JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

GREEN PROPELLANT : A REVIEW

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1. ABSTRACT:

For decade ,enlarge range of propellant and propulsion system which is used in space exploration by aircraft and space vehicle was studied, developed, investigated and commercialized . From this paper we known about the recent advancement and experimental research on green propulsion for replacement of hydrazine ,hydrazine derivative and nitrogen tetera oxide as propellent in space – propulsion .

The objective of this research was to associate propellent that are able of surpass the performance of current propellent used for space propulsion . Green propellant are remarkable less hazardous ,destructive for human and their domains . There are two type of propellent are studied: being mono -propellent and bi -propellant .This study describes about the advanced and wide uses of green propellent for large mission ,mainly for environments sustainability and safety concern. Payable progressive expeditious research undertaking in the green propulsion field it was necessary to extensively study and collect the data of green monopropellants .

Keyword: green propellant, monopropellant, space propulsion, bi-propellant, environment sustainability

2.INTRODUCTION:

A fifty years space propulsion have using highly toxic and hazardous chemical propellant ,government and experts are urging the change of the highly toxic propellent with green alternatives , a new green alternative and a fresh perspective is needed to address.

The propellant that used for space programs present in three specific environmental concerns: Ground-based Impacts which includes from groundwater contamination to explosions caused by triggered by improper handling of propellants. Atmospheric Impacts generally arise from the interaction between propellant exhaust and the atmosphere. Biological Impacts contribute to toxicity, hazard, distructive and corrosiveness of propellants. Space system developers aim to be mitigate these impacts as doing so , it could possibly reduce both cost and risk related to propellant transportation and storage, clean-up of harmful releases, human exposure to toxic compounds, setup requirements for handling hazardous propellants, and orbital debris. The entrenched utilization of highly toxic propellants that harm environmental pollutants maintain program costs high—but the cost of evolving and be suitable for green replacements with more advantageous performances. That is why the performance of slowed even when a green propellant provides latent performance benefits.

Moreover, the people are misconstrued the meaning of the term "Green Propellant" as totally environment-friendly. All propellants affect the environment in some way or the other. For example, all launch vehicles emit exhaust which may contains carbon dioxide, soot, water vapuor, sulphates, oxides of nitrogen, and inorganic chlorine. Each and every exhaust compounds have their own environmental impact in one way or other. These facts of green propellant are more favorable viewed as one that aim to minimize and eliminate an environmental impact that effect in one or more of the three areas.[1] A green propellant might have its own significant environmental impacts, which may be similar to the present methods. For instances , many green propellants are capable to replaced hydrazine, but they still pose atmospheric and space-predicated effects.

Two types of GREEN propellants were investigated, being monopropellants and bipropellants

Classification of green monopropellants into three more collective major categories:

1. Energetic Ionic Liquids (EILs) (or premixed oxidizer/fuel ionic aqueous solutions).

2. Liquid NOx Monopropellants (either in binary compound, nitro compound, or premixed/blend form). 3. Hydrogen Peroxide Aqueous Solutions (HPAS).

3.GREEN MONOPROPELLANT's CLASSIFICATION :

Referring to some modern green propellants, by calling them the term "monopropellants" or by more equivalent terms such as premixed propellants, fuel blends, or mixtures. Monopropellants are that types of propellants that consisted chemical compounds (for example N2H4), due to exothermic chemical decomposition an energy is released. With the advancement of liquid gun propellants. This particular section describe each of the three classes proposed for monopropellants. This advance development are accompanied with technical data and characteristics including the chemical formulations and each monopropellant constituents . By focusing on the study of propellants thermochemistry-this is necessary to considered or gathered the Thermodynamic and thermochemical properties from various literature sources

3.1. Energetic Ionic Liquids (EILs)

Energetic Ionic Liquids (or premixed oxidizer/fuel ionic propellant blends) also called Ionic liquid(ILS) that contains oxidizer salts and it dissolved in aqueous solutions, mixed with Ionic Fuel (IF) or Molecular Fuel (MF), producing a premixed propellant (i.e., the rocket propulsion community widely use Energetic Ionic Liquid [8]). By adding or blend fuel component in the propellant increase the performance by reducing the high adiabatic temperature of the ionic liquid binary aqueous solution and further stabilizing the combustion process. For instance, methanol is used to regulate and controll the burning rate of the monopropellant while the ammonium nitrate (AN) along with other stabilizing additives is used as a stabilizer [10] . on further different EILs will be describe (i.e., HAN, HAN/HN, HNF, ADN) based on green monopropellants accentuating on their composition, physical properties, performance, stability of storage and handling, toxicity, material compatibility, ignition methods, and in-flight heritage or proposed missions.

3.1.1 HAN

Hydroxylammonium nitrate (HAN) is a liquid monopropellant known for its ionic solution with the chemical formula [NH3OH+][NO3 -], this is considered as a energetic ionic liquids (EILS) and now -a-day it garnered full attention because of their favorable properties including high density, smooth combustion characteristics and considerable Isp × d values [24–29]. Furthermore , it possesses low toxicity and is easy to manipulate or handling (Fig. 3). Therefore, the HAN eco-friendly chemical propellant has emerged as a alternative to hydrazine.

The development of liquid gun propellants (LGPs) in the U.S. Army [13] have origins of HAN based monopropellant . Three specific formulations of LGPs were identify , namely LP1846, LP1845, and LP1898 [5] and their properties are listed in Table 1. The first two columns of these aqueous solutions are HAN/TEAN-based (tri-ethanol-ammonium nitrate) and the third column is HAN/DEHAN-based (di-ethyl hydroxyl ammonium nitrate). Due to relatively low combustion pressure [14], as well as the high combustion temperature (2500 K [5]) ,these propellants are not suitable for rocket propulsion system. Therefore this lead to the formation of the state-of-the-art AF-M315E (Air Force Monopropellant 315E) HAN-based green monopropellant which is suitable for space propulsion innovates by the U.S. Air Force Research Laboratory (AFRL) [15].

Table 1. Composition of US Army liquid gun propellants (LGPs) [28,29].

Propellant	Component, wt%			
	HAN $[NH_3OH]^+$ $[NO_3]^-$	TEAN $[NH(C_2H_4OH)_3]^+$ $[NO_3]^-$	DEHAN $[(CH_3CH_2)HNOH]^+$ $[NO_3]^-$	Water H_2O
LP1846	60.8%	19.2%	0.0%	20.0%
LP1845	63.2%	20.0%	0.0%	16.8%
LP1898	60.7%	0.0%	19.3%	20.0%

Furthermore, HAN propellants are more favorable than compare to the hydrazine, including high chemical stability, enhanced performance, and low development costs. Having these properties HAN particularly well-suited for small spacecraft and satellites [30–32]. Table 3 summarizes the performance comparison of various chemical propellants.

Table 3
Toxicity comparison of different propellants against sodium chloride [8, 9]

Propellants	LD_{50} oral (mg kg^{-1})	LD_{50} skin (mg kg^{-1})
Hydrazine	59	91
HNF	128	-
HAN	325	-
AF-M315E	550	-
LP1846 (XM46)	815	-
SHP163	500-2000	> 2000
ADN	832	-
NaCl	3750	-

3.1.2 ADN

The development of ADN (ammonium dinitramide)-based green propellants began at the Swedish Defense Research Agency (FOI) in Europe in 1997 [22,50,51]. ADN-based monopropellants have arisen as an another type of environmentally-friendly "green" propellant, having high specific impulse, safety, and low maintenance costs. Their more advantageous characteristics make them well-suitable for use in low pollution space shuttle propulsion systems and transportation power systems [38, 39]. The family of ADN-based monopropellants mainly consists of FLP-103, 105, 106, 107 and LMP-103S, among them the latter was developed by Bradford ECAPS Co. LMP-103S and FLP-106 are the most mature and more developed , and LMP-103S was approved by the European Space Agency (ESA) and in-space demonstrated successfully through the High Performance Green Propulsion system (HPGP) on the Mango-PRISMA satellite launched in June 2010 [52–54]. A range of Different fuels were used within energetic ionic liquid mixture such as methanol, monomethyl-formamide MMF and dimethyl-formamide DMF. However, in methanol the addition of ammonia (NH3) is necessary increase the pH of the mixture [22,55] otherwise it will incompatible with ADN

3.2 LIQUID OXIDES OF NITOGENS:

Nitrogen consist many binary compounds by making the bond with oxygen. In this research we only discussed about mono and dinitrogen oxides being NO, NO_2 , N_2O, N_2O_3 , N_2O_4 and N_2O_5 . They are evaluated for working as potential oxidizers for a bipropellant system. Nitric oxide (NO) is gaseous in the pressure-temperature so it excluded from considerations, and is therefore it is outlined from requirement 1. Nitrogen dioxide (NO_2) and nitrogen tetroxide (N_2O_4) form an equilibrium mixture but these propellants are highly toxic (GHS acute toxicity class 1) and that's why they also excluded from consideration and are not included in the trade-off due to non-compliance of requirement 10. This is also applicable for dinitrogen trioxide (N_2O_3), due to falls in GHS class 1. Dinitrogen pentoxide N_2O_5 has a melting point of 41°C and is considered a solid. Therefore, N_2O_5 is excluded as a potential propellant candidate due to non-compliance of requirement 1. The only propellant in this group that is left and could be a potential of viable 'green' propellant is nitrous oxide (N_2O). This propellant have both requirements :relatively nontoxic (GHS class 5) and is liquid in part of the temperature-pressure envelope specified by requirement 1. Therefore, nitrous oxide has been considered in the trade-off as a promising candidate.

3.3 HYDROGEN PEROXIDES

Hydrogen peroxide is categorised as category 3 in the GHS ATC system. Hydrogen peroxide can be procured in concentrations up to 98% (in water). As a monopropellant, hydrogen peroxide decomposes into oxygen (O_2) and water (H_2O), at: Hydrogen peroxide (H_2O_2) is a well-known monopropellant as well as an oxidizer for a bipropellant combinations. Hydrogen peroxide is miscible with water, liquid at atmospheric pressure and room temperature, and relatively non-toxic. Based on its LC50 value, a decomposition temperature around 1000K (for the higher concentrations). However, the specific impulse of hydrogen peroxide is only 186s at a chamber pressure of 10 bar and a nozzle area ratio of 50. Therefore, hydrogen peroxide as a monopropellant is not included in the trade-off due to its noncompliance with requirement 6. As an oxidizer in a bipropellant system, hydrogen peroxide can reach a specific impulse of >310s, depending on the fuel that is used. Therefore, this propellant is included in the trade-off as a bipropellant candidate

Table 11
Comparative properties of green propellant used for reaction control systems (RCS)

Parameters	Propellant currently in use	HAN-based propellant		ADN-based propellant	H_2O_2 propellant	N_2O propellant (liquid)
	Hydrazine	SHP163	AF-M315E	LMP-103S		
Freezing point (°C)	2	←30	-22	-6	-7	n/a
Density (g cm^{-3})	1.0	1.4	1.5	1.4	1.3	0.7
Theoretical specific impulse (s)	239	276	266	182	255	206
Density specific impulse (g cm^{-3} s)	241	390	390	256	332	153
Adiabatic flame temperature (K)	1183	2166	2166	1154	2054	1640

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NEED FOR GREEN PROPELLANT:

• . In composite solid rocket propellants, Ammonium perchlorate (AP) is widely used and it has its own disadvantages i.e. during its decomposition HCl release, and Smoke Trail. HCl gas formed and react with water vapours which leads the formation of HCl (l) this causes Acid Rain. The smoke trail left by the rocket and missile can result in reveal the launching site which is undesirable from the combat point of view. Another point that is also of concern is in exhaust, due to high temperatures, HCl gas further dissociates into H+ and Cl- ions. The Cl- radicals react with the O3 (Ozone layer) molecules, start decomposing it to O2 and start forming compounds like ClO , ClO2, ClO3, etc. which results in depletion of Ozone layer.

• In liquid Propellant, Hydrazine (N2H4) derivatives such as Mono Methyl Hydrazine (MMH) or Unsymmetrical Dimethyl Hydrazine (UDMH) . Hydrazine is extremely toxic, hazardous during fuelling & handling in nature . Therefore there is a necessary to find the substitute of AP & Hydrazine based composition with the minimum compromise of performance and having environment friendly tendency.

• In recent years low toxicity liquid rocket propellants have become an interest and potential substitutes for hydrazine and N2O4 in lower to medium thrust engines because of its cost reduction and minimized environmental impact and, also benifical ,more favorable with the simplification of the long sought health and safety precautions. High-energy based green propellants (like ADN, HAN and HNF) are based on organic compounds and although they produce the high molecular weight of their decomposition products with proportionally higher operational temperatures, which posses significant paramount challenges to durability of catalytic reactors and radiative cooled thrust chambers. Hydrogen peroxide (H2O2) is now being considered as a favorable green monopropellant and bipropellant due it does not suffer from these shortcomings (when paired with hydrocarbons) for low and medium thrust applications. While ,Ammonium Nitrate (AN) Based propellants are always green and environment friendly but it is challenging to manufacture. As AN has multiple crystal phases, which transform at different temperatures into each other . That cause inhomogeneous effect in Solid Composite, which ultimately leads to cracks in grain.

• Many propellants exhibit different density variation at different temperature. This is especially true for N2O (relative density 1.2 near boiling point and 0.7 near 30°C). From the system point of view, it is very efficient to increasing the propellant density. This implies that most light hydrocarbons and N2O should be cooled before tank filling large and immense quantities like boosters. Therefore it shows added advantage of cooling is the reduced vapour pressure (preferably below atmospheric pressure, except for N2O) give low pressure manoeuvre for all ground equipment. In additionally, the cooling requirements are much less than for cryogenic liquids. A conventional industrial refrigerator, like those utilized in deep freeze industry, is sufficient to cool the propellant, vapours can be easily recondensed. Cooling also help to pull down the vapour pressure for toxic or very flammable products. This minimize the peril of toxic fumes (e. g. N2O4) or explosion (air / light HC vapour amalgamation) in case of spillage.

APPLICATIONS:

- Boosters :

The volume of the propellant in luiquid booster is huge, propellant cost also effect. The explosion risk is also an important factor. The behaviour of oxidizers or fuels having potential monopropellant are not very good contenders from safety perspective. All these constrictions are fulfilled by LOX-hydrocarbons combinations such as kerosene. Many US and Soviet launchers are using special kerosene amalgams to reduce adversities like coking and combustion instabilities. The green propellant that can be used in place of kerosene is methane. The biggest advantage of methane over kerosene is the possibility to use a fuel rich gas generator without soot formation and noble cooling efficiency of methane. Moreover, methane is injected in gaseous state lowering the risk of combustion instabilities. Besides the conventional LOX-kerosene and LOX-methane recipes, some light hydrocarbons and ethers offer striking properties such as greater Isp, higher density and regenerative cooling followed by gaseous injection.

- Manned Capsule RCS And Landing Retrorockets: Till this date the reference propellants are MMH / N2O4. The substitution by non-toxic propellants would offer a significant improvement for the crew safety and for post recovery operations. Possible solution emerge viz. new monopropellants such as organic nitrate salts and mixtures or safe combinations like N2O and organic liquids. Certainly, they offer lower Isp than MMH-N2O4 but they are much nontoxic. A critical point would be the ignition reliability which is unconditionally essential for the crew safety.
- AIM (Automatic Interplanetary Missions):

Currently MMH-N2O4 or hydrogen are used extensively in AIMs. For manned missions LOX-LH2 is perhaps the finest choice but may require considerable developments for the landing phase. For less severe Delta V requirements, N2O / hydrocarbons or new monopropellants (ADN or HAN) are preferble solutions.

CONCLUSION:

In this review, we summarized the current state of research and development in green rocket propellants. It is true that the propellant that we used for a half of century for rocket propulsion system , such as hydrazine, are highly toxic and pose risks to human health and the environment. As a result, this research describe about the alternative propellants that are more favorable and environmentally friendly, safer to handle and offer comparable or better performance.

In summary , the development of green rocket propellants is an exciting area of research, and it is likely that we will see more prioritizing eco-friendly and collaborative innovation in this field in the years to come. These developments help us improve the safety and environmental impact of space missions but also help in exploration opportunities that were previously impossible.

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