HAN-Based Monopropellant Assessment for Spacecraft

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The growing cost of space missions, the need for increased mission performance, and concerns associated with environmental issues are changing rocket design and propellant selection criteria. Whereas a propellant's performance was once defined solely in terms of specific impulse and density, now environmental safety, operability, and cost are considered key drivers. Present emphasis on these considerations has heightened government and commercial launch sector interest in Hydroxylammonium Nitrate (HAN)-based liquid propellants as options to provide simple, safe, reliable, low cost, and high performance monopropellant systems.

Introduction

Monopropellant system development has been pursued for decades. The simplicity of monopropellant feed and control systems make them very attractive for missions where the high performance ($I_{sp}$) of bipropellants can be traded for high reliability and low cost. Many monopropellants have been investigated, but only a few have found continued applications. Hydrazine ($N_2H_4$) is by far the most widely used monopropellant and is applied in many types of attitude control thrusters, insertion stages, and gas generators. It has relatively high performance (compared to cold gas systems), an extensive flight heritage, and is commonly referred to as the state-of-the-art. Toxicity & flammability hazards, however, are $N_2H_4$'s major drawbacks. These hazards necessitate expensive ground handling procedures that limit $N_2H_4$'s utility for small cheap spacecraft. This has led NASA to establish a program to develop an advanced monopropellant rocket system for future applications.

Specifically, the NASA Advanced Monopropellant Program is emphasizing the requirements of several mission scenarios. These include, for example, orbital insertions and attitude control for small Earth-science spacecraft and injection retro for planetary spacecraft. In general, the advanced monopropellant thruster being developed will be of high value in missions where simple, cost-effective, relatively high thrust systems are desired or where insufficient power is available for electric propulsion options. The primary goal of the program is to demonstrate a flight-type monopropellant thruster that is environmentally benign and has a specific impulse greater than that of $N_2H_4$, nominally 220 seconds.

Based on the search for monopropellants that could meet these goals Hydroxylammonium Nitrate-based (HAN-based) liquid monopropellants were identified. HAN-based monopropellants have been pursued by the Army as liquid gun propellants (LGP) for many years. Through the Army liquid gun program, HAN-based propellants have shown promise in the areas of environmental/health and safety, performance, density, and thermal management. The impact on satellite design of the anticipated propellant enhancements were assessed in a number of studies. One such study compared a HAN-based monopropellant and a hydrazine monopropellant propulsion subsystem for three NASA missions, Total Ozone Mapping Spectrometer-Earth Probe (TOMS-EP), Tropical Rainfall Measuring
**Baseline Propellant Formulation**

The Army has developed a number of HAN-based monopropellants for use in artillery guns. Three of these formulations are LP1846, LP1845 and LP1898. Table I shows the formulations of LP1846 and LP1898 with 20 percent water by weight along with LP1845, a variation of LP1846 with reduced water content. They are all HAN-based and differ only in the carbon containing component. LP1846 and LP1845 use triethanolammonium nitrate (TEAN) and LP1898 uses diethylhydroxylammonium nitrate (DEHAN).2 These formulations are salts dissolved in water. HAN is oxygen rich, and is commonly referred to as the oxidizer, the other salt is fuel rich and is referred to as the fuel. Variations on these formulations are being developed for rocket monopropellant applications. They are being derived from the aforementioned Army formulations as aqueous mixtures of HAN and one or more nitrate salts. Issues specific to rocket monopropellants, such as low pressure ignition and combustion with a clean exhaust plume, are being considered.

To date, though, LP1846, LP1845 and LP1898 are the most closely studied HAN-based formulations and have the largest body of data available. Therefore, the discussion herein will use LP1846, LP1845 and LP1898 as examples to illustrate the advantages of HAN-based monopropellants.

**Benefits Over State-of-Art**

Based on the considerable amount of work done on the Army’s HAN-based LGPs, benefits of a HAN-based monopropellant propulsion system are anticipated in the areas of safety, performance, density, and thermal management as discussed below.

**Safety**

HAN-based propellants, mostly LP1846, have been the subject of numerous studies concerning the health and safety risks associated with them. To date all data collected is favorable. Both the generant and the exhaust are benign. No extraordinary clothing is required for handling. Water repellent materials and elastomeric gloves are sufficient. Utility clothing is acceptable if it is removed and the skin is washed after a spill. Animal studies have shown that toxicity is not a major concern. LP1846 has proven negative as both a carcinogen and mutagen.4 No inhalation hazards are associated with these propellants (unless aerosolized5), or their exhaust products (CO2, N2 and H2O). In addition, the propellant has proven not to be flammable or sensitive at atmospheric pressure. The health and safety characteristics of N2H4 are a stark contrast to the ones just described for HAN-based monopropellants. N2H4 poses a threat both in terms of toxicity and flammability. N2H4, both as a liquid and vapor, is a confirmed carcinogen, mutagen in animals and is flammable at atmospheric pressure. It requires specialized clothing, facilities, and equipment. This all translates into large infrastructure and high costs associated with handling N2H4.4,6

**Performance**

A comprehensive investigation of potential formulations and a careful balance of the critical issues of performance, ignition, material limitations, and contamination is underway. Variables being considered for formulation of a HAN-based rocket monopropellant are the fuel ingredient and amount of water. Performance of HAN-based liquid propellants is highly dependent on the amount of water in the mixture. The more water, the lower the exhaust temperature and, to first order, the lower the specific impulse. The fuel ingredient trades are maximizing the heat of formation or fuel value.
while minimizing the molecular weight of the exhaust.

The fuel ingredient trades are still continuing, therefore, for purposes of benchmarking the performance of HAN-based monopropellants, LP1846, LP1845, and LP1898 were used.

Figure 1 is a graph of theoretical specific impulse ($I_{sp}$) vs. area ratio for LP1846 (XM46) and LP1898 with variations in water content. These predictions were obtained using a one-dimensional equilibrium code. Further refinement of the theoretical $I_{sp}$ predictions to account for decomposition inefficiencies and heat losses can be found in Table II. Two estimates of specific impulse efficiency ($\eta I_{sp}$) are made, a conservative $\eta I_{sp}$ estimate of 85% along with an anticipated $\eta I_{sp}$ of 92%. It can be seen that a delivered $I_{sp}$ of between 220 and 240 seconds is achievable with the Army LGP's, and even higher $I_{sp}$ in the range of 270 seconds is achievable, with a reduced water version of these baseline formulations.

Comparitively, N$_2$H$_4$ monopropellant thruster systems have delivered $I_{sp}$ of between 220 and 230 seconds.

Density

The density of a HAN-based rocket monopropellant can be estimated by looking at the Army LGP formulations in Table III. The similarity between LP1846, LP1845, LP1898 and the rocket monopropellant under development is in both the ingredients and their quantities (~60 wt % HAN and ~20 wt % H$_2$O). Therefore, the storage density of the advanced rocket monopropellant can be estimated as ~1.4 g/cc. This is a 40% improvement over the 1.0 g/cc of N$_2$H$_4$.

Thermal Management

Thermal management of a HAN-based monopropellant system is driven by the viscosity. Figure 2 has a graph of the viscosity of the Army monopropellants as a function of temperature. From this, it can be seen that at approximately 240 K the propellants transition into a region of dramatic viscosity variation. This sets the lower bound on the usable temperature range of the propellant. Increased viscosity below this temperature makes the propellant incompatible with typical propellant feed systems. Therefore, the practical limits of these types of monopropellants appears to be approximately 240 K. The exact temperature limit of the propellant and amount of thermal management ultimately will depend on the exact formulation, propulsion system design, mission, and satellite design. In contrast, a N$_2$H$_4$ propulsion system is limited not by viscosity variations, but rather the freezing point of the propellant (see figure 2). N$_2$H$_4$ freezes at 273K and is generally maintained at a minimum temperature of 280K. This 40K difference in propulsion system temperature requirements translates into possible reduction or elimination of thermal management power requirements for HAN-based systems.

Critical Demonstrations

A large body of work has been done under the Army funded gun program that is directly applicable to the NASA rocket effort. Work in such areas as safety, handling, materials compatibility, modelling, ignition and combustion fundamentals, to mention only a few, have all been leveraged. The fundamental differences in the Army gun effort and the NASA rocket effort to be addressed are operating pressure, duty cycle, and material limits. Liquid monopropellant artillery guns under development operate at approximately 200 MPa and fire a few rounds a minute. High pressure operation enhances the combustion kinetics and the low duty cycle allows the gun to act as a heat sink to survive the extreme combustion temperatures. Rocket monopropellant systems under development must be designed to operate in the range of 0.5-1.4 MPa, at a variety of duty cycles in both pulse and steady-state modes, and at the highest possible performance (i.e. highest temperature). At low pressures the turbulence levels will not be present to enhance ignition and combustion. At multiple duty cycles and with high performance (>220 seconds), selection of thruster materials (specifically catalyst materials) will present a challenge.

Two NASA contracts have been let via the IHPRPT program to address these issues and develop a flight-type thruster operating on a HAN-based monopropellant. The thruster/propellant development has achieved very promising results to date. Specifically, over one-hundred different ingredients for possible fuel alternatives have been investigated. This list has been trimmed to five ingredients through both laboratory and thruster/reactor testing. Thruster testing used a pyrotechnic ignition system and heavyweight hardware
to investigate the critical thresholds of the thruster and propellant designs. In this configuration many HAN-based rocket monopropellant formulations were tested at chamber pressures that varied from 2.5-4.8 MPa. One of the formulations tested in this configuration was optimized for performance and demonstrated an Isp of 270 seconds (projected for area ratio of 50:1 at vacuum conditions) at a TIC* (characteristic exhaust velocity efficiency) of 95%. The combustion temperature in this case approached 2500K and had an exhaust that was largely water.

For the baseline thruster system, ignition studies have focused on catalytic ignitors. Catalytic ignition and combustion at pressures of 1.4-2.8 MPa with a non-optimized HAN-based monopropellant has been demonstrated. The catalysts primarily being considered use a Pt-group metal as the active metal and require a minimal amount of preheat, much the same as in hydrazine systems. However, as demonstrated in the pyrotechnic/heavyweight hardware testing, operating at the maximum potential performance of this type propellant results in a very high temperature oxidizing environment. This environment will preclude the use of conventional catalyst materials. Therefore, additional ignition concepts will be developed along with a baseline thruster system that will operate at a reduced temperature so that a conventional catalyst bed ignition system can be used. The alternate ignition concepts to be considered for the next generation advanced monopropellant thruster system include laser ignition, electrical ignition, chemical injectant ignition, and an enhanced catalytic ignition system.

Conclusion

HAN-based monopropellant systems will provide a step-change in monopropellant technology. Once available, reduced costs, increased capability, and decreased complexity will all result. The primary technical challenges which need to be addressed before these monopropellants can be applied to satellite propulsion systems are reliable, repeatable ignition at low pressure and high temperature oxidation resistant materials. Low pressure ignition (1.4-2.8 MPa) has been accomplished with both a pyrotechnic and catalytic ignition system, but repeatability and durability of the ignition system is still an issue at this time. Design changes from the state-of-the-art N₂H₄ system such as combustion chamber material, ignition concept, and thermal management system may be required, but with very little affect on overall system mass. A dramatic impact on mass and volume is anticipated when compared to N₂H₄ propulsion systems because of increased performance and density of this new propellant. However, the overriding benefit of HAN-based propellants will be reduced toxicity and flammability hazards and the corresponding reduction in ground operation costs.

References

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<td>60.8</td>
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Table I - Composition of Army developed monopropellants for liquid gun applications

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<tr>
<th>LP1846</th>
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<tr>
<td>Combustion Gas Molecular Weight, lb/lb mol @ 100 psi</td>
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<td>C*, ft/sec @ 100 psi</td>
<td>4356</td>
<td>4455</td>
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<td>Theoretical Isp, @ 100 psi / 50:1 expansion, vacuum</td>
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<td>Estimated Isp (Theo. x 0.92)</td>
<td>232.7</td>
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Table II - Theoretical Performance of Reference Monopropellants

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<td>Density, g/cc @ 25 C</td>
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Table III - Density of Reference Monopropellants
Figure 1 - Theoretical Rocket Performance Predictions

Figure 2 - Viscosity of HAN-based Monopropellants and Hydrazine
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