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Rocket Performance of Red Fuming Nitric Acid with Blends of Norbornadiene, Carene and Cardanol

R. Chhibber, C. Prabhakaran, S.G. Kulkarni and S.P. Panda
Institute of Armament Technology, Pune–411 025

ABSTRACT

The fuel blends of norbornadiene and carene (50:50 by weight) and norbornadiene, carene and cardanol (40:40:20 by weight) exhibit synergistic hypergolic ignition with red fuming nitric acid (RFNA) as oxidiser. These fuel blends have been evaluated by theoretical calculations of performance parameters and subsequently verified by static firing in a 10 kg_f thruster at a chamber pressure of around 20 atm, using RFNA (with 21 per cent N_2O_4 by weight) as oxidiser. The theoretical calculations show maximum specific impulse and C^*values at the O/F, 3 to be 227.8 s and 1598.7 m/s respectively for the norbornadiene-carene blend. The corresponding values for the norbornadiene, carene and cardanol blend were found to be 226.8 s and 1586.0 m/s respectively at the O/F, 4. For theoretical calculations, the chamber pressure (P_c) and the exit pressure (P_e) were assumed to be 20 and 1 atm, respectively. The static firing of the propellants in a 10 kg_f thruster exhibited smooth pressure-time curves with the experimental C^* values in close agreement with those calculated and the non-deposition of carbon in the nozzle. This indicated low combustion instability and high combustion efficiency under rocket conditions (> 0.9). The fuel blends with their low cost and toxicity and relatively high density can replace *G*-fuel used in several Indian missiles without impairing the performance.

1. INTRODUCTION

Panda *et al* have reported the synergistic hypergolic ignition[1,2], the pre-ignition reactions[3,4], and the performance evaluation of blends of carene and cardanol[5] and cyclopentadiene and cardanol[6] mixed in 70:30 weight proportion, using red fuming nitric acid (RFNA) as oxidiser. Recently, it was observed by the authors that carene, when mixed with norbornadiene or dicyclopentadiene in different weight proportions exhibited synergistic hypergolic ignition with the same oxidiser. It was also oberved that the addition of 20–30 per cent by weight of cardanol to the fuel blends increased the synergy in ignition. Cationic copolymerisation was proposed as one of the important pre-ignition reactions[7] (along with oxidation and nitration), based on IR and mass spectral data obtained for the oligomers isolated through copolymerisation of carene with norbornadiene or dicyclopentadiene and their condensation with cardanol in the presence of concentrated sulphuric acid. The performance of the new fuel blends with RFNA as oxidiser, both by computer calculations and by static firing of a suitable thruster, was studied. The new fuel blends, being of low cost with large indigenous and renewable contents having no or low toxicity can be considered as possible replacement of *G*-fuel used in several Indian missiles. *G*-fuel is an equal mixture of xylidines and triethylamine. Xylidines are known to be toxic and triethylamine with its high vapour pressure is irritant and highly inflammable; causing handling, health and storage problems.

2. EXPERIMENTAL

2.1 Materials

Carene and cardanol, obtained from Camphor and Allied Products, Bombay and Card-Chem Ltd,

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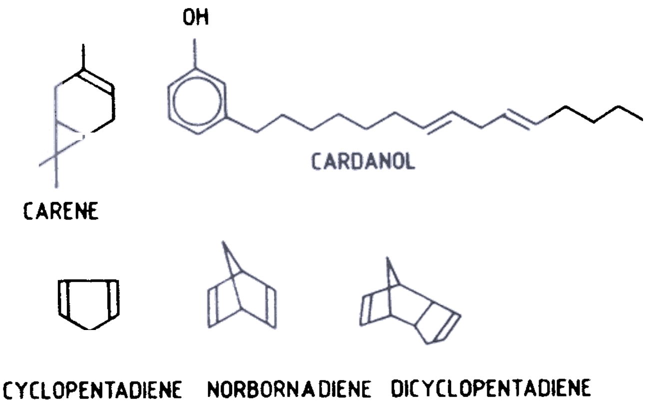

Figure 1. Structure of fuel molecules.

Hyderabad, respectively, were used without further purification. Norbornadiene (*Fluka*) was obtained from the trade and distilled. The red fuming nitric acid with HNO_3 (76 per cent), N_2O_4 (21 per cent) and water (3 per cent) of a density of 1.56 g/cc, was obtained from High Explosives Factory, Kirkee, Pune.

2.2 Methods

Ignition delay (ID) measurements were carried out in a modified Pino's apparatus described by Kulkarni and Panda[8]. Theoretical evaluation of performance parameters was carried out, using the NASA CEC-71 programme[9]. Heat of combustion values of various fuel blends were determined, using a Gallenkamp adiabatic bomb calorimeter. Heats of formation of the fuel blends were calculated from the corresponding heats of combustion.

The static firing trials were conducted at the Liquid Propulsion Systems Centre (LPSC), ISRO, Thiruvananthapuram, in their PRED Test Facility at TERLS. A 10 kg_f thruster with a throat dia 6.15 mm, chamber dia 26 mm, chamber length, 55 mm, exit dia of divergent nozzle 28.7 mm, and a half divergent nozzle angle 15°, was used. The thruster was provided with a silicide-coated tungsten nozzle insert, refracil-lined combustion chamber, a triplet impinging stream type of injector, and a remote controlled pressure-time recording system[5,6]. The results were recorded by three pulsed firings, each of 500 ms duration with 5 min interval at three different oxidiser-to-fuel (O/F) weight ratios. Using equivalent water-flow rate values, suitable orifices were selected to get the desired O/F weight ratios[5]. The ID values under firing conditions were determined at different O/F weight ratios. These ID values are defined as the lapse of time between the complete opening of the solenoid valves for oxidiser and fuel, and the rise in pressure in the combustion chamber to the 90 per cent of its final value. Such values recorded for the second and the third pulses were more realistic and consistent than those recorded for the first pulse. From the pressure-time curves, the maximum pressure developed in the combustion chamber at each O/F weight ratio was noted. By using these data, the experimental characteristic velocities were determined with the help of the formula

$$C^* = \frac{P_c \cdot A_t \cdot g}{\dot{w}} \qquad (1)$$

where A_t is the throat area (= 0.297 cm^2); $\dot{w}$ is the total flow rate which is equal to the weight flow rate of oxidiser + weight flow rate of fuel; P_c is the chamber pressure; C^* is the characteristic velocity; and g is the acceleration due to gravity.

3. RESULTS AND DISCUSSION

Table 1 gives the properties of carene, norbornadiene, and blends of carene and norbornadiene (50:50 by weight) and carene, norbornadiene, and cardanol (40:40:20 by weight). Table 2 shows the ID values of different blends of carene and norbornadiene with RFNA as oxidiser. It can be seen from the ID data that carene exhibits synergy in ignition when blended with norbornadiene in various weight proportions. The maximum synergy is achieved for a 50:50 blend as indicated by the ID values given in Table 2. The ignition takes place with a very strong flame and loud report in all the cases. The addition of 20–30 per cent (by weight) of cardanol to the fuel blends further increases the synergy in ignition as shown by the ID values reported in Table 3. Based on these observations, the blends of carene-norbornadiene and carene-norbornadiene-cardanol were selected for their performance evaluation studies.

Tables 4 and 5 give some of the important theoretical performance parameters of these fuel blends at chamber pressure (P_c) of 20 atm and exit pressure (P_e) of 1 atm. For carene-norbornadiene-RFNA system, it can be seen from Table 4 that the characteristic velocity (C^*) and specific impulse (I_{sp}) increase gradually from O/F weight ratio, 1.0 to 3.0, after which both the parameters show a gradual decrease. The maximum C^* and I_{sp}

obtainable for the propellant are 1598.7 m/s and 227.8 s, respectively.

Similar values are obtained at O/F weight ratio 3 for carene-norbornadiene-cardanol-RFNA propellant also i.e. 1598 m/s and 227.1 s, respectively (Table 5). Interestingly, the maximum C^* and I_{sp} values of both the propellants are very close to each other, indicating thereby that the addition of 20 per cent by weight of cardanol to a blend of carene and norbornadiene does not affect the theoretical performance of the blend. However, such addition results in enhanced synergy in ignition (Table 3). Hence, it was felt necessary to study the experimental behaviour of the propellants by carrying out static firing trials in the 10 kg_f thruster readily available at LPSC, Thiruvananthapuram. Both the propellants were pulse-fired three times for 500 ms

Table 1. Properties of different fuels and fuel blends

Property	Carene	Cardanol	Norbornadiene	Blend of carene-norbornadiene (50:50 by weight)	Blend of carene-norbornadiene-cardanol (40:40:20 by weight)
Molecular formula	$C_{10}H_{16}$	$C_{21}H_{32}O$	C_7H_8	$C_{7.4798}H_{10.3839}$ (arbitrary)	$C_{7.3839}H_{10.3144}O_{0.660}$ (arbitrary)
Boiling point, °C	170-172	290-300	89	130	160
Freezing point, °C	–43	–52	–19.1	< –55	< –55
Density, g/cc	0.8561	0.9523	0.909	0.880	0.8940
Viscosity at 30 °C, cps	4.1138	52	1.5577	2.2269	4.1357
Heat of combustion, cal/g	10,614	10,645	10,682.3	10,667.86	10,634.9

Table 2. ID values of carene and norbornadiene blends with RFNA as oxidiser using Pino's apparatus

Carene (% by weight)	Norbornadiene (% by weight)	O/F weight ratio (by volume-optimum)	Average ignition delay (ms)	Remarks
100	–	3.6 (6.55)	377.6	Good flame with sticky residue
0	100	2.0 (3.43)	45.3	Strong flame with loud report
60	40	2.0 (3.55)	83.6	Strong flame with sound
50	50	2.0 (3.54)	51.5	Strong flame with very loud report
40	60	2.0 (3.51)	55.0	Strong flame with loud report
30	70	2.0 (3.49)	60.0	Strong flame with sound

Values in the parentheses are of O/F by weight

Table 3. ID values of carene, norbornadiene and cardanol blends with RFNA as oxidiser using Pino's apparatus

Carene (% by weight)	Norbornadiene (% by weight)	Cardanol (% by weight)	O/F weight ratio (by volume-optimum)	Average ignition delay (ms)	Remarks
70	–	30	2.5 (4.41)	68.5	Strong flame with residue
60	10	30	2.5 (4.42)	46.0	Strong flame with very loud report
50	20	30	2.5 (4.38)	41.6	Strong flame with very loud report
45	35	20	2.5 (4.33)	36.2	Strong flame with very loud report
40	40	20	2.5 (4.31)	32.5	Strong flame with very loud report
	40	30	2.5 (4.29)	33.5	Strong flame with very loud report
	50	30	2.5 (4.24)	41.3	Strong flame with sound
		100	2.0 (3.27)	>3000	Sporadic ignition with large carbon residue

Values in the parentheses are of O/F by weight.

at three O/F weight ratios. The ID values (under firing conditions) and the maximum pressure developed in the combustion chamber were recorded from the pressure-time curves. The C^* values were calculated using Eqn (1). Table 6 gives the propellant flow rates and equivalent water-flow rates at different O/F weight ratios. Table 7 lists the ID values (static firing), maximum pressure developed during firing and the calculated and experimental C^* values. It can be seen that for carene-norbornadiene-RFNA system the ratios of $C^*_{experimental}$ and $C^*_{calculated}$ (combustion efficiency) are high (> 0.9) at all the three O/F weight ratios. The

Table 4. Theoretical performance* parameters of carene-norbornadiene blend (50:50) with RFNA as oxidiser

O/F weight ratio	Average molecular weight of combustion products, M_c(g/mole)	Chamber temperature T_c (K)	Exhaust temperature T_e (K)	Characteristics velocity C^* (m/s)	Specific impulse I_{sp} (s)
1.0	18.119	1429	744	1226.2	173.7
2.0	19.011	2142	1072	1457.3	205.9
3.0	22.741	2996	1671	1598.7	227.8
4.0	25.160	3222	1870	1588.4	227.1
5.0	26.377	3197	1881	1544.2	221.1

* Frozen flow conditions with P_c, 20 atm and P_e, 1 atm.

Table 5. Theoretical performance* parameters of carene-norbornadiene-cardanol blend (40:40:20) with RFNA as oxidiser

O/F weight ratio	Avergae molecular weight of combustion products M_c (g/mole)	Chamber temperature T_c (K)	Exhaust temperature T_e (K)	Characteristic velocity C^*(m/s)	Specific impulse I_{sp} (s)
1.0	18.03	1408	729.4	1220	172.7
2.0	19.07	2155	1082	1459	206.2
3.0	22.80	2999	1678	1598	227.1
4.0	25.08	3217	1871	1586	226.8
5.0	26.41	3188	1878	1542	220.7

* Frozen flow conditions with P_c, 20 atm and P_e, 1

Table 6. Propellant and equivalent water flow rates*

O/F weight ratio	C^* (m/s)	Weight flow rate		Equivalent water flow rates	
		Oxidiser (g/cc)	Fuel (g/cc)	Oxidiser (g/cc)	Fuel (g/cc)
a. Norbornadiene-carene-RFNA system					
2.0	1457.3	27.468	13.734	22.42	14.63
3.0	1598.7	28.166	9.389	22.99	10.00
4.0	1588.4	30.240	7.560	24.69	8.05
b. Norbornadiene-carene-cardanol-RFNA system					
2.0	1459	27.439	13.719	22.4	14.51
3.0	1598	28.183	9.394	23.01	9.93
4.0	1586	30.287	7.571	24.72	8.00

* Chamber pressure, 20.6 kg_f/cm^2

Table 7. Results of static firing of a 10 kg_f thruster using norbornadiene, carene and cardanol based fuels and RFNA as oxidiser

O/F weight ratio	Average ignition delay (ms)	Average chamber pressure (kg_f/cm^2)	C^* Calculated (m/s)	C^* Experimental (m/s)	C^*_{expt}/C^*_{calc}
a. Norbornadiene-carene-RFNA system					
2.0	10.0	19.5	1457.3	1379.26	0.946
3.0	12.5	19.5	1598.7	1513.09	0.946
4.0	15.0	19.5	1588.4	1503.27	0.946
b. Norbornadiene-carene-cardanol-RFNA system					
2.0	15.0	18.0	1459.0	1273.16	0.872
3.0	15.0	18.5	1598.0	1435.48	0.898
4.0	15.0	19.0	1586.0	1464.73	0.923

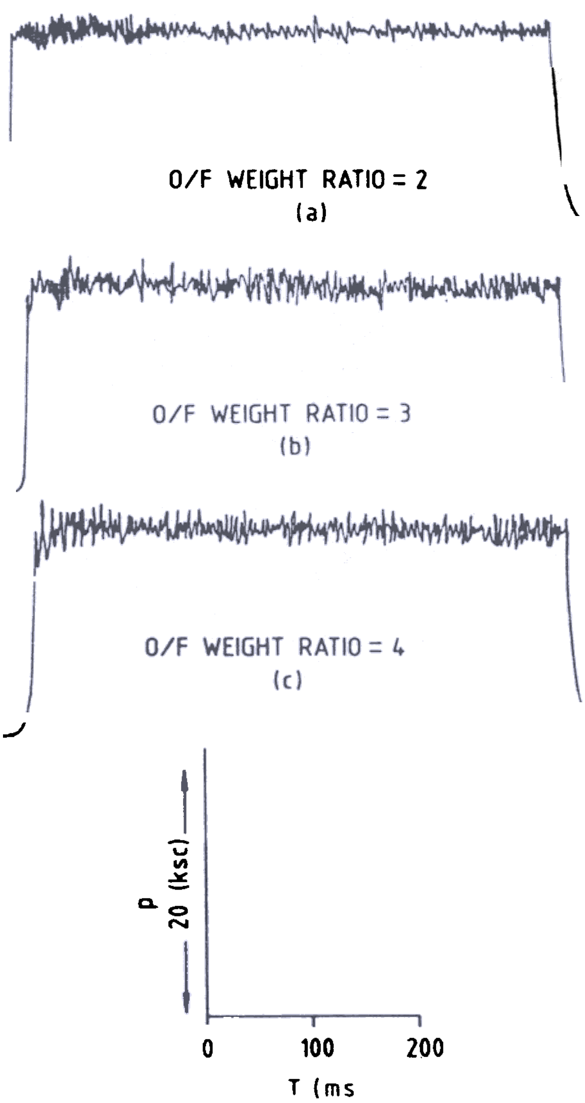

Figure 2. Pressure-time curves for carene-norbornadiene-RFNA at different O/F weight ratios.

pressure-time curves, as shown in Fig. 2, are reasonably smooth with low ignition spikes (pressure variation is within ± 5 per cent of the mean pressure). No carbon residue was noticed in the combustion chamber. These facts indicate the high combustion efficiency of the propellant under the rocket conditions, particularly at the optimum O/F weight ratio with a density 1.3076 g/cc and density impulse 297.87 g s/cc.

In the case of carene-norbornadiene-cardanol-RFNA system, the values of combustion efficiency are 0.872, 0.898 and 0.923 at O/F, 2.0; 3.0 and 4.0 respectively. However, the ID values at these O/F ratios were 15 ms under the rocket conditions. The pressure-time curves for the propellant, as shown in Fig. 3, are adequately smooth. Thus the propellant can be used at O/F ratio 4.0 having the highest combustion efficiency (0.923) and density impulse (307.98 g s/cc with the density of the propellant, 1.3579 g/cc).

The present work is aimed at finding a suitable alternative to *G*-fuel (equal mixture of xylidines and triethylamine) used in some of the missiles with RFNA as oxidiser. The isomeric xylidines like 2, 3; 2, 4; 2, 5; 2, 6; 3, 4; 3, 5-dimethyl anilines are all described to be toxic by Reagents Diagnostica Chemicals, MERCK, 1987-88. The same catalogue labels triethylamine as flammable and irritant. The precautions prescribed involve avoiding all contacts with human body, eyes and skin as the effects may be severe or even lethal. Inhalation of the vapours of the irritants is prohibited. Kit and Evéred[10] have described triethylamine as a dangerous fire hazard chemical. Its vapours form flammable mixture with air at all

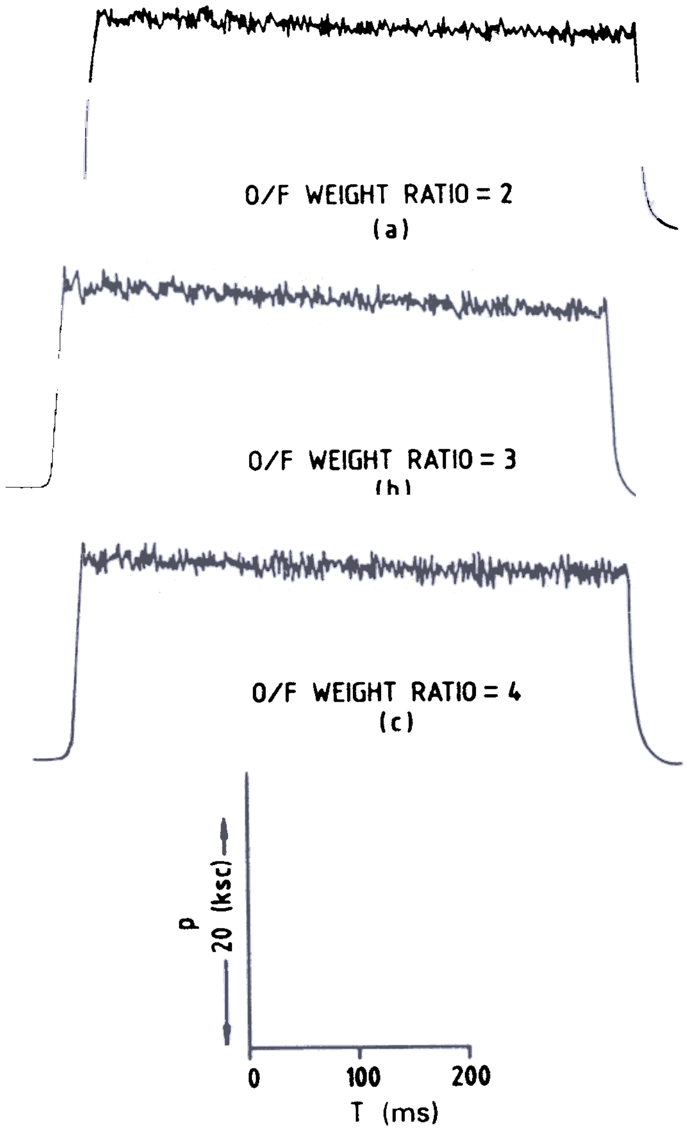

Figure 3. Pressure-time curves for carene-norbornadiene-cardanol-RFNA at different O/F weight ratios.

temperatures exceeding 20 °F making it a difficult liquid for storage. Its vapour pressure and rise in vapour pressure with temperature are rather high[10]. In addition *G*-fuel produces a strong obnoxious smell. As a result, all operations from the production to the level of filling of the fuel into the rocket motor become problematic creating resentment among the workers. The users dissatisfaction with the fuel is bound to come as a negative factor for its future use. Like the xylidines, the liquid rocket fuels such as monomethylhydrazine (MMH) and *N, N*-dimethylhydrazine (UDMH) are now manufactured indigenously. However, both these chemicals are flammable and toxic. Even UDMH has been listed under possible carcinogenics by the above-mentioned catalogue. Therefore it becomes necessary to investigate carene-norbornadiene or carene-norbornadiene-cardanol as a suitable replacement for *G*-fuel and other amino fuels currently being used for rockets in India. These new fuels are neither toxic nor irritant. They have very low freezing points, high boiling points, comparatively higher densities and better density impulse values as compared to *G*-fuel and UDMH, when used with RFNA as oxidiser at optimum O/F weight ratios. Cardanol, being a phenol, is corrosive to human skin; however because of the dilution at which it is proposed to be used, it does not pose any serious handling problems.

Both, carene and cardanol, are natural products obtained indigenously from turpentine and cashew-nut shell liquid, respectively. They are easily available in India at a cost less than Rs. 25 per kg. Norbornadiene, though not manufactured in India, can be produced from acetylene and cyclopentadiene[11] which, in turn, is made by thermal cracking of a petrochemical, dicyclopentadiene[12]. Unlike UDMH and xylidines, norbornadiene is a versatile chemical used for a variety of purposes in chemical industries. As the manufacture of norbornadiene is not established in India like that of xylidines, MMH or UDMH, it will not be fair to make a cost comparison at this stage. However, even if we import norbornadiene, the price of the new fuel blends having a substantial content of indigenous low cost components will not be exorbitant.

4. CONCLUSION

It is concluded that if the combustion is synergistic with an ID value around 20 ms under rocket conditions, it exhibits low combustion instability and good combustion efficiency for propellants with predominantly hydrocarbon fuels and RFNA as oxidiser. However, the optimization of the performance of the above propellants is necessary through proper hardware design using larger thrusters, particularly when they have certain important advantages as stated above over the accepted liquid propellants being used in rockets in India.

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