PROPELLANTS—THE FEASIBILITY OF THEIR MANUFACTURE IN INDIA

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ABSTRACT

In the light of the recent Chinese aggression, the modernization of our defence forces has become a vital necessity. In this paper, one aspect of this problem has been considered in detail viz. the development of an indigenous rocket and missile force. While it is true that many factors e.g. rocket motors, propellants, guidance systems etc. are involved, it is also true that a start in one area will act as an impetus to developments in the other fields. Solid/liquid propellant and oxidizer systems have been considered, the properties of solid and liquid propellants evaluated and on the basis of such comparison, it has been concluded that effort concentrated on the development of liquid propellants will be well expended. Liquid propellant/oxidizer systems have been compared amongst themselves and it has been concluded that the hydrazine fuels oxidized by RFNA/WFNA/IRFNA would represent systems fulfilling the country's immediate military needs best. The availability of raw materials for the manufacture of hydrazine fuels (and also of some solid propellants) has been considered and it is shown that the necessary raw materials are available in sufficient quantities to support an indigenous propellants industry.

INTRODUCTION

Recent events have shown up the inadequacy of India's defence capacity and have also heavily underlined the fact that the defence forces of the country have to be rapidly modernised. Since rockets and missiles of various types are now being increasingly regarded as necessary and basic equipment for the armed forces, it is proposed to discuss in this article the feasibility of manufacturing in this country the propellants that power these missiles and to show that with judicious selection it is entirely possible for India to have a largely indigenous rocket or missile force based on indigenously manufactured propellants. Propellants are broadly classified into solid and liquid propellants, the two types having significant differences particularly in specific impulse and thrust control.

The merits of the various propellants will be briefly considered in order to enable a selection to be made from the numerous propellants of the one or of those which are most suitable to our needs. Among the criteria of suitability will, necessarily, be possibility of manufacture from indigenous raw materials, high specific impulse (lbs. thrust/lb. of propellant/sec.) storability i.e. the ability to be stored for long periods without undergoing significant decomposition, etc.

SOLID PROPELLANTS

A solid propellant is usually a mixture of at least two substances one of which is the fuel and the other an oxidizer. The most common fuels are such complex hydrocarbons or hydrocarbon derivatives as the synthetic rubbers, and synthetic resins; polymers like polyurethane, polyethylene etc. are gaining increasing prominence[1]. While polyurethane and polysulfide have very superior binding qualities and fuel value, the availability (even in the U.S.A.) is poor and the cost high[1]. However, polyesters, polyethylene and synthetic rubbers represent solid propellant binders and fuels with good to medium binding qualities and fuel values[1] which can be manufactured in the country from indigenously available raw materials; the case of butadiene is discussed in some detail only in the context that if it is decided to have a solid propellant based missile force and if butadiene rubbers are chosen as the propellant (for which there is sufficient justification both on grounds of fuel value and raw material availability) what are the possibilities? The most common oxidizers are ammonium and potassium perchlorates and nitrates and various organic nitrates like glyceryl trinitrate. The setting up of the 30,000 tons per year synthetic rubber plant at Bareilly therefore acquires a new defence significance; alcohol from the sugar factories will be the raw material for this plant. Other important sources of raw materials for the manufacture of solid propellants are the petroleum refinery gases which contain significant quantities of butadiene and other unsaturates which are important starting materials for certain types of synthetic rubbers and polymers; butane and butylenes present in petroleum refinery gas can also be converted into butadiene. Table 1 gives the yields (wt. %) of butane, butylene, butadiene and methane from the cracking of liquid hydrocarbons different by processes[2].

TABLE 1

YIELDS (Wt%) OF BUTANE, BUTYLENE, BUTADIENE & METHANE.

Product	Thermal naphtha refining	Thermal gas oil cracking	Cat. gas oil cracking	Naphtha cracking (Caterole)	High temp. regenerative gas oil cracking
Methane	3·3	1·0	1·0	17·8	10·2
Butadiene	0·2	0·1	0·1	—	—
n-Butane	3·8	2·9	0·4	—	—
n-Butylenes	2·8	0·6	2·8	—	—

It has been estimated that by 1965 there will exist in the country a refining capacity of about 12m. tons. The total yield of liquid hydrocarbons suitable for processing into petroleum products varies with the nature of the crude being as high as 45% by wt. in the case of Nahorkatiya crudes and as low as 27% by wt. in the case of the Cambay crudes. Considering only the lower figure for making a safe estimate, therefore, nearly 3·24 million tons of liquid products will be available for processing into petroleum products. Considering again, only the lowest figures in Table 1, at a conservative estimate 3,240—6,480 tons of butadiene will be available from the refineries for processing into synthetic rubber. This figure can be augmented by the conversion of at least 12,960 tons/yr. of n-butane to butadiene and 19,440 tons/yr. of n-butylenes to butadiene by dehydrogenation according to the following reactions —

$$CH_3.CH_2.CH_2.CH_3 \xrightarrow{-2H_2} CH_2 = CH - CH = CH_2.$$

$$CH_3.CH_2.CH = CH_2 \xrightarrow{-H_2} CH_2 = CH - CH = CH_2.$$

12,960 tons of butane would yield about 12,000 tons of butadiene/year and 19,440 tons of butylenes would yield about 18,662 tons of butadiene/year. There is thus a possibility that at least 34,000—37,000 tons of butadiene may be available for processing into synthetic rubbers suitable for use as solid propellants. In addition, the unsaturates in coke oven gas may yield some more butadiene.

The great advantage of a solid propellant so far has been instant readiness which, till recently, was not possible with liquid propellants. Another advantage possessed by solid propellants is that the thrust can be programmed relatively easily by manipulating the shape of the propellant grain. However, these considerable advantages are offset by the complexity of their manufacture as a solid propellant consists of inhibitors, ballistic modifiers, stabilizers etc. in addition to the actual propellant and oxidizer. Also solid propellants have specific impulses as much as 10—20% lower than liquid propellants; the performance can be improved by the incorporation of metal additives in the propellant grains but that further increases the complexity of the manufacture of solid propellants. The advantages and disadvantages of solid propellants may be summarized as follows:—

Credit	Debit
1. Instant readiness	1. Specific impulse 10—20% lower than liquid propellants
2. Programmed thrust	2. Complex manufacturing process involving manufacture of organic fuel, inorganic oxidizer, modifier, inhibitor, metal base additive.

LIQUID PROPELLANTS

In the field of liquid propellants one of the most important system is alcohol oxidized by liquid oxygen (LOX) because of the very high specific impulse obtainable when 100% ethyl alcohol is used. However, the fact that the rocket had to be 'fuelled' with 'LOX' before it could be fired and also because this fuelling was a lengthy process, for a long time liquid propellant systems have not found military use where instant readiness is of the essence, though they are uniquely successful in space rockets. Another disadvantage in the use of such fuels and oxidizers as alcohol, liquid oxygen, liquid hydrogen, liquid fluorine etc. is their low bulk density due to which rocket motors have to be of enormous size leading to a poor total impulse/weight ratio. Moreover, the picture has changed completely with the advent of semi-storable, storable and packageable liquid propellants and oxidizers of high densities and specific impulses. The design of highly efficient instantly (and constantly) ready, simple, liquid propellant based rockets is now possible and as a matter of fact a number of well-tried, liquid propellant based military rockets now exist e.g. Able Star, Titan II, Atlas-Thor-Agena Upper and Redstone. A great advantage of many liquid propellant systems is that they are hypergolic i.e. ignition occurs on contact of propellant and oxidizer or they can be readily made so.

TABLE 2

MISSILES BASED ON STORABLE PROPELLANT SYSTEMS[3]

Missile	Oxidizer	Fuel
Able Star	IRFNA	*UDMH*
Aerobee	IRFNA	Aniline
Atlas Thor Agena-Upper	IRFNA	*UDMH*
Bomarc	IRFNA	JP-X
Bullpup	IRFNA	MAF
Titan	N_2O_4	*Aerozine*

Characteristics of semi-storable, storable and packageable propellants will now be considered briefly not only to define them but also to select propellant-oxidizer systems with the best combination of characteristics for our needs; much of the material in this section is taken from an excellent review of storable propellants by Grelecki and Tannenbaum[3]. A storable propellant is defined as a liquid whose critical temperature is higher than 160°F or 70°C (maximum ambient temperature). In addition the liquid must not have a vapour pressure greater than 500 p.s.i.a. at 160°F and must not decompose during storage at a rate greater than 1 per cent per year at a constant temperature of 120°F (49°C). Even though these conditions are arbitrarily chosen they provide a practical set of standards for differentiating between storables and non-storables. Semi-storable propellants are those that can be made storable under a restricted temperature regime. They can therefore be treated as storables if they are kept at temperatures well below the maximum of 160°F and 70°F (21°C) is set as the upper limit for semi-storables; this temperature can be maintained in most places, without difficulty, by air conditioning. A packageable propellant meets all the requirements of a storable material and in addition can be hermitically sealed for at least 5 years with minimum ullage (vapor space). It must be extremely thermally stable at ambient temperatures at least towards decomposition into non-condensable gas; a packageable propellant must not decompose at 120°F. **This group of propellant contains the most desirable and versatile types and represents the ultimate in useful liquid propellants. Based on these, it is possible to have prepackaged rocket engines which can be filled with propellant and sealed shut to give self-contained units that require no last minute filling and need only be armed and fired as required.** Most of the storables are also packageable. Table 3 gives a list of current storable propellants and propellant blends.

TABLE 3

COMMON NEAT STORABLE PROPELLANTS AND BLENDS[3]

Name	Formula/composition
Fuels	
Hydrazine	N_2H_4
Monomethyl hydrazine (MMH)	$CH_3N_2H_3$
Unsymmetrical dimethyl hydrazine (UDMH)	$(CH_3)_2N_2H_2$
Pentaborane (not packageable) (PB)	B_5H_9
Ammonia (borderline case; vapour press. at 100 °F 495 psia).	NH_3
Diethylene triamine (DETA)	$(H_2NC_2H_5)_2NH$
MAF—1	Mixed amines
MAF—3	"
MHF—1	Mixed hydrazines.
MHF—3	"
U-DETA	60% UDMH, 40% DETA
Aerozene—50	50% UDMH, 50% N_2H_4
JP Fuels RP Fuels	Mixture of hydrocarbons
Oxidizers	
RFNA	Nitric acid containing 15% No_2 and 2% H_2O, when 0·5 % HF is added material is known as IRFNA
Chlorine Trifluoride (CTF)	C_1F_3
Bromine pentafluoride (BPF)	BrF_5
Nitrogen tetroxide	N_2O_4
CTF/BPF	Miscible in all proportions.
CTF/ClO_3F	Miscible in all proportions. Storable only over a restricted composition range.

The advantages and disadvantages of liquid propellants may be summarized as follows:—

Credit	Debit
1. 10—20% higher specific impulse	1. Greater propellant cost
2. Storable and packageable	2. Greater handling hazards
3. Greater reliability	3. Limited 'know-how'.
4. Hypergolic or easily made so	
5. Minimum field service problems	
6. Simpler engine design	
7. Greater versatility.	

It is thus seen that the advantages far outweigh the disadvantages and with the advent of prepackaged propellant systems the utmost simplicity in engine design and the minimum of field service problems are achieved. These are paramount considerations in military use. The current developments in the field of liquid propellants thus make them objects of serious consideration by a nation trying to strengthen and modernize its defence forces in a hurry. Table 4 gives the rating of some storable propellants.

TABLE 4

RATING OF STORABLE PROPELLANTS[3]

Propellant/oxidizer	Physical properties	Handling and storability
Hydrazine	good	excellent
Monomethyl hydrazine	good	excellent
Unsym. dimethyl hydrazine	good	excellent
Ammoni	fair	good
Amines	good	excellent
Hydrocarbons	good	excellent
Pentaborane	good	fair
Nitrogen tetroxide	good	good
IRFNA	excellent	good
Chlorine trifluoride	excellent	fair
Bromine pentafluoride	good	fair
Hydrogen peroxide	good	fair
Perchloryl fluoride	fair	good

The performance of some storable propellant/oxidizer systems is given in Table 5.

TABLE 5

COMPARISON OF THE PERFORMANCE OF STORABLE PROPELLANT/OXIDIZER SYSTEMS[3]

Fuel	Oxidant	Isp.	Id.
Hydrocarbons	N_2O_4	276	348
	H_2O_2	279	555
	ClF_3	258	386
Hydrazine	N_2O_4	292	357
	H_2O_2	288	253
	ClF_3	294	444
Pentaborane	N_2O_2	306	337
	H_2O_2	312	311
	ClF_3	288	423
Monomethyl Hydrazine	N_2O_2	288	348
	ClF_3	283	404
Unsymmetrical dimethyl hydrazine	N_2O_2	286	334
	ClF_3	279	382

COMPARATIVE ADVANTAGES OF SOLID & LIQUID PROPELLANTS

Many of the advantages of solid propellants are now available in storageable/packageable liquid propellant systems and in addition solid propellants suffer from certain drawbacks. "They have in general a lower performance, thrust control and termination are difficult, although the problems involved are supposedly near to solution. But still solid propellants cannot be turned on and off. Also the firing time of solid propellant rockets is shorter and consequently the total impulse is smaller. In addition, the performance of solid propellant is quite sensitive to variations in temperature, whereas liquid propellants are within very wide range, insensitive to temperature changes. Finally the manufacture of a solid propellant grain is always a very involved process, frequently requiring costly machinery "[4].

Having seen the overall advantages of liquid propellants over solid propellants it should be possible to select for manufacture propellants on the basis of performance, chiefly, but also at the same time paying some attention to the availability of the necessary raw materials in the country. A preliminary selection can be made by excluding from our list such exotic propellants and oxidizers as pentaborane, chlorine trifluoride, perchloryl fluoride and bromine pentafluoride which do not have performances superior to some of the commoner and more easily manufactured systems and have poorer handling and storing characteristics. The field of selection thus narrows to the hydrocarbon and the hydrazine propellants and fuming nitric acid and nitrogen tetroxide oxidizers.

HYDROCARBONS

Here the synthetic rubbers, synthetic resins and other solid rocket propellants are not being considered but only the pure liquid hydrocarbons and their mixtures or solutions. The lower members of the aliphatic series of hydrocarbons are gases and pentane is the first member of the series which is liquid. The liquid members of the series suffer from the defect of low bulk density entailing a poor total impulse/weight ratio. The higher mmbers of the series are solid and thus unsuitable for use. The possibility of using soluons of solid hydrocarbons in liquid hydrocarbons can be considered but there is the danger of the solids separating out at the low temperatures obtaining at high altitudes. However, hydrocarbon compositions can be satisfactorily used in tactical or combat rockets e.g. anti-tank rockets that practically leaves the hydrazines as the sole contenders for strategic rockets carrying nuclear or other effective war heads.

Sources of hydrocarbons :

While petroleum is the largest source of hydrocarbons, petroleum hydrocarbons suffer from a poor density/volume ratio. Recently Letort[5] has discussed the properties of high energy fuels and shown the feasibility of their manufacture from selected coal tar fractions by hydrogenation. Considering that nearly 16 million tons of coal will be charged into coke ovens for the productions of metallurgical coke by 1965/66[6] nearly 400,000 to 480,000 tons of tar will be available assuming that 2·5 to 3 % by weight of the coal carbonized appears as tar[6]. Further, the fraction of tar oil considered suitable for hydrogenation (anthracene oil) amounts to 20% of the tar and thus 80,000 to 96,000 tons of appropriate fraction will be available for hydrogenation to fuels which when oxidized by oxygen rich oxidizers like fuming nitric acid can power tactical rockets or which can be used as superior fuels for air breathing jet engines.

HYDRAZINES

It has already been pointed out that as far as large, strategic rockets are concerned, the most suitable of the numerous propellants from all points of view are the hydrazines viz. hydrazine, monomethyl hydrazine (MMH) and unsymmetrical dimethyl hydrazine (UDMH). Of the hydrazines, hydrazine itself suffers from the drawback of a high freezing point (34°F) and tendency to detonate in the vapour phase when heated. Monomethyl hydrazine is a comparative newcomer in the field while UDMH is admirable in all respects but has a low density.

Routes to the hydrazines :

Of the many methods proposed for the manufacture of hydrazine and its derivatives, two have assumed commercial significance viz. the modified Raschig process and the nitrosation-reduction process.

Modified Raschig synthesis :

This method has been in use as the chief commercial method for the production of hydrazine.

$$NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH.$$

$$NH_3 + NH_2Cl + NaOH \longrightarrow NH_2.NH_2 + NaCl + H_2O.$$

Substitution of monomethylamine or dimethylamine instead of ammonia in the second step of the reaction gives monomethyl or unsymmetrical dimethyl hydrazine as the final product. However the process suffers from the disadvantage of low concentration of product in the synthesis liquor. Large quantities of water are required as monchloramine is stable only in dilute solutions. The yield of hydrazines is only 2·3% by weight the rest being salt and water. Although UDMH does not form an azeotrope with water, it cannot be obtained from dilute solutions by simple distillation.

Nitrosation-reduction method :

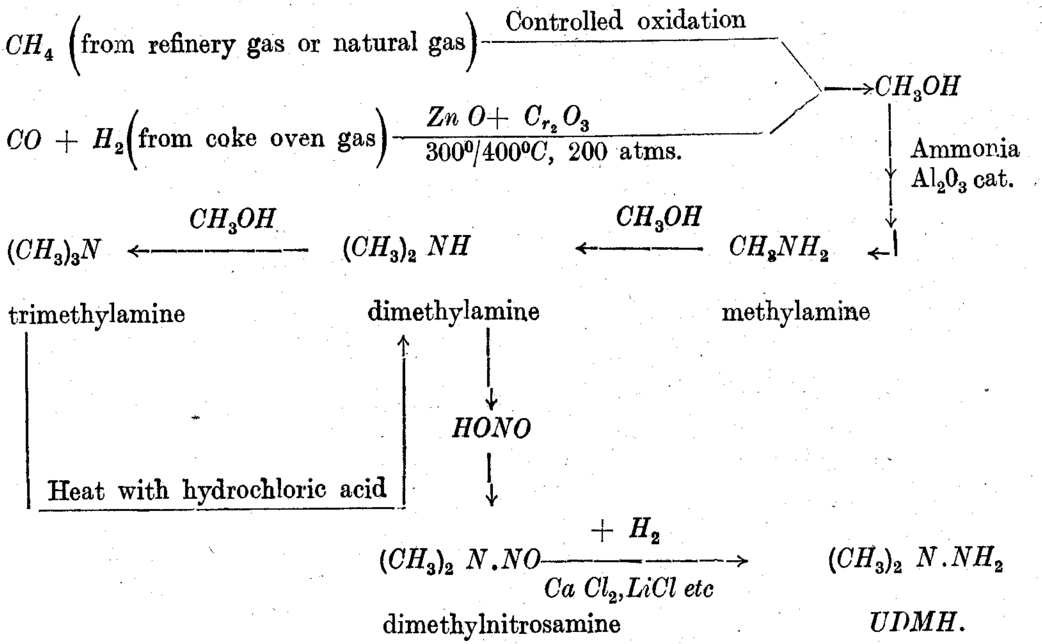
The other important commercial method of obtaining the hydrazines is by converting the corresponding amine into the nitrosoamine and reducing the nitrosoamine to the hydrazine.

$$R_2NH + HONO \longrightarrow R_2N.NO + H_2O.$$
$$R_2N.NO + 4H \longrightarrow R_2N.NH_2 + H_2O.$$

The nitrosoamine can be obtained in high concentrations (ca. 90%) from the reaction products and can be reduced to UDMH by one of several methods using Gr. VIII metals as catalysts. Unfortunately, in the catalytic reduction considerable quantities of UDMH are also reduced to the amine but recent studies have shown that the addition of small quantities of salts of lithium, calcium, lanthanum etc. effectively suppresses the formation of the amine during hydrogenation. In the presence of such salts conversions ranging from 76—87% have been realized while even in their absence conversions upto 62% are still possible. The nitrosation-reduction process, therefore, is obviously the route of choice for the manufacture of UDMH.

Raw Materials :

The starting material for the synthesis of UDMH is dimethyl amine which in turn is obtained from methyl alcohol and ammonia or from methyl chloride and ammonia. Of the two, methyl chloride is the more difficult to synthesize while a number of well tried commercial methods exist for the synthesis of methyl alcohol from petroleum refinery gases, natural gas or coke oven gas which thus constitute the most abundant raw material sources for the manufacture of propellants in India.



One prolific source of raw material for the synthesis of UDMH from methane, is natural gas of which the present proved and indicated reserves are 756,000 million cubic feet equivalent to 20 million tons of oil and consisting almost entirely of pure methane. The other source is the gases produced in the cracking of liquid hydrocarbons in a petroleum refinery (Table 6).

TABLE 6

YIELD OF METHANE IN THE CRACKING OF LIQUID HYDROCARBONS (WT. $_0/^\circ$)[2]

Thermal Naphtha Refining	3·3
Thermal Gas Oil cracking	1·0
Catalytic Gas Oil cracking	1·0
Low pressure, high temperature Gas Oil cracking	5·8
High Temperature Regenerative Gas Oil cracking	10·2
Naphtha Cracking by Caterole Process	17·3

By 1965 India will be refining 12 million tons of crude oil which will be largely indigenous. The total yield of liquid hydrocarbons varies with the crude, being as high as 45% by weight in the case of Nahorkatiya crudes and as low as 27% by weight from Cambay crudes. Taking the lower figure for the sake of making a cautious and safe estimate, at least 3·25 million tons of liquid hydrocarbons will be treated in the refineries for the production of gasolene and other petroleum products. Again, taking only the lowest yield of methane as the basis of making a safe estimate of the availability of this material *at least* 32,400 tons of methane will be available for controlled oxidation to methyl alcohol from the refineries alone. In addition, the carbonization of 16 million tons of coal by 1965-66 for the production of metallurgical coke will give the following yields of appropriate gaseous raw materials for the establishment of a liquid propellants industry.

Methane	0·74 million tons/yr.
Carbon Monoxide	0·42 million tons/yr.
Hydrogen	0·22 million tons/yr.

Thus, at least 0·8 million tons of methane will be available by 1965-66 from the refineries and coke ovens for controlled oxidation to methyl alcohol; additionally, there are proved and indicated reserves of nearly 15,000 million tons of methane available in situ as natural gas.

Of course, other hydrocarbons can also be oxidized to methyl alcohol but from Table 7 it can be seen that the oxidation of hydrocarbon higher than methane[7], yield a number of oxygenated products (listed in order of decreasing yield) of which methyl-alcohol is only one compound and apart from low yields, separation is difficult.

TABLE 7

OXIDATION OF HYDROCARBON HIGHER THAN METHANE

Hydrocarbon Oxidized	Oxygenated products in order of decreasing yield.
C_1	2, 3
C_2	3, 2, 1
C_3	1,3,2,4,
N—C_4	1,3,2,4
i—CS	4,1,3,2

Acetaldehyde (1); Methylalcohol (2); Formaldehyde (3); Acetone (4).

Location:

The immense reserves of natural gas clearly indicate that the best possible location of a liquid propellants industry would be in the natural gas fields viz. in the Jwalamukhi area of Punjab and in the Cambay-Ankleswar Kalol area of Gujerat. In the former case, it might be advisable for strategic reasons to locate the actual plant as far away from the border as possible and pipe the gas to the site though this might not make any significant difference to enemy's long range bombers operating from their bases. Therefore, for purely economic reasons it will be desirable to have the plant in the Jwalamukhi gasfield itself. The Gujerat gasfield has the advantage of being near the refineries at Bombay and Koyali from which also additional supplies of methane can be drawn.

However, if dispersion of a strategic industry is desired then some of the plants can be located in the eastern region of the country where a large number of steel plant and other coke ovens are already functioning and from whose gaseous byproducts, methane, carbon monoxide and hydrogen can be recovered for the use of the propellant industry.

CONCLUSIONS

In the foregoing, a comparison has been made of solid and liquid propellant systems and it has been shown that storable and packageable liquid propellant systems are now available which are highly efficient and versatile. From a consideration of the various liquid propellant/oxidizer systems currently in active military use, it is shown that the system, MMH/unsymmetrical dimethyl hydrazine/Red fuming nitric acid is an excellent system round which India's rocket and missile force can be built up on account of its high specific impulse and density impulse and all-round excellent physical, handling and storability characteristics. It has also been shown that the raw materials for their manufacture are available in abundance in the country. Undoubtedly, propellants like pentaborane and oxidizers like bromine pentafluoride and chlorine trifluoride have superior performances but for the immediate purpose of arming our forces with rockets/missiles they do represent systems of all-round general superior characteristics which can be manufactured from abundantly available raw materials in the country.

The manufacture of propellants indigenously from raw materials available in abundance is clearly not only a feasible proposition, but also a proposition which deserves serious consideration at the highest level. It is entirely within the bounds of possibility to develop a completely indigenous propellant manufacturing capacity based on the abundant raw materials available in the country.

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