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# Propellant Technologies: A Persuasive Wave of Future Propulsion Benefits

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### **PROPELLANT TECHNOLOGIES: A PERSUASIVE WAVE OF FUTURE PROPULSION BENEFITS**

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#### SUMMARY

Rocket propellant and propulsion technology improvements can be used to reduce **the** development time and **operational** costs of new space vehicle programs. Advanced propellant technologies can make the space vehicles safer, more operable, and higher performing. Five technology areas are described: Monopropellants, Alternative Hydrocarbons, Gelled Hydrogen, Metallized Gelled Propellants, and High Energy Density Materials. These propellants' benefits for future vehicles are outlined using mission study results and the technologies are briefly discussed.

#### INTRODUCTION

Space exploration and utilization require vehicles that are **operable,** safe, and reliable. **Technologies** for improving rocket performance are also desirable. As space missions become more ambitious, the needs for reducing cost and increasing the capability of rocket systems will increase. Propellant technologies have the power to make space **flight** more affordable and deliver higher performance.

Throughout the world, a new set of space related activities is being formulated. Many nations are taking advantage of the powerful viewpoint of Earth from orbit and beyond. New space activities in the USA are planned which include small expendable boosters, larger reusable launch vehicles, high speed aircraft, and new small spacecraft for many commercial and civilian space operations. These new space planning activities have identified the need for new lower cost ways of gaining access to space, and many ideas are coming to bear on this difficult issue. The cost of space access is particularly vexing, as many people and much infrastructure is usually associated with large orbital aerospace and rocket vehicles. One option to reduce space access costs is propellant technologies. Advances made over the last 60 years in propellants have shown that propellants can be made safer, less costly, and/or more energetic. Investing in propellant technologies can provide benefits across the board to all major international programs and **the NASA** Enterprises (ref. 1)

With the recent advent of reusable launch vehicles (RLVs), the investigation of combined cycle and combination propulsion, and the development of small boosters for low cost spacecraft, the interest in advanced propellants has arisen. With RLVs, the need is for propellants that improve the vehicle mass fraction, as the idea of single stage to orbit makes unceasing demands on the performance of lightweight materials, cryogenic systems, and, of course, rocket propulsion. Combined and combination propulsion, using both air-hreathing and rocket propulsion, are another set of options for single stage and two stage to orbit vehicles. These vehicles will also stress the limits of many technologies, and high density, high energy hydrocarbons and hydrogen will be needed. Advanced cooling techniques with endothermic fuels is also attractive for many applications. Small boosters are also in vogue. The use of

small boosters for space access has become more attractive, especially for entrepreneurs attempting to use space for profitable gain, and universities who wish to use space flight, satellite construction, and operation as learning tools.

High speed aircraft, with fleet foot, perhaps approaching orbital velocities, are also in the plans for commercial gain, national power projection, observation, and space access. These aircraft require cooling technologies for their airframes as well as their internal systems, passengers, and payloads. Typically, the fuel is used as a heat absorber, but hypersonic flight requires cooling capacities that exceed that of traditional fuels. Endothermic fuels have the capacity to thermally break up and split into components. This breakup of the fuel absorbs heat and increases the fuel cooling capacity.

Many studies have also shown the powerful leverage gained with high performance upper stages. High specific impulse propellants with high density can reduce the size of launch vehicles, thereby performing the same mission with a smaller launch vehicle, reducing the cost of space access. Improving these upper stages has led to the use of  $O<sub>2</sub>/H<sub>2</sub>$  propellants, but the density of H<sub>2</sub> has hampered the ability of upper stages in the search for high density. Additives to  $H_2$  or the use of alternative hydrocarbons may allow the upper stage to deliver the same payload performance while occupying a smaller volume, and reduce the overall launch vehicle mass and cost.

Spacecraft propulsion technology improvements are critically important in reducing space vehicle costs. Just as with the upper stages, reducing the mass and size of the spacecraft can reduce the size of the launch vehicle needed. As the propulsion system is often the largest and most massive component of a spacecraft, there is a powerful leverage to be gained with higher density, higher performance propellants. Size reductions can often allow the integration of functions that further reduce overall vehicle costs, such as the combining of apogee propulsion for orbit circularization, and the use of the same propellants and engines for on-orbit maneuvering and orbit maintenance.

The future also beckons with new propellants born of the computer and the propellant designer. A dream of many is the harnessing of the most powerful chemical bonds between individual atoms, of hydrogen, boron, carbon, and aluminum. The atoms, once created, are arrested within a cryogenic solid, and released as they enter the rocket engine. Though these propellants are currently difficult to fabricate in large quantities, there is hope that the power of molecular manipulation from microtechnology, and ultimately nanotechnology, will make these new, and in some cases not vet known, propellants a shining reality.

Five major areas of propellant technologies will be discussed in the paper. The influence of these technologies on vehicle design, some of the current research interests, and the status of the technologies will be addressed.

#### THE TECHNOLOGIES

Five major areas have been identified for fruitful research. The five areas are Monopropellants, Alternative Hydrocarbons, Gelled Hydrogen, Metallized Gelled Propellants, and High Energy Density Propellants. During the development of the NASA Advanced Space Transportation Plan, these technologies were identified as the most likely to have high leverage for new NASA vehicles for each of the Enterprises. Several NASA research programs had fostered work in fuels under the topic, "Fuels and Space Propellants for Reusable Launch Vehicles," (ref. 3) in 1996 and 1997. One of it's components was formulated to promote the development and commercialization of monopropellant rocket fuels, hypersonic fuels, and high energy density propellants. This research has resulted in the teaming of small business with large industry, universities, and government laboratories. This work is on-going with 7 contractors, and the commercial products from these contracts will bolster advanced propellant research. This work is continuing under other programs, recently realigned under the Three Pillars of NASA: Global Civil Aviation, Revolutionary Technology Leaps, and Access to Space.

The five technologies are described and their applications and their effect on future missions is discussed.

#### MONOPROPELLANTS

Current spacecraft and satellite users and manufacturers are looking for more environmentally benign, safer propellants. Environmental, safety, and cost concerns with hydrazine  $(N_2H_4)$  and its derivatives have led to the development of monopropellants with a high water content and high energy additives. Though the first versions of the fuels may be lower performing than hydrazine, the cost associated with launch processing and the ground crew's safety are significantly reduced with the new monopropellants. Safer propellants can reduce costs by eliminating the need for self-contained atmospheric protective ensemble (SCAPE) suits (ref. 2) that are needed for toxic propellants. Also, extensive and prohibitive propellant safety precautions, and isolation of the space vehicle from parallel activities during propellant loading operations can be minimized or eliminated (ref. 3). If used on future satellites, the costs for operating them will be lowered, in some cases dramatically. Monopropellant testing of hydroxyl ammonium nitrate (HAN)-based fuels has begun to show promise and will soon be adopted for on-board propulsion systems on communications satellites and LEO satellites and constellations (ref. 4).

Technologies for igniting the monopropellants are important. Current monopropellants use a catalytic ignition system, but some of the high energy additives can foul the catalyst, making it less effective. Laser and combustion wave ignition are potential alternatives. Materials compatibility of the monopropellants with the tank materials is also very critical for long term space missions. Polymeric liners or chemical passivation of metallic fuel tanks may be required to alleviate this problem. The high water content of the monopropellant will create a highly oxidizing environment in the rocket chamber and nozzle. High temperature coatings will be required to minimize the chemical attack of the exhaust on the rocket engine walls.

Advanced monopropellants are potentially simpler to handle than traditional bipropellants, and have a density comparable to solid rocket motors. Figures 1 and 2 show the benefits of monopropellants for Liquid Rocket Boosters (LRB) for the Space Shuttle. The monopropellant shown here is TEGDN/AP/A1 (ref. 5) and it can reduce the overall gross liftoff weight (GLOW) of the Shuttle, and reduce the booster length, making them more compact. In figure 1, the GLOW of the Space Shuttle is reduced by 9.3 percent when using a TEGDN/AP/A1 monopropellant LRB. The booster length for this option is 124 ft. By allowing the booster length to grow to 142 ft, the payload is increased from 50 000 to 70 500 lbm, and the resulting booster is still considerably shorter than the 149-ft SRB, as shown in figure 2. These options for increasing payload and reducing booster length give the designer more options that can lead to further reductions in vehicle mass and increases in payload performance.

Other monopropellants using gelled fuels can also improve performance and increase safety (ref. 5). Gelled  $H_2O_2$  and liquid TEGDN/AN/Al have the potential for very high density, excellent performance, and safety. Metal particles could be added to the gelled  $H_2O_2$ , further increasing it's density.

#### ALTERNATIVE HYDROCARBONS

The regenerative cooling of spacecraft engines and other components can improve overall vehicle performance. Endothermic fuels can absorb energy from an engine nozzle and chamber and help to vaporize high density fuel before entering the combustion chamber (refs. 6 to 10). For supersonic and hypersonic aircraft, endothermic fuels can absorb the high heat fluxes created on the wing leading edges and other aerodynamically heated components. Dual fuel options are also possible, where the endothermic hydrocarbon (HC) fuels are used for the lower speed portions of flight below Mach 8, and the hydrogen fuel is used for the final acceleration to the upper stage separation velocity.

Figure 3 shows the GLOW for several airbreathing space vehicles. The baseline case is a hydrogen fueled Single Stage to Orbit (SSTO) vehicle, whose GLOW is less than 1 million lbm. Both Two Stage to Orbit (TSTO) cases have GLOW values that are 1.5 and 1.7 million lbm, respectively. Endothermic hydrocarbon fuels, because of their greater heat load absorption, require an increased GLOW over H<sub>2</sub>-fueled Two Stage to Orbit vehicles. This increase in GLOW is relatively small at 0.2 million lbm, however, and eliminates the need for  $H_2$  for the first stage. Several types of related hydrocarbons can increase fuel density and reduce the overall mass of the vehicle structure, tankage and related thermal protection systems.

Material compatibility is also a crucial factor in the design of these endothermic fuel aircraft. Figure 4 shows the effect of different feed system metals on the phase change (or gasification) of aircraft fuels for cooling applications. These design issues are especially important for long lived operational vehicles, such as military and civilian aircraft or reusable spacecraft.

A research area that has gained emphasis is Hypersonic Fuels. With the planned development of Reusable Launch Vehicles and airbreathing Rocket Based Combined Cycle systems, higher density fuels will be desirable for airbreathing vehicles in the speed range of Mach 1 to 25. Endothermic fuels and fuel additives are sought to increase the heat-sink capacity or cooling capacity of the fuel for hypersonic flight. Gelled  $H_2$ ,  $O_2$ , or methane  $(CH<sub>A</sub>)$  (with appropriate gellants, such as water, ethane or other frozen cryogenic gellants) or nanoparticulate gellants are also of interest due to the potential for higher propellant density for alrbreathing ramjet or scramjet propulsion. Fuel systems supplemented by radical recombination catalysts, such as phosphorus species, to accelerate recombination of hydrogen, oxygen, and hydroxyls (OH) to form water, with net improvement in thrust efficiency for high speed nozzle expansions, without severe specific impulse (Isp) losses, are also of interest. This research includes analytic assessments of feasibility, practical demonstrations of fuel additive techniques using minimal, efficient, smart delivery systems, and demonstrations of thrust augmentation in nozzle test flows. Liquid air systems that can produce an oxidizer from captured air are also being investigated. The oxidizer produced from the air would be stored on board the aircraft for later use.

#### **GELLED HYDROGEN**

The benefits of gelled hydrogen have been known for many years and experimentally proven in the past (refs. 11 to 15) There are five major benefits: safety increases, boiloff reductions, density increases with the attendant area and volume related mass reductions for related subsystems (thermal protection system, structure, insulation, etc.), slosh reductions, and Isp increases (in some cases). All of these benefits together can provide GLOW reductions for airbreathing vehicles and rocket powered vehicles. Early tests of gelled H<sub>2</sub> used silica gellants, but required large weight percent (wt%) values of the gellant to be successful. Later work identified solid cryogenic methane and ethane, as well as nanoparticulate materials, as more appropriate gellants for H<sub>2</sub>.

Specific analyses of the performance gains for various missions are dependent on the vehicle and mission design. Figure 5 shows the GLOW for a gelled  $O_2/H_2$  (H<sub>2</sub> gelled with CH<sub>4</sub>) SSTO rocket versus one using liquid  $O_2/H_2$ . The gelled H<sub>2</sub> SSTO rocket has a very similar GLOW, so only a small mass penalty is paid for the benefits of the gelled  $H_2$ . This vehicle used the gelled hydrogen at a 4.2:1 mixture ratio and a 10-wt% gellant value. These analyses have not yet included the benefits of slosh reduction, boiloff reduction, and these impacts on reducing the vehicle GLOW and the improvements on the overall vehicle performance. Systems analyses performed for other high density hydrogen vehicles have shown that the reductions of the GLOW for increased density hydrogen are very significant. In cases where another high density hydrogen, slush hydrogen was used, the density increased by 16 percent, the GLOW was reduced by 10.2 percent, or 102 000 lbm. For airbreathing vehicles, such as the National Aerospace Plane (NASP), the estimated reduction in GLOW for slush hydrogen was from 20 to 50 percent. Thus, a gelled hydrogen with a 10 percent density increase may deliver a significant fraction of these airbreathing vehicle GLOW reductions and other subsystem mass savings. Supporting references for these analyses are provided in reference 11.

Safety can be significantly increased with gelled fuels. A higher viscosity reduces the spill radius of the gelled hydrogen and limits the potential damage and hazard from a fuel spill. Another important advantage is the potential for leak reduction or elimination. The leak paths from the feed systems would be minimized and the possible explosion potential would be reduced. The extended down time for the Space Shuttle due to hydrogen leaks has shown the high cost of spacecraft sitting idle, unable to launch their expensive cargoes.

Boiloff reduction is another feature of gelled hydrogen. The boiloff reductions are up to a factor of 2 to 3 over ungelled liquid hydrogen (refs. 11 and 12). This feature will assist in long term storage of hydrogen for upper stages that must sustain on-orbit storage or long coast times. Also, lunar flights and interplanetary missions with large hydrogen fuel loads will derive a benefit, reducing the overall tank size by minimizing the cryogenic boiloff. Taking advantage of the boiloff reduction will require some redesign of the propellant acquisition system, as the gelled hydrogen viscosity is higher in the quiescent state. Once the hydrogen is flowing, the viscosity drops, and the thixotropic fluid is easily moved from the tank to the engine.

Significant density increases are possible with gelled hydrogen. A 10 percent density increase is possible with 10 percent added ethane or methane. These gellants are introduced into the hydrogen as frozen particles that form a gel structure in the hydrogen. Figure 6 depicts the gelled hydrogen density and the rocket performance when combusted with  $O_2$ . A maximum Isp is attained at 5-wt% methane gellant. However, the past data shows that the hydrogen should be gelled with 10-wt% of the frozen cryogen. The density of the gelled hydrogen and the rocket performance were used to estimate the "best" operating point for current rocket powered SSTO vehicles. A design point using a 7.0:1 mixture ratio, and a 10-wt% gellant level appeared to deliver the most attractive design with the lowest vehicle GLOW. This result is in contrast to the earlier results noted above, and shows that there is not a single design point that is attractive for all applications. References 3, 11, and 12 provides some additional analyses of gelled hydrogen density and performance and some additional discussion of its benefits.

#### METALLIZED GELLED PROPELLANTS

Metallized gelled rocket propellants have been considered for many different applications (refs. 16 to 18). While operational usage has not yet come to fruition, there are many technology programs that are underway to eliminate the unknowns with gelled propellants and the propulsion systems that will use them. Numerous studies have shown the potential benefits of gelled fuels and oxidizers. Technology programs to prove the combustion performance of gelled propellants have been conducted most recently by the U.S. Army Missile Command, with their industry and university partners, for tactical missile applications.

The NASA Lewis Research Center and its partners have investigated  $O<sub>2</sub>$  /H<sub>2</sub>/A1 and  $O<sub>2</sub>$ /RP-1/A1 for NASA missions and conducted experimental programs to validate elements of the combustion and fuel technology. Gelled and metallized gelled hydrogen and RP-1 have been emphasized because hydrogen and RP-1 are typical propellants for NASA launch vehicles and upper stages. Derivatives of these propellants are therefore preferred to minimize the incremental risk for a newly introduced propulsion concept. Gelled hydrogen onto itself is also related to this technology. It's likely applications would be for rocket powered launch vehicles and upper stages, rocket based combined cycle airbreathing vehicles, and combination (rocket and airbreathing) propulsion options.

Figure 7 illustrates the GLOW reductions for O<sub>2</sub>/RP-1/A1 and NTO/MMH/A1 propellants for a Space Shuttle Liquid Rocket Booster (LRB). These analyses were conducted to find ways to improve Space Shuttle's payload performance to the Space Station. The performance can be increased several ways. Very significant booster length reductions are possible with these high density metallized fuels. These length reductions can ease the ground handling of the boosters, and reduce the drag during ascent, thus improving the Shuttle's performance. Alternatively, the metallized gelled booster length can be allowed to grow to that of the Solid Rocket Booster, and the payload performance of the Space Shuttle increases by 15 percent with 55-wt% RP-1/A1 and 35 percent with 50-wt% MMH/ A1. Additional increases in payload performance were possible with small diameter increases in the metallized gelled LRB. A 1-ft diameter increase (from 12 to 13 ft) would in increase the Shuttle payload in LEO by from 50 000 to 70 500 lbm using 55-wt% RP-1/Al.

Heat transfer with the metallized fuels is an important combustor and nozzle design issue. The results of the first experiments with 55-wt% O2/RP-1/Al heat transfer are shown in figure 8. Four different fuels are were tested to determine their performance: traditional RP-1, 0-, 5-, and 55-wt% RP-1/Al. The 0-wt% case is a gelled RP-1 with no added aluminum. The engine tests used a 30-lbf thrust rocket engine. The formation of a substantial protective gelled layer formed on the injector and chamber from using a silica gellant in the 0- and 5-wt% RP-1/A1. This gelled layer caused the heat flux reductions in the second half of the chamber, and this effect is noted particularly the 0- and 5-wt% RP-1/A1 cases. The peak heat flux in the nozzle for the 5- and 55-wt% RP-1/A1 were nearly double that of the baseline RP-1 fuel. The 55-wt% cases produced a metal oxide coating on the nozzle throat, which had strong insulating properties. Improved high temperature coatings, ablative materials, or  $O_2$  cooling are possible avenues to accommodate these higher fluxes.

#### HIGH ENERGY DENSITY PROPELLANTS

New technologies in atom formulation and physics of material manipulation has led to the discovery and synthesis of materials that can be used in rocket propellants (refs. 3 and 19 to 28). Solid cryogenic propellants storing atoms of H, Al, B, C, or other atomic additives, require a unique propulsion system design where the fuels are stored at liquid helium temperatures during ground handling and flight. Figure 9 shows the benefits of atomic hydrogen as a launch vehicle propellant and several vehicles are compared. The baseline case is the National Launch System (NLS) using O<sub>2</sub>/H<sub>2</sub> propellants at an Isp of 430 s. The reductions in GLOW that are possible with atomic hydrogen are over 50 percent with a 750 sec specific impulse. This Isp performance level requires a 15-wt% of atomic hydrogen stored in solid  $H_2$ .

The overarching vision for HEDM is to create a propellant combination which has at least the performance of  $O<sub>2</sub>/H<sub>2</sub>$  (typical of the Space Shuttle, which delivers a specific impulse of 452 s in vacuum) but with higher overall propellant density. Current materials of interest are cubane, strained ring compounds, polymeric oxygen  $(O_4, O_6,$  $O_8$ ), polymeric nitrogen (N<sub>4</sub>, N<sub>6</sub>, N<sub>8</sub>), B-N analogs of prisimane (B<sub>3</sub>N<sub>3</sub>H<sub>6</sub>), and additives to cryogenic liquids and solids, such as oxygen and hydrogen. Stabilization and production of polymeric oxygen and polymeric nitrogen, and the formation and production of high energy density materials in solid hydrogen or other appropriate solid cryogenic solids is important. Formulation of high energy density materials (HEDM) requires use of sophisticated computer

modeling to guide the experimental production. Laser experiments are being formulated to create and detect polymeric oxygen and polymeric nitrogen.

Other propellants and additives that are not cryogenic are also being developed. Methods of modeling, creating, using, and stabilizing these materials for use as rocket propellants are being sought and implemented. Formulation of monopropellants and bipropellants with high energy density materials are taking advantage of the extensive theoretical developments of the last 50 years and turn them into realistic propellants and additives. Some of the near term materials that are being implemented are methods for large scale cubane ( $C_8H_8$ ) propellant production. Cubane as an additive to hydrocarbon propellants may increase the payload of rocket systems by 10 to 20 percent. Another important aspect of the HEDM research is the demonstration of the integrated use of computational modeling software to assist in experimental formulation of high energy density materials

Using these propellants is more complex than traditional propellants because of their unique chemistry. While the above mentioned monopropellants are often simpler fuels with additives that are traditional molecules which are stable in storage, the high energy species must be formulated very meticulously because they are not occurring in nature. These formulations offer increased energy density, but they must be manufactured and stored in a stabilizing medium. This medium may be solid hydrogen particles (or other cryogenic material) that surround the newly created atoms or molecules and isolate them, preventing their recombination. Figure 10 illustrates the experimental results of the formation and storage lifetime of atomic hydrogen in solid hydrogen (ref. 28). A heat spike occurs when the atoms recombine, and it is noted in the figure when the number of atoms drops to zero. The release of a heat spike is the result of the atoms reaching a critical storage density, where no more than a certain number of atoms can be stored in the solid H<sub>2</sub>. Next generation RLV propulsion systems can use these frozen hydrogen particles in a cryogenic liquid carrier, such as helium (ref. 19).

Stored metal atoms in solid hydrogen are the penultimate step in the development of higher performance, higher density propellants. These more advanced propellants will require longer development times, so they would not be the first propellants to be commercialized. Near term aspects related to these high energy species might be the production methods of the atoms or species, the cryogenic feed system components, such as superinsulation, valves and other flow control components, feed lines, cryogenic storage, and leak detection systems.

#### CONCLUDING REMARKS

Using improved propellants can lower operations cost, simplify spacecraft processing, and make space flight more accessible and affordable. Other capabilities that are enabled with these propellant technologies are better vehicle cooling, reduced cryogenic boiloff, reduced vehicle structural mass, reduced thermal protection requirements, and improved safety.

Many advanced vehicles are being planned for future aeronautics and space missions. All are able to take advantage of the extensive and well known benefits of advanced propellants and propellant additives. Monopropellants that are safer and denser than traditional propellants can reduced space access costs. Aeronautics missions, both atmospheric and transatmospheric, can use endothermic fuels to simplify the vehicle operations and processing and allow high speed flight without using liquid  $H_2$ . Gelled fuels can increase the density of liquid fuels, improve their safety, and reduced cryogenic boiloff and minimize fuel slosh. The addition of metal particles to the gelled fuels can further increase booster and vehicle density, giving more benefit to spacecraft designers. Future missions using high energy density materials could reduce the GLOW of launch vehicles, and if they can be simplified, may enhance or enable large fast human planetary missions. Many options for the human expansion into the solar system are possible by using advanced propulsion.

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**Figure 1 .--Monopropellant benefits for Liquid Rocket Boosters.**



**Figure 2.--Monopropellant Liquid Rocket Booster length and diameter.**



**Figure 3,--Alternative hydrocarbons for airbreathing TSTO.**



**Figure 4.--Dependence of the maximal specific rate of decomposition of hexene and the energetic catalyzer productivity from the catalyzer layer temperature (pressure = 1.03 MPa).**







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**Figure 10.mHigh energy density propellants: atomic hydrogen storage versus time. (a) ESR measurements of T-atom concentration in D-T at three different temperatures. (b) Effect of thermal spikes on total D-atom concentration as seen by ESR in solid D2 containing 2% tritium held at 1.3 K. These spikes were not intentionally triggered (ref. 28).**