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Polycyclic Alkanes Based High Density Hydrocarbon Fuels Preparation and Evaluation for LFRJ Application

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Abstract

Two polycyclic alkanes based high density thermally stable hydrocarbon fuels DPCR-2 and DPCR-3 were prepared from processed special petroleum fraction DPCR-1 for LFRJ application. These fuels were subjected to detailed physio-chemical characterization and found to have improved density (0.844 to 0.846 g/cc @ 20 °C), low aromatic content (<5%), low sulphur content and high flash point (> 62 °C). These newly developed fuels exhibits better properties than aviation turbine fuel (ATF/Jet A-1). The theoretical as well as experimental ramjet performance such as characteristic velocity and chamber pressure for both the fuels are higher than ordinary Jet-A1 and comparable with similar high density T-6 fuel. These fuels are showing superior storage characteristics in elastomeric fuel system such as acrylonitrile butadiene rubber used in missile applications. DPCR-2 and DPCR-3 developed for LFRJ application are found to be very promising in terms of performance, density, availability and cost effectiveness in comparison with Jet A-1 fuel which is presently being used in a number of air breathing propulsion systems.

Key words: Hydrocarbon fuels, Density, Jet A-1, RJ-4, Ramjet, Static test

1. Introduction

Missiles are typically volume limited, rather than weight limited, so that fuel volumetric energy is a key parameter. The reason is that such missiles are always volume limited with

their fuel tanks designed to be as small as practical so the remaining space can be allocated for ordinance, electronics and other missile components¹⁻³. A comparison of readily available liquid fuels suitable for use as air breather fuels indicates that hydrocarbons exhibit the highest heat of combustion. High density and thermally stable hydrocarbon fuel are in great demand for RAMJET and SCRAMJET applications⁴⁻⁸. Liquid fuel based ramjet (LFRJ) propulsion system is preferred for air breathing engines as it offers higher payload and range. For a given range performance, ramjet propulsion results in significant weight reduction in comparison with either solid or liquid propulsion system which exhibit specific impulse in the range of 250 to 300 s⁹. In order to increase thrust force of rockets and jet engines, fuel having high combustion energy as much as possible per unit volume, i.e., liquid fuel having high density and high heat of combustion is required for fueling ramjet propelled limited volume missile systems. Furthermore, since liquid fuel is supplied to combustion chambers through pipes, or employed for flying objects in ultrahigh altitude region at low temperature beyond the need for a fuel of high energy content in order to maximize range performance of the missile, there are other critical requirements depending on the manner in which the missile is to be deployed. For instance in airborne deployment, the fuel must exhibit a combination of suitable viscosity, very low freezing point, easy ignitability in terms of its flash point and be acceptably fluid at the low temperatures encountered¹⁰⁻¹¹. Ramjets must meet the requirements of high volumetric heating value, low viscosity, excellent combustion characteristics, low toxicity, low cost, low volatility, low freezing point and flash point no lower than 60 °C. Combustion value, density and cost are primary factors in choosing a fuel for ramjet application¹²⁻¹³. Thus, over the years, there has been a major focus to seek fuels with increasingly high density content concurrently with the development of ever more versatile systems.

A high density fuel of the foregoing type does not occur in nature but rather must be chemically synthesized or blended. A number of synthesized high energy hydrocarbon based fuel blends such as hydrogenated norbornadiene (RJ-5), hydrogenated and isomerised dicyclopentadiene (JP-10) and mixture of these two with methylcyclohexane (JP-9) have been developed in the recent years for air breathing engine¹⁴⁻²⁰. These polycyclic alkanes based high energy fuels meet most of the requirements such as low flash point, low viscosity, low freezing point and high densities²¹. However, JP-10 fuel is very expensive and has relatively higher viscosity, low flash point, whilst the viscosity of liquid fuel RJ-5 is high enough to limit the systems effectiveness in which it is employed and also cost is extremely

high because synthesis of the fuel is difficult, besides a raw material of norbornadiene is insufficiently supplied. Also, most of these synthetic fuels are unsuitable for operation at $-54\text{ }^{\circ}\text{C}$. Because of their non-availability in sufficient quantities and cost factors involved in large scale production these fuels were having restricted use. Hence, Jet A-1 is still preferred due to its easy availability, appropriate boiling, freezing and flash points, without any handling problems. It also exhibits reasonably good calorific value (approx. $10,250\text{ cal/gm}$) and Isp (approx 1200 seconds) at A/F (ranging between stoichiometry and 20) and thus is a proven fuel. Jet A-1, however, exhibits low density, high aromatic content (allowed up to 25%) and comparatively low Isp value and needs to be replaced with more energetic fuel to achieve higher specific and density impulse values and increased range with reduction in weight.

Based on these shortcomings, it is clear that development of new improved fuels would constitute a critical technological enhancement in the field of chemical propulsion. In this work, we have developed two polycyclic alkanes based high density thermally stable hydrocarbon based fuel blends and evaluated its performance parameters. This paper discusses formulation of these fuels, physio-chemical characterization and its swelling studies with NBR rubber. Both theoretical and experimental ramjet performance of these fuels has also been investigated under similar conditions and compared with T-6 fuel²².

2. Experimental

2.1. Materials

Processed hydrocarbon base fuel (DPCR-1) was purchased. JP-10 was supplied by DMSRDE, Kanpur, India. Dimethyldicyclopentadiene (DMCPD) was obtained from TCI Chemicals, India and methanol from Finar Chemicals, Ahmedabad, India. Decalin was procured from Loba Chemie Pvt Ltd., Mumbai, India. 5% Palladium catalyst on activated carbon was procured from Arora-Matthey Ltd., Kolkata, India. IOLAR Grade-II Hydrogen gas was used for hydrogenation of DMCPD. Nitrile rubber compound sheet procured from RAP, Vijayawada, India is used.

2.2 Preparation of base fuel DPCR-1

The special petroleum fraction is processed in de-aromatisation by continuous deep saturation/hydrogenation followed by de-waxing to obtain base fuel DPCR-1. The initial

boiling point of DPCR-1 is 175 °C. DPCR-1 is modified by carrying out distillation up to 195°C to remove low boiling fractions to prepare fuel blends DPCR-2 and DPCR-3.

2.3 Preparation of DPCR-2

Fuel blend DPCR-2 was prepared by addition of 16 mL of JP10 and 20 mL of decalin to the 64 mL of modified DPCR-1 fuel. The theoretical and experimental densities of the fuel DPCR-2 was 0.841 g/cc and 0.846 g/cc at 20°C respectively.

2.4 Preparation of RJ-4

A solution of dimethylcyclopentadiene dimer (4 Litres), ethyl acetate (2 Litres) and 500 g of 5% Pd-on-carbon catalyst dispersed in 2 Litres of ethyl acetate was taken in a properly cleaned and dried 20 Litres high pressure reactor. The inside air content was purged out three times by filling hydrogen gas and vented carefully. The reactor was pressurized to 7 bar with hydrogen and leak check was carried out. Stirring was carried out at 500 rpm and reactor was heated to 50 °C temperature. The reaction was allowed for 24 hours and the completion of reaction was initially checked by thin layer chromatography (TLC). After the completion of the reaction, the reaction products are filtered to remove catalyst, transferred to a 20 Litres round bottom flask and ethyl acetate was removed by rotary vacuum evaporation. The liquid product, hydrogenated dimethylcyclopentadiene dimer (RJ-4) was analyzed by FTIR, CHNS elemental analysis, ¹H NMR, ¹³C NMR and ESI-MS techniques.

2.5 Preparation of DPCR-3

Fuel blend DPCR-3 was prepared by addition of 16 ml of RJ-4 and 20 ml of decalin to the 64 ml of modified DPCR-1 fuel. The theoretical and experimental densities of the fuel blend DPCR-3 is 0.842 g/cc and 0.844 g/cc @ 20°C respectively.

2.6 Swelling studies

Samples of 25 mm x 25 mm of weight approx. 1 g (W_1) were cut from the central portion of the moulded NBR sheet and allowed to swell in fuel blends DPCR-2 and DPCR-3 at ambient conditions. After 72 h, the swollen samples were removed, wiped dry and weighed again (W_2). The degree of swelling is calculated using the following equation:

$$\text{Swelling (\%)} = \frac{W_2 - W_1}{W_1} \times 100$$

Density, tensile strength, elongation, modulus, shore hardness were calculated before and after swelling.

2.7 Predictive performance

Predictive performance of fuels DPCR-2 and DPCR-3 in ramjet mode was determined using NASA CEC-71 code and compared to T-6 fuel. Heat of formation data calculated from heat of combustion value is used for the theoretical performance evaluation. Performance parameters were obtained with varying air to fuel (A/F) ratio.

2.8 Static test performance

2.8.1 Static test on DPCR-2 at ambient temperature with burn time 19 sec

The LFRJ combustor of dia 178 mm was operated at ambient temperature with air as an oxidizer. The fuel used was DPCR-2, at a weight ratio of air to fuel of 14.65 to 193. The pressure measured in the combustion chamber was 2.55 to 4.94 bar. The density of fuel DPCR-2 is 0.846 g/cc. The air flow rate is 7 kg/s corresponding to Mach 2, sea level and fuel DPCR-2 flow rate is 466 g/s to 80 g/s. The A/F range is 14.65 to 193 and heater temperature is 540 K. The motor was operated for 20 seconds.

2.8.2 Static test on DPCR-3 at ambient temperature with burn time 20 sec

The fuel blend used was DPCR-3, at a weight ratio of air to fuel of 14.4 to 203. The pressure measured in the combustion chamber was 2.8 to 4.93 bar. The density of fuel blend DPCR-3 is 0.844 g/cc. The air flow rate is 7 kg/s corresponding to Mach 2, sea level and fuel DPCR-3 flow rate is 466 g/s to 80 g/s. The A/F range is 13.54 to 91.23 and heater temperature is 540 K. The motor was operated for 20 seconds.

2.8.3 Static test on T-6 fuel at ambient temperature with burn time 20 sec

The fuel blend used was T-6, at a weight ratio of air to fuel of 14.5 to 193. The pressure measured in the combustion chamber was 2.7 to 5.01 bar. The density of T-6 fuel is 0.840 g/cc. The air flow rate is 7 kg/s corresponding to Mach 2, sea level and T-6 fuel flow rate is 466 g/s to 80 g/s. The A/F range is 14.8 to 189 and heater temperature is 540 K. The motor was operated for 20 seconds.

3. Instrumentation

FT IR spectra were recorded using Perkin Elmer Spectrum One spectrometer. The samples were examined with a spectral resolution of 4 cm^{-1} and scanned from 400 to 4000 cm^{-1} in the transmission mode. ^1H and ^{13}C NMR spectra were measured on an NMR spectrometer

working at 400 MHz (^1H frequency) of make Bruker Avance III (400 MHz). The mass spectra were recorded on Varian 410 prostar LCMS-MS using electrospray ionization method. The elemental analyses were performed on ThermoQuest microanalysis and Flash EA 1112 series CHNS elemental analyser.

Physico-chemical characteristics of fuel formulations DPCR-1, DPCR-2 and DPCR-3 were carried out as per ASTM test methods. Calorific value of the blend was determined using bomb Parr calorimeter model 6200. The mechanical properties such as the tensile strength, modulus and elongation at break of the NBR swollen and unswollen samples were carried out on dumbbell-shaped samples using a DAK Systems INC, model no: 9052 Universal testing machine (UTM) operated at room temperature with a gauge length of 25 mm and a crosshead speed of 500 mm min⁻¹ as per the ASTM D 412. The tensile values reported herein are the average of the results of tests run on at least six specimens. The hardness was determined with a Wallace model 1 HT 16A digital Shore-A durometer as per ASTM D 2240.

4. Results and Discussions

The suitable liquid hydrocarbon base fuel DPCR-1, a highly refined kerosene is produced from special petroleum fraction (light normal paraffin) which is similar to Jet A-1. DPCR-1 fuel has advantages in number of aspects like low aromatic and total sulphur content etc. The initial boiling point of DPCR-1 fuel is 175 °C. Distillation has been carried out till 195 °C in order to remove low boiling fractions. The properties of hydrocarbon fuels Jet A-1 and fuel DPCR-1 is compared in Table 1.

4.1 Formulation of fuel DPCR-2

To develop a thermally stable jet fuel an optimum chemical composition is essential to meet performance requirements. Initial boiling point of DPCR-1 fuel is 175 °C and the density of distilled DPCR-1 fuel is 0.804 g/cc at 20°C. The second component of the fuel blend is JP-10, which is a C₁₀ cyclic hydrocarbon, and contains >98.5 Wt % of exo-tetrahydrodicyclopentadiene (exo- THDCPD). The improvement of density, freezing point, net heat of combustion and is done by the addition of JP-10. The requisite initial and final boiling point requirements is imparted to the blend by the addition of decalin as a third component which is a high boiling hydrocarbon. Chemical structures of JP 10 and decalin are given in Figure 1. The chemical composition of DPCR-2 fuel is given in Table 2.

4.2 Formulation of fuel DPCR-3

JP-10 is a synthetic fuel with limited availability and is very expensive. Hence, alternate fuel blend DPCR-3 is developed by using RJ-4, which is a mixture of C₁₂ cyclic hydrocarbons i.e. *endo* & *exo*-tetrahydrodimethyldicyclopentadiene (*endo* & *exo*-THDMDCPD) as an additive instead of JP-10. The reaction mixture within a range of C₁₀—C₁₅ comprising butadiene and cyclopentadiene as major basic structural units, is utilized as a raw material for the preparation of hydrogenated cyclic hydrocarbons component in the fuel composition. The reaction product of below C₁₀ is not preferable because of its low density. On the other hand, the reaction product exceeding C₁₆ is also not preferable, because the freezing point is high, and its viscosity is also high. Since these adducts are obtained from Diels-Alder reaction products of acyclic conjugated diene and cyclopentadiene as the mixture in the form of fraction, when such mixture is adjusted to have a prescribed range of carbon atom by means of distillation, the mixture thus adjusted can be utilized as a raw material. The above described reaction mixture for *eg* dimethyldicyclopentadiene (DMCPD), however, comprises unsaturated compounds involving diene as the major components so that such reaction mixture is deficient in calorific value and long-term storage stability. Thus, the reaction mixture is unsuitable for fuel composition without any modification. In this respect, such reaction mixture is subjected to hydrogenation to preferably make diene to be a perhydro-compound, whereby the reaction mixture is hydrogenated and comprises saturated hydrocarbons. The hydrogenated products have high density and high heat of combustion, and sufficiently low freezing point.

RJ-4 was synthesized by hydrogenating DMPCD by using Palladium metal catalyst to yield a mixture of *endo* and *exo*-tetrahydrodimethyldicyclopentadiene. The dimer is first hydrogenated preferably in a two-stage operation. In the first stage, the 8, 9 positions of the dimer are hydrogenated at 50 °C temperature under 7 bar hydrogen gas pressure to obtain dihydro derivative. The dihydro derivative is relatively thermally stable, thus permitting the use of a substantially prolonged temperature in the second stage; i.e. heating to be carried out for 24 hrs to complete hydrogenation. Schematic representation of formation of RJ-4 is shown in Figure 2. FTIR shows disappearance of strong peak at 1660 cm⁻¹ corresponding to olefinic double bonds in RJ-4 upon saturation. Similarly, ¹H NMR shows absence of two doublets at 5.1 and 5.5 ppm after hydrogenation.

The improvement of density, freezing point, net heat of combustion and decreasing of viscosity is taken care by the addition of synthesized RJ-4 to the fuel blend DPCR-3. Similar to DPCR-2, the third component decalin imparts the requisite initial and final boiling point requirements. The chemical composition of DPCR-3 is given in Table 3.

4.3 Characterization of DPCR-2 & DPCR-3

Fuels DPCR-2 and DPCR-3 were characterized for the properties such as density, viscosity, boiling point, heat of combustion, etc. Physico-chemical characterisation of these fuels provided in Table 4a & 4b was carried out as per ASTM test methods. The addition of greater percentages of the minor component of exo-THDCP, of course, further lowers the freezing point of the DPCR-2. However, formulations which freeze at just below $-65\text{ }^{\circ}\text{C}$ have been found to be preferable over other lower freezing mixtures as rocket ramjet fuels because the addition of more of the minor component adversely affects the density and volumetric heating value of the fuel. For long term storage and safe handling of fuels DPCR-2 and DPCR-3 the additives such as anti-oxidant, 2,6-ditert-butyl 4-methylphenol; anti-static, sigbol; Lubricity, naphthenic acid and anti-icing inhibitor, diethyleneglycol monomethylether were added at ppm level.

The formulated high density fuels of the present work contains substantial portion of inexpensive base fuel DPCR-1 and hence overcome problems such as high cost and availability when compared to fuels like JP 10, RJ 4 and RJ 5. These fuels by blending with the suitable bicyclic organic compounds and hydrogenated $\text{C}_{10}\text{-C}_{12}$ cyclic hydrocarbons can be tailored to provide properties such as density, viscosity, freezing point, flash point and heat of combustion while exhibiting the ability to better or comparable specific impulse (Isp) than that of already available fuels. The fuel composition of these fuel blends is characterized by a mixture consisting of plural components so that the present fuel composition has an advantage in that the freezing point reduce remarkably as compared with the case wherein each fuel composition consists of a single component. In addition, the fuel composition of the present work has such advantages that the density of which is extremely high, i.e., 0.844 or more and the net heat of combustion is also extremely high, i.e., 43730 KJ/Kg or more. These fuels have advantages in that it is non-corrosive to metal and that it has long-term storage stability, because the fuel composition contains no unsaturated component. Also, as these fuels are mixed from chemical materials which can be easily obtained in relatively pure form, the properties of the fuels are highly reproducible.

4.4 Swelling properties

The compatibility of fuel blends DCPR-2 & DCPR-3 over acrylonitrile butadiene rubber was estimated with swelling studies. Changes in the rubber were determined by standard elastic property determinations after swelling. The deterioration of the rubber property is mainly due to fuel aromatic levels. Aromatic content was particularly effective in promoting swell and softening. The swelling effect of the fuel blends NBR-DPCR-2 and NBR-DPCR-3 with acrylonitrile butadiene rubber was investigated after getting swollen in it for 72 hrs. Density, shore hardness and percentage volume swelling of NBR before and after swelling were given in Table 5. Figure 3 compares the percentage of retention of the tensile strength, elongation at break and modulus of the NBR samples before and after swollen in fuels DPCR-2 & DPCR-3, the retention values were given in Table 6. From Figure 3 it was clearly evident both these fuels possess very good retained tensile strength, elongation at break and modulus after swelling in NBR. The decrease of tensile strength, elongation at break and modulus of DPCR-2 and DPCR-3 when compared to NBR is due to the presence of aromatic content. The minor loss in the elongation at break after aging may be due to the increase in cross linking density, which leads to restriction for chain extension and decreases the chain length between cross-linking points. However, not much difference of tensile strength is observed for both DPCR-2 and DPCR-3 because of the low aromatic content i.e less than 5% (3.4% in DPCR-2 and 2.46% in DPCR-3). The volume swelling percentages for the NBR in both DPCR-2 and DPCR-3 were more or less the same.

4.5 Predictive performance evaluation for both DPCR-2 and DPCR-3 fuels

The predictive performance parameters of DPCR-2 and DPCR-3 were determined using NASA CEC-71 code. Various performance parameters such as characteristic velocity (C^*), specific impulse (Isp) were determined assuming frozen flow conditions at 5 bar chamber pressure and compared to T-6 fuel. T-6 is a high density speciality Russian fuel (840 Kg/m^3) using in missile applications widely. The parameters were evaluated in chamber, throat and nozzle exit. Supersonic area ratio (A_e/A_t) was assumed to be one. A/F ratio was varied from 5 to 140.

Heat of formation data calculated from heat of combustion value was used for the theoretical performance evaluation. Performance parameters obtained with varying air to fuel (A/F) ratio were given in Figure 4. The characteristic velocity and chamber pressure data obtained for Russian T-6 at varying A/F ratio were almost equivalent to DPCR-2 and DPCR-3. Hence it

was expected that DPCR-2 and DPCR-3 will perform in similar way to that of T-6 fuel in actual static/ flight tests. Fuels DPCR-2, DPCR-3, T-6 shows maximum characteristic velocity (C^*) i.e. 1279.75, 1305.34, 1273.19 m/s respectively at A/F = 14.

4.6 Static tests evaluation on DPCR-2 and DPCR-3

Fuels DPCR-2 & DPCR-3 were evaluated by using a bipropellant thruster in pulse mode at ambient temperature and compares the performance parameters such as chamber pressure, characteristic velocity and specific impulse with T-6. The performance of the DPCR-2 and DPCR-3 as rocket propellants was investigated by operating stationary rocket motors by conducting static tests in ramjet mode of dia 178 mm LFRJ engine at ambient temperature. Both the fuels DPCR-2 & DPCR-3 has been tested in Ramjet mode for A/F ranging from 14 to 55 approximately with LFRJ static test. The LFRJ engine used for the static tests was represented in Figure 5. The LFRJ engine has two cheek mounted rectangular air intakes. Fuel injection was done in both air intakes through four parallel pairs of straight hole injectors. Fuel modulation was achieved through a set of solenoid valves which can switch ON or switch OFF any pair of injectors. Flame holding was done through two numbers pressure swirl injectors placed in the dome region. The combustion chamber was unlined and a convergent nozzle was used at the exit of combustor. Chamber pressure was measured at nozzle entry.

Static tests on DPCR-2 and DPCR-3 fuels were planned with a cumulative burn time of 20 s. The performance of LFRJ engine with these fuels in terms of chamber pressure & combustion efficiency as a function of air fuel ratio has been generated. Another static test was operated under similar operation conditions with T-6 fuel in order to have comparison. Air fuel ratio was varied from stoichiometric value of 15 to lean value of 79. Sea level, Mach 2.0 condition was simulated for the test. Figure 6 represents variation of absolute chamber pressure with time and characteristic velocity with time for static tests on DPCR-2, DPCR-3 & T-6 fuel respectively. The absolute chamber pressure (P_c) of DPCR-2 and DPCR-3 is quite comparable. However, the difference in the data observed in the Fig. 6 is due to the difference in the time scale taken. Time scale difference is due to the invariable time difference in switch on and off of the recorder in both the tests. Uniform control of air and fuel flow rates is not possible in the two different static tests. Hence, it is always preferable to take absolute values into consideration. The characteristic velocity (C^*) for all the three tests are comparable. Figure 7 represents the LFRJ test comparison of fuels DPCR-3 and T-6.

Chamber pressures and combustion efficiencies at various air fuel ratios of fuels DPCR-2 & DPCR-3 were found to be close to those obtained with T-6 fuel.

Table 7 compares the air and fuel flow rates, A/F ratio and combustion efficiency of fuels DPCR-2, DPCR-3 and T-6 fuel. The combustion efficiency has been close to 100% for stoichiometric air to fuel ratio. The combustion efficiency has been high for air fuel ratio up to 20. The combustion efficiency obtained with fuels DPCR-2 and DPCR-3 is comparable with T-6 fuel. It can be mentioned here that both the T-6 fuel and fuels DPCR-2 and DPCR-3 delivered combustion efficiencies much higher than those obtained with Jet A-1 fuel. Hence, the performance of fuel DPCR-2 & DPCR-3 show them as a promising ramjet fuels. The combustion efficiency during the last step, when only dome fuel remains ON and fuel flow in air intakes is stopped completely, is found to be more than 100%, This is possibly due to hot walls of bare motor to comparatively cooler combustion products. When a flight rocket is operated employing T-6 fuel and fuels DPCR-2 and DPCR-3, satisfactory flight performance, with no detrimental explosions, is observed. The achieved chamber pressure, specific impulse and characteristic velocity of fuels DPCR-2 and DPCR-3 is in comparable with T-6 fuel.

5. Conclusions

The polycyclic alkanes based high density hydrocarbon fuels DPCR-2 and DPCR-3 developed for LFRJ application are very promising in terms of performance, density, availability and cost effectiveness in comparison with Jet A-1 fuel which is presently being used in a number of air breathing propulsion systems. It has been found that these newly developed fuels are having better properties than aviation turbine fuel (ATF/Jet A-1). The new fuels have improved density (0.844 to 0.846 g/cc @ 20 °C), low aromatic content (<5%), low sulphur content, high flash point (> 62 °C). The theoretical as well as experimental ramjet performance such as characteristic velocity and chamber pressure for both the fuel blends are higher than ordinary Jet-A1 and comparable with similar high density T-6 fuel. These new fuels are exhibiting superior storage characteristics in elastomeric fuel system such as acrylonitrile butadiene rubber used in missile applications. The fuels of the present work can be used in liquid ramjet and scramjet propulsion applications.

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References

- 1) H. S. Chung, C. S. H Chen, R. A. Kremer and J. R. Boulton, *Energy Fuels*, 1999, **13**, 641.
- 2) G. W. Burdette, *U S Patent*, 1983, 4410749.
- 3) T. Edwards, *J. Propul. Power*, 2003, **19**, 1089.
- 4) F. F. Webster, AIAA/SAE 14th Joint Propulsion Conference, AIAA 1978-1108.
- 5) S. Ronald and S. Fry, *J. Propul. Power*, 2004, **20**, 27.
- 6) G. L. Dugger, *ARS Journal*, 1959, **29**, 819.
- 7) P. J. Waltrup, *J. Propul. Power*, 1987, **3**, 515.
- 8) G. Gafani, A. Kuznetsov and D. Har-Lev, 49th AIAA/ASME/SAE/ASEE Joint propulsion conference, AIAA, 2013-3078.
- 9) H. A. Meylemans, L. C. Baldwin and B. G. Harvey, *Energy Fuels*, 2013, **27**, 883.
- 10) A. Gany, *Defence Sci. J.*, 2006, **56**, 321.
- 11) N. K. Smith and W. D. Good. *AIAA*, 1979, **17**, 905.
- 12) L. Wang, X. Zhang, J- J. Zou, H. Han, Y. Li and L. Wang, *Energy & Fuels*, 2009, **23**, 2383.
- 13) G. W. Burdette, and A. I. Schneider, *U.S. Patent*, 1983, 4401837.
- 14) A. Osmont, I. Gökalp, L. Catoire, *Propell. Explos. Pyro.*, 2006, **31**, 343.
- 15) T. S. Kokan, J. R. Olds, J. M. Seitzman and P. J. Ludovice, *J. Thermophys. Heat Transfer*, 2008, **22**, 727.
- 16) G. Liu, Z. Mi, L. Wang and X. Zhang, *Ind. Eng. Chem. Res.*, 2005, **44**, 3846.
- 17) E. J. Janoski, A. Schneider and R. E. Ware, *U.S. Patent*, 4086286, 1978.
- 18) E. J. Janoski, R. E. Mitchell and A. Schneider, *U.S. Patent*, 4177217, 1979.
- 19) Y.-Y. Tsao, C.-N. Liao, C.-Y. Chen, C. -M. Lin and K. -M. Wei, *U.S. Patent*, US8450544B2, 2013.

- 20) J.-J. Zou, X. Zhang, J. Kong and L. Wang, *Fuel*, 2008, **87**, 3655.
- 21) T. Edwards, *38th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, AIAA*, 2002-3874.
- 22) Pustyrev. U, *Proceedings of the second international symposium on aviation turbine fuel specification*, 1993.

Tables

Table 1: Comparison of specifications of Jet A-1 and DPCR fuel

Properties	Jet A-1	DPCR-1 Fuel
Density (g/cc) @ 20 ⁰ C	0.775 – 0.840	0.799 – 0.815
Boiling Range (⁰ C)	205 – 300	170-275 max
Viscosity @ 20 ⁰ C	8.0	16.5 max @ - 34.4 ⁰ C
Heat of Combustion, KJ/g	42.8	43.03
Acidity mg KOH/g	0.015	--
Flash Point Closed Cup (⁰ C)	38	53 min
Freezing Point	- 47 ⁰ C	- 51.1 ⁰ C
Aromatic Hydrocarbon	25% max	5 % max
Common sulphur	0.3 max	0.003 max
Mercaptan sulphur	0.003 max	0.0003 max
Copper Corrosion Test	Not worst than No.1	1b max
Ash Content	--	1.0 max (mg/gal)

Table 2: Chemical composition of DPCR-2

HC Fuel	Volume (ml)	Density (g/ml) @ 20°C	Boiling point (°C)	Weight (g)
DPCR-1	64	0.804	195-275	51.456
JP-10	16	0.94	183	15.04
Decalin	20	0.88	187	17.6
Total weight				84.096

Table 3: Chemical composition of DPCR-3

HC Fuel	Volume (ml)	Density (g/ml) @ 20°C	Boiling point (°C)	Weight (g)
DPCR-1	64	0.804	195-275	51.456
HDMCPD	16	0.94	188	15.040
Decalin	20	0.88	187	17.600
Total weight				84.096

Table 4a: Physico-chemical characteristics of fuel blends DPCR-1, DPCR-2 & DPCR-3

Properties	ρ @ 20°C	B. P. °C	F.P. °C	A.C. % wt	Fr.P. °C	ΔH_c , KJ/Kg
DPCR-1	0.799-0.815	175-275	53 min	5 max	-51 max	43030
DPCR-2	0.846	181-245	59	3.4	< -60	43730
DPCR-3	0.844	193-259	65	2.46	< -75	43060

* ρ : Density; B.R: Boiling Range; F.P: Flash Point; A.C: Aromatic content; Fr.P: Freezing Point; ΔH_c : Enthalpy of Combustion

Table 4b: Physico-chemical characteristics of fuel blends DPCR-1, DPCR-2 & DPCR-3

	VIS*	ACI	R.C.	SUL.	C.S.C	ASH	JFTOT
DPCR-	3.1	Nil	-	0.00	1	Nil	-
DPCR-	3.2	Nil	14.	0.02	1	Nil	1.0
DPCR-	3.7	Nil	14.	0.00	1	Nil	1.0

*VIS: Kinematic Viscosity, mm^2/s @ 20°C; ACI: Acidity, mg of KOH/100 mL fuel; R.S: Resin content, %wt; SUL: Sulphur content, %wt C.S.C: Copper strip corrosion @ 100 °C for 2 h; Ash: Ash content, %wt; JFTOT: Thermo-oxidizing stability dynamic conditions at 150-180 °C for 5 h

Table 5: Density, shore hardness A and percentage of volume swelling of NBR samples

Property	NBR	NBR-DPCR-1	NBR-DPCR-2
Density (g/cc)	1.16	1.09	1.10
Shore hardness A	30	40	38
Volume swelling in % after 72 hrs	--	1.82	1.82

Table 6: Percentage of retention of mechanical properties after swelling (for 72 hrs)

Property	NBR-DPCR-1 (%)	NBR-DPCR-2
Tensile strength	92.96	93.88
Elongation at break	90.40	89.55
Modulus at 100%	93.58	95.27

Table 7: Comparison of the air and fuel flow rates, A/F ratio and combustion efficiency of fuels DPCR-2, DPCR-3 and T 6 fuels

Test No.	AFR* (Kg/s)	MFR (g/s)	DFR (g/s)	A/F	P _c (bar)	C.E.
T-6	7.086	443.5	36	14.8	5.01	98.02
	7.086	323.5	36	19.7	4.67	100
	7.086	128.6	36	42.6	3.45	93.17
	7.086	79.7	36	60.6	2.87	87.97
	7.086	0	36	189	2.69	104.3
DPCR-2	6.82	433	35	14.65	4.94	98.85
	6.82	322	35	19.15	4.47	99.5
	6.82	135.6	35	40.0	3.28	90.4
	6.82	75.2	35	62.0	2.75	87.5
	6.82	0	35	193.0	2.55	102.4
DPCR-3	6.87	444.7	32	14.4	4.93	98.92
	6.88	346	32	18.21	4.7	99.2
	6.89	143.7	33.3	39.05	3.4	90.6
	6.92	88.23	33.3	56.44	3.0	88.1
	6.93	0	40.4	203	2.8	101.2

Figures

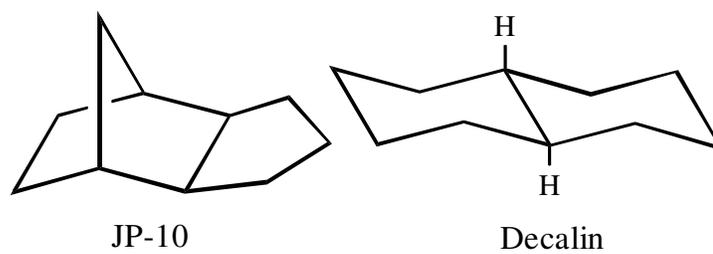


Fig.1 Structures of JP 10 and Decalin

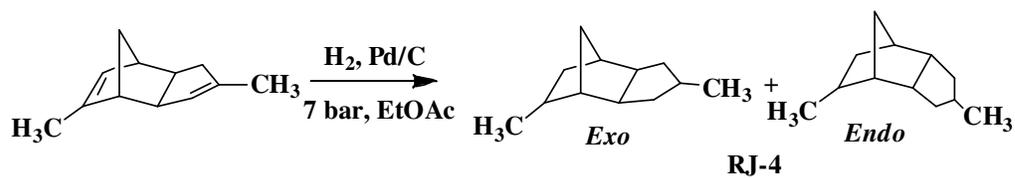


Fig. 2: Schematic representation of synthesis of RJ-4

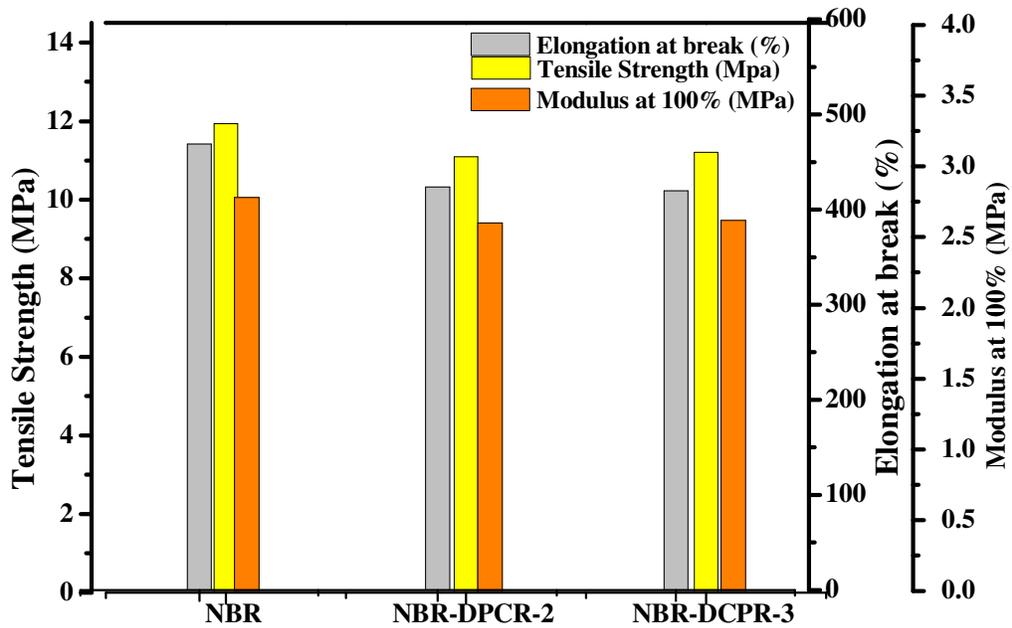


Fig. 3: Comparison of tensile, elongation and modulus properties of NBR samples in DPCR-2 and DPCR-3 fuels

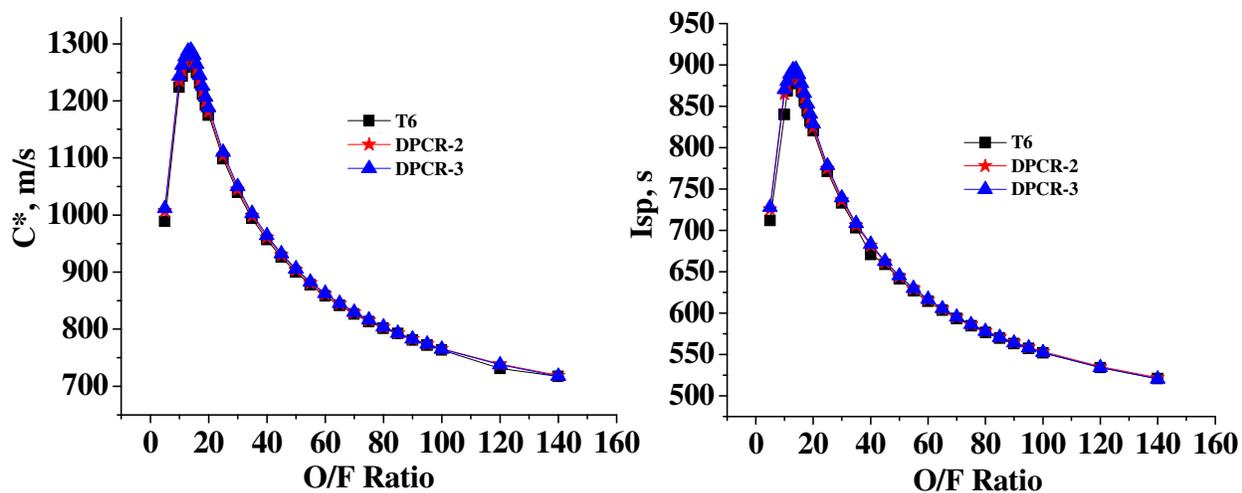


Fig. 4: Comparison of predictive performance of three fuels

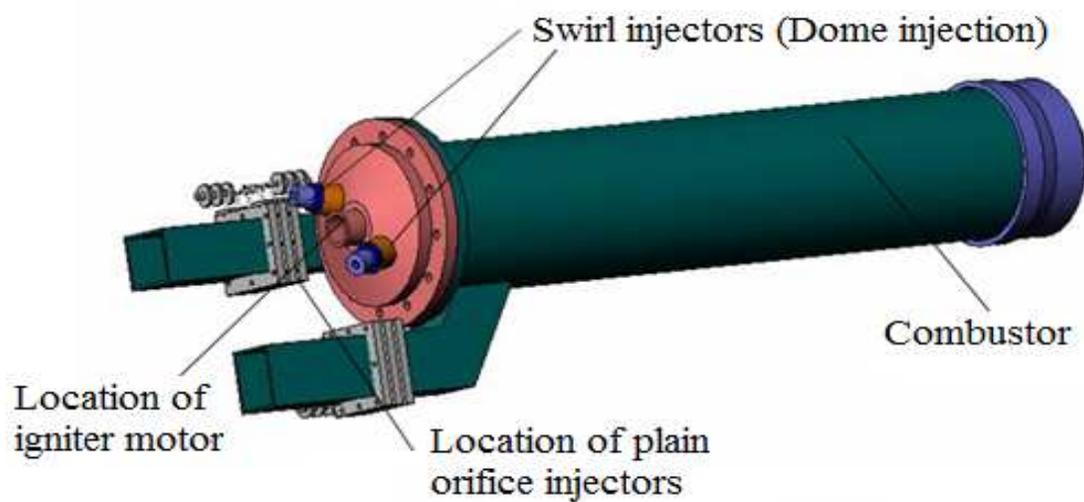
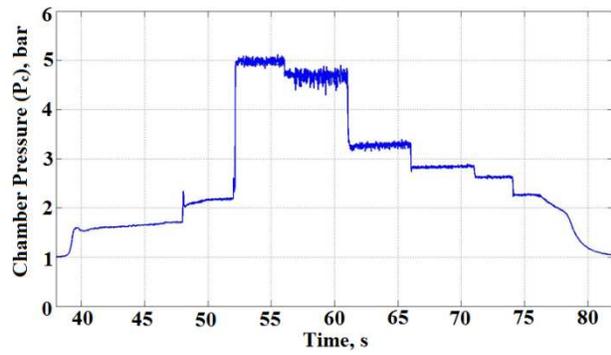
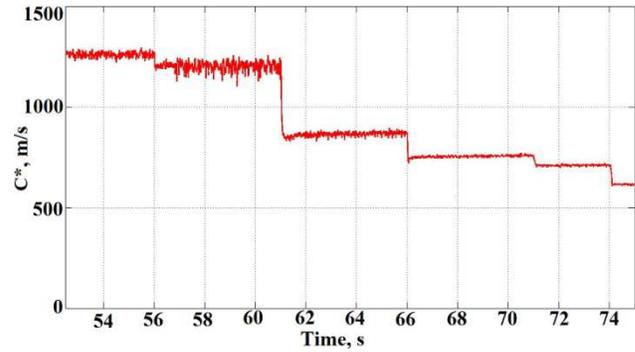
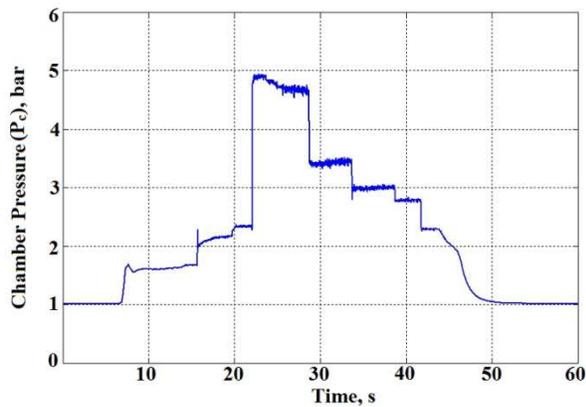


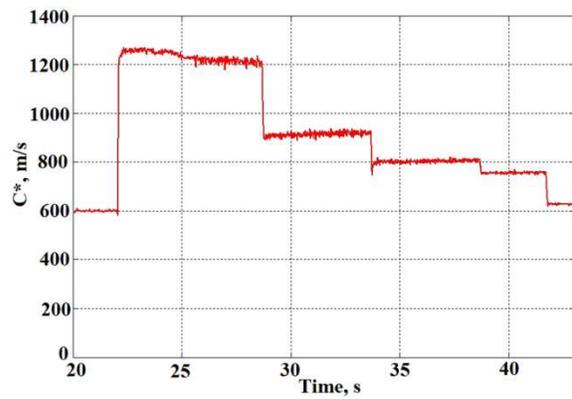
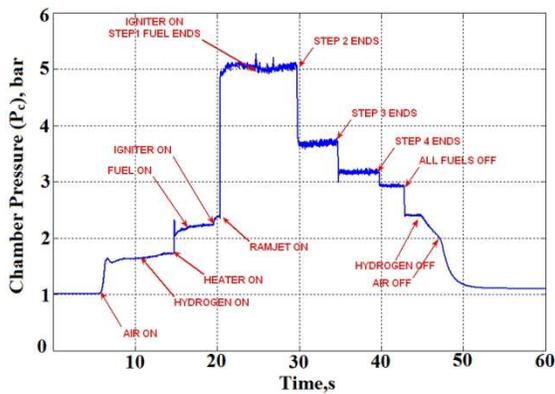
Fig. 5: LFRJ engine used for static test



a

a¹

b

b¹

c

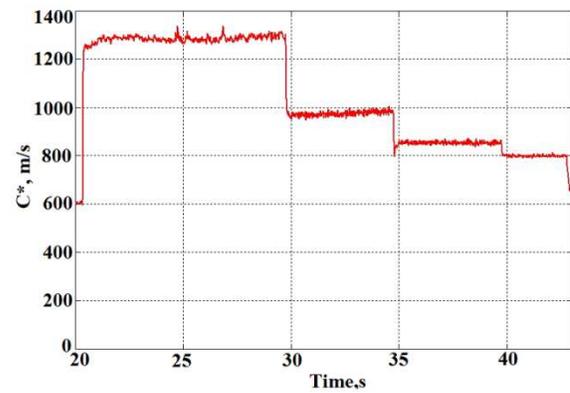
c¹

Fig. 6: Variation of absolute chamber pressure (a, b, c) with time and characteristic velocity (a¹, b¹, c¹) on DPCR-2, DPCR-3 & T-6 fuel respectively

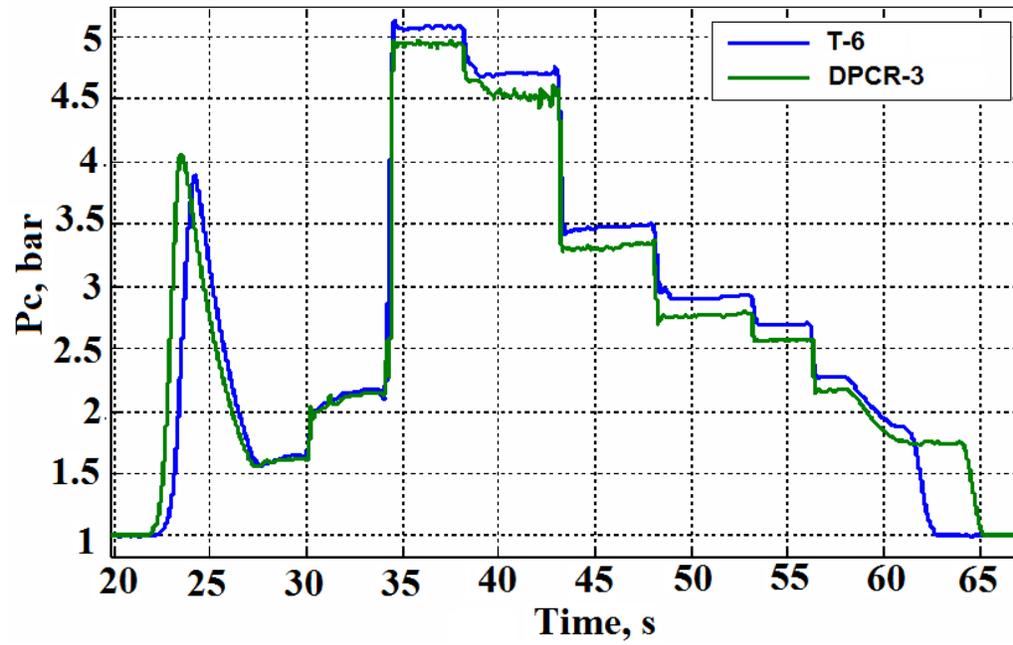
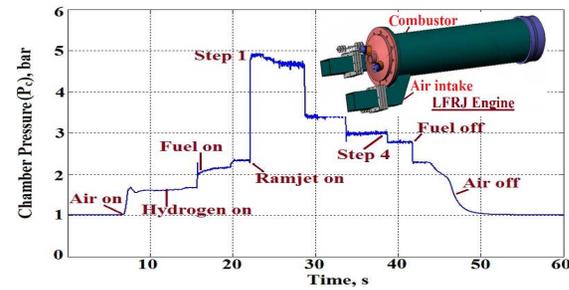


Fig. 7: Comparison of chamber pressure obtained for DPCR-3 and T-6 during LFRJ static test

GRAPHICAL ABSTRACT

TEXT: Preparation and performance evaluation of high density hydrocarbon fuel for liquid ramjet engine application