

Development of a Mixed Bed Catalytic System for Providing Endothermic Cooling with in-situ Generation of Hydrogen Gas for Scramjet Combustors

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Abstract— When hypersonic vehicles operate at Mach numbers 4-8, the temperature of the hot parts of the combustor would increase from approximately 1000K to 4000K, and the thermal management of such large quantities of waste heat becomes an important design consideration. Endothermic cooling provides an efficient method of cooling scramjet combustors by making use of certain endothermic reactions, like for example, the catalytic cracking reaction. Apart from providing endothermic cooling, this technology can also be used for the in-situ generation of hydrogen gas in the cracked fuel. The presence of hydrogen decreases the ignition time and ignition delay of kerosene and it also helps in anchoring flames at high speeds of airflow in a scramjet combustor. We have developed a mixed bed catalytic system consisting of molecular sieves and reformat-100 catalysts for providing endothermic cooling as well as the in-situ generation of hydrogen gas. The results of our findings are described in this communication.

1. INTRODUCTION

NAL is playing an active role in the strategically important area of hypersonic air breathing propulsion and NAL's contributions in this area are well known [1,2]. When hypersonic vehicles operate at Mach numbers 4-8, the temperature of the hot parts of the combustor would increase from approximately 1000K to 4000K due to the increase in the stagnation temperature of the inlet air, and the thermal management of such large quantities of waste heat becomes an important design consideration. Although thermal effects can be somewhat accommodated by improved materials and passive cooling, sustained hypersonic flight in the atmosphere requires a substantial heat sink. The fuel itself can be used as a coolant for the engine elements. Since preheating of the fuel is desirable before combustion, it can be circulated in heat transfer passages embedded inside the hot engine parts so that the

excess heat of the engines is removed by the fuel and in the process the fuel is also regeneratively preheated to the desired temperature. For example, fuels such as liquid hydrogen and liquid methane can contribute cooling effects only through the absorption of sensible and latent heat. Hence, it is important to investigate the ways and possibilities of increasing the effective heat absorption capacity of the fuel so that the fuel can achieve even more efficient cooling. Endothermic cooling provides an efficient method of cooling scramjet combustors by making use of certain endothermic reactions, like for example, the catalytic cracking reaction. The catalysts will be maintained at a chosen temperature and pressure, and the fuel will be made to pass through the catalytic bed. The fuel will absorb the heat from the catalytic bed and undergoes a catalytic cracking reaction on the catalyst surface. Whenever the fuel undergoes such a catalytic reaction it absorbs upto five times more heat than what it does when there are no catalysts. What is more, after endothermic heating, the long polymeric chains of the fuel decompose into short simple one, and the fuel becomes a better fuel with as much as 10 percent more energy content than the chemical energy of the unheated original fuel. At the Propulsion Division, NAL, the concept of endothermic cooling has been experimentally demonstrated using aviation kerosene as the fuel.

1.1. The need for the addition of hydrogen to kerosene combustion

Hydrocarbon fuels like kerosene are attractive candidates for fuelling scramjet engines in the Mach number (≤ 8) flight regimes due to their significant advantages in terms of energy density and handling issues, as compared to hydrogen. However, there are also shortcomings regarding

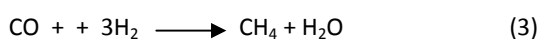
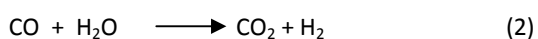
the use of hydrocarbon fuels in supersonic combustion. Notably their relatively long ignition delay times far exceed the available residence time of air flow through the combustors. Moreover, liquid hydrocarbons require rapid vaporization before mixing and subsequent combustion. Considerable research has been devoted to the improvement of hydrocarbon combustion in supersonic flow.

For the requirement of anchoring flames at very high speeds of airflow in a ramjet/scramjet combustor, it is frequently desired to establish combustion zones beyond the traditional boundaries of rich/lean limits and aerodynamic limits. It is well known that free radicals (FR) play very important roles in the initiation, propagation branching and termination of combustion reactions. The unavailability of key free radicals at requisite sites and times is believed to be the cause of flame extinction.

Many studies have demonstrated that a hydrogen pilot flame can provide a high temperature reacting gas with a large radical pool so that the subsequent hydrocarbon ignition is enhanced. The presence of hydrogen in the pilot flame has been shown to considerably decrease the ignition delay of hydrocarbon fuels and to also firmly stabilize the flame at high flow velocities. A catalytic reaction known as steam reformation can be used for the introduction of hydrogen in the cracked components of a fuel.

1.2. Steam Reformation reaction for the in-situ generation of hydrogen

The reaction of hydrocarbons with steam on suitable catalysts is called steam reforming (STR). The reactions occurring are represented by the three reactions given below. Generally, the STR process involves three reactions, namely the splitting of hydrocarbons with steam (eq. 1), a water gas shift (WGS) reaction (eq. 2) and by the formation of a smaller hydrocarbon, for example, methane (eq.3).



However, for kerosene - a mixture of wide variety of hydrocarbons-, the steam reformation reaction will produce a range of products. The catalysts used for the steam reforming of hydrocarbons are based on nickel. To prevent coke formation, nickel is coated on basic supports like

MgAl₂O₄, CaAl₂O₄, BaAl₂O₄, SrAl₂O₄, ZrO₂Al₂O₄ or Al₂O₃ containing rare earth oxides. In the present investigation we have employed a commercial catalyst sold in the brand name Reformax 100.

1.3. Literature information on the development of endothermic fuels

Reports on the development of endothermic fuels are seen in literature as early as in 1962 [3]. The development of endothermic fuels has been reviewed. [4,5,6]. There are several types of endothermic reactions possible during regenerative cooling. Dehydrogenation, cracking (thermal or catalytic) and steam reforming are the most important reactions that are being investigated in literature. A large number of such reactions have been reported by Lander and Nixon [4]. For example, naphthenic (cycloparaffin) fuels can be dehydrogenated to an aromatic and hydrogen. A classic example is the dehydrogenation of saturated ring compounds like methyl cyclohexane and decalin to form aromatics and this has been successfully demonstrated by Nixon and coworkers [7] and Lipinski et al [8]. This reaction is shown to provide a heat sink of 2190 kJ/kg of the fuel. Petley and Jones used the catalytic endothermic reaction of methylcyclohexane as a heat sink for the thermal management for a Mach 5 cruise aircraft [9]. Huang, Sobel and Spadaccini demonstrated that hydrocarbons fuels such as JP-7, JP-8 + 100, and JP 10 can undergo endothermic reactions and provide sufficient heat sink, and demonstrated the endothermic potential of these fuels for hypersonic scramjet cooling. A high pressure bench scale reactor was used by them to determine the overall heat sinks, endothermic reforming products and coking rates for the fuels [10]. Sobel and Spadaccini carried out investigations on n-heptane and Exxon Norpar 12 (an inexpensive mixture of decane, undecane dodecane and tridecane) to arrive at practical endothermic fuels with a high cooling capacity and performance and handling characteristics very similar to current aircraft fuels [11].

Reports are also available in literature regarding the development of new catalysts for the catalytic cracking of hydrocarbon fuels. O'Rear Dennis et al reported a method for upgrading the hydrocarbon fuels by contacting the product stream with an acidic olefin cracking catalyst (eg ZSM-5 or ZSM-4 zeolite) at 260-454°C and 68 atmosphere pressure. The product has been reported to be rich in lighter olefin fractions [12]. Yurkina et al reported that kerosene fractions can be hydrogenated by passing over a Pd/alumino-silicate catalyst. Jet fuels of improved properties containing ≤5% aromatics were obtained [13].

Brabbs, Theodore et al reported a catalytic bed for the fuel rich catalytic combustion of Jet A fuel at equivalence ratios of 4.7 to 7.81 which yielded combustion temperatures of 1250 to 1060 K. No soot was visually observed in their combustion..However the paper does not give any detail regarding the nature of the catalyst used [14].

The Propulsion Division, NAL has developed a mixed bed catalytic system consisting of molecular sieves and reformax-100 catalysts for providing endothermic cooling as well as for the in-situ generation of hydrogen gas. The results of these findings are described in this communication.

2. EXPERIMENTAL DETAILS

In order to carry out the catalytic cracking reaction, a high pressure, high temperature catalytic reactor was designed, fabricated and installed by M/s High Tech Engineering, Pune. This reactor can heat kerosene upto 450°C and maintain a pressure upto 10 atm. Fuel pump and mass flow controllers precisely control the amount of the fluid which enters the reactor tube. Fig.1 shows the schematic diagram of the reactor tube. At the centre of the reactor tube is situated another inner tube, the thermo-well and the temperature of the reactor tube is precisely controlled by three thermocouples inserted at three different locations inside the thermo-well. The SCADA computer software automatically records the change in temperature observed by these three thermocouples. Another thermocouple is positioned close to the external skin of the reactor tube and the temperature of the reactor tube is maintained at the set value by sensing the skin temperature with the help of this thermocouple. The reactor also consists of a preheater. In this set of experiments, the preheater was maintained at 375°C, the nitrogen flow rate was maintained at 90 ml/min, and the kerosene flow at 4.5 ml/minute.

The reactor tube was filled with the properly activated cracking catalyst. In this investigation, sodium aluminium silicate (molecular sieves), Reformax-100 and ZSM-5 were used as the catalysts. The gas chromatographic measurements were made using a Thermofisher (Chemito) Gas chromatograph model GC 8610.

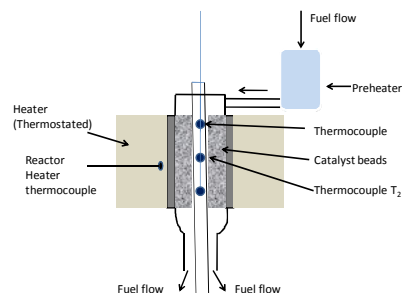


Fig. 1. Schematic diagram of the cross-section of the reactor

The carrier gas is nitrogen and its flow is arbitrarily fixed at 90 ml /min in this set of experiments. The catalytic reaction is a vapour phase reaction, and in order to ensure a uniform gaseous mixture, the temperature of the preheater is maintained at 648K. The experiment was conducted when the temperature of the thermocouple T_2 reached ≈ 626 K.

3. RESULTS AND DISCUSSION

3.1. Cracking of kerosene over a mixed bed column

Earlier it was observed that kerosene could be catalytically cracked by passing through a column of molecular sieves as the catalyst. The presence of an additive ZSM-5 improves the cracking process. Therefore a mixed catalytic bed was prepared wherein the bottom portion of the reactor tube was filled with Reformax-100 catalyst and the upper portion with a mixture of molecular sieves and ZSM-5 as the catalysts. Kerosene saturated with water was used as the fuel, and the reactor temperature was maintained at 648K, and the experiment started when the temperature of the thermocouple T_2 reached 626K.

Fig.2 show the variation in temperature with time when pure nitrogen gas at 90 ml/min (curve 1) and that of a mixture of nitrogen gas (90 ml/min) and steam (4.5 ml/min) (curve 2) were passed through the reactor. It is seen that when nitrogen gas alone is passed through the reactor bed, the temperature of T_2 fell from 626 K to 610 K, a fall by 16 K. When nitrogen plus water mixture was passed through the system the temperature fall was from 626K to 608 K, a fall by 18 K. The heating of the reactor was temporarily switched off i.e., during the above period of measurement. The temperature of the reactor tube was once again heated

and when T_2 reaches 626K, the experiment of the next flow was carried out.

Fig.2 (curve3) shows the results obtained when a mixture of nitrogen gas and kerosene was passed through the reactor tube. The preheater ensures that all the kerosene is present as a gas and a uniform mixture of gases enter the reactor tube. As the gases pass through the heated catalyst particles in the reactor tube, the catalytic cracking reaction takes place. i.e., kerosene absorbs the heat from the catalyst particles and splits into smaller hydrocarbon molecules. Because of this heat absorption by kerosene, the temperature of thermocouple T_2 drops from 626K to 514K, a drop by 112 K. Such a drop in temp is due to the occurrence of the endothermic catalytic cracking reaction.

Time (min)	Temperature of T2 (K)		
	Nitrogen alone	Nitrogen + Water	Nitrogen +Kerosene
0	626	626	626
1	625	627	627
2	627	630	626
3	626	631	626
4	631	630	580
5	631	629	571
6	631	630	574
7	630	628	561
8	629	629	545
9	630	628	541
10	628	626	537
11	626	625	533
12	624	623	530
13	622	621	529
14	621	619	528
15	619	616	526
16	617	615	524
17	615	613	528
18	613	611	521
19	612	609	521
20	610	608	514

Table 1 Variation of temperature with time for nitrogen flow, nitrogen plus water flow and nitrogen plus kerosene flow over the catalytic bed in the reactor

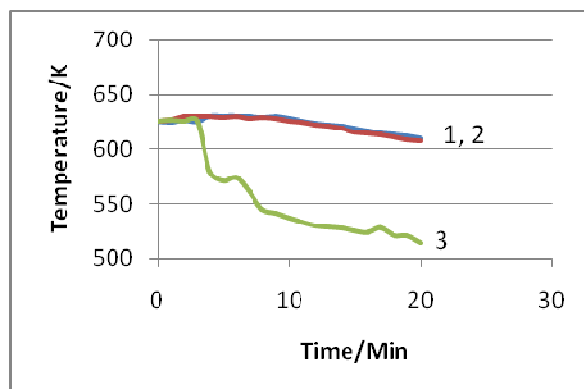


Fig. 2 Experimental demonstration of endothermic cooling. Temperature variation with time for the flow of (1) 90 ml/min nitrogen alone; (2) 90 ml/min nitrogen plus 4.5 ml/min water; (3) 90 ml/min nitrogen plus 4.5 ml kerosene.

3.2. Gas chromatographic investigations of cracked kerosene samples

Gas chromatography can be used as an important diagnostic tool for monitoring the catalytic cracking process. The difference in the gas chromatograms (GC) of pure and cracked kerosene provides valuable information regarding the cracking process that has taken place.

Kerosene distills in the range of approximately 478K to 533K and kerosene contains a very large number of hydrocarbons and other organic compounds in much smaller amounts. As kerosene (a mixture of a large number of hydrocarbons) passes through the GC column the individual components separate into different groups and each group leaves the column at different times. Each peak corresponds to the presence of a group of substances. Hydrocarbons with smaller chain length are the first to leave the column and they give rise to the first peak in the GC. The retention time of this peak will be the smallest. Their peak height and area will be proportional to their respective concentration in the original kerosene. In the same way, as the chain length of the hydrocarbon increases, the retention time of their GC peaks will also increase and their peak height and area will be a measure of their relative concentration in kerosene. Fig 3 illustrates this point. Fig.3 is the GC of a 1:1:1:1 molar mixture of n-hexane, iso octane, n-decane and n-dodecane.

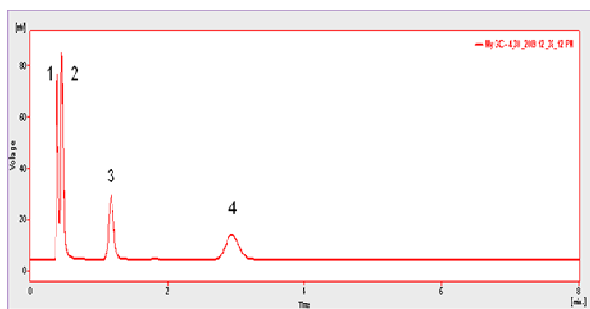


Fig.3 GC of 1:1:1:1 equimolar mixture of n-hexane, iso octane, n-decane and n-dodecane.

Peak No	Reten. Time [min]	Area [mV.s]	Height [mV]
1	0.39	148.366	72.443
2	0.46	224.817	81.207
3	1.18	139.575	25.273
4	2.94	134.5	9.8

Table 2 Peak location, area and height of GC peaks of n-hexane (1), iso octane (2), n-decane (3) and n-dodecane (4).

Table 2 shows the peak location, area and height of these GC peaks. The first peak at 0.39 min was due to n-hexane, the next one at 0.46 min was due to iso octane, the peak at 1.18 was due to n-decane and the last peak at 1.83 min was due to n-dodecane. The shift in peak height with increase in carbon number of the hydrocarbon is clearly illustrated in this GC.

In the case of catalytic cracking the longer chain length hydrocarbons will be converted into smaller chain length hydrocarbons. Therefore when the GC of cracked kerosene was recorded, depending upon the extent of cracking, there should be an increase in the population of shorter-retention-time peaks and there should also be a decrease in the population of the longer-retention-time-peaks. Hence by careful comparison of the GCs of the cracked and uncracked kerosene samples, valuable information could be obtained regarding the catalytic cracking process.

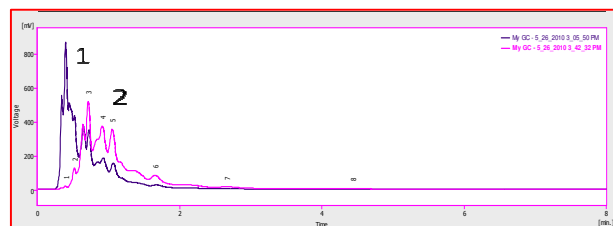


Fig.4. Gas chromatograms of (1) cracked and (2) uncracked kerosene fractions

Fig 4.1 shows the GCs of a kerosene fraction wherein no catalytic cracking was performed and Fig.4.2 that of the cracked kerosene sample. It is seen that the peak area in the residence time range of 0-1 min show an increase in the case of the cracked kerosene fraction. Quantitatively this result is summarized in Table 3.

Peak No	Peak areas for each retention time/ min					
	1	2	3	4	5	6
Retention time/ min	0.390/ 0.393	0.513	0.643	0.710	0.907	1.047 / 1.060
Peak area of uncracked kerosene/ mV.s	82.8	473.3	---	3996.1	3746.0	5047.2
Peak area of cracked kerosene/ mV.s	7578.0	---	5286.8	-----	---	2086.0

Table 3 Comparison of peak areas of GC in the retention time 0-1 min

A look at the data in the table shows that the kerosene peak at 0.390 minutes has increased by many – fold in the cracked kerosene sample (82.8 mV.s vs 7578 mV.s). The combined peak heights of the first three peaks (i. e. upto the residence time 0.643 minutes) in the case of uncracked kerosene is 556.1 mV.s whereas in the case of the cracked kerosene this value is 12864.8 mV.s, an increase by a factor of 23.13. This is a definite proof for the occurrence of the catalytic cracking reaction.

3.3. Investigations for the presence of hydrogen molecules in the cracked fuel

As the fuel passes through the Reformax-100 catalyst beads present in the mixed bed system, as a result of the steam reformation reaction taking place in the reactor tube, hydrogen will be released as one of the products of the reaction. The emitted gaseous products

from the reactor were collected using a gas sampling bag and subjected to gas chromatographic investigations. For detecting hydrogen the recommended gas chromatographic column is a dual column consisting of 10% Apiezon L and molecular sieves. The detector used was a thermal conductivity detector.

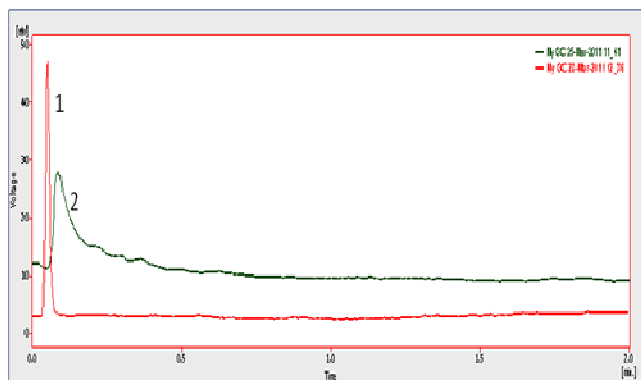


Fig.5. GCs of standard hydrogen (1) and the emitted gas (2) from the catalytic reactor.

Fig.5.1 shows the GC of 0.3 ml of pure hydrogen as well as that of the cracked kerosene vapours. The data are given in Table 3.

Description	Peak location/ min	Peak area/ mV.s	Peak height/ mV
Pure hydrogen	0.050	55.8	44.1
Hydrogen present in the cracked kerosene vapours	0.080	57.9	12.7

Table 4. GC peaks of pure hydrogen and that of hydrogen present in cracked kerosene vapours.

It is seen that a single peak was obtained for hydrogen at 0.050 (residence time) and the peak area was evaluated to be 55.8 mV.s. Fig.5.2 shows the GC when 1.0 ml of the gas sample collected after kerosene had passed through the mixed bed column was injected into the GC. Again a single peak is obtained at a residence time of 0.08 minutes with a peak area of 57.9 mV.s. The appearance of this GC peak in the kerosene vapours clearly indicated the presence of hydrogen in the vapours. A comparison of peak heights show that pure kerosene gave a peak height of 44.1 mV and that of the cracked kerosene vapour 12.7 mV. Though the location of the peak has been shifted to the

right and the peak broadened, this peak of kerosene vapour obtained in a column of Apiezon L and molecular sieves with TCD as the detector is definitely attributed to the presence of hydrogen in the kerosene vapours. The shift in the peak location and broadening of the hydrogen peak were due to the chemical interference of the other constituents of the vapour on the hydrogen peak.

The endothermicity of the reaction has also been worked out. The catalytic cracking reaction is a vapour phase reaction. The specific heat of kerosene vapour is 1.6 kJ/kg.K, that of nitrogen gas is 1.054 kJ/kg.K and the heat capacity of the combined catalytic bed has been worked out to be ≈ 1.2 kJ/kg.K. As kerosene passes through the catalytic bed, the temperature of the thermocouple T_2 , positioned at the center of the reactor tube falls from 626 K to 514 K. For the experimental conditions employed, the endothermic cooling has been evaluated to be about 0.82 MJ.

5. Conclusion

A mixed bed catalytic reactor was developed to address the twin issues of providing endothermic cooling to scramjet combustors by cracking kerosene to simpler molecules and the in-situ generation of hydrogen which helps in anchoring hydrocarbon flames. However, some more important parameters like influence of flow rate and residence time, wall heat flux rate etc have to be studied and catalytic cracking core designed and fabricated. When this catalytic cracking core is integrated with the scramjet combustor, it will provide an efficient cooling for the combustor. The work is in progress.

6. Acknowledgement

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