Green Propellant: A Study

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Abstract- The present study focuses simply on propellants which are environment friendly i.e. Green propellants. In Propulsion Systems, there are two ingredients burned together which are fuel & oxidizer and the resultant energy is used to propel the system. In composite solid rocket propellants, Ammonium perchlorate (AP) is being used extensively which has its own disadvantages i.e. HCl release during its decomposition, and Smoke Trail. HCl gas thus formed tends to react with water vapours resulting in the formation of HCl (l) which causes Acid Rain. The smoke trail left behind the rocket/missile can result in detection of the launching site which is not acceptable from the combat point of view. One more area that is of concern is in exhaust, due to high temperatures, HCl gas further dissociates into H^+ and Cl^- ions. The Cl^- radicals react with the O_3 molecules (Ozone layer), start decomposing it to O_2 and start forming compounds like ClO, ClO_2, ClO_3, etc. which results in depletion of Ozone layer. In liquid Propellant, Hydrazine (N_2H_4) derivatives are commonly used such as Mono Methyl Hydrazine (MMH) or Unsymmetrical Dimethyl Hydrazine (UDMH). Hydrazine is extremely toxic in nature which can be hazardous during fuelling & handling. Hence there is a need to find the substitute of AP & Hydrazine based composition with the minimum compromise of performance and having environment friendly tendency.

Keywords – Green Propellant, Ammonium Nitrate, Ammonium dinitramide, Hydrazinium Nitroformate, Hydroxyl Ammonium Nitrate, High Energy Materials

I. INTRODUCTION

The propellants used in space programs pose specifically three environmental concerns: *Ground-based Impacts* which range from groundwater contamination to explosions caused by inopportune handling of propellants. *Atmospheric Impacts* generally caused by interaction of propellant exhaust with the atmosphere. *Biological Impacts* encompass toxicity and corrosiveness of propellants.

These impacts have sought to be alleviated by space system developers as doing so could possibly reduce both cost and jeopardize- especially 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 perpetuated utilization of highly toxic propellants that engender environmental pollutants keeps program costs high—but the cost of evolving and be suitable green replacements withal inclines to be high. This has customarily slowed advance even when a green propellant provides latent performance benefits. Moreover, the term “Green Propellant” is often misunderstood as totally environment-friendly. All propellants affect the environment in some way or the other. For example, all launch vehicles produce exhaust which can comprise carbon dioxide, soot, water vapour, sulphates, oxides of nitrogen, and inorganic chlorine. All of these compounds have an environmental impact in one way or other. Given these facts, a green propellant is more acceptably viewed as one that seeks to minimize or eliminate an acute environmental impact in one or more of the three areas.[1] A green propellant is liable to have its own environmental impacts, which may be identically tantamount to the present methods. For example, many green propellants can be replaced to hydrazine, but they still present atmospheric or space-predicated effects.

II. NEED FOR GREEN PROPELLANT

To lessen air pollution through rocket launches, much research has been done to develop propellants that are environmental amicable (“green”) and contribute towards non-toxic propellants. These propellants are generally more facile and safer to use than the traditional ones, and are likely to bring down the costs associated with propellant convey and storage. In recent years low toxicity liquid rocket propellants have become captivating as possible substitutes for hydrazine and N_2O_4 in lower to medium thrust engines due to the cost reduction and minimized environmental impact and, more so, the benefits associated with the simplification of the long sought health and safety precautions. High-energy based green propellants (like ADN, HAN and HNF) are predicated on organic compounds and reimburse the high molecular weight of their decomposition products with proportionally higher operational temperatures, which still pose paramount challenges to the entelechy of durable catalytic reactors and radiative cooled thrust chambers. Hydrogen peroxide (H_2O_2) does not suffer from these shortcomings and is now being reviewed as a favourable green monopropellant and bipropellant (in conjunction with hydrocarbons) for low and medium thrust applications. Ammonium Nitrate (AN) Based propellants are always green but it is quite difficult to manufacture. As AN has many crystal phases, which transform into each other at different temperatures. This cause inhomogeneous effect in Solid Composite based on it, which ultimately leads to cracks in grain.

III. DEVELOPMENT IN VARIOUS COMPOSITIONS

Fresh class of high energy propellant compositions, often in the literature verbally expressed as High Performance Green Propulsion (HPGP), comprises of ingredients such as Ammonium Di-Nitramide (ADN, e.g. Swedish propellant LMP-103S). Its specific impulse is around 235 seconds. The development of HPGP was initiated to meet the requirements for future outpost missions. After more than 10 years of research and development and a successful in-orbit demonstration throughout the PRISMA mission, the HPGP technology has confirmed to provide enhancement in performance and volumetric efficiency, lessening of propellant handling hazards and safer launch operations.[2]

Another important alternative for liquid storable propellant for small spacecraft and satellite ACS or RCS, especially taking into account the health and environmental concerns, is 98% hydrogen peroxide of HTP (High Test Peroxide) class. The substance is essentially non-toxic with exceptional environmental compatibility and no risk connected to use of high explosives. AND is high explosive compound that hypothetically may be separated from its solution or even may crystallize spontaneously under adverse conditions such as, vacuum. What more, the 98% HTP may certainly be applied in lieu of hydrazine monopropellant and it additionally might accommodate as an efficacious oxidizer in nontoxic bipropellant cumulations to develop and control a satellite propulsion system for a share of the cost of traditional systems. With the correct materials of construction, felicitously prepared in the laboratory and tested, the compounds showed stability throughout long storage duration– customarily decomposing at profoundly low rates (attainable rates of self-deterioration with present HTP technology may be far below 0,1% per year).[3]

Certainly, the primary advantage of using liquid propellant in the form of 98% HTP for many space propulsion applications such as, satellites, will be the reduction of costs, largely by eliminating the requirement for SCAPE suits required for traditional toxic propellants; no requirement of extensive propellant safety measures and remoteness of the space vehicle from ongoing activities during propellant loading operations; high density of 98% HTP would be the key feature for the reduction of mass of the entire satellite boards and quite lower cost compared to other thruster propellants.[4]

Other oxidizer that can be used as a substitute for both hydrazine and ammonium perchlorate (AP, in solid rocket propellant) is Hydrazinium Nitroformate (HNF). Though substantial advances in recent years, there are numerous issues that argue against the use of HNF. There are unsettled problems regarding characteristics such as thermal stability and rasping sensitivity of this compound, as well as various problems related to compatibility. HNF is additionally quite sumptuous to engender and due to its carcinogenic hydrazine base not stringently a green propellant.[5]

Another chemical compound that can be a better substitution for hydrazine monopropellants is hydroxyl ammonium nitrate (HAN), in the form of liquid solutions. However, it has not yet reached any practical applicability so far mostly due to the quandaries regarding lack of opportune ignition catalysts, perplexed combustion mechanisms, relatively high sensitivity and material incompatibility.

The last but not least example includes the whole group of chemical compounds soi-disant ionic liquids (salts with very low melting points) that typically show substantial benefits over mundane fuels or solvents, such as high stability, reduced toxicity, noble solvent characteristics, and virtually no vapour pressure. Unconventional propellants predicated on energetic ionic liquids have been proposed. Some of them have already been proved to be plenarily hypergolic with 98% HTP. [6][7]

Yet there is need for further development of green chemical space propulsion technologies for their future implements in thrusters. New oxidizers, energetic materials and manufacturing materials are still a requisite. The development of these elements requires the use of many theoretical and experimental implements that indeed are previously made available in modern chemistry, such as quantum chemical analysis, analytical chemistry and through powerful spectroscopic methods.

IV. ADN BASED PROPELLANT

A. Solid Propallent–

Solid propellants, in current era are widely used in booster in large boosters for launchers and, to minor extent, for in-space propulsion. Propellants for these applications are primarily based on the oxidizer ammonium perchlorate, NH_4ClO_4, and metal Al - powder embedded in a polymer binder matrix such as HTPB (Hydroxyl Terminated Polybutadiene) or PBAN (poly acrylonitrile-co-butadiene-co-acrylic acid). Although AP is an excellent oxidizer due to its relatively low hazardousness and the possibility to mould its airborne properties, it has negative impacts on the environment and on personal health. By replacing AP with ADN there will be no hydrochloric emission since ADN only contains hydrogen, oxygen and nitrogen as constituents. Calculations show that ADN-based solid propellant can achieve performance equal to or higher than that of the conventional AP-based propellants.[8]

It is not feasible to employ newly developed propellant to a large sized vehicle such as, launcher boosters. Thus smaller and less cost-sensitive applications seem to be a better choice. Hence, ADN-based propellants are expected to be employed for in-space propulsion applications, where liquid propulsion system is vastly used. Liquid rockets provide high performance and modifiable thrust, but they are costly and use toxic propellants for instance hydrazine, nitrogen tetroxide (NTO) and monomethyl hydrazine (MMH).

Solid propellants possess benefits such as simplicity, storability and compactness. Furthermore, no propellant distribution system is required which enables immensely colossal amelioration in reliability and cost. One disadvantage is however their relatively low specific impulse. In spite of this, solid propellant rocket motors have been used to propel spacecraft in numerous missions since first used in the upper stage of the first U.S. Satellite Explorer I in 1958. In recent times solid propellant rocket motors are considered to be used for the ascend module in the Mars sample return mission. Substituting the AP-based propellant with ADN will provide higher performance and reduced environmental impact. Future work concerning solid ADN-based propellants will focus on improving the mechanical properties and to characterize the sensitivity.[9]

B. Liquid Monopellant –

One of the most promising alternatives to monopropellant hydrazine is blends predicated on an oxidizer salt dissolved in a fuel/dihydrogen monoxide coalescence. Hydroxyl ammonium nitrates (HAN) has been studied for this purport .Due to its high solubility, ADN can be utilized in the same way as HAN.[10][11][12][13][14] The development of ADN-predicated monopropellants commenced at FOI in 1997 on a contract from the Swedish Space Corporation, SSC, and several different propellant formulations have been technologically advanced and substantiated. Future work concerning liquid ADN-based monopropellants will focus on ignition and thruster development.

V. HYDRAZINIUM NITROFORMATE: A NOVEL SUBSTITUTE FOR AMMONIUM PERCHLORATE

Utilization of high performance oxidizers into solid propulsion system provide high specific impulse, reduced or low toxicity and have anticipated exhaust profile characteristics, when compared to other using traditional solid propellants. Solid propulsion system could provide very high specific impulse by utilizing high performance oxidizers such as Hydrazinium Nitroformate (HNF). HNF is much anticipated oxidizer to use in solid propellant formulations due to its energetic nature which provides high performance.

Many oxidizers suffer from varying degrees of instability, such as photosensitivity, shock, friction and impact sensitivity, decomposition in presence of moisture, sensitivity to pH and incompatibility (such as hypergolic reactions) to other propellant materials. A typical example of incompatibility is the reaction between HNF and curing agents used in solid propellant binder grain such as HTPB and GAP. In order to improvise compatibility of the propellant and to diminish the risks by abrasion sensitivity during mixing and casting operation, Cesaroni et al. 2002) taught an oxidizer package comprising a solid oxidizer in the form of discrete pellets from a predetermined geometric shape, the pellets were arranged in an array with spaces amongst the pellets and a holder for maintaining them in the array to receive a binder introduced to spaces amongst the array of pellets. The binder presented provides a support matrix to give harmonizing burn rates for the pellets and the support binder matrix. The pellets were made with HNF or ADN and the composition can present yet ballistic modifiers, other additives and, additionally, ultrafine aluminium.[15]

A monopropellant used in the conventional manner for spacecraft propulsion in existing systems, whereby it is to be noted that due to the properties of the system, less rigorous requirements concerning storage, transport, and handling are possible, was proposed by van den Berg *et al.* (2004).[16] Their research showed that solid high-energy oxidizers, such as HNF or ADN, when dissolved in water, render a liquid monopropellant system with a specific impulse that could be equal to the specific one of the conventional monopropellant.

VI. THE CONSIDERATION

Use of Ammonium perchlorate in composite propellant and that of hydrazine in liquid propulsion is extensive. Yet they both shows high risk of adverse impacts on environment as well as human health. ADN and HNF are emerging as possible eco-friendly substitutes to the AP and hydrazine monopropellants. Even with the ADN hygroscopicity and HNF sensitivity, they have considerably higher specific impulse than AP based propellant systems, reduced toxicity and desirable exhaust gas profile characteristics, when compared to traditional solid oxidizer (AP). Moreover they do not comprise chlorine, thus eliminating the generation of harmful chloric acids. These are the reasons why there is elevated interest in utilization of these propellants.

VII. APPLICATIONS

Probable application is the main driving force for the selection of a green propellant as exemplified by three examples following:

- *Boosters*

  Since the volume of propellant contained in launcher boosters is huge, propellant cost plays a vital role in selection. The explosion risk is also an important factor. As oxidizers or fuels having potential monopropellant behaviour are not very good contenders from safety point of view. 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 I_{sp}, higher density and regenerative cooling followed by gaseous injection.

- *Manned Capsule RCS And Landing Retrorockets*

  Till this date the reference propellants are MMH / N_2O_4. 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 N_2O and organic liquids. Certainly, they offer lower I_{sp} than MMH-N_2O_4 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-N_2O_4 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, N_2O / hydrocarbons or new monopropellants (ADN or HAN) are preferable solutions.

VIII. TOXICITY & CONTROL

Many green propellants are certainly quite toxic. Toxicity level is defined as {Threshold Limit Value (TLV) – Time Weighted Average (TWA); 8 hours per day upon weekly exposure}. Many green propellants have toxicity level in the 1 to 100 ppm range. But there are some which represents astonishingly low limits viz. HTP, toxicity level is 1 ppm (like NTO) and it is 25 ppm for ammonia. Nonetheless the effective exposure risk is lower for HTP than for NTO, which is even worse in the case of ammonia. On the other hand, light hydrocarbons and N_2O are non-toxic, they only have narcotic effect at high concentrations.

This toxicity can be alleviated in some cases by sub cooling. The explosion hazards should also be analysed carefully if large propellant quantities are used. This is a special concern for monopropellants, but N_2O and HAN / ADN seem reasonably safe from this point of view.

Many propellants exhibit an astronomically immense density variation with change in temperature. This is especially true for N2O (relative density 1.2 near boiling point and 0.7 near 30°C). From the system perspective, it is very efficient to increment the propellant density. This betokens that most light hydrocarbons and N2O should be cooled afore tank filling for astronomically immense quantities (boosters). The integrated advantage of cooling is the reduced vapour pressure (preferably below atmospheric pressure, except for N2O) ensuing low pressure manoeuvre for all ground equipment. In additament, the cooling requisites are much slacker than for cryogenic liquids. A conventional industrial refrigerator, like those utilized in deep freeze industry, is sufficient to cool the propellant, vapours can be facilely recondensed. The integrated advantage of cooling is the vapour pressure-pull down for toxic or very flammable products. This will reduce the peril of toxic fumes (e. g. N2O4) or explosion (air / light HC vapour amalgamation) in case of spillage. All these points are taken into account for the trade-off.

IX. CONCLUDING REMARKS

Finally, the providence of green propulsion will depend on its ability to satisfy the two primary requisites for its progress – higher performance and lower costs. U.S. space agencies have already begun to move towards green propellant with acceptance of LOX/hydrogen and LOX/kerosene launch vehicles and greater use of electric propulsion for spacecraft. Till this date environmental impact of launch vehicles might felt low, because launch rates are nominal. Green technology could make interplanetary missions more proficient and sample return missions from distant bodies more practicable. Green technology isn’t just a future prospect – it is already a part of space development, and further development seems highly prospective.

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