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Fuel Rich Catalytic Combustion—the First Stage of a Two-Stage Combustor

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FUEL-RICH CATALYTIC COMBUSTION - THE FIRST STAGE OF A TWO-STAGE COMBUSTOR

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ABSTRACT

An experimental program demonstrated that fuel-rich (φ = 4.8 to 7.8) catalytic combustion can be accomplished soot free as long as the combustion temperature is less than the temperature at the rich limit of combustion. Although soot was not measured directly, three pieces of data strongly suggest that it was not present: (1) the product gases were completely transparent and produced no radiation characteristic of soot, (2) measured reaction temperatures followed closely those calculated for equilibrium with no soot present, and (3) over 99 percent of the carbon was accounted for in the measured reaction products. Data for two catalyst configurations were taken along with gas samples at two locations downstream of the catalyst bed.

INTRODUCTION

Soot formation in gas turbine combustors is a problem that is expected to get worse as the quality of fuel deteriorates. This increased soot loading has adverse effects on liner temperature and fails to meet environmental standards. The mechanism of soot formation has received a great deal of attention recently; a number of studies have been undertaken to relate combustion parameters and fuel properties to the mechanism. Another approach to the problem of soot is a two-stage combustion system in which the first stage is a fuel-rich catalytic combustion fuel processor. Catalytic combustion can be soot free at equivalence ratios beyond the rich limit of combustion and can produce a fuel-rich gaseous mixture containing mostly small hydrocarbon molecules. This approach was prompted by the research of Street and Thomas (ref. 1), who studied the formation of carbon (soot) in premixed flames. They observed that carbon was not formed in flames when the gas mixture was being burnt near the rich limit of combustion. This same observation was made by Burgoyne and Neal (ref. 2). Street and Thomas suggested that the reason for this behavior was that rate-controlling step in the formation of soot has a high activation energy and thus carbon would form very slowly at these temperatures.

Recently an experimental program was undertaken to demonstrate that soot-free combustion of very fuel-rich gaseous mixtures is possible as long as combustion occurs at temperatures below the rich limit of combustion. This paper describes preliminary results of the catalytic combustion of iso-octane at equivalent ratios in the range φ = 4.5 to 8.0.

EXPERIMENTAL APPARATUS

A 5.1 cm insulated flow reactor (fig. 1) was built to experimentally demonstrate that soot-free fuel-rich catalytic combustion is feasible in a practical combustion system. Platinum-Palladium on a honeycomb substrate was selected as the catalyst because it is an excellent oxidation catalyst and the substrate has only a small pressure loss. Iso-octane was used as the base fuel because it is a pure single component liquid which was relatively inexpensive. A multitube conical fuel injector (ref. 3) produced a uniform gaseous mixture of fuel and air entering the catalyst bed. A simple gas sampling system (fig. 2) withdrew samples from two locations downstream of the catalyst bed. These were stored in 1 L stainless steel bottles and later analyzed on a gas chromatograph with a thermal conductivity detector. Thermocouple ports were located along the reactor for monitoring the temperature and an optical port was located 7.6 cm downstream of the catalyst for visual observations. The reactor was designed always to operate in the fuel-rich mode so that the catalyst was not destroyed by the temperature of a stoichiometric burn.

The catalyst was a 10 percent coating of Platinum-Palladium on 2.54 cm thick honeycomb substrates. Table I gives a description of the catalyst substrate and the four configurations used in the testing program. Results for the 1290 and 1900 cm^2 catalyst configurations will be presented in this report.

RESULTS AND DISCUSSION

In order to have uniform reaction occurring in the catalyst it is necessary to have a near homogeneous fuel-air gas mixture entering the bed. Temperature profiles measured diametrically across and reactor upstream of the catalyst demonstrated that good mixing and vaporization had been obtained. Figure 3 shows a comparison between the measured temperature and the theoretical one calculated for an air inlet temperature of 800 K and liquid iso-octane at 298 K. The agreement is excellent. Combustion temperature profiles across the outlet of the catalyst bed were much flatter than those for the vaporized fuel-air mixture upstream of the catalyst.

The first thing to be shown is that the reactions taking place in the catalyst bed produces a soot free product. Although direct measurements of soot were not taken, other measurements and observations strongly suggest that the gaseous products are soot free. These are (1) the reaction temperature, (2) visual observations of the gaseous products, and (3) the carbon atom balance across the catalyst bed.

The reaction temperature is the temperature measured 3.7 cm downstream of the catalyst bed. Figure 4 is a plot of the temperature as a function of equivalence ratio for two theoretical equilibrium calculations. The solid line shows the calculated temperatures when solid carbon is not a product while the dashed line shows the temperatures when it is a product. The difference in the temperature for the two calculations is about 150 K. The measured temperature agrees very well with the no soot calculations and strongly suggests the gases are soot free.

Visual observations of the hot reaction products 7.6 cm downstream of the catalyst bed show a completely transparent gas quite different from the luminous gas of the soot producing flame of a Bunsen burner. A small amount of light was observed through the window but this was found to emanate from the hot substrate of the catalyst bed. This is the second bit of information which tends to justify the no soot assumption.

The final piece of evidence is the carbon balance across the catalyst bed calculated from the measured reaction products. Figure 5 shows the ratio of the carbon out to the carbon in expressed as a percent plotted versus the measured reaction temperature for the data found in table II. The dashed line is the 100 percent line drawn across the plot. The fit of the data to the line is excellent and the average value of the ratio is 99.6 percent.

Having established that combustion was soot free, the effect on the product distribution of changing parameters such as catalyst surface areas and gas phase dwell time was investigated. Table III compares the temperature and product distribution at the same equivalence ratio for catalyst configurations having 1290 and 1900 cm^2 of surface area. As can be seen only small changes were observed for most of the products formed with the exception of hydrogen and water, which changed by more than a factor of two. For the smaller catalyst configuration 0.068 cm^3 of water per liter of product gas was collected (about 8.5 percent water as a product) and 5.35 mole percent hydrogen. The larger area produced only about 3.5 percent water but 12.11 mole percent hydrogen. Thus increasing the catalyst surface area increased the mole percent of hydrogen and decreased the fraction of water produced. This yields a more energy rich and clean burning product gas which is one of the objectives of this work. At present there is not enough data to determine what the mechanism might be for this conversion, but reformation of the hydrocarbons by water appears to be a good candidate.

Another difference in the data was the decrease in the temperature when the surface area was increased. At first glance this was unexpected and difficult to understand until it was noted that there was a significant difference in the volume of water collected for the two samples. The analysis of the reaction products have consistently shown that reactions involving oxygen lead ultimately to the formation of CO, CO_2, and H_2O. The heats of formation of these compounds at 1200 K are -27.2, -94.4, and -59.5 kcal/mole, respectively. Since the formation of CO is exothermic by only 27 kcal while water is exothermic by 59.5 kcal, its clear that the catalyst configuration producing the most water would have a higher temperature.

Table II compares the reaction products for the 1900 cm^2 catalyst configuration as a function of temperature (equivalence ratio) for samples taken at two locations along the drift tube. The first location (about 16 msec of gas phase reaction time) describes the product distribution resulting from surface and gas phase reactions. The second location (about 60 msec) gives some insight into the types of gas phase reactions occurring. The major products (>2 percent) are H_2, CO, CO_2, H_2O, CH_4, C_2H_4, C_3H_6, and C_4 hydrocarbons. Figure 6 shows the change in the mole percent of some of these compounds as the reaction temperature changes. The lines are eyeball fits to the data and were meant to demonstrate that the trends at the two dwell times are very similar even though the mole percents are difficult. The most significant changes in the two sets of data are the decrease in the mole percent of H_2, C_3H_6, and C_4 hydrocarbons and increase in CH_4 with increase in gas phase reaction time. This indicates that pyrolysis of the larger molecules is occurring followed by consumption of the molecular hydrogen by the hydrocarbon fragments. Figure 7 shows the carbon atom balance presented previously with data showing the amount of carbon present in molecules having two or fewer carbon atoms. It is clear that as the temperature increases pyrolysis of the larger molecules result in more of the carbon appearing in the smaller molecules, thus demonstrating the fuel processing mechanism.

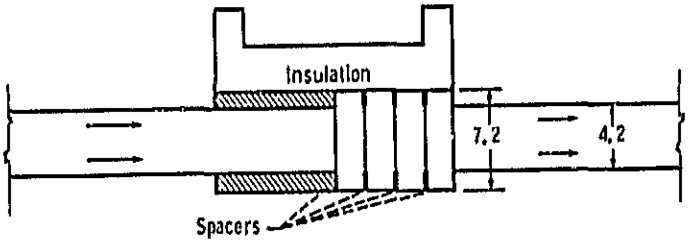
SUMMARY

Fuel-rich catalytic combustion producing a soot free pyrolyzed fuel appears to be a viable approach to a two-stage combustion system. Such a soot free process is feasible as long as the combustion temperature is less than the temperature at the rich limit of combustion. Although direct measurements of soot were not taken, three pieces of data strongly suggest that soot was not present. These are (1) the product gases are completely transparent and produce no radiation which would be characteristic of soot being present, (2) measured reaction temperatures follow closely those calculated for equilibrium with no soot present, and (3) over 99 percent of the carbon was accounted for in the measured reaction products. Analysis of gas samples for two catalyst configurations indicated that the mole percent of water, an undesirable product, can be greatly reduced by using more catalyst. Gas samples taken at two locations along the drift tube showed that the pyrolysis of the larger molecules produced mainly methane and ethylene.

REFERENCES

1. Street, J.C. and Thomas, A.: Carbon Formation in Pre-mixed Flames. Fuel 34, 4 (1955).
2. Burgoyne, J.H. and Neale, R.F.: Limits of Inflammability and Spontaneous Ignition of Some Organic Combustibles in Air. Fuel, 32, (1953).
3. Tacina, R.R.: Degree of Vaporization Using an Airblast Type Injector for a Premixed-Prevaporized Combustor. NASA TM-78836, 1978.

TABLE I. - DESCRIPTION OF CATALYST, CONFIGURATION, AND HOLDER



Monolith description		
Number	Cell density[a]	Surface area[b]
1	31	768
2	15.5	522
3	7.75	334
4	3.88	275

[a] Cells/cm^2.
[b] cm^2.

Area	Stacking order			
1290			2	1
1900	4	3	2	1

TABLE II. - REACTION PRODUCTS FOR CATALYST SURFACE AREA 1900 cm^2

Reaction temp., K	1200	1170	1138	1114	1093	1213	1198	1181	1145
Equivalence ratio	4.00	5.50	6.56	7.22	7.87	4.82	5.11	6.61	6.26
Moles fuel/min	1.266	1.465	1.751	1.937	2.099	1.265	1.359	1.468	1.666
Moles air/min	15.75	15.89	15.93	16.00	15.92	15.66	15.86	15.90	15.86
Dwell time, msec	15.9	16.1	17.3	18.5	19.5	59.6	60.3	60.9	64.2
Catalyst bed pressure drop, psia									
Upstream pressure	28.77	28.63	28.61	28.79	28.81	28.85	28.96	28.61	28.66
Downstream pressure	28.53	28.63	28.53	28.66	28.69	28.69	28.77	28.54	28.62
ΔP across bed	.24	.00	.08	.13	.12	.16	.19	.07	.04
Reactor temperature, K									
Preheat air	815	813	814	813	811	820	818	815	811
Vaporization	549	532	508	491	476	551	543	533	513
Gas sample concentrations, percent, groups 1 and 2									
Hydrogen	12.54	12.11	8.28	5.84	4.58	10.93	10.30	9.46	7.9
Oxygen	.73	.75	.79	.87	.92	.65	.63	.66	.69
Nitrogen	53.23	53.10	55.86	58.14	59.93	52.69	53.18	53.76	54.66
Carbon monoxide	17.41	16.32	13.28	11.49	10.33	17.43	16.64	15.47	14.58
Carbon dioxide	1.78	2.07	2.68	3.10	3.37	1.53	1.83	2.20	2.70
Methane	6.34	5.83	6.12	5.71	4.91	8.86	8.82	8.79	8.16
Acetylene	.15	.08	.06	.03	.04	.61	.40	.30	.14
Ethylene	4.08	3.21	4.20	3.29	2.00	4.62	4.85	4.65	4.43
Ethane	.42	.50	.59	.51	.48	.21	.29	.42	.55
Group 1 total	96.68	93.97	91.86	89.00	86.56	97.53	96.94	95.71	93.81
Propylene	1.66	2.57	3.61	4.13	4.13	.62	1.13	1.52	2.76
Allene	.24	.25	.22	.16	.13	.12	.16	.20	.29
Methyl acetylene	.20	.16	.12	.10	.10	.23	.26	.29	.26
C_4 hydrocarbons	1.42	2.77	4.05	5.59	6.17	.54	.26	.94	2.54
C_5 hydrocarbons	.06	.23	.48	.91	.95	.06	.04	.11	.31
Benzene	.12	.09	.10	.09	.09	.36	.39	.43	.35
Toluene	.03	.03	.04	.21	.00	.07	.08	.11	.13
Iso-octane	.00	.03	.24	.89	2.04	.00	.00	.00	.00
Total groups 1 and 2	100.42	100.10	100.74	101.26	100.26	99.53	99.26	99.32	100.47
Liquid sample data									
Liquid deposit cm^3/l	0.033	0.028	0.061	0.059	0.073	0.024	0.033	0.028	0.043
Density g/cm^3	1.00	1.05	1.01	1.05	1.03	1.01	1.02	1.00	1.02
pH	4.5	4.5 to 5	4.5 to 5	4 to 4.5	4 to 4.5	4.5	4.0	6.0	6.0

TABLE III. - REACTION PRODUCTS AND TEMPERATURE AS A FUNCTION OF CATALYST SURFACE AREA

Catalyst surface area, cm^2	1290	1900
Reaction temperature, K	1192	1170
Equivalence ratio	5.49	5.50
Reaction products, percent		
Hydrogen	5.35	12.11
Oxygen	.96	.75
Nitrogen	59.59	53.10
Carbon monoxide	13.14	16.32
Carbon dioxide	2.40	2.07
Methane	6.55	5.83
Acetylene	.16	.00
Ethylene	4.15	3.21
Ethane	.53	.50
Propylene	2.91	2.57
Allene	.36	.25
Methyl acetylene	.23	.16
C_4s	2.98	2.77
C_5s	.30	.23
Benzene	.17	.09
Toluene	.05	.03
Iso-octane	00	.03
Mole ratio across catalyst	1,200	1.347
Liquid, cm^3/liter	.068 (8.5 percent)	.028 (3.5 percent)

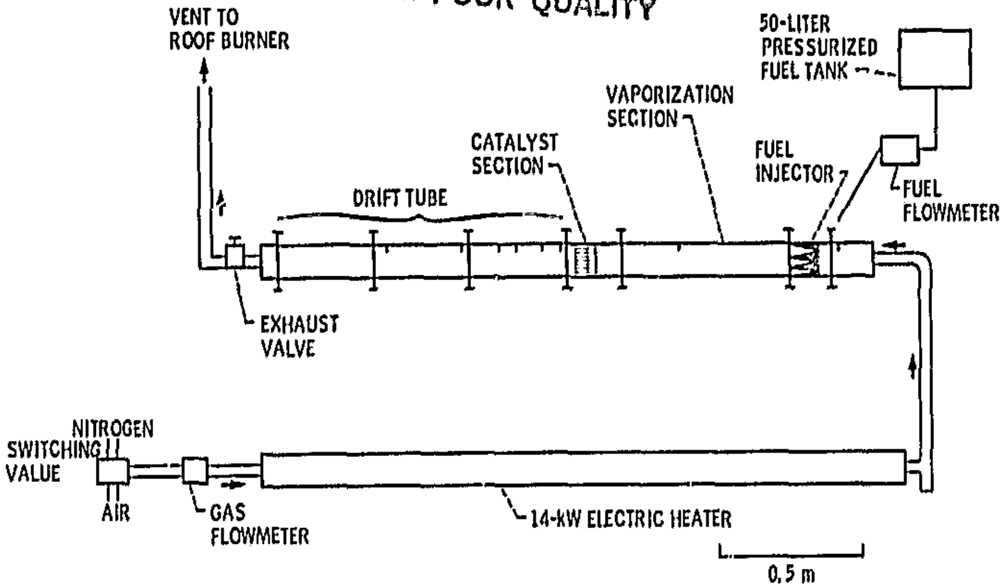


Fig. 1. - Schematic drawing of catalytic flow tube reactor.

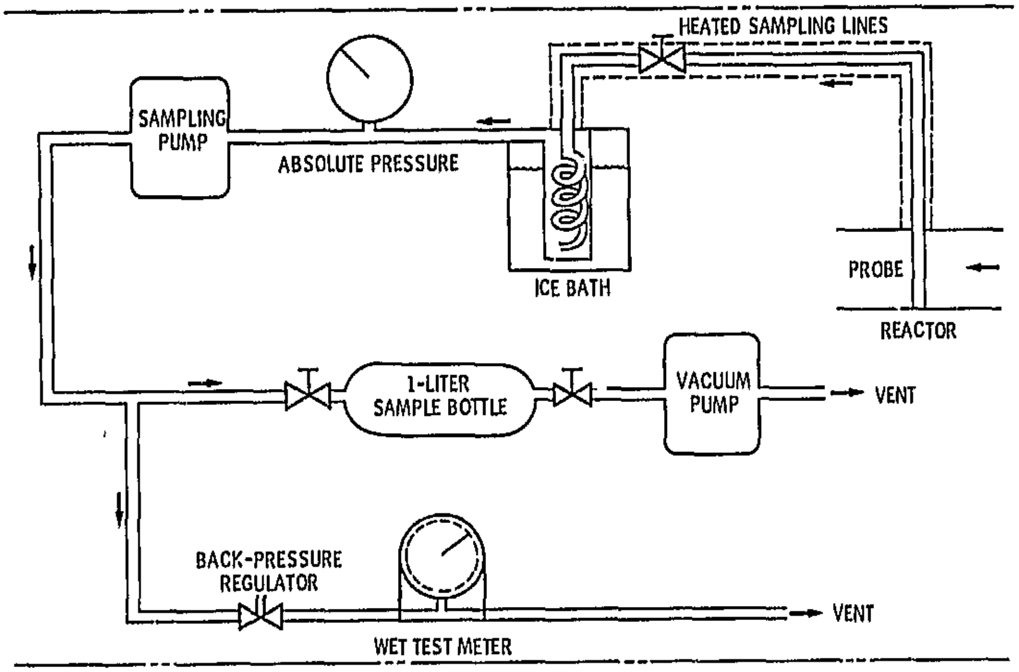


Fig. 2. - Sampling system.

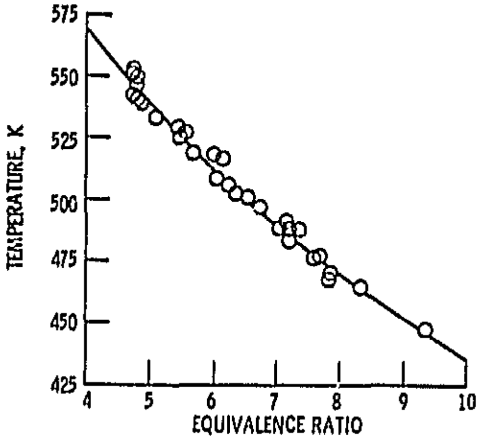


Fig. 3. - Comparison of measured vaporization temperature with theoretical temperature as function of equivalence ratio.

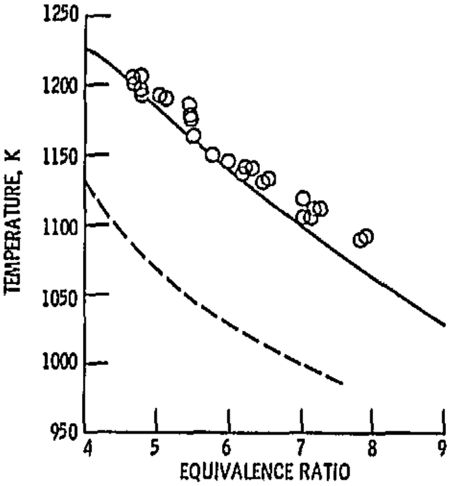


Fig. 4. - Comparison of measured reaction temperatures with calculated equilibrium temperatures. All reaction temperatures corrected to inlet conditions of calculation.

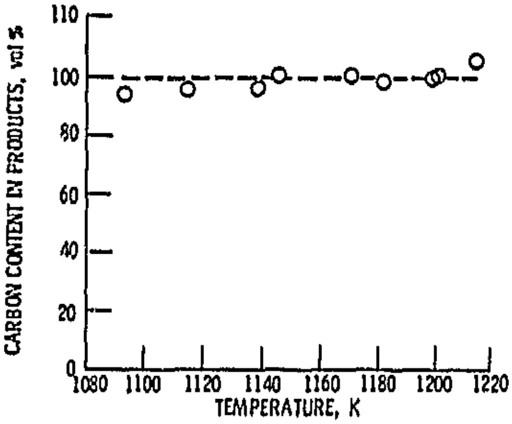
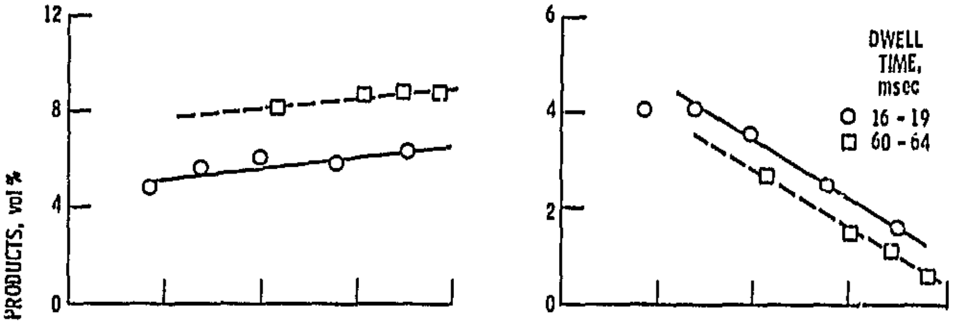
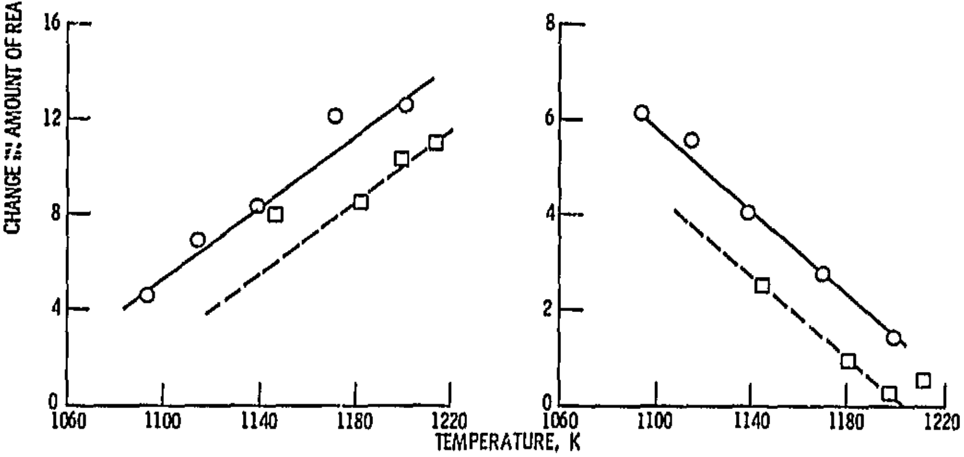


Fig. 5. - Carbon atom balance - percent of initial carbon in reaction products (table 2) as function of temperature.



(a) Methane.

(c) Propylene.



(b) Hydrogen.

(d) C_4 hydrocarbons.

Fig. 6. - Change in the percentage of reaction products as function of temperature and dwell time.

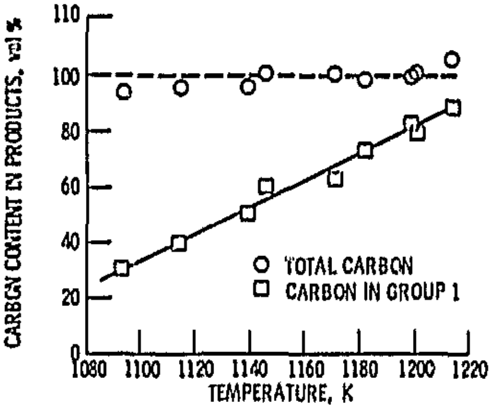


Fig. 7. - Carbon atom balance and percent of carbon found in molecules having two or fewer carbon atoms.

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16. Abstract
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Catalytic combustion; Fuel-rich combustion; Two-stage combustion system; Soot-free combustion

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