A COMPREHENSIVE REVIEW OF PROPELLANTS USED IN CRYOGENIC ROCKET ENGINE

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ABSTRACT

Very powerful rockets are required to conduct research activities outside the atmosphere of the Earth. At the same time, these rockets also have an important role in placing various communication, security, weather, information and intelligence satellites in their respective orbits. Through these powerful rockets, scientists are trying to reach Mars and beyond it. Liquid propellants have a special contribution to operate these rockets. These rockets evolved at a very rapid pace after the development of cryogenic technology. This technology is very important from a strategic point of view, so every nation wants to achieve it. However, very few nations are capable to overcome the technical complexities of this technology. So far, there are only six nations that have mastered this technology. This has become possible due to intensive research activities in this field. This study attempts to compile research work related to liquid propellants. Special attention has been given to the work done in the field of cryogenic propellants. The major problems encountered during the use of liquid propellants and the research work done for their diagnosis are also included in this review paper. Use of an appropriate heat exchanger can solve some tank pressurization related problems, especially where helium is used. Using cryo-cooler and passive insulation techniques can effectively reduce the boil-off effect. Advanced materials and advanced manufacturing technology are required to control fatigue-related problem such as dog-house failure. Specific chemical nature also restricts the use of some liquid propellants as well.

Keywords: *Cryogenics, Liquid Propellant, Rocket, Liquid Hydrogen, Liquid Nitrogen*

Introduction

The term cryogenics is related to very cold temperatures, typically around -150 °C and below. At such low temperatures, common gases begin to liquefy, e.g., oxygen gas liquefies at -182.96 °C and nitrogen gas at -210.15 °C(Ventura and Risegari 2010). In typical jet engines, atmospheric oxygen/air is utilized to burn the fuel(Royce 2015). Gases have a high specific volume than liquid and need more space to store it(Morin et al. 2011).The usefulness of cryogenic increases here in managing the size of the rocket.By converting these gases into the liquid, their specific volume is reduced so that more fuel can be carried. Additionally, oxidizers used to burn the fuel are readily unavailable outside the Earth's atmosphere. Therefore, it becomes necessary to carry the oxidizer along with the fuel in the rocket engine. For this reason, liquid propellant rocket engines (LPRE) are commonly used in space technology (Casiano et al. 2010).Cryogenic rocket engines are designed in such a way that the fuel and oxidizer can be refrigerated and used in a liquid state. The technology of cryogenic engines is a sophisticated technique. There are many challenges associated with it. Being refrigerated at extremely cold temperatures, excessive heat is generated during the leak. Heat transfer is very rapid, owing to substantial temperature differences. Also, heat transfer by radiation becomes significant in these conditions (BRENNAN 1967; Chen et al. 2004). The highest quality heat insulation system is required to avoid such situations. Proper venting is also required to avoid a sudden increase in pressure in such situations(Chen et al. 2004). Additionally, a cryogenic engine requires unique materials that do not change their properties at extremely low temperatures (Asraff et al. 2015; Murty et al. 2016). Apart from these, many other challenges put this technology in the category of the most complicated technologies. Owing to the extremely complex manufacturing process, very few countries have succeeded in acquiring the cryogenic rocket engine technology.

This article attempts to review the liquid propellants used to operate rocket engines. Of these, special attention has been paid to compile the work done on cryogenic rocket propellants.

Brief History of Cryogenic Rocket Engine

The first liquid-propellant rocket was designed by Robert Goddard, which first flew in 1926. In this rocket, liquid oxygen and gasoline were used as propellants. Significant progress in this field was reported from 1926 until the start of World War II. Some major advantages associated with liquid-propellant rocket engines are extremely high thrust, high thrust to weight ratio, easy throttling, easy to control, etc. In this, the heat release rate can also be completely controlled. With the development of this technology, the rocket became more viable and advanced (GODDARD 1958; Clary 2003; Hunley 2013). The liquid-propellant rocket engine was first used in the V-2 ballistic missiles developed by German scientists during World War II. This was the first practical use of this engine in which liquid oxygen and alcohol were used as propellants. Over time, liquid-propellant rocket engine developed by Germany became more and more efficient, although the original schematic remained the same. Rockets equipped with liquid-propellant rocket engines can be used multiple times. Owing to that, the main engines of the space shuttle are always liquid propellant rocket engines (Sutton 2005; Zaloga 2013: 1942–52).

Mono-propellant, bi-propellant and tri-propellant rockets evolved over time. In a mono-propellant rocket, a single chemical is used as a propellant and the energy required for propulsion is obtained by dissolution of its chemical bonds. In contrast, a bi-propellant rocket uses different liquid fuels and oxidizer propellants simultaneously. Bi-propellant systems are more efficient than mono-propellant systems although their structure and functioning are very complex. Thousands of combinations of fuels and oxidizers have been tested for this purpose over the years. Three propellants are used in tri-propellant rockets which help to generate high specific impulses. It is being developed in the context of rocket designs that will be able to reach in the orbit in a single stage(Alexander 2005; Haidn 2008).

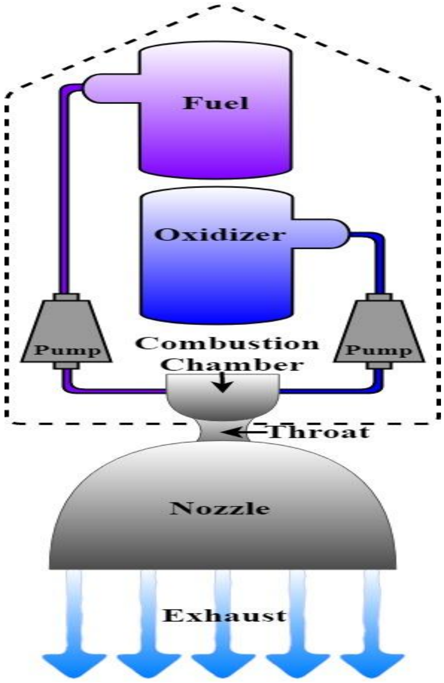

Figure 1: Schematic diagram of cryogenic rocket engine

Table 1: Countries equipped with cryogenic rocket engine technology and description of their first cryogenic engine (liquid oxygen/liquid hydrogen)(Chhaniyara 2013; Gupta 2019).

Sr. No.	Nation	Rocket Engine	Launch vehicle	Thrust (vacuum), kN	Cycle	Year
1.	United States of America	RL-10	Atlas	110.1	Expander	1963
2.	Japan	LE-5	H-1	89	Gas generator	1977
3.	France	HM-7	Ariane 1	62.2	Gas generator	1979
4.	China	YF-73	Changzheng-3	44.15	Gas generator	1984
5.	Soviet Union	RD-0120	Energia	1863.9	Staged combustion	1987
6.	India	CE-7.5	GSLV Mk-2	73.5	Staged combustion	2014

Liquid Propellants

Liquid propellants used in rocket science are generally categorized into three sections, i.e., petroleum-based fuel, cryogenic fuel and hypergolic fuel (Hogoboom et al. 2017; Pelton 2017).Petroleum-based fuels are a mixture of complex hydrocarbons that are refined from crude oil. Highly refined kerosene oil is commonly used as petroleum-based rocket fuel, technically referred to RP-1 (Ott et al. 2008). This fuel is used in conjunction with a liquid oxygen oxidizer. The operating life of rocket engines driven by this fuel is limited as they have been found to produce excessive soot, coke and other harmful residues (Goodger 1995). Some rockets or launch vehicles that have been propelled from this fuel are mentioned in the table 2.

Cryogenic propellant has special significance in rocket science and is also known as a clean-burning fuel. These are liquefied gases stored at subzero temperatures. In this class, liquid hydrogen as fuel and liquid oxygen as oxidizer have been used extensively in rocketry. Since this fuel has to be stored at extremely low temperatures, it is impractical and expensive to store it for a longer duration of time. Owing to the low density of liquid hydrogen, it requires a larger vessel to store than other fuels. In spite of these shortcomings, it is also an attractive fuel for rocketry because it provides much more specific impulses than other fuel. Different types of cryogenic fuels and their usage history are shown in the table 2.The combination of liquid methane and liquid oxygen has also been used as a cryogenic liquid propellant in many space missions(Wang et al. 2010).This combination is relatively a clean-burning and non-toxic cryogenic combination. Cryogenic engines that use liquid fluorine as fuel have also come into existence. Experimentally it was observed that fluorine can act as a super-oxidizer resulting in a high specific impulse to the rocket engine(Bond 1980). It is frequently used in combination with liquid oxygen to further improve its performance as an oxidizer. The combination of liquid fluorine and liquid oxygen is known as FLOX. However, its toxicity has limited its usage(Rothenberg and Ordin 1954).

Hypergolic is the term used for propellant fuels and oxidizers that ignite spontaneously when coming in contact with each other. They do not require any additional ignition source. These fuels are considered as ideal fuels for rocket maneuver systems. In addition, hypergolic fuel is usually liquid at operating temperatures, so they do not pose storage-related problems. Due to the highly toxic nature of hypergolic fuels, extreme care is required during handling and storage. Compounds named hydrazine, monomethyl hydrazine (MMH) and unsymmetrical dimethyl hydrazine (UDMH) are commonly used hypergolic fuels of the liquid propellant engine (Perlee et al. 1962; Mahakali et al. 2011).

Table 2: Common types of liquid propellants

Sr. No.	Type	Composition	Use/Test	Ref.
1.	Petroleum-based Fuels	RP-1/LOX	Atlas, Delta II, First stage of Saturn 1B and Saturn V, Falcon 1, Zenit-3SL	(Bjelde et al. 2007; Training)
2.	Cryogenic Fuels	LH2/LOX	Space Shuttle, Upper stages of the Centaur, Saturn V, Saturn 1B, GSLV Mark III (3rd Stage)	(Vernin and Pempie 2009; Training)
		LOX/CH4	SpaceX Raptor, Suitable for Future Mars Mission	(Vernin and Pempie 2009; Markusic 2010)
		FLOX(LF2/LOX)/RP-1	Tested in Atlas booster engine. No Operational Use	(Propellants, 2020)
3.	Hypergolic Fuels	Aerozine-50/N2O4	Titan II, Apollo Lunar Module,	(Clark 1972; Davis and Yilmaz 2014)
		UDMH/N2O4	Proton Rocket, Ariane 1, GSLV Mark III (2nd Stage)	(Davis and Yilmaz 2014)
		Monomethylhydrazine (MMH)/ N2O4	Ariane 5 EPS, Draco thrusters, SpaceX Dragon	(Davis and Yilmaz 2014)

Alcohol has also been used as a liquid propellant in the early years of rocket science. The combination of liquid oxygen and ethyl alcohol has been used as a propellant in German V2 and American Redstone missile program. With the exploration of increasingly advanced fuels, their use began to be reduced. H_2O_2 was also employed as an oxidizer in Black Arrow rocket, but its poor freezing point and unstable nature hampered its future application badly. Besides, nitrous oxide was also used as an oxidizer or as a monopropellant in some rockets.

Cryogenic Propellants

The most commonly used cryogenic propellant fuel is liquid hydrogen (LH2) and oxidizer is liquid oxygen (LOX). Hydrogen (LH2) is liquefied at -253 °C and oxygen (LOX) at -183 °C. By using cryogenic propellants, rockets are capable of carrying heavy payloads because they have great efficiency to generate high thrust output. This efficiency is usually measured in terms of specific impulse and the measurement unit of specific impulse is second. High specific impulses can be achieved when exhaust gas has a high temperature and very low molecular weight. For this purpose, the propellants must have a large heat of combustion. The presence of lighter elements in the combustion products of propellants is also a very necessary condition here. The density of propellants is also a critical factor as high-density propellants can be carried in smaller and lighter containers than low-density ones. Liquid propellants have a much higher specific impulse than solid propellants (Shen et al. 2019). Therefore, less volume of cryogenic liquid propellants is required to carry similar payloads than solid fuels. In practice, most cryogenic engines powered by liquid oxygen and liquid hydrogen typically operate at mixture ratios of 5 to 6 of LOX/LH2 (Tokudome et al. 2009).The combustion cycle also has its own utility in the context of the efficiency of cryogenic engines. The specific impulse of the rocket can also be increased by choosing a suitable combustion cycle. The staged combustion cycle is capable of generating more specific impulses than the gas generator combustion cycle. However, it has a complex operating mechanism than that of the gas generator combustion cycle.In a staged combustion cycle, the exhaust gas is used again in the combustion chamber with little more oxidizer to get a high specific impulse. However, ejected exhaust gases are wasted in the gas generator combustion cycle (Notardonato 2012).

Efforts to get an efficient liquid propellant are still progressing today. Research is underway to develop cryogenic rocket engine technology worldwide. In this sequence, there has also been commendable progress in the development of liquid propellants. However, most of them are still in the experimental phase. There is a need for further research on the feasibility of using them commercially. In the below-mentioned table, i.e., Table 3, an attempt has been made to compile the research conducted in the context of liquid propellants for the cryogenic rocket engine.

Common Problems Faced in Liquid Propellant Rockets

Apart from the advantages, some problems are also associated with liquid propellants. Efforts are continued unabated for many years to solve these problems. In this section, some problems related to liquid propellants have been referred. This section also includes research activities undertaken globally to overcome these problems.

Tank pressurization related problems

The most commonly used rockets that derive power from liquid propellants are bipropellant type. As described in previous sections, liquid fuel and liquid oxidizers are utilized in them. These are stored in separate tanks and are mixed only when they enter into the combustion chamber. These components are transported into the combustion chamber by pumps or by pressure in the tanks. In both methods, tank pressurization is needed. The tank pressure is required to maintain a positive suction head for the pump in a pump-fed system. However, in pressure-fed systems, it acts as the main driving force to push the propellant into the combustion chamber. The most common method adopted for this task is to use pressurized gas such as helium. This gas is injected from the top of the propellant tank(Lei, Yanzhong, Kang, et al. 2015; Hermsen 2017).Ensuring the availability of sufficient data to accurately estimate the amount of gas required to pressurize and evacuate the tank is a challenge. The availability of such type of data plays an important role in creating an effective design of rockets. The pressurization system should not be so large that it makes the rocket too heavy, nor so small that the engine cannot function to its full potential(Hermsen 2017).The research work done on the problems related to the tank pressurization system is compiled in the Table 3.During long burning hours, necessary precautions should be taken to avoid the excessive cooling of helium gas to maintain the adequate flow rate. If the fuel and oxidizer freeze due to extremely cold helium gas, their flow rate becomes largely unbalanced. This problem can be overcome by using a suitable heat exchanger.

Table 3: Propellants used in liquid cryogenic engine

Cryogenic Propellant	Experiment	Outcomes	Year	Ref
LOX, LCH4, LH2	Minimizing the storage issue	Their technique provides mass savings when mission durations are 7 days for LOX, 14 days for LCH4, and roughly 2 months for LH2.	2002	(Plachta and Kittel 2002)
LH2	cryogenic propellant subsystem for STRATOFLY MR3 vehicle	200 tons of LH2 shall be properly cryogenically stored and managed on board	2020	(Fusaro and Viola 2020)
Zero boil-off				
LOX/LH2	Zero boil-off storage concept	Using cryo-cooler & passive insulation technique can depreciate the boiloff problem	2001	(Hastings et al. 2001)
LN2	Zero boil-off storage	Cryo-cooler was successful at removing 6.8 watts of heat at approximately 75K and 150 watts of input power	2004	(Plachta2004)
LH2	Zero boil-off densified cryogen storage system model	Active cooling and passive insulation systems minimize the overall mass and volume of the storage system.	2004	(Haberbusch et al. 2004)
LO2 & LN2	Zero boil-off system	Boil-off eliminated by the integration of cryo-cooler to the propellant tank.	2016	(Plachta et al. 2016)
Heat Transfer				
LCH4	Conjugate heat transfer of cryogenic methane at supercritical pressures	Heat transfer via convection mode plays a dominating role than conduction in the solid fin	2013	(Leilei Wang et al. 2013)
LCH4	Heat transfer of supercritical cryogenic methane in miniature tube	Jackson acceleration criterion works well in predicting heat transfer deterioration	2013	(Gu et al. 2013)
LOX/CH4	Numerical study of the turbulent convective heat transfer	With the increase of inlet methane pressure, heat transfer was improved at supercritical pressures	2010	(Wang et al. 2010)
LCH4	Turbulent supercritical heat transfer of the cryogenic-propellant methane flowing in a rectangular engine cooling channel	A shallow cooling channel does well for supercritical heat transfer but undergoes severe pressure loss	2012	(Ruan and Meng 2012)
LCH4	Effects of rib geometry, rib height, wall thermal conductivity, and surface heat flux on heat transfer improvement and pressure loss	Ribbed tube surface leads to heat transfer drop at a supercritical pressure	2015	(Xu et al. 2015)
LN2 & LH2	Quenching characteristics were compared between two LN2 & LH2	LH2: annular flow & high mass flux LN2: inverted annular flow & low mass flux	2015	(Hartwig et al. 2015)
Tank Pressurization				
LOx	Investigation on pressurization performance of LOx tank using CFD	Aerodynamic heat mostly impacted the tank performance during pressurized discharge.	2016	(Liu et al. 2016)
LH2	CFD model of the large-sized liquid propellant tank was formulated to study the depiction of pressure fluctuation.	Vaporization rate is largely influenced by heat leaks through the tank wall when the tank is vented.	2013	(Chen and Liang 2013)
LH2	A mathematical model was developed for explaining thermal stratification induced by natural convection in the LH2 tank.	A decline in stratified layer temperature was observed with time in hot test owing to varying LH2 tank pressure.	2017	(Xavier et al. 2017)

LOx	Experimental study on pressurized cryogenic tank performance when high-temperature helium was used as pressurant.	The use of high-temperature helium gas as pressurant in the pressurization system can provide a stable discharging liquid rate.	2015	(Lei, Yanzhong, Yonghua, et al. 2015)
LH2	Developed a CFD model for studying the helium impact on pressurization performance in a liquid hydrogen tank.	For long-duration pressurization, the fluid properties may change owing to diffusion and consequently, the heat and mass transfer rate may alter inside the cryogenic tank	2017	(Wang et al. 2017)
LH2, LOx	A CFD model of the double-side insulated cryogenic tank is investigated to minimize the requirement of pressurant gas.	A lesser amount of pressurant gas is required when an inner insulation layer is introduced in the cryogenic tanks.	2016	(Wang et al. 2016)
LH2	Numerical study on the influence of phase change on self-pressurization in a cylindrical LH2 tank.	The pressure rise was altered by tiny vapor regions (created by evaporation).	2015	(Fu et al. 2015)
LH2	CFD approach to investigate the pressurization performance of LH2 tank loaded with helium gas	With the increased inlet gas temperature, the requirement of gas is significantly reduced during discharge.	2014	(Wang et al. 2014)
LOx	A CFD model was constructed to investigate the pressurization performance of LO2 tank during pressurized discharge.	The foam layer of the tank prevented the outside aerodynamic heating; consequently, no facilitation in pressurization performance was achieved.	2013	(Lei Wang, Li, Zhao, et al. 2013)
LH2	A CFD model was created to examine pressurization performance in LH2 tank	Pressurization performance was better in case of H2 supplies than He.	2013	(Lei Wang, Li, Li, et al. 2013)
LH2, LOx	Comparison of pressurization characteristics obtained for thermodynamic equilibrium model, one-dimensional stratified model and computational fluid dynamics model were done.	Thermodynamic equilibrium model has good acceptability in the pressurization estimate	2015	(Lei, Yanzhong, Kang, et al. 2015)

Acoustic combustion instability problem

In liquid rocket engines, acoustic combustion instability is one of the most complex phenomena. This problem emerges extensively during the design of high-power rockets. In this phenomena, oscillatory combustion occurs that increases pressure with larger amplitudes. It has the potential to damage the combustion chamber walls and injector plates by local burnout. The rate of heat transfer increases substantially due to high-frequency pressure and gas velocity fluctuations(Anderson and Yang 1995).

Chehroudi(Chehroudi 2010) has presented a physical hypothesis related to this phenomenon in his article.Popov et al.(Popov et al. 2015) found that the length of injector channels has a significant impact on stability characteristics.

Boil-off gas problem

Boil-off is a major problem encountered when storing liquid gases at cryogenic temperatures. This usually happens when the heat is transferred to the storage tank by some means resulted in the boiling of liquid. Owing to that process, pressure in the tank increases abruptly. As such, cryogenic gases are always stored below their boiling point. Heat is more likely to enter into the cryogenic tank during the storage or transportation operations. Extensive research efforts have been made to reduce this problem and achieve zero boil-off (Hastings et al. 2001), out of which the results of some articles are placed in the Table 3.

Heat transfer related problems

The reliability of a rocket combustion chamber is dependent on the accurate information of heat transfer in cooling and combustion chamber. The highest heat flux and pressure differential occur at the throat of the nozzle which produces the much-discussed dog-house effect. This effect reduces the lifetime of the structure (Quentmeyer 1977).Doghouse effect is the failure mode of the rocket combustion chamber wall. In this event, the sidewall of the hot gas chamber becomes thinner. As a result, the combustion chamber bulges inwards. It is a visco-plastic deformation caused by load and thermo-mechanical fatigue (Fassin et al. 2014).Dog-house failure is a material related problem. To build high pressure, high performance and reusable cryogenic engine, research needs to be conducted on advanced material and advanced manufacturing technology (Macdonald and Badescu 2014).

Propellant chemistry

Some fuels that are capable of producing excellent specific impulses can also cause problems in the operation of the engine. A major example of such type of fuel is liquid fluorine propellant. It is highly toxic and corrosive and the products resulting from its combustion are also highly corrosive and dangerous.

In table 3, an attempt has been made to summarize the research work done in the context of solving these problems. In addition to these problems, research work is also being done on other problems of liquid propellants to find possible solutions. The rapid development of this field has been possible due to the ongoing research activities around the world. To make very powerful rockets, it is important to diagnose problems related to existing liquid propellants and, it is also necessary to search for possible alternatives to existing liquid propellants.

Conclusion

Cryogenic rocket technology has a special significance in space science. With the help of this technology, it was possible to design better rockets which made it easier to explore space. Placing satellites in their designated orbits, collecting information about other planets, providing logistics or technical support to space stations, carrying astronauts, launching manned or unmanned space missions are also easier. Additionally, with the development of this technique, the percentage of success in these complex missions also enhanced. Liquid propellants have played a crucial role in the development of rocket technology. Cryogenic liquid propellants are liquefied gases stored at subzero temperatures. This is clean rocket fuel, due to which no harmful products are produced by combustion, as a result, the environment is also not getting polluted. In the past, various types of cryogenic rocket fuels were discovered, of which liquid hydrogen gained special significance. In this article, cryogenic liquid propellants used in rocketry other than liquid hydrogen are also described in detail. The common problems encountered during the use of liquid propellant engines and the details of the research work related to improving them is also a major part of this review. Since the outer environment of the Earth behaves in a very unpredictable manner, there is always room for improvement in the efforts made to understand it. Therefore, there will always be a need to design better and higher capacity rockets. To operate these rockets, cryogenic fuel producing more powerful impulse will be required which will be accountable for their development. Helium gas is used prominently for tank pressurization purpose. Use of an appropriate heat exchanger is recommended to solve some tank pressurization related problems. Boil-off problem can be effectively addressed using cryo-cooler and passive insulation technique. Research on advanced materials and advanced manufacturing technology is needed to control dog-house failure. Some liquid propellants that are capable of producing high impulses lose their importance due to their chemical nature. Thus, it can be concluded that potential solutions to existing cryogenic liquid propellant problems and identification of new cryogenic liquid propellants may play a key role in designing better rockets for future space missions.

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