LOW TOXICITY REACTIVE HYPERGOLIC FUELS FOR USE WITH HYDROGEN PEROXIDE

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ABSTRACT

The need for low toxicity hypergolic fuels has brought rocket grade hydrogen peroxide (RGHP) to the forefront as the oxidizer of choice for future hypergolic systems. The search for a hypergolic mate for RGHP has been primarily focused on using transition metal salts dissolved in energetic liquids to create hypergolic fuels. These dissolved salts catalytically decompose RGHP on contact, producing heated oxygen and steam which ignite the remainder of the fuel. The use of transition metal salts in these fuels is therefore necessary to induce hypergolicity, but these compounds reduce the specific impulse of these fuels due to the presence of high molecular weight transition metal oxides in the exhaust. Reactive hypergolic fuels can eliminate this problem by using light metal hydrides dissolved in energetic liquids for fuels. These metal hydrides combust directly with RGHP upon contact and ignite the remainder of the fuel. Due to the low atomic weights of the metals used, these metal hydrides can enhance the specific impulse of such fuels instead of degrading the performance as transitional metal salts do. Tests of such reactive fuels are promising and indicate that fuels of this type can be successful hypergolic fuels for use with hydrogen peroxide.

INTRODUCTION

Hypergolic, or self-igniting propellant combinations have been investigated since the 1930's. In fact, one of the first known hypergolic propellant combinations consisted of highly concentrated hydrogen peroxide and hydrazine hydrate.[1] Throughout the years since World War II, several successful hypergolic combinations have been employed in missiles and spacecraft. Nitrogen tetroxide (NTO) paired with monomethyl hydrazine (MMH) and inhibited red fuming nitric acid (IRFNA) paired with unsymmetrical diemethyl hydrazine (UDMH) have been the most used because of their high performance. However, these propellant combinations are also toxic and carcinogenic. Due to their high performances and lack of suitable non-toxic alternatives, they have been the hypergolic combinations of choice for many years.

CATALYTIC HYPERGOLIC FUELS
Fuels that are hypergolic with RGHP can be divided into two groups. The first group consists of catalytic hypergolic fuels, each of which is composed of an energetic liquid in which a metal salt is dissolved. This salt is usually the salt of a transition metal that catalytically decomposes hydrogen peroxide. When RGHP and fuel impinge, the hydrogen peroxide is decomposed by the catalyst, producing superheated oxygen and water vapor. This heat vaporizes the fuel until the auto-ignition temperature is reached, and then combustion begins.

The primary disadvantage of these fuels is the use of transition metals. In general, to minimize the ignition delay of a fuel more of the metal salt is added.[2] Increasing the concentration of transition metals reduces the exhaust velocity of the rocket exhaust, and therefore the specific impulse, since the exhaust velocity is inversely proportional to the square root of the average molecular weight of the exhaust products. To maximize the specific impulse requires the reduction of the transition metal concentration of the fuel, but if the metal concentration is reduced significantly, then the ignition delay of the fuel may be long, and hard-starts may result. A balance between kinetic and thermodynamic performance must be determined for catalytic hypergols.

REACTIVE HYPERGOLIC FUELS
Reactive hypergolic fuels differ from the catalytic hypergols in that the mechanism of reaction is a direct combustion reaction instead of a decomposition reaction *leading* to a combustion reaction. A reactive metal compound, typically a compound of the light metals, such as lithium, boron, or aluminum, is dissolved in an energetic liquid. When RGHP and the fuel impinge, the RGHP and the metal compound react directly, generating heat which vaporizes and ignites the remainder of the fuel and oxidizer.

These fuels can ignite much faster than their catalytic counterparts because combustion via RGHP can liberate much more heat than its decomposition. This is demonstrated by the comparison in Table 1. In this table the heat generated by the combustion of one mole of hydrogen peroxide with a metal hydride is compared to the heat generated by the decomposition of one mole of hydrogen peroxide.

| Reaction	Heat of Reaction
$H_2O_2(l) \Rightarrow H_2O(g) + O_2(g)$	54.0 kJ/mole
$H_2O_2(l)$ + 1/4 metal hyd. (s) $\Rightarrow$ 11/4 $H_2O(g)$ + 1/4 $LiOH(s)$ + 1/8 $Al_2O_3(s)$	446.3 kJ/mole

Table 1: Comparison of Heats of Reaction for H_2O_2 Decomposition vs. H_2O_2 Combustion

Table 1 indicates that far more heat is liberated per mole of hydrogen peroxide consumed in the combustion reaction than in the decomposition reaction. The generation of more heat leads to a more rapid vaporization and temperature rise in the energetic liquid, and more rapid ignition than in a catalytic fuel.

The use of low atomic weight metals in these reactive metals benefits specific impulse, which is a further advantage over catalytic hypergolic fuels. Also, in contrast to the catalytic hypergols, increasing the concentration of reactive metals both reduces ignition delay and increases specific impulse. Reactive hypergolic fuels have a significant advantage over catalytic fuels.

RESULTS AND DISCUSSION

To verify the advantages of the reactive metal fuels, experiments were performed with two distinct fuels. Fuel A consists of a metal hydride (comprising 4.2% by mass) in an ethereal solvent, and Fuel B consists of a metal hydride, (comprising 20% by mass) dissolved in a different ethereal solvent. The hypergolic ignition of both fuels with 97% hydrogen peroxide was tested by drop test to verify ignition. Both fuels ignited rapidly. The fuels were also compared to NTO/MMH thermodynamically by using the United States Air Force Specific Impulse Code. Figure 1 presents the comparison of vacuum Isp over a range of O/F values. For this comparison, a chamber pressure of 500 psi and an expansion ratio of 10 were used.
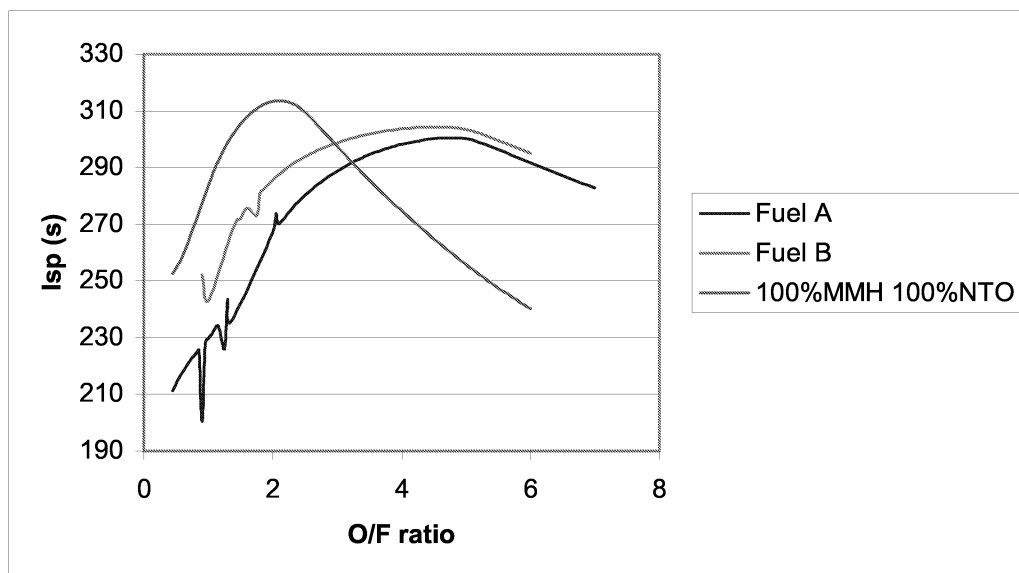
Figure 1: O/F vs. Isp for Reactive Hypergolic Fuels Using 100% RGHP and NTO/MMH

As the graph indicates, the theoretical Isp of both reactive fuel combinations approach the performance of NTO/MMH, with both reaching peak performance at an O/F about 5. Also, due to the high O/F optimum

values and the density of RGHP, the density specific impulse values of these fuels may exceed that of NTO/MMH. The theoretical performance of these fuels suggests that these fuels could be potential replacements of NTO/MMH for certain applications.

FUEL SAFETY AND HANDLING

Neither fuel is pyrophoric, but both solutions are moisture sensitive. Water actively hydrolyzes each of these metal hydrides, liberating hydrogen. This problem is not acute when the hydrides are in solution, but care must be taken to avoid contact with water. These fuels must be stored under an inert atmosphere, and the stability of these solutions can degrade rapidly in the atmosphere. This is a concern in testing, as it is difficult to test these fuels in a completely inert atmosphere. Prolonged contact with the atmosphere or contaminants may lead to the reaction of significant portions of the hydrides in solution, which could degrade kinetic or thermodynamic performance.

Both solutions are somewhat corrosive and ether has a relatively high vapor pressure, but neither fuel is as aggressively toxic as NTO; neither is listed as a carcinogen.

IGNITION DELAY TESTING

Ignition delay testing was performed using a high-speed video camera and using the *Hypertester*, a drop-test device which can determine the ignition delay value of a propellant combination to within one millisecond. The *Hypertester*, developed at Purdue University, is displayed in Figure 2. The *Hypertester* is simply a drop–test device which uses an oscilloscope to record the timing of events characterizing ignition delay. To determine the ignition delay, a specified amount of fuel is placed in the crucible (approximately 20 microliters). A drop of oxidizer (20 to 30 microliters) falls from its syringe suspended above the crucible. When the drop impacts the crucible, the velocity transducer below senses the impact and transmits the vibration to the oscilloscope. When the fuel and oxidizer ignite, the light given off is detected by the photodiode, and this data is also transmitted to the oscilloscope on a separate channel. The time between the impact of the oxidizer drop and the beginning of the flash from the combustion is recorded as the ignition delay.

Using 96.8% hydrogen peroxide, Fuel A was tested in the *Hypertester*, as was U.S. Navy Block 0, an early catalytic hypergolic fuel developed at China Lake. Block 0 was tested for comparison. The LAH fuel was unavailable for testing at the time of this writing. Five tests of each fuel were conducted. The average ignition delay for Block 0 was 11.2 milliseconds with the values ranging between 9 and 13 milliseconds. For Fuel A, the average was 3 milliseconds with no measurable deviation. Such a small delay for this fuel is competitive with NTO/MMH, which produced an ignition delay of less than 3 milliseconds for the same device.[3] In an engine, the difference between RGHP/Fuel A and NTO/MMH should be even less as the propellants are slammed together at high pressure.
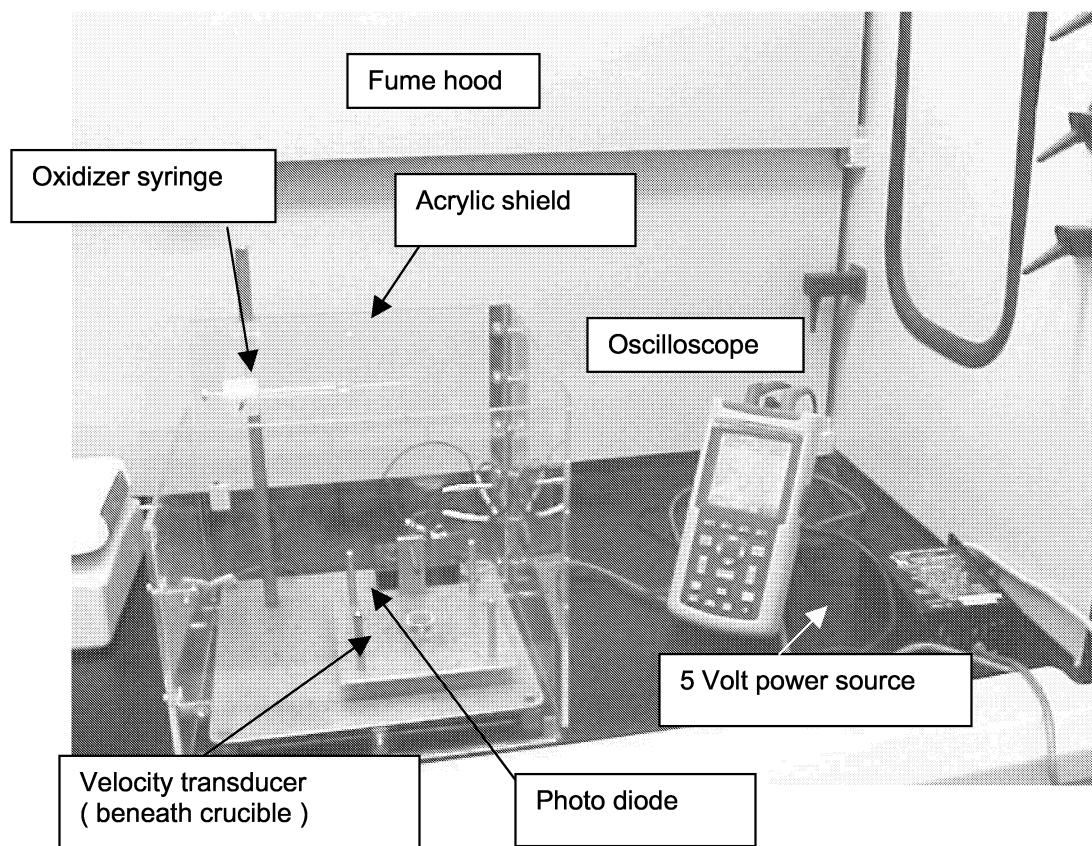
Figure 2: The *Hypertester*

Using a high-speed video camera, the ignition process of RGHP/Bock 0 and RGHP/Fuel A was visible. The camera captured video of a drop test of each combination at a rate of 1000 frames per second. For Block 0, a catalytic hypergolic fuel, the high-speed camera displayed the influence of the fluid properties upon the ignition delay. After the drop of peroxide impacted the fuel in the crucible, a vapor cloud of fuel, oxygen, and water began to expand from the impact point. The ignition of this cloud occurred more than an inch above the impingement point. Once the initial combustion occurred, the flame spread rapidly throughout the cloud. In contrast, the ignition of Fuel A was much more rapid. No fuel and oxidizer cloud was noted before the ignition.

These ignition tests indicate that the ignition delay of Block 0 is limited by smaller amount of heat produced by the decomposition reaction as opposed to a combustion reaction, and the longer time required to heat the fuel and oxidizer vapor mixture to its ignition point after the decomposition takes place. Block 0 contains approximately 5% by weight of manganese, the active catalytic species, while the other fuel contains 4.2% by weight metal hydride. Therefore, the amounts of the active species in each fuel are comparable, and even though the solvents are different, it is reasonable to say that Fuel A ignites much more rapidly due to the larger amount of heat produced by the combustion reaction of RGHP/metal hydride as opposed to the decomposition reaction of the RGHP. Because of the higher heat evolved, the ignition point of the remainder of Fuel A is reached much faster. The decomposition reaction does not produce enough heat to ignite the remainder of the Block 0 as rapidly.

In order to reduce the ignition delay of Block 0, more of the catalytic salt would be needed. However, this would reduce the Isp. With Fuel A and other such reactive hypergolic fuels, increasing the amount of the metal hydride has the potential to reduce the ignition delay and increase the Isp. This is the major advantage of reactive hypergolic fuels over catalytic hypergolic fuels.

ENGINE TESTING

Open injector engine testing of Fuels A and B was performed at the Advanced Propellants and Combustion Lab at Purdue University using its 1000-lbf bipropellant test stand. A 0.5 liter fuel tank and new plumbing were used for these tests. All hardware was cleaned thoroughly with ethanol and then flushed with THF to remove the ethanol and to remove any other soluble material from the tank. The engine chosen was a pintle injector design, with a pintle designed by IN Space, LLC. The open injector tests were performed to determine if the ignition delays produced by the fuels were suitable and to determine the appropriate fuel lead times to be used when the chamber and nozzle would be attached. All tests were recorded with a 1000 frame per second high-speed camera. An effort was made to fire the fuels as quickly as possible after loading due to the highly reactive nature of the fuels. It was feared that any residual contaminants in the tank could react with the hydrides and reduce the ignition delay to unacceptable levels. The fuels were tested with 97.6% hydrogen peroxide, and both fuels ignited rapidly, as could be seen with the high-speed video camera. Injector pressures varied between 200 and 300 psi. These tests provided confidence that tests using the chamber and nozzle would be successful. Table 2 displays the data of these firings.

Fuel	Duration (s)	Avg. oxidizer inlet press. (psi)	Avg. fuel inlet press. (psi)	Total mass flow (lbm/s)	O/F	Ignition
A						
Test 1	3	260	240	0.645	4.92	rapid
Test 2	3	260	240	0.643	4.87	rapid
B						
Test 1	3	350	235	0.650	4.10	rapid
Test 2	3	350	250	0.649	4.09	rapid

Table 2: Injector Firing Data

Firings were conducted with Fuel A and 97.5% hydrogen peroxide. Three two-second firings were conducted, and all firings went well, with no hard starts or combustion instabilities noted. Thrust, chamber pressure, and mass flow data were collected, but due to an incorrectly installed purge line, mass flow data was incorrect, and calculation of the specific impulse of the combination was not possible.

CONCLUSIONS

Reactive hypergolic fuels have potential advantages over their catalytic counterparts due to the use of reactive metal hydrides instead of transition metal salts to induce hypergolicity. The theoretical and experimental work conducted in this research indicate that this enthusiasm is justified due to the rapid and smooth ignitions witnessed in both the drop tests and open injector tests. More testing must be done to verify the specific impulse predictions and assess the actual performance of these fuels for current and future systems.

FUTURE WORK

- ### CONTINUED ENGINE TESTING

Continued engine testing is planned so that experimental specific impulse and C* values over a reasonable O/F range can be determined. Future firings are planned using a similar pintle injector, and chamber pressures of 300 to 400 psi are planned for full scale testing.

- ### HIGH ENERGY SOLVENTS

The ethereal solvents used are not ideal rocket fuels, but currently used because of the availability of the metal hydrides in these solvents. Higher energy hydrocarbons and amines will be investigated, as well as higher energy ethers. Solvents to be considered are liquids at room temperature with low boiling points, high density, high energy, hydrophobic, and that can dissolve a large weight percentage of the hydrides.

- <u>GELLED FUELS</u>

Another method to create a reactive metal fuel with a large percentage of a light-metal hydride is to gel a suspension of the hydride in an energetic fuel. This approach could be successful as long as both the solvent and the gelling agent are hydrophobic and unreactive with the hydride. This method could maximize the Isp of the fuel, and could be used for some short-duration reaction and control missions.

REFERENCES

1) Clark, Dave, <u>Ignition!</u>, Rutgers University Press., 1972.

2) Frolik, Steve, "Hypergolic Liquid Fuels for use with Rocket Grade Hydrogen Peroxide", M.S. Thesis, Purdue University, August 2000.