STORABLE HYPERGOLIC SOLID FUEL FOR HYBRID ROCKET ENGINES

R.V. Singh, R. Srinivasan & V.K. Srivastava

Defence Research & Development Laboratory, Hyderabad

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A solid fuel was synthesised by condensing aniline with furfuraldehyde. The product was directly cast in the rocket motor casing. After curing, a hard solid mass was obtained. This was found to have good hypergolicity with RFNA (Red Fuming Nitric Acid), good storability at room temperature and the required mechanical properties. The paper presents the technique of casting, ignition delay measurements and indicates the future programme for this study.

The development of the hybrid rocket propulsion concept which uses solid fuels and liquid oxidisers instead of conventional all solid or all liquid combinations for both the fuel and oxidiser has been recognised and widely discussed for past few years,but no significant development was made in India due to lack of extensive knowledge on the subject. The hybrid system may provide[1] a number of propulsion system capabilities in combinations not readily achievable with all-solid or all-liquid systems. These capabilities are controllable thrust, high energy performance, throttling; safety in manufacturing, handling and operation; smokelessness and low development cost.

In the hybrid system, the solid fuel does not burn[2] in small cracks or voids, thereby eliminating, for all practical purposes, the concern for structural integrity of the solid charge.

Hypergolicity i.e., the ability to ignite spontaneously on direct contact with oxidiser, is a desirable property in the fuel for almost every conceivable hybrid engine application, since it renders a separate ignition system superfluous. With fluorine containing oxidisers such as fluorine (F_2), flox ($F_2 + O_2$) or chlorotrifluoride (ClF_3), all hydrocarbon based fuels as well as many others are hypergolic. More problematical is the position in regard to nitrogen tetroxide (N_2O_4) and fuming nitric acid (HNO_3) called WFNA and RFNA (White and Red Fuming Nitric Acid). Only a few solid substances such as certain amines, hydrazine derivatives, metallic hydrides and certain metallic tetra hydroborates are hypergolic with these easily available and cheap oxidisers. Normally these compounds are unsuitable as fuels due to their high cost, high fragility, etc.

Therefore, for achieving an acceptable level of hypergolicity with the above mentioned oxidisers, other solid fuels have to be synthesised.

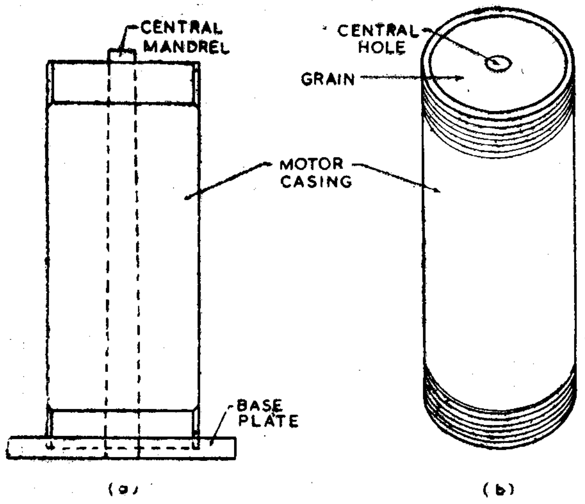

Fig. 1—(a) Casting fixture; (b) Case-bonded grain

EXPERIMENTAL

Aniline Furfuraldehyde Condensate—as Hybrid Fuel

Sixty grams of freshly distilled aniline and 20 grams of concentrated hydrochloric acid (A.R.) were mixed together and cooled to room temperature. This mixture was then added to 400 grams of aniline taken in two litre three necked flask fitted with a mechanical stirrer, dropping funnel and a thermometer. The flask was immersed in ice-salt freezing mixture with continuous stirring. The temperature of the mixture was adjusted between 10-15° C. Now 320 grams of freshly distilled furfuraldehyde was added, drop by drop, with vigorous stirring. An exothermic reaction started with each drop of furfuraldehyde. The temperature of the mixture was adjusted between 20-30° C and kept constant throughout the reaction. At the end, a very thick and sticky mass which was difficult to stirr by means of mechanical stirrer was obtained.

Casting and Firing of the Fuel in Hybrid Motors

Dark coloured, non-pourable mass was thoroughly mixed with about 1% K_2CrO_4 and heated to 50-60°C in a water bath for about 10-15 minutes. During this time, the whole mass softened and became pourable. It was then poured directly in the motor casing having a central mandrel to get a central hole in the grain. Curing of the fuel was complete at ambient temperature within about 12 hours and then the mandrel was removed. A very hard, case bonded grain with the central hole, was obtained. The motor was fitted with the nozzle at one end and injector at the other end as shown in Figs. 1, 2 and 3.

By adopting the same procedure, several motors were filled and fired to judge the proper injector conditions of pressure and rate of flow of RFNA.

Curing of the fuel was complete within few hours and could be moulded into any shape. During curing the fuel developed good bonding with metallic motor casing and no binder was required. The storability was unlimited at room temperature (25-30° C). It was unaffected by moisture and other atmospheric conditions and even after keeping for several months there was no change in hypergolicity with RFNA as well as in other properties of the fuel.

The fuel had good hypergolicity with RFNA and no external device was required to start the combustion. It may, therefore, provide the capability of variable or preprogrammed thrust together with the option of start-stop-restart operation, if required. For all practical purposes the fuel is non-explosive, does not burn without oxidiser and therefore, has no problem or limitation of conventional solid propellant from the consideration of manufacturing, handling and operational safety.

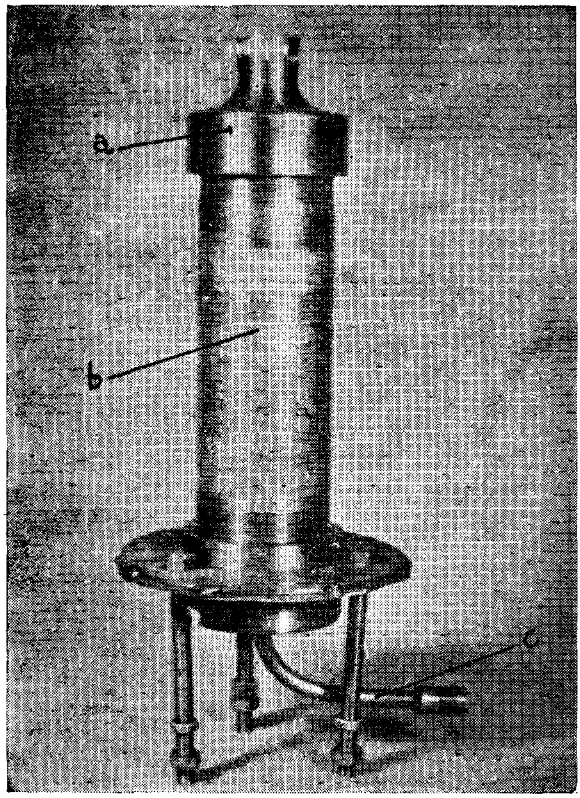

Fig. 2—Motor ready for firing : (a) Nozzle (b) Motor casing loaded with grain (c) Injector.

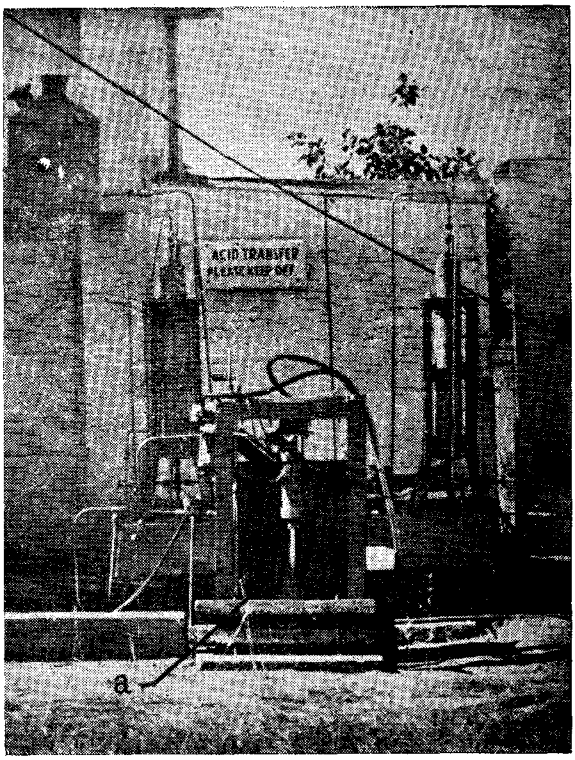

Fig. 3—Ignition started : (a) Ignition flame.

During firing of these hybrid motors, it was observed that the charge does not deform and retains its original shape. This indicates that the fuel has the required mechanical properties for this type of combustion. The smoke free burning of this fuel-nitric acid combination was also observed which can be of significant military value.

Ignition Delay of the Fuel with RFNA

Closely coupled to the combustion is the ignition delay *T*. This gives the time interval from the first contact between the fuel and oxidiser to the appearance of the first flame. A short ignition delay is desirable for several reasons. With fluorine containing oxidiser such as F_2 Flox Or OF_2; the ignition delay is extremely short ($<$ 25 ms) with practically any ordinary fuel. In the case of HNO_3 and N_2O_4, the *T* can vary from a few milliseconds for metallic hydrides upto several tens of seconds for some of the solid amines. For the solid amine in general, it can be stated that an ignition delay of $<$ 1000 ms (1 second) is good, and $<$ 500 ms, very good.

In the present study, several catalysts were tried to increase the rate of burning of the propellant and it was found that in presence of such catalysts as K_2CrO_4 $KMnO_4$, Cu_2O, V_2G_5, $(NH_4)_2Cr_2O_7$, etc., the combustion of the propellant becomes very fast and flame comes with great velocity. The effects of these catalysts, on the ignition delay of the fuel with RFNA, were also measured. For this, a laboratory method, depicted in Fig. 4, was developed and adopted for this hybrid fuel. This idea came from Pino's measurement of *T*-value of liquid propellants.

The inner cone of the tester displaces the acid in the outer cone whereby the acid closes an electrical circuit at the platinum electrode and is then forced through the injection holes into the fuel mass in the inner cone. The resulting flame is detected by the photo cell. The time interval between electrode contact and the first flame is the ignition delay.

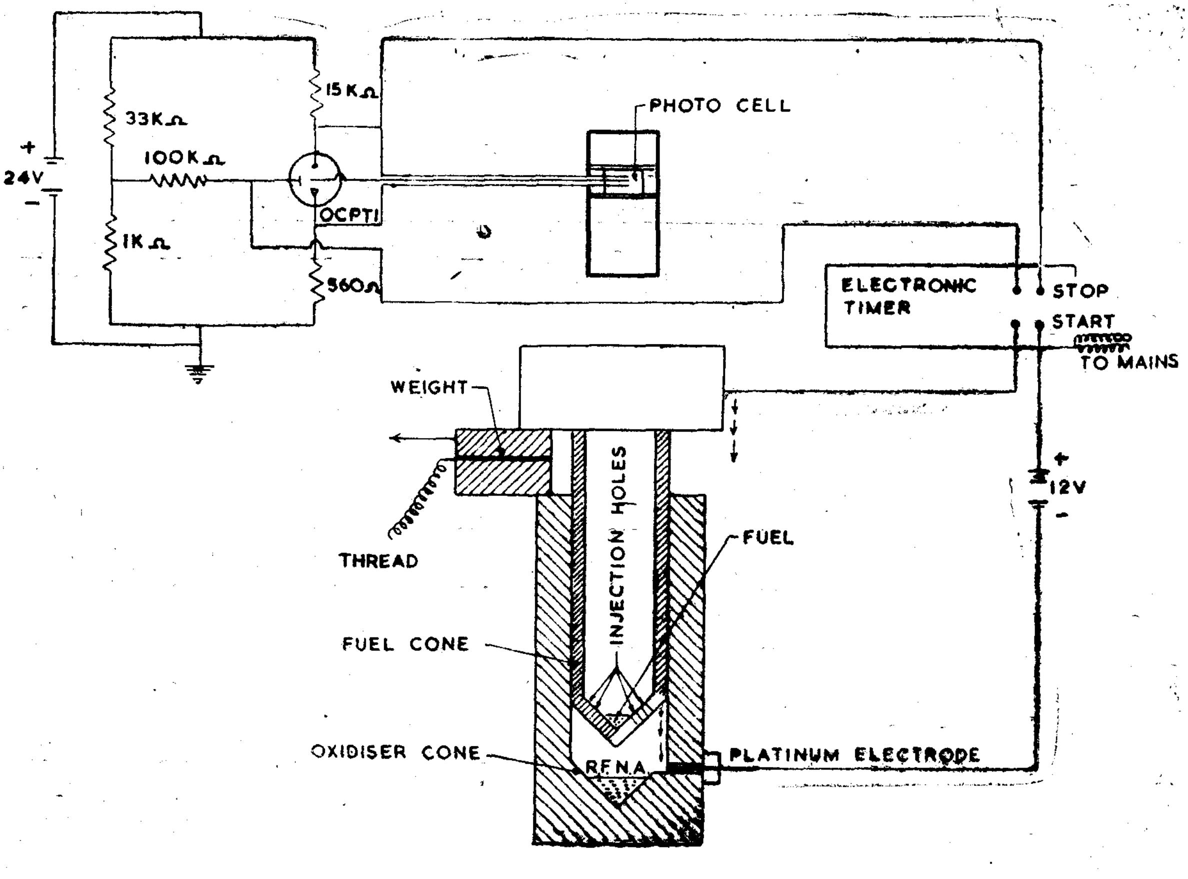

Fig. 4—Apparatus for determination of ignition delay of hybrid rocket engine fuel.

From Table 1 it is clear that the measured ignition delay of the fuel lies between 80–100 ms at an O/F ratio 1·5 to 3·0. The catalysts, used to increase the rate of combustion, do not reduce the ignition delay at all (except $(NH_4)_2 Cr_2O_7$) but they increase it considerably. For K_2CrO_4 the T-value lies between 173–181 ms; for Cu_2O between 84–88 ms; for V_2O_5 between 107–301 ms; for $KMnO_4$ between 94–103 ms; for $(NH_4)_2 Cr_2O_7$ between 71–83 ms; for the same O/F ratio.

In the comparative studies Fig. 5 of ignition delay of the fuel (0·5 gm) with different amounts of RFNA used for combustion, it has been observed that the optimum value of oxidiser and fuel ratio is 3. With this combination i.e., O/F = 3 this fuel (with or without catalysts) represents the least ignition delay.

These catalysts were also tested by dissolving them in RFNA instead of mixing with fuel. The results are shown in Table 2.

From these results (Fig. 6) it can be concluded that these catalysts effectively reduce the ignition delay, when dissolved in RFNA. $KMnO_4$ reduces the ignition delay upto 41 ms at the concentration of 3·0%. V_2O_5 reduces it upto 53 ms at the concentration of 1·0%. But their use was ruled out on the basis that these solutions coagulated after keeping for few days and cannot be suitable for pre-packaging from operational point of view.

TABLE 1

IGNITION DELAY OF FUEL WITH RFNA (IN PRESENCE OF CATALYSTS MIXED IN THE FUEL)

Amount of fuel = 0·5 gm, Catalyst = 5%

Sl. No.	RFNA used for ignition (ml)	Ignition delay of fuel (ms)					
		Without catalyst	With catalyst				
			K_2CrO_4	Cu_2O	V_2O_5	$KMnO_4$	$(NH_4)_2Cr_2O_7$
1	0·3	—	213	—	—	—	—
2	0·4	141	192	85	118	99	83
3	0·5	80	176	84	116	103	77
4	0·6	81	178	87	107	98	73
5	0·8	84	181	88	168	94	75
6	1·0	83	173	86	301	95	71
7	1·2	94	195	106	328	92	90
8	1·4	98	269	109	3340	102	95
9	1·6	100	—	110	4350	105	95
10	1·8	—	—	381	—	113	145
11	2·0	200	—	—	—	190	288

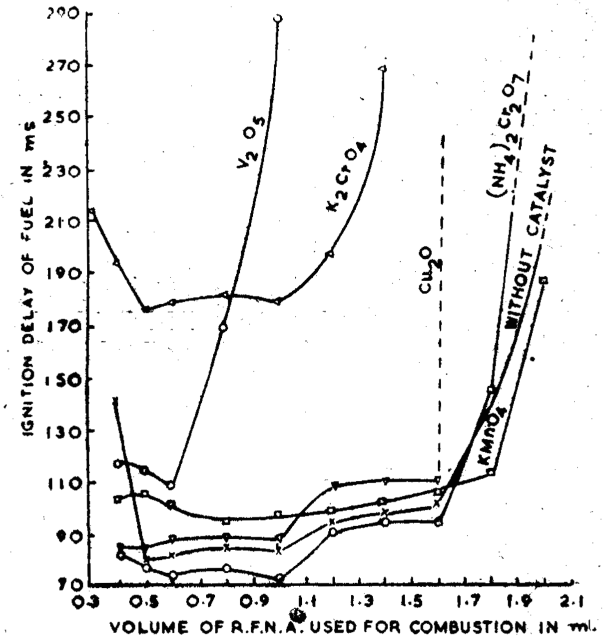

Fig. 5—Comparison of the effect of various oxides (mixed with fuel) on the ignition delay of fuel with RFNA.

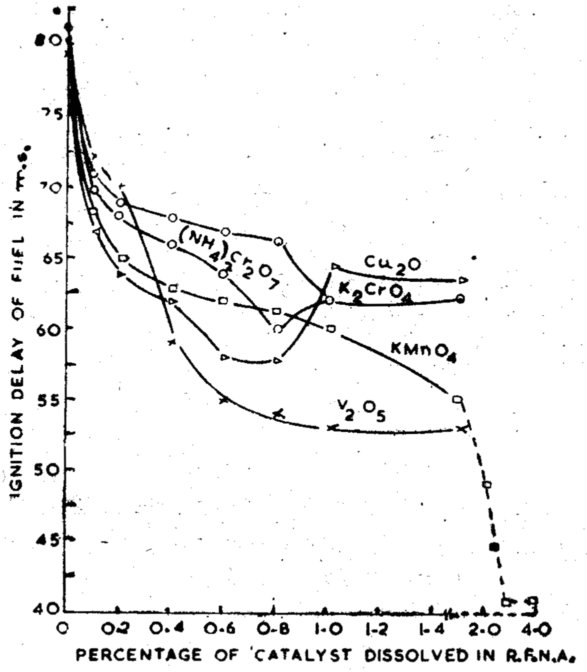

Fig. 6—Comparison of the effect of various catalysts (dissolved in RFNA) on the ignition delay of the fuel with RFNA.

These ignition delays, for this type of propellant, can be considered as extraordinarily short. An even shorter ignition delay is, however, desirable for certain applications. To understand the extent to which the ignition delay can be shortened, we can cite the *T*-value of 50 ms which is normal for hypergolic liquid rockets with liquid amines and nitric acid.

TABLE 2

IGNITION DELAY OF FUEL WITH RFNA (IN PRESENCE OF CATALYST DISSOLVED IN RFNA).

Weight of fuel = 0·5 g, Weight of oxidiser (RFNA) = 1·2 g, O/F ratio = 2·4

Sl. No.	Percentage of catalyst dissolved in RFNA (W/W)	Ignition delay of fuel (ms)					Remarks
		K_2CrO_4	Cu_2O	V_2O_5	$KMnO_4$	$(NH_4)_2Cr_2O_7$	
1	0·0	80	80	79	80	81	K_2CrO_4, Cu_2O, V_2O_5, $(NH_4)_2Cr_2O_7$ are completely soluble upto 1·5% and $KMnO_4$ is completely soluble upto 3%
2	0·1	71	67	72	68	70	
3	0·2	69	64	70	65	68	
4	0·4	68	62	59	63	66	
5	0·6	67	58	55	62	64	
6	0·8	66	58	54	61	60	
7	1·0	62	64	53	60	62	
8	1·5	62	63	53	55	62	
9	2·0	—	—	—	49	—	
10	2·5	—	—	—	45	—	
11	3·0	—	—	—	41	—	
12	4·0	—	—	—	41	—	

After intensive experimentation, this problem has been tackled in the case of this fuel, by introducing minute quantities of a metallic hydride which reduced the ignition delay to a satisfactory level.

CONCLUSION

It is apparent from the foregoing that the hybrid rocket engine, as a concept, has many potential advantages. This fuel, synthesised from aniline and furfuraldehyde has the desirable properties required for solid hybrid fuels.

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