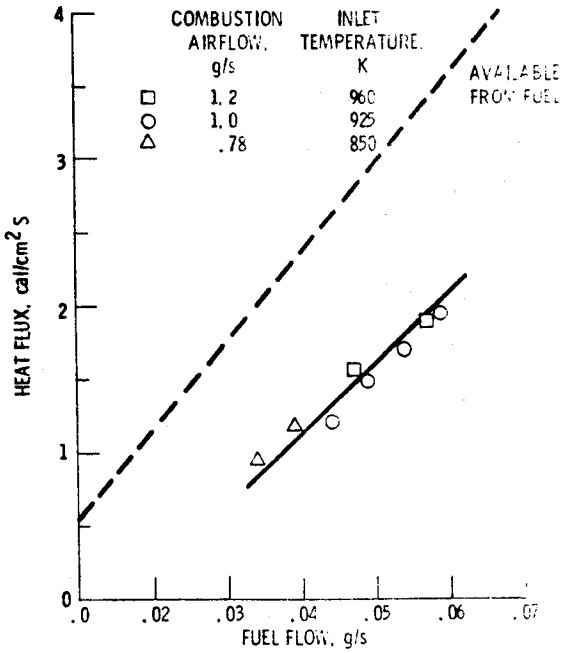

Figure 5. - Heat flux to cooling air versus fuel flow; radiation-cooled configuration. Propylene fuel; combustion efficiency, 99.5 percent; pressure, 1.5×10^5 Pa.

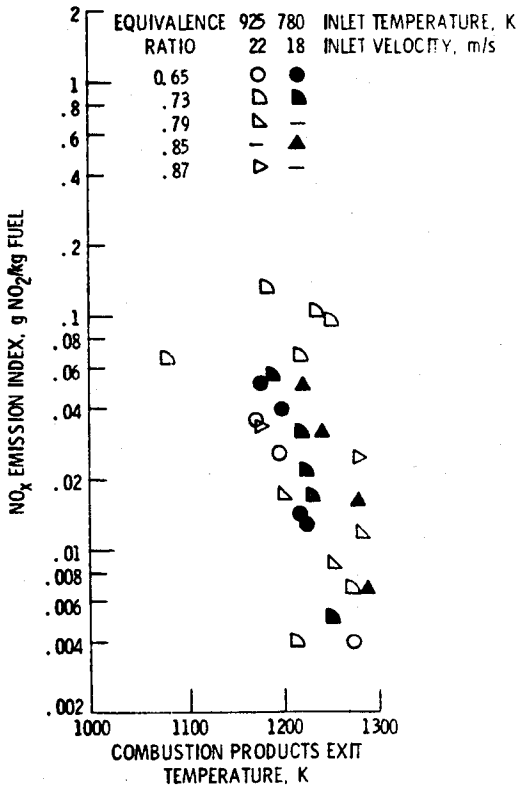

Figure 6. - NO_x emission index versus combustion products exit temperature. Propylene fuel; radiation-cooled configuration; combustion airflow, 1 g/s; pressure, 1.5×10^5 Pa.

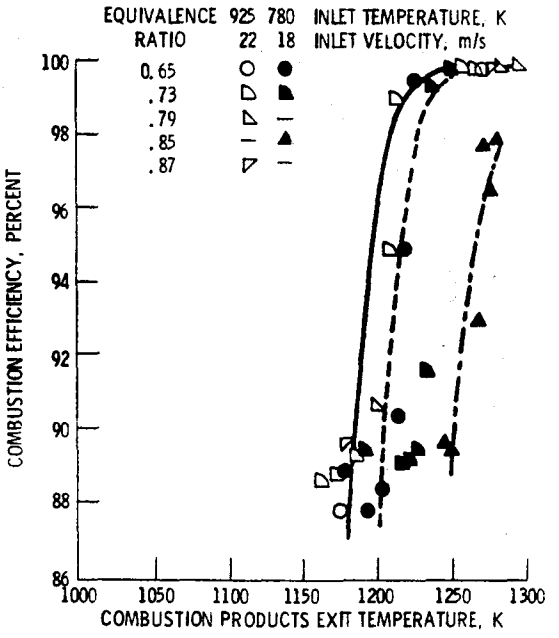

Figure 7. - Effect of combustion products exit temperature on combustion efficiency; radiation-cooled configuration. Combustion airflow, 1.0 g/s; propylene fuel; pressure, 1.5×10^5 Pa.

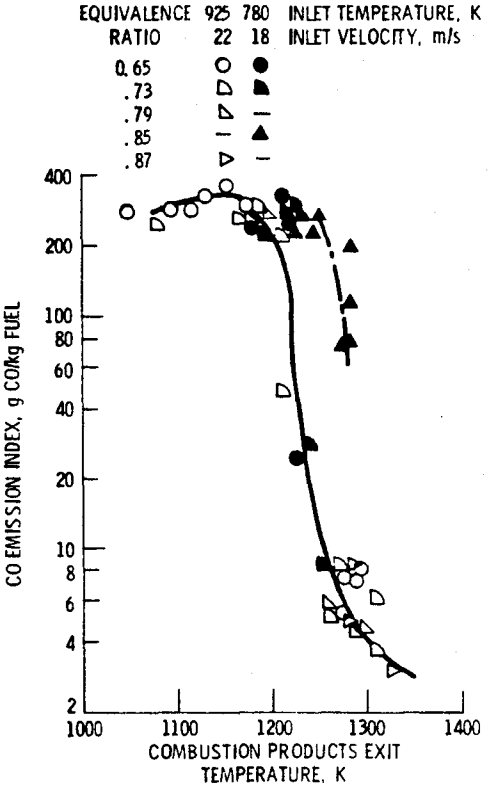

Figure 8. - Effect of combustion products exit temperature on CO emission index. Combustion airflow, 1.0 g/s; pressure, 1.5×10^5 Pa; propylene fuel.

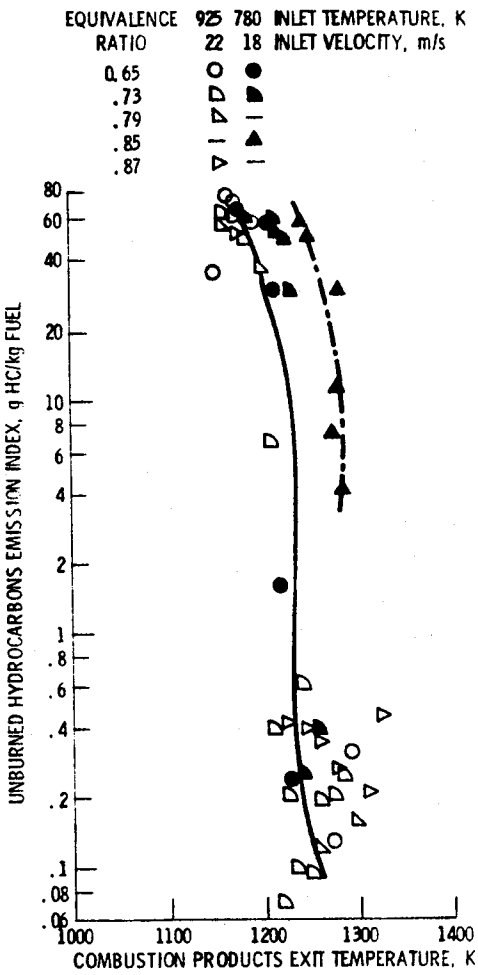

Figure 9. - Effect of combustion products exit temperature on unburned hydrocarbons emission index. Combustion airflow, 1 g/s; pressure, 1.5×10^5 Pa; propylene fuel.

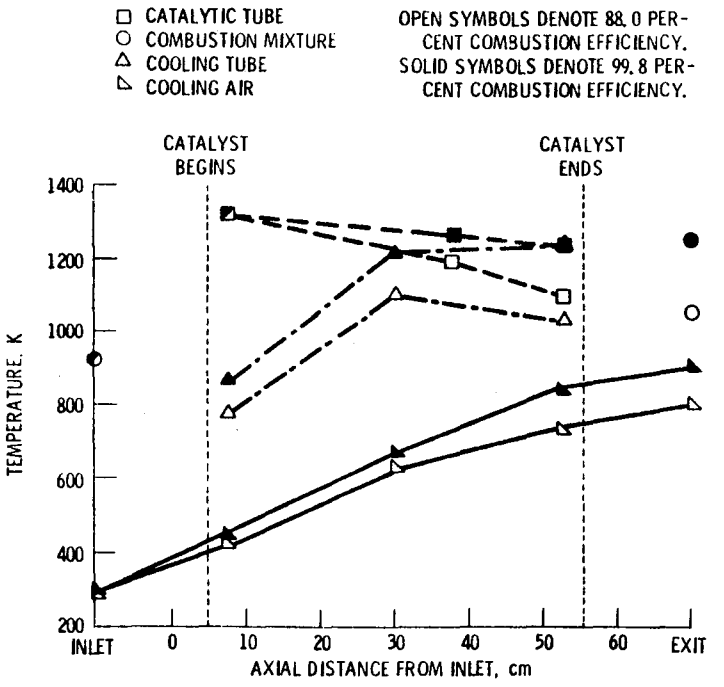

Figure 10. - Axial temperature profile of radiation-cooled configuration. Combustion airflow, 1.0 g/s; inlet velocity, 22 m/s; inlet temperature, 927K; pressure, 1.5×10^5 Pa; propylene fuel; equivalence ratio, 0.72.

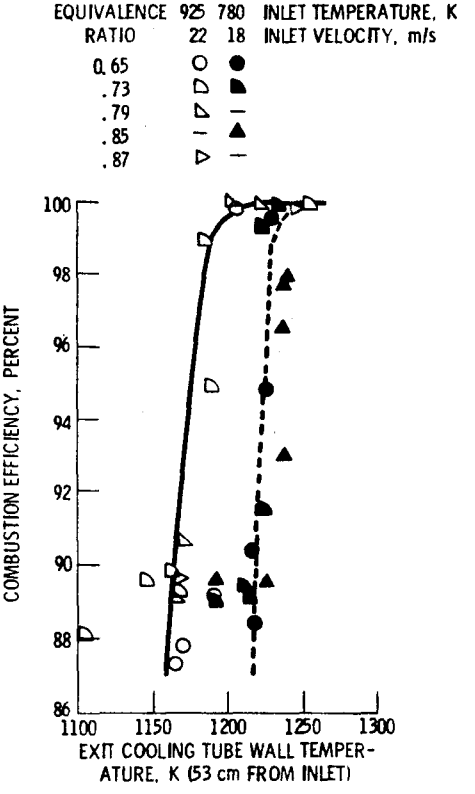

Figure 11. - Effect of cooling-tube wall temperature on combustion efficiency. Combustion airflow, 1.0 g/s; pressure, 1.5×10^5 Pa; propylene fuel.

1. Report No. NASA TM-81748	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle EXPERIMENTAL EVALUATION OF CATALYTIC COMBUSTION WITH HEAT REMOVAL AT NEAR STOICHIOMETRIC CONDITIONS		5. Report Date 6. Performing Organization Code 778-35-03
7. Author(s) Daniel L. Bulzan		8. Performing Organization Report No. E-814 10. Work Unit No.
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135		11. Contract or Grant No. 13. Type of Report and Period Covered Technical Memorandum
12. Sponsoring Agency Name and Address U.S. Department of Energy Office of Transportation Programs Washington, D.C. 20545		14. Sponsoring Agency ~~Code~~ Report No. DOE/NASA/51040-23

15. Supplementary Notes

Prepared under Interagency Agreement DE-AI01-77CS51040. Prepared for the Fourth Workshop on Catalytic Combustion, Cincinnati, Ohio, May 14-15, 1980.

16. Abstract

Two concentric tube configurations were tested to evaluate catalytic combustion with heat removal at near stoichiometric conditions. Tests were conducted at an inlet pressure of 1.5×10^5 Pa, inlet fuel-air mixture temperatures from 780 to 960 K, combustion air flow rates from 0.78 to 1.5 g/s, equivalence ratios up to 0.90, and a range of cooling air flow rates. Propane and propylene fuels were used. Both configurations used air flowing through the center tube for cooling and combustion in the annulus on the catalytic surface. One configuration had the catalyst applied to the outside surface of the inner tube. Conversion of the fuel was very low for this configuration. At an inlet fuel-air mixture temperature of 960 K, a combustion air flow rate of 1.5 g/s, an inlet velocity of 11 m/s, and a propylene fuel flow rate of 6.0×10^{-2} g/s, 34 percent of the heat available from the fuel was transferred to the cooling air in the center tube using a platinum catalyst. The other configuration had the catalyst applied to the inside surface of the outer tube. Conversion of the fuel was considerably better in this configuration. At an inlet mixture temperature of 925 K, a combustion air flow rate of 1.0 g/s, an inlet velocity of 22 m/s, and propylene fuel flow rate of 6.0×10^{-2} g/s, 58 percent of the heat available from the fuel was transferred to the cooling air in the inner tube using a platinum/rhodium catalyst. At equivalence ratios as high as 0.87 NO_x emissions less than 0.2 g NO_2/kg fuel were obtained. Combustion efficiencies greater than 99.5 percent were measured for certain operating conditions with this configuration.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Catalytic combustion Stirling engine Combustion	Unclassified - unlimited STAR Category 44 DOE Category UC-96

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified		

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