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Liquid Rocket Propellants: Past and Present Influences and some Future Considerations

Abhinav Madan[1], Mohammad Salman[1], Ganesh Panday[2*] and James Kunjwal[1]

[1]*Department of Mechanical Engineering, Graphic Era Hill University,*
Bhimtal Campus, Nainital, Uttarakhand, India.
[2]*Department of Chemistry, Graphic Era Hill University, Bhimtal Campus,*
Nainital, Uttarakhand, India.

Abstract

During last few decades, propellant chemists are struggling to find high – energy liquid rocket propellants, better suited to the defence and civilian. Rocket propellant is a material used by a rocket as, or to produce in a chemical reaction, the reaction mass (propulsive mass) that is ejected, typically with very high speed, from a rocket engine to produce thrust, and thus provide spacecraft propulsion. A good liquid propellant is one with a high speed of exhaust gas ejection which implies a high combustion temperature and exhaust gases with small molecular weights. Liquid oxygen and gasoline were the first used rocket propellants by Robert H. Goddard. Germany had used alcohol / liquid oxygen with hydrogen peroxide to drive the fuel pumps during world war II .During 1950's and 1960's, hydrogen, kerosene, lithium, fluorine and methane were believed to be a marvelous propellant due to their high specific impulse .One of the most efficient mixtures, oxygen and hydrogen, suffers from the extremely low temperatures required for storing hydrogen and oxygen as liquids (around 20 K or −253 °C)) and low fuel density (70 kg/m³), necessitating large and heavy tanks. This review article is an approach towards the need of ease of operation, low cost and good performance of a liquid rocket propellant. Approximately 170 different liquid propellants have undergone for lab testing till now. The future challenges includes an ecofriendly, easily available liquid rocket propellant having low energy cost.

Keywords: liquid rocket propellant, liquid oxygen, hydrogen, combustion temperature.

1. Introduction

Rocket propellant is a material used by a rocket as, or to produce in a chemical reaction, the reaction mass (propulsive mass) that is ejected, typically with very high speed, from a rocket engine to produce thrust, and thus provide spacecraft propulsion. In a chemical rocket propellants undergo exothermic chemical reactions to produce hot gas. There may be a single propellant, or multiple propellants; in the latter case one can distinguish fuel and oxidizer. The gases produced expand and push on a nozzle, which accelerates them until they rush out of the back of the rocket at extremely high speed. For smaller attitude control thrusters, a compressed gas escapes the spacecraft through a propelling nozzle. A potential other method is that the propellant is not burned but just heated. In ion propulsion, the propellant is made of electrically charged atoms (ions), which are electromagnetically pushed out of the back of the spacecraft. Magnetically accelerated ion drives are not usually considered to be rockets however, but a similar class of thrusters use electrical heating and magnetic nozzles. In pulse propulsion, a heavy, metallic base acquires the force from an explosion behind it, for example from an atomic bomb, and a transfers it to a dampening system that reduces the shock to the payload [1].

Rockets create thrust by expelling mass backwards in a high speed jet (*Newton's Third Law*). Chemical rockets, the subject of this article, create thrust by reacting propellants within a combustion chamber into a very hot gas at high pressure, which is then expanded and accelerated by passage through a nozzle at the rear of the rocket. The amount of the resulting forward force, known as thrust, that is produced is the mass flow rate of the propellants multiplied by their exhaust velocity (relative to the rocket), as specified by Newton's third law of motion. Thrust is therefore the equal and opposite reaction that moves the rocket, and not by interaction of the exhaust stream with air around the rocket. Equivalently, one can think of a rocket being accelerated upwards by the pressure of the combusting gases against the combustion chamber and nozzle. This operational principle stands in contrast to the commonly-held assumption that a rocket "pushes" against the air behind or below it. Rockets in fact perform better in outer space (where there is nothing behind or beneath them to push against), because there is a reduction in air pressure on the outside of the engine, and because it is possible to fit a longer nozzle without suffering from flow separation, in addition to the lack of air drag [2].

2. Review of Literature

Robert H. Goddard on March 16, 1926, holding the launching frame of his most notable invention—the first liquid-fueled rocket. On March 16, 1926, Robert H. Goddard used liquid oxygen (*LOX*) and gasoline as propellants for his first partially successful liquid rocket launch. Both are readily available, cheap and highly energetic. Oxygen is a moderate cryogen — air will not liquefy against a liquid oxygen tank, so it is possible to store LOX briefly in a rocket without excessive insulation. Gasoline has since been replaced by different hydrocarbon fuels, for example RP-1 - a highly refined grade of kerosene. This combination is quite practical for rockets that need not be stored, and to this day, it is used in the first stages of many orbital launchers.

Germany had very active rocket development before and during World War II, both for the strategic V-2 rocket and other missiles. The V-2 used an alcohol/LOX liquid propellant engine, with hydrogen peroxide to drive the fuel pumps. The alcohol was mixed with water for engine cooling. Both Germany and the United States developed reusable liquid propellant rocket engines that used a storeable liquid oxidizer with much greater density than LOX and a liquid fuel that would ignite spontaneously on contact with the high density oxidizer. The German engine was powered by hydrogen peroxide and a fuel mixture of hydrazine hydrate and methyl alcohol. The U.S. engine was powered by nitric acid oxidizer and aniline. Both engines were used to power aircraft, the Me-163B Komet interceptor in the case of the German engine and RATO units to assist take-off of aircraft in the case of the U.S. engine [3].

During the 1950s and 1960s there was a great burst of activity by propellant chemists to find high-energy liquid and solid propellants better suited to the military. Large strategic missiles need to sit in land-based or submarine-based silos for many years, able to launch at a moment's notice. Propellants requiring continuous refrigeration, and which cause their rockets to grow ever-thicker blankets of ice, are not practical. As the military is willing to handle and use hazardous materials, a great number of dangerous chemicals were brewed up in large batches, most of which wound up being deemed unsuitable for operational systems. In the case of nitric acid, the acid itself (HNO_3) is unstable, and corrodes most metals, making it difficult to store. The addition of a modest amount of dinitrogen tetroxide, N_2O_4, turns the mixture red and keeps it from changing composition, but leaves the problem that nitric acid corrodes containers it is placed in, releasing gases that can build up pressure in the process. The breakthrough was the addition of a little hydrogen fluoride (HF), which forms a self-sealing metal fluoride on the interior of tank walls that *Inhibited* Red Fuming Nitric Acid. This made "IRFNA" storeable. Propellant combinations based on IRFNA or pure N2O4 as oxidizer and kerosene or hypergolic (self igniting) aniline, hydrazine or unsymmetrical dimethylhydrazine (UDMH) as fuel were then adopted in the United States and the Soviet Union for use in strategic and tactical missiles. The self-igniting storeable liquid bi-propellants have somewhat lower specific impulse than LOX/kerosene but have higher density so a greater weight of propellant can be placed in the same sized tanks [4].

Many early rocket theorists believed that hydrogen would be a marvelous propellant, since it gives the highest specific impulse. As hydrogen in any state is very bulky, for lightweight vehicles it is typically stored as a deeply cryogenic liquid. This storage technique was mastered in the early 1950s as part of the hydrogen bomb development program at Los Alamos. It was then adopted for hydrogen fueled stages such as Centaur and Saturn upper stages in the late 50s and early 1960s. Even as a liquid, hydrogen has low density, requiring large tanks and pumps, and the extreme cold requires tank insulation. This extra weight reduces the mass fraction of the stage or requires extraordinary measures such as pressure stabilization of the tanks to reduce weight. Pressure stabilized tanks support most of the loads with internal pressure rather than with solid structures. Most rockets that use hydrogen fuel use it in upper stages only.

Gaseous hydrogen is commercially produced by the fuel-rich burning of natural gas. Carbon forms a stronger bond with oxygen so the gaseous hydrogen is left behind. Liquid hydrogen is stored and transported without boil-off because helium, which has a lower boiling point than hydrogen, is the cooling refrigerant. Only when hydrogen is loaded on a launch vehicle (where there is no refrigeration) does it vent to the atmosphere.

Launch pad fires due to spilled kerosene are more damaging than hydrogen fires, primarily for two reasons. First, kerosene burns about 20% hotter (absolute temperature) than hydrogen. The second and more significant reason is buoyancy. Since hydrogen is a deep cryogen it boils quickly and rises due to its very low density as a gas. Even when hydrogen burns, the gaseous H_2O that is formed has a molecular weight of only 18 u compared to 29.9 u for air, so it rises quickly as well. Kerosene on the other hand falls to the ground and burns for hours when spilled in large quantities, unavoidably causing extensive heat damage that requires time consuming repairs and rebuilding. This is a lesson most frequently experienced by test stand crews involved with firings of large, unproven rocket engines. Hydrogen-fueled engines also have some special design requirements such as running propellant lines horizontally so traps do not form in the lines and cause ruptures due to boiling in confined spaces. These considerations, however, apply to all cryogens such as liquid oxygen and liquid natural gas as well. Use of liquid hydrogen fuel has an excellent safety record and superb performance that is well above that of all other practical chemical rocket propellants [5].

The highest specific impulse chemistry ever test-fired in a rocket engine was lithium and fluorine, with hydrogen added to improve the exhaust thermodynamics (all propellants had to be kept in their own tanks, making this a tripropellant). The combination delivered 542 s specific impulse in a vacuum, equivalent to an exhaust velocity of 5320 m/s. The impracticality of this chemistry highlights why exotic propellants are not actually used: to make all three components liquids, the hydrogen must be kept below -252°C (just 21 K) and the lithium must be kept above 180°C (453 K). Lithium and fluorine are both extremely corrosive, lithium ignites on contact with air, fluorine ignites on contact with most fuels, including hydrogen. Fluorine and the hydrogen fluoride (HF) in the exhaust are very toxic, which makes working around the launch pad difficult, damages the environment, and makes getting a launch license that much more difficult. The rocket exhaust is also ionized, which would interfere with radio communication with the rocket. Finally, both lithium and fluorine are expensive and rare, enough to actually matter. This combination has therefore never flown [6]

In November 2012, SpaceX CEO Elon Musk announced a new direction for propulsion side of SpaceX: developing methane/LOX rocket engines.[5] SpaceX had previously used only LOX/RP-1 for all of their primary propulsion engines. LOX and kerosene (RP-1). Used for the first stages of the Saturn V, Atlas V and Falcon, the Russian Soyuz, Ukrainian Zenit, and developmental rockets like Angara and Long March 6. Very similar to Robert Goddard's first rocket. This combination is widely regarded as the most practical for boosters that lift off at ground level and therefore must operate at full atmospheric pressure. LOX and liquid hydrogen, used in the Space Shuttle orbiter, the Centaur upper stage of the Atlas V, Saturn V upper stages, the newer Delta IV rocket, the H-IIA rocket, and most stages of the European Ariane 5 rocket. Nitrogen tetroxide (N_2O_4) and hydrazine (N_2H_4), MMH, or UDMH. Used in military, orbital, and deep space rockets because both liquids are storable for long periods at reasonable temperatures and pressures. N_2O_4/UDMH is the main fuel for the Proton rocket, Long March rockets, PSLV, and Fregat and Briz-M upper stages. This combination is hypergolic, making for attractively simple ignition sequences. The major inconvenience is that these propellants are highly toxic, hence they require careful handling. Monopropellants such as hydrogen peroxide, hydrazine, and nitrous oxide are primarily used for attitude control and spacecraft station-keeping where their long-term storability, simplicity of use, and ability to provide the tiny impulses needed, outweighs their lower specific impulse as compared to bipropellants. Hydrogen peroxide is also used to drive the turbopumps on the first stage of the Soyuz launch vehicle [7].

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