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Fuel-Rich Catalytic Combustion of Jet-A Fuel—Equivalence Ratios 5.0 to 8.0

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INTRODUCTION

Fuel-rich catalytic combustion (E. R. > 5.0) is a unique technique for preheating a hydrocarbon fuel to temperatures much higher than those obtained by conventional heat exchangers. In addition to producing very reactive molecules, the process upgrades the structure of the fuel by the formation of hydrogen and smaller hydrocarbons and produces a cleaner burning fuel by removing some of the fuel carbon from the soot formation chain. Temperatures higher than the 1200 K measured in a previous study with iso-octane (ref. 1) can be obtained by altering the air inlet temperature and/or the equivalence ratio (E. R.). The maximum temperature for the processed gases is probably 1350 K which is the threshold temperature for the formation of soot (ref. 2).

With fuel-rich catalytic combustion as the first stage of a two stage combustion system, these enhanced fuel properties can be utilized by both high speed engines, where time for ignition and complete combustion is limited, and engines where emission of thermal NO_x is critical. Two-stage combustion (rich-lean) has been shown to be effective for NO_x reduction in stationary burners where residence times are long enough to burn-up the soot formed in the first stage. Such residence times are not available in aircraft engines. Thus, the soot-free nature of the present process is critical for high speed engines. Hustad and Sonju (ref. 3) studied the lower flammability limit of hydrocarbons as a function of temperature and showed that the limit goes to zero at about 1473 K. Thus, the high temperature produced by this process enables one to use fuel lean combustion as a technique for controlling the combustion temperatures and the formation of thermal NO_x .

In a previous publication (ref. 1), results were presented for the fuel-rich catalytic combustion of iso-octane. Success of this concept will be highly dependent on the ability to apply it to practical and commonly used fuels, such as DF-2, Jet-A, JP-4, etc. This paper will describe the successful application of fuel-rich catalytic combustion to Jet-A, a multicomponent fuel used in gas turbine combustors.

EXPERIMENTAL APPARATUS AND PROCEDURES

The catalytic flow tube reactor has been described in reference 1 and the present fuel injector in reference 4. The fuel used for this work is specified by the ASTM Jet-A turbine fuel designation. This is a multicomponent kerosene type fuel commonly used in gas turbine engines. Jet-A with a H/C ratio of 1.92 has an autoignition temperature of 533 K and contains 15% aromatic and 1% olefin hydrocarbons. The fuel was metered to the reactor from a pressurized fuel tank. Flow rates measured with a calibrated turbine flow meter varied from 150 to 220 cm³/min, depending upon the equivalence ratio desired.

Standard procedures were followed for each run. These included a warm-up of at least 90 minutes with hot nitrogen followed by an additional warm-up of 30 to 50 minutes at the desired test conditions. This procedure assured steady-state temperatures in the reactor.

After the reactor reached a steady state temperature, start-up was initiated by adding fuel to the hot nitrogen. To ensure that the equivalence ratio in the reactor was always beyond the rich limit of combustion, the flow system was designed to permit switching the gas from nitrogen to air without interrupting the flow. By adjustment of the regulated pressure of the two gases, the fuel-air equivalence ratio could be established with hot nitrogen and then switched to air. In this way the catalyst never experienced stoichiometric burn. Shut down was accomplished by reversing the process. A calibrated strain gauge flow meter measured the airflow which was kept constant at about 0.3 std m³/min. The pressure at the inlet to the catalyst bed was maintained at about 160 kPa.

The catalyst used in these experiments was the same type as that used in the iso-octane experiments. To assign a numerical value to the amount of catalyst being used, the external surface area was calculated for each monolith size. Two catalyst configurations were used. Configuration #1 consisted of 4 catalyst discs, each of different cell density value, stacked in increasing density value. Configuration #2 was the same as #1 with an additional disc of 7.75 cells/cm² in front of the other four discs. The catalyst surface area was calculated to be 2067 cm² for configuration #1, and 2479 cm² for configuration #2. The catalyst configuration used in the iso-octane experiments corresponds to the same catalyst surface area as configuration #1 in the Jet-A experiments. The slight difference in the calculated surface area from that reported in reference 1 is due to a very small difference in the measurement of the catalyst cell dimensions.

Ten gas samples were withdrawn from the reactor from a probe located 17.8 cm downstream of the catalyst bed, corresponding to about 20 msec of gas phase reaction time. The sampling system and procedure has been previously described (ref. 1). The gaseous combustion products were analyzed by gas chromatography with

thermal conductivity and flame ionization detectors. Three columns were used for the separation of the gas components: washed Molecular Sieve, Sphercarb, and Porapak R.

RESULTS AND DISCUSSION

Fuel-rich catalytic combustion of a practical fuel is a viable technique for preheating the fuel to very high temperatures without forming soot. The soot-free nature of the process was demonstrated by observing the hot reaction product gases 7.6 cm downstream of the catalyst bed. As with iso-octane, the gases were always completely transparent and showed none of the characteristic radiation associated with a sooting flame. Jet-A fuel was studied over the equivalence ratio range of 4.8 to 7.8 with combustion temperatures ranging from 1180 to 1060 K. Flashback and spontaneous ignition of the fuel were not a problem for the test conditions used in the present study.

The reaction temperature was measured 3.8 cm downstream of the catalyst bed with a shielded closed-end thermocouple. Figure 1 is a plot of the measured reaction temperatures versus equivalence ratio. These temperatures compare well with those calculated using the NASA Lewis Chemical Equilibrium Calculations program (ref. 5) assuming soot was not a reaction product. This was the same character shown by the iso-octane data in the previous work. Although at present it is not clear why this combustion temperature can be calculated with an equilibrium program since the product distribution does not correspond to the equilibrium products, the experimental data clearly show that such a calculation is an acceptable way to estimate the temperature.

The size of the catalyst bed was increased from 2067 to 2479 cm² by adding another catalyst disc in front of the original configuration. This caused a 15 K drop in the combustion temperature (see Figure 1) and showed a measurable increase in the pressure drop across the catalyst bed. Cold flow measurements showed no change in the pressure drop. The next effect was a small reduction in the amount of solid collected in the cold trap.

Table 1 shows a side-by-side comparison of the reaction products, temperatures, and equivalence ratios for the two catalyst configurations. The products are divided into two groups to show the fuel-processing character of the preburner. Group 1 contains H₂, O₂, N₂ and all C₁ and C₂ carbon containing compounds, while group 2 contains larger hydrocarbons. The analysis shows that the breakdown of Jet-A is very similar to that found for iso-octane with the exception of hydrogen and the aromatics. The smaller hydrogen concentration is probably due to the lower hydrogen to carbon ratio of the Jet-A fuel. Although Jet-A had an initial aromatic content of about 15%, it is not clear whether the benzene and toluene concentrations measured came from the initial fuel or from gas phase reactions downstream of the catalyst. In the case of iso-octane, samples withdrawn at two gas phase dwell times showed that benzene was formed by gas phase reactions downstream of the catalyst bed. Although the Jet-A data were not

obtained for two dwell times, a comparison of the measured benzene concentrations versus temperature for the two catalyst configurations showed that the concentration of benzene was independent of the amount of catalyst present and increased with temperature. See Figure 2. This suggests that the formation of benzene in the present experiments may be by gas phase reactions also. In addition, it was noted the amount of benzene found in the iso-octane analysis at 60 msec was very similar to that found at 20 msec for Jet-A.

In the study of iso-octane, a grease-like solid was found in the cold trap. Jet-A produced much more of this grease-like solid. The amount of solid collected was greater at the higher temperatures than at the lower ones. This solid was soluble in acetone, stable at high temperatures, and slowly oxidized by air at room temperature. Oxidization caused the solid to change from a light yellow color to brown and finally to a black liquid. At present we have been unable to identify the solid or the black liquid. An unexpected result was the reduction in the quantity of solid formed when the size of the catalyst bed was increased.

The carbon-atom balance across the catalyst bed was calculated from the measured reaction products in Table 1. Changes in the number of moles of gas due to chemical reaction were accounted for by using nitrogen as a reference gas and balancing the carbon-nitrogen ratio across the bed. Figure 3 is a plot of the percentage of the initial fuel carbon found in the product gases as a function of the reaction temperature. Unlike the iso-octane study, we were unable to account for all the fuel carbon of Jet-A with the gaseous products.

The ability of a fuel to form soot in a gas turbine combustor is related to the hydrogen to carbon ratio of the fuel, i.e., the smaller this ratio the more soot produced. Fuel-rich catalytic combustion enhances the fuel by forming hydrogen and smaller hydrocarbons and removes some of the fuel carbon from the soot formation process. This carbon removal is accomplished by the formation of carbon monoxide and carbon dioxide, both of which are known not to form soot at the combustion temperatures of a hydrocarbon fuel. The effective hydrogen to carbon ratio of the processed fuel was calculated by subtracting the amount of carbon in carbon monoxide and carbon dioxide from the total fuel carbon and dividing the initial hydrogen by the balance of the carbon. Figure 4 shows the increase in the hydrogen to carbon ratio for the processed Jet-A fuel.

The appearance of carbon dioxide is interesting as one would not expect to find it as a product under such fuel rich conditions. Carbon dioxide is formed in the gas phase by the reaction of carbon monoxide and the OH radical. Since this reaction is much slower than the reaction between the OH radical and a hydrocarbon molecule, very little CO_2 should be formed. Thus, carbon dioxide must be formed by a surface reaction in the catalyst bed. Figure 5 shows the carbon dioxide concentration as a function of temperature for three catalyst configurations. The

middle line (CSA = 1977-2070 cm²) shows data for both iso-octane (refs. 1 and 6) and Jet-A. Note that the amount of carbon dioxide found in the analysis was independent of the fuel type or the high temperature dwell time. Smaller or larger catalyst configurations yield larger or smaller concentrations of carbon dioxide, suggesting that the carbon dioxide formed initially was then consumed by a secondary surface reaction. The rate of this secondary reaction requires an activation energy of about 5 kcal in order to account for the observed temperature dependence of the data.

Fuel-rich catalytic combustion provides a unique window to view the product of the thermal breakdown of a large fuel molecule prior to the formation of soot. Experiments have been conducted with two fuels to date, iso-octane, a branched chain paraffin, and Jet-A, a multicomponent fuel containing both aromatic and other cyclic compounds. Although the products of these two fuels are similar, there are differences which are interesting. Jet-A with a hydrogen to carbon ratio of 1.92, produced much more of the grease-like solid and had higher concentrations of acetylene, ethylene, benzene, and toluene than iso-octane. The amount of the solid collected increased as the temperature increased. Expected behaviour for a precursor to soot as the soot formation process is known to have a strong temperature dependence. The solid is readily oxidized by air and forms a black liquid, which might appear as a solid at high temperatures. Now, if this solid is related to one of the precursors to soot, its formation must then be related to the species whose concentrations increased. All four of these compounds are known to be strong "sooters". At present, the data is not adequate to proceed any further, but better sampling and the analysis of the solid and liquid may be very informative.

SUMMARY

Fuel-rich catalytic combustion of Jet-A fuel was studied over the equivalence ratio range 4.8 to 7.8, which yielded combustion temperatures of 1180 to 1060 K. The process was soot free and the gaseous reaction products were similar to those obtained in the iso-octane study with the exception of hydrogen and the aromatics. This study demonstrated the viability of using fuel-rich catalytic combustion as a technique for preheating a practical fuel. The effective hydrogen to carbon ratio of the products showed a maximum increase of 44% (1.92 to 2.79) which results in a much cleaner burning fuel. We were unable to account for all of the fuel carbon with the gaseous products but most of the missing carbon may be in the solid and liquid collected in the cold trap. We believe that fuel-rich catalytic oxidation may be a useful tool for studying intermediate stages in the soot formation process. It is suggested that the solid collected in the cold trap may include a precursor to soot.

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Table 1 - Gaseous Reaction Products

	Catalyst surface area - 2067 cm ²					Catalyst surface area - 2479 cm ²				
Reaction Temp., K	1166	1146	1124	1107	1083	1141	1126	1109	1094	1077
Equivalence Ratio	5.25	5.68	6.16	6.52	7.07	5.41	5.79	6.25	6.61	7.09
Fuel flow, g mole/min	0.757	0.823	0.895	0.958	1.037	0.771	0.830	0.895	0.950	1.013
Air flow, g mole/min	12.22	12.28	12.32	12.46	12.44	12.07	12.14	12.13	12.15	12.11
Residence time, msec	19.8	20.2	20.3	21.0	22.0	20.3	20.2	21.2	21.8	22.7
PRESSURE, kPa										
Upstream	160.3	159.7	159.0	159.2	159.4	157.9	157.7	157.9	158.4	158.4
Downstream	159.7	159.3	158.8	159.2	158.5	156.8	156.8	157.3	157.7	157.7
ΔP across bed	0.6	0.4	0.2	0.0	0.9	1.1	0.9	0.6	0.7	0.7
TEMPERATURE, K										
Preheated air	800	801	801	803	803	799	800	801	802	803
Fuel	304	303	303	302	301	299	298	297	297	296
GROUP 1:										
Hydrogen	5.58	4.76	3.92	3.43	2.83	5.20	4.45	3.84	3.32	2.76
Oxygen	1.05	1.03	1.13	1.22	1.40	1.27	1.31	1.40	1.59	1.72
Nitrogen	59.90	60.43	59.80	61.68	63.15	60.18	59.58	61.49	62.16	63.41
Carbon monoxide	15.02	13.89	12.39	11.96	10.94	14.59	13.47	12.66	11.91	11.41
Carbon dioxide	2.29	2.61	2.93	3.23	3.49	2.32	2.56	2.81	2.98	3.22
Methane	4.91	4.58	4.03	3.71	3.32	4.67	4.33	4.31	3.97	3.72
Acetylene	0.360	0.237	0.151	0.124	0.076	0.304	0.214	0.147	0.113	0.079
Ethylene	7.02	7.57	7.37	7.61	6.76	7.01	7.34	7.34	7.34	6.96
Ethane	0.38	0.47	0.55	0.64	0.59	0.51	0.57	0.60	0.61	0.59
Total Group 1	96.51	95.58	92.27	93.60	92.56	96.05	93.82	94.60	93.99	93.87
GROUP 2:										
Propylene	1.23	1.77	2.23	2.44	---	1.37	1.83	2.30	2.52	2.58
C3 hydrocarbons	0.191	0.162	0.075	0.058	---	0.182	0.157	0.082	0.064	0.042
C4 hydrocarbons	0.74	1.14	1.45	1.59	---	0.86	1.24	1.50	1.67	1.77
C5 hydrocarbons	0.16	0.28	0.44	0.56	---	0.19	0.31	0.47	0.61	0.71
C6 hydrocarbons	0.004	0.026	0.066	0.11	---	0.014	0.025	0.056	0.10	0.16
Benzene	0.43	0.42	0.38	0.34	---	0.42	0.38	0.35	0.32	0.29
Toluene	0.27	0.31	0.31	0.32	---	0.33	0.31	0.32	0.30	0.25
C7 hydrocarbons	0.000	0.005	0.015	0.027	---	0.001	0.004	0.016	0.026	0.067
Styrene	0.030	0.011	0.017	0.011	---	0.048	0.017	0.020	0.013	0.010
C8 hydrocarbons	0.038	0.029	0.056	0.061	---	0.051	0.042	0.067	0.068	0.077
Total Group 2	3.09	4.15	5.04	5.52	---	3.47	4.32	5.18	5.69	5.96
Total Group 1 and 2	99.60	99.73	97.31	99.12	---	99.52	98.14	99.78	99.68	99.83

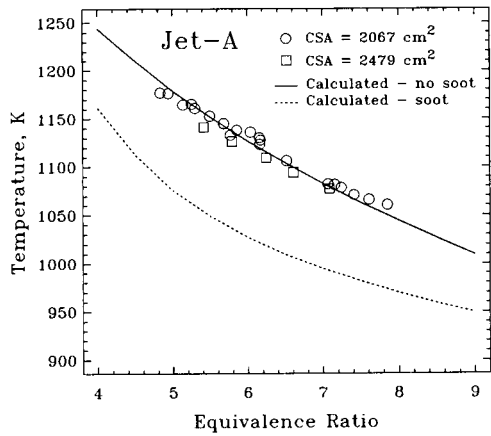


Figure 1 - Comparison of measured reaction temperatures with calculated equilibrium temperatures.

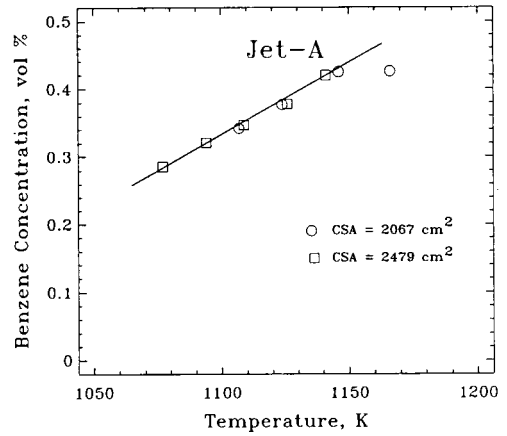


Figure 2 - Concentration of benzene in reaction products versus temperature for two catalyst configurations. (Note the amount formed is independent of the size of the catalyst bed.)

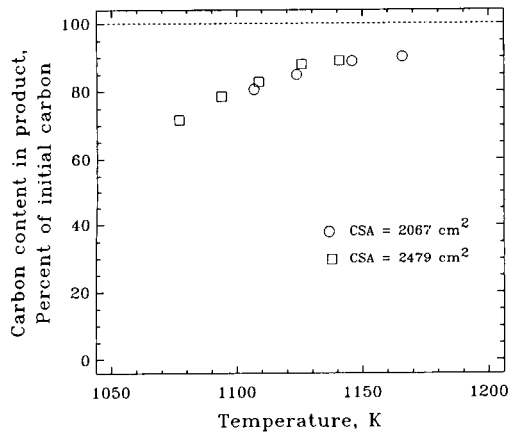


Figure 3 - Percentage of fuel carbon atoms found in gaseous reaction products.

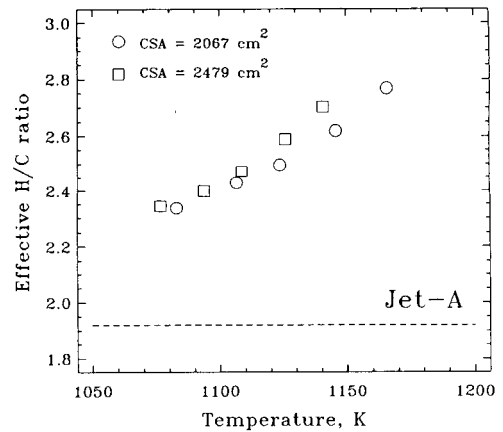


Figure 4 - Effect of removing some of the fuel carbon from the soot formation chain.

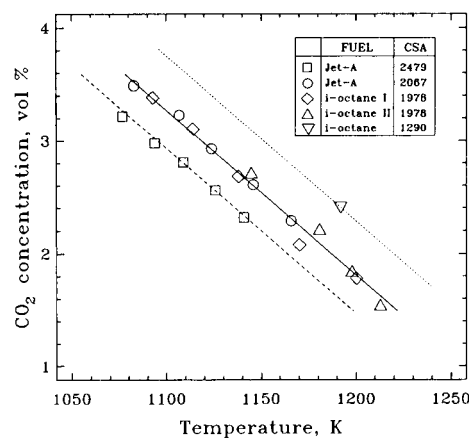


Figure 5 - Concentration of carbon dioxide versus temperature for three catalyst configurations and two fuels; (i-octane I and i-octane II have dwell times of 18 and 60 msec, respectively).

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