Rocket Propellants

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Introduction:

THE history of the rocket can be traced back to 1300 A.D., when rockets with gunpowder were introduced from China. However, the principle on which the rocket works was recognized as early as 300 B.C. by Hero of Alexandria. The importance of rockets was not stressed right up to the first World War. The Germans and Americans were first in the field. Goddard in America worked on liquid fuel rockets while the Germans whose work was characterised by disorganisation till 1935, evolved the famous V-2 rocket in the second world war. Since then rockets have assumed increasing importance in warfare and exploration at high altitudes; they are also being seriously suggested for interplanetary travel.

Rockets move forward due to the momentum set up in opposition to the momentum generated by the rocket motor. This momentum is generated by allowing the hot gases, produced by rapid burning of fuel, to expand through a diverging nozzle thus converting the thermal energy of the gases into mechanical energy. The ideal nozzle would have to be infinitely long and require the gases to exhaust into vacuum. Long nozzles are however not used since they increase the rocket weight and the resistance to rocket flight. The Germans claimed a 40% conversion of energy in their V-2 rocket.

Fuel for rockets:

Fuel in the rocket makes up a considerable part of the total rocket weight and it is necessary that it burn quickly and produce the maximum thrust. Rocket fuels are known as propellants and as distinguished from ordinary fuels, carry their oxidant with them. Both solid and liquid fuels are used, their relative values being characterised by the specific impulse which is defined as the thrust produced per pound of fuel per second.

Solid propellants

Solid propellants are characterised by low specific impulses from 170 to 220, small burning times and high combustion chamber pressures. A typical solid propellant system is shown in Figure 1.

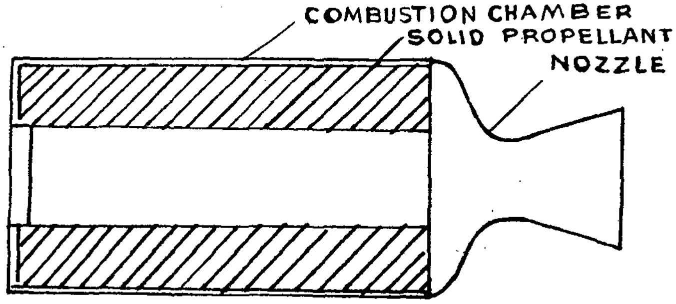

FIG. 1
SCHEMATIC DIAGRAM
OF
SOLID PROPELLANT SYSTEM

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The propellant " grain " is filled round the periphery of the combustion chamber in various ways, the main idea being the proper distribution of weight and the provision of a burning surface which is either constant in area, or increases or decreases uniformly with the progress of combustion. The weight of propellant used is governed by the thrust it must produce while the thickness of the bed will be decided by the rate of burning.

The rate of burning of solid propellants is found to be governed by the chamber pressure, the propellant composition and the initial propellant temperature. The relation is expressed in an equation-[1] $r = ap^n$ where r = rate of burning and p is the chamber pressure. The power term "n" is found to depend on the propellant composition and a value lower than unity is desirable as higher values mean uncontrolled combustion and rapid development of pressure; "a" depends on the propellant and its initial temperature, increasing with higher initial temperatures. The rate of burning is known to increase with the increase in gas velocity parallel to the burning surface.[2] This is known as erosive burning.

Most rockets using solid propellants work in the pressure range of 500-2000 psia, with burning rates ranging from 0.05 inches per second to 2 inches per second.[3] An ideal pressure time curve for such rockets is shown in Fig. 2. The usual curve obtained is also shown. Unstable combustion is known to occur in solid propellant systems,[4] this being accompanied by high frequency oscillations. This is explained as being due to sudden increase in heat flux from the gases to the burning surface. The oscillations increase the burning rate by as much as 150 per cent. Unstable combustion can be reduced by using solids which evolve little heat in the solid phase.

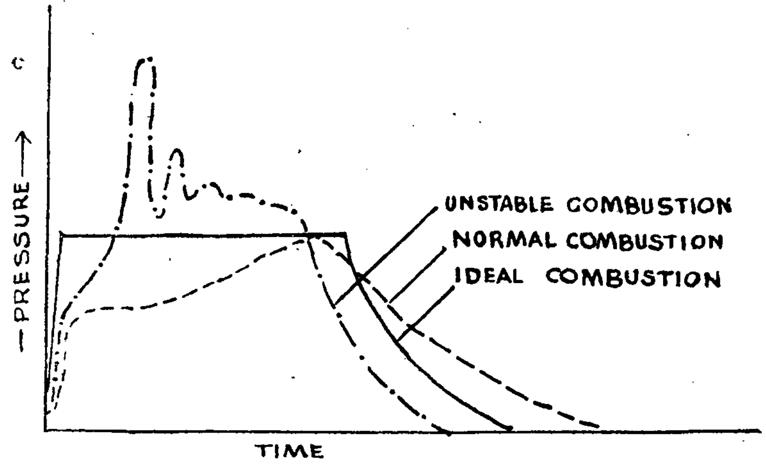

FIG 2
PRESSURE TIME CURVES
For
SOLID PROPELLANTS

Typical solid propellants requiring oxygen would contain perchlorates and nitrates of potassium and ammonium bonded by a combustible material like asphalt or some plastic bonding agent. Double base propellants containing nitroglycerine and nitrocellulose, require no oxidant and give high specific impulses up to 210. Powdered zinc and sulphur have also been used.[5]

Solid propellant systems are preferred in warfare for short range work because of their ease of loading and firing in quick succession.

Liquid propellants

Liquid propellant systems may be bipropellant in which case oxidant is carried separately, or monopropellant in which case separate oxidant is not required. Typical systems are shown in Fig. 3.

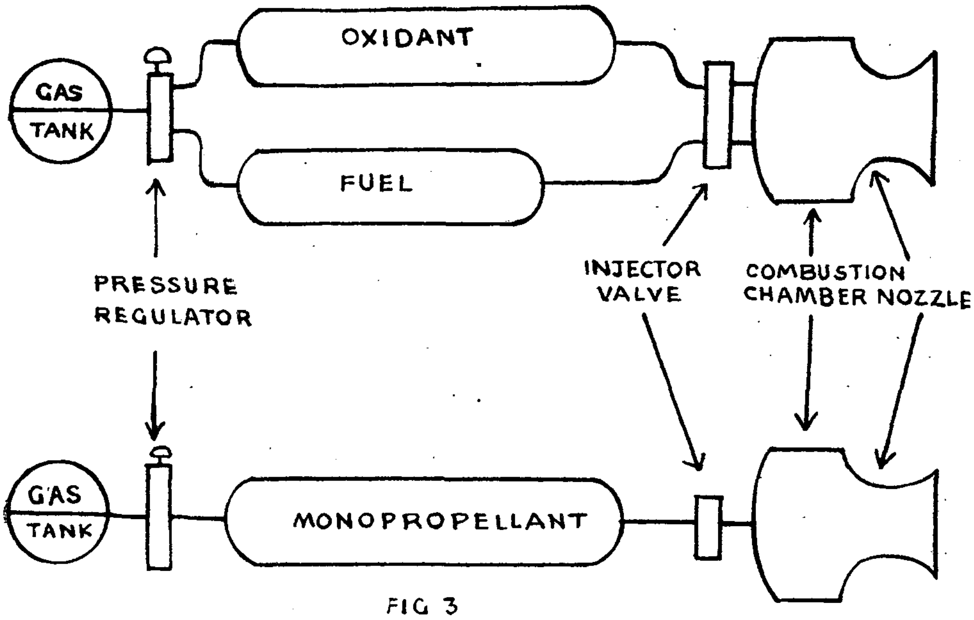

FIG 3
SCHEMATIC DIAGRAM
MONO-PROPELLANT AND BIPROPELLANT SYSTEMS.

To be good propellants, the fuel must satisfy the following important conditions:

(a) High heat of combustion.
(b) Negative heat of formation.
(c) Ease and rapidity of combustion.
(e) Low molecular weight and high density.
(e) Low freezing point and high boiling point.
(f) Safety in storage, handling and transport.
(g) Availability and cheapness.
(h) Low molecular weight of combustion products.

Liquids that have been suggested or are being used (see Table 1) are liquid hydrogen, petroleum hydrocarbons, methyl and ethyl alcohol, ammonia, hydrazine, aniline and the metal hydrides. Since density is important, high density being favourable; the density impulse defined as the thrust per unit volume of fuel per second is used as a characteristic of the fuel.

Liquid hydrogen though having the highest specific impulse, has a low density and boiling point which make it unpopular for general work. However it has been suggested for interplanetary travel. Petroleum oils have good specific impulses, the unsaturated hydrocarbons giving better performance.[6] They are easily available and cheap. The alcohols are more popular being good in performance and cheap. Moreover admixture with water does not reduce performance much but decreases the chamber temperature markedly.[7] Hydrazine is preferred to ammonia though costlier than the latter. Using the monohydrate reduces the cost to some extent. It has a high density and boiling point but its freezing point is low. The high freezing point of aniline can be lowered by mixing with furfural. Aniline is used with nitric acid oxidant in self-igniting systems. Fuels used thus are known as hypergolic and require smaller combustion chambers and simpler injectors. Metal hydrides have been suggested[8],[9] instead of Hydrogen, using the light metals Li, B, Mg, Al, Si. They have high heats of combustion and specific impulses, but they are highly unstable and costly.

The various oxidants are given in table No. 2. Tetra nitromethane and liquid oxygen have almost the same available 0_2 per unit volume but the former is toxic and explosive and 0_2 is always preferred. N_20_4 and $HN0_3$ are popularly used in self-igniting systems for almost all types of fuels. Corrosiveness of HNO_3 increases with NO_2 content greater than 15%. 10% H_2SO_4 may be added to decrease corrosion. Use of less concentrated, nitric acid leads to ignition lag. H_2O_2 is popularly used in bi-propellant systems. Its negative heat of formation suggests its use as a monopropellant. Fluorine is found to be theoretically better than Oxygen[10] but it presents several difficulties owing to its toxic and corrosive nature.

Operation difficulties:

In the performance of rocket motors, the nozzle expansion ratio, the combustion chamber pressure and the propellants used undoubtedly play an important part. But the real limiting condition is the wall temperature. When combustion temperature is 3000°C, the wall temperature is kept down to 1500°C[11] using regenerative or film cooling. Lower wall temperatures are also obtained by using excess fuel which results in the presence of hydrogen in the exit gases and the low molecular weight of the gases offsets to some extent the decrease in temperature. High temperatures do not allow the full chemical energy to be utilised since the gases like H_2O and CO_2 dissociate at high temperatures and decrease the specific impulse. Higher operating temperatures than those used at present could be possible using special materials like ceramet.[11]

Carbon deposition when using petroleum fuels or alcohols is undesirable in the combustion chamber as it can lead to hot spots which can burn out the wall. Studies on carbon deposition[12] show that it is governed by fuel volatility, density, C/H ratio and the strength of the C-C bonds. Carbon deposition increases in the sequence paraffinic → naphthenic → aromatic. For a given C/H ratio, carbon deposition decreases with increase in fuel volatility. Stronger C-C bonds increase carbon deposition. It is hence necessary to specify a low percentage of aromatics as also a lower final boiling point for the fuel.

Ignition delay or lag is an important factor in liquid propellants. Large lags lead to excessive oscillation of chamber pressure during fiiring.[13] It is found advisable to inject oxidiser first and fuel next. However simultaneous injection is best for hypergolic fuels. Lean mixtures have larger lags than rich ones. Higher initial temperature of the fuel reduces the lag substantially. Addition of surface active agents is found beneficial.[14] Reactivity of the fuel is also an important factor in reducing time lag.

Combustion instability in liquid systems is now-a-days being given a great deal of attention.[15] This phenomenon manifests itself in the form of uncontrollable cyclic variations in feed and chamber pressure. Low frequency variations from 40-200 c.p.s. are common. Variation in chamber pressure at rates greater than 1000 c.p.s. is known as " Screaming." These variations have been explained as being maintained by the interaction of the fuel consumption rate and the chamber pressure resulting in shock waves. Low frequency oscillations are governed by the chamber pressure and the fuel to oxidant ratio. These oscillations are not harmful but result in inefficient operation. On the other hand high frequency variations though resulting in better performance, cause a large increase in the heat transfer to the walls of the combustion camber resulting in burnouts.

Rockets in space travel:

All these operating difficulties have not prevented scientists from examining the suitability of rockets for space travel. A great obstacle is the large amount of energy which has to be expended in order to get away from the earth's gravitational field. The velocity of escape which is a measure of the minimum energy required for this purpose, has been found out to be 7 miles per second.[16] A rocket using liquid H_2 and O_2 would if used, require 95.9% of its total weight to be utilized for fuel.[17] A suggestion that the rocket be made in a number of steps, each step containing its own tanks, combustion chamber etc., has been examined.[18] The results show that to carry a ten pound cargo to the moon, a five step aniline-nitric acid rocket would weigh 367 tons initially. A ten step rocket would weigh 60 tons. This looks attractive but is very costly.

The use of nuclear energy is automatically suggested and this would reduce the fuel weight to an insignificant amount but the reaction chamber and heat transfer set-up would be important. Using H_2, heated by nuclear energy to high temperatures of the order of 11,000°F, would give on expelling, speeds greater than 28,000 miles per hour. However these are mere scientific speculations and the operating difficulties are too many to suggest a solution at present.

TABLE 1

Propellant	*Specific impulse*
Liquid H_2	343
Metal Hydrides	290
Alcohol	200-300
Hydrazine	257-264
Ammonia	255
Hydrocarbons	225
Aniline	200
Hydrazine hydrate*	180
80% H_2O_2	120

* contains
57% $N_2H_4 \cdot H_{20}$
30% Methanol
11% Potassium cyanocuprate

Data from Encyclopedia of Chemical Technology, Vol. II and Victor, Rev. Alumin, 24, 69, 1947.

TABLE 2

Oxidant	*Wt.* % O_2	*Density* (20°)	*Grams* O_2 *per litre at* 20°
Nitromethane	69.5	1.65	1150
Liquid O_2 at 1 atm., b.pt.	100.0	1.14	1140
N_2O_4 ..	69.5	1.48	1030
HNO_3 ..	63.5	1.52	970
100% H_2O_2	47.0	1.46	690
90% H_2O_2 ..	42.2	1.405	590

Reproduced from Tschinkel, Chem. Eng. News., 32, 2582, 1954.

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