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Enhancement of Volumetric Specific Impulse in HTPB/Ammonium Nitrate Mixed Hybrid Rocket Systems

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ENHANCEMENT OF VOLUMETRIC SPECIFIC IMPULSE IN HTPB/AMMONIUM

NITRATE MIXED HYBRID ROCKET SYSTEMS

by

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ABSTRACT

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ACRONYMS

AN	ammonium nitrate
AP	ammonium perchlorate
C	carbon
C*	characteristic velocity
CEA	chemical equilibrium with applications
G	oxidizer mass flux
GOX	gaseous oxygen
HTPB	hydroxyl-terminated polybutadiene
I_{sp}	specific impulse
O/F	mass ratio of fluid oxidizer to solid propellant
VI_{sp}	volumetric specific impulse

NOMENCLATURE

a	empirical constant
$\dot{m}_{fuel}$	fuel mass flowrate
M_{GOX}	gaseous oxygen mass
M_{HTPB}	hydroxyl-terminated polybutadiene mass
$M_{NH_4NO_3}$	ammonium nitrate mass
$\dot{m}_{ox}$	oxidizer mass flowrate
n	burn rate exponent
$\dot{r}$	regression rate
t	time
T_{burn}	burn length
ρ_{GOX}	oxygen density
ρ_{HTPB}	hydroxyl-terminated polybutadiene density
$\rho_{NH_4NO_3}$	ammonium nitrate density

CHAPTER I

INTRODUCTION

When compared to conventional liquid- and solid-propelled rocket systems, hybrid rockets -- where the propellants typically consist of a moderately benign liquid or gaseous oxidizer and an inert solid fuel -- possess well-known operational safety and handling-advantages. A study by the U.S. Department of Transportation concluded that most hybrid rocket motor designs can be safely stored and operated without a significant risk of explosion or detonation. Because hybrid rockets store fuel and oxidizer in two separate phases, they are much safer to manufacture, transport, and operate than solid rockets. Hybrids can also have the ability to start, stop, relight, and throttle unlike solid motors. Hybrid rocket systems offer higher performance than hydrazine-based systems and their inherent design safety offers a significant potential for ride-share spacecraft applications. Thus, such systems offer the potential to significantly reduce operating costs for commercial launch vehicles. However, in spite of these well-known safety and handling advantages, conventionally-designed hybrid rocket systems have not seen widespread commercial use due to several key drawbacks that exist with conventional hybrid-system designs.

Foremost amongst these disadvantages are internal motor ballistics that result in fuel regression rates typically 25-30% lower than solid fuel motors in the same thrust and impulse class. One cannot simply increases the oxidizer massflow to compensate for the low fuel regression rate due to resulting combustion instabilities that result from high oxidizer massflux levels. These lowered fuel regression rates tend to produce unacceptable fuel lean conditions that lead to poor mass-impulse performance, erosive fuel burning, nozzle erosion, reduced motor duty cycles, and potential combustion instability. To achieve stoichiometric propellant mixtures that produce acceptable combustion characteristics, traditional cylindrical fuel ports have been fabricated with very long length-to-diameter ratios. This high aspect ratio results in poor volumetric efficiency. Another source of volumetric inefficiency in hybrids results from large storage tanks for low-density fluid oxidizers. These two sources of poor volumetric efficiency lead to form factors that are incompatible with SmallSat applications and are also more susceptible to lateral buckling when subjected to longitudinal launch loads.

CHAPTER II

LITERATURE REVIEW

A. Increasing Fuel Massflow Rates in Hybrid Motors with Compact Form Factors.

The fuel regression rate of a hybrid rocket can theoretically be increased by increasing the oxidizer massflux; however the resulting combustion instabilities at high flux rates limit the effectiveness of this option [1]. To achieve enhanced fuel massflows for lower oxidizer massflux levels, hybrid fuel grain designers have resorted to increasing the fuel grain surface burn area by casting complex fuel grain geometries with multiple fuel ports and a large pre-combustion chamber or multiple injectors. A classic realization of this high surface area technique is the original AMROC 15-port grain design [2]. There are several disadvantages to the multiple port approach [3]. First, the overall fuel regression rate decreases as the number of ports increases and the motor diameter size grows accordingly. Second, the potential for uneven port burning is significant. Uneven burning presents a potential for compromised fuel grain integrity, especially towards the end of the burn. Also, multi-port fuel grain designs typically produce unburned mass fraction of greater than 10%. Third, multiple port designs present an increased risk of feed-coupling instabilities related to dynamic flow interactions between the injector(s), the multiple fuel ports, and the pre-combustion chamber [1]. Finally, complex casting of multi-port geometries using conventional propellants requires the development of extensive tooling, and presents an unavoidable difficulty with removing the tooling once the grain material is cured. There is often a requirement for an embedded structure to support the fuel port as it regresses. The presence of this supporting web adds complexity to the fuel port design, and has the potential to allow voids within the fuel grain structure. Voids such as these can potentially cause fuel grain fractures [4].

B. Hybrid Fuel Regression Rate Enhancement Techniques

Other techniques for increasing fuel regression rates that have been tested are generally based on increasing the heat transfer from the combustion zone to the fuel grain surface [5]. Unfortunately, most of these methods suffer significant operational shortcomings. These techniques include, adding metal particles to the fuel grain [6], the use of swirl injection to increase the local oxidizer surface massflux [7], and the use of paraffin based fuels [8]. All of these techniques have demonstrated some ability to enhance regression rates, but have also introduced multiple disadvantages.

Introducing micron-sized metal particles has been shown to increase regression rates in hybrid fuels by increasing heat transfer to the fuel grain surface. However, the resulting increase in the effective exhaust product molecular weights results in only marginal end-to-end motor performance improvements, especially when higher performance oxidizers are used [9]. Introducing nano-sized metal particles increases motor production costs, and uniform fuel grain material properties are more difficult to achieve.

Swirl injection has been demonstrated to be effective in increasing the fuel regression rate [10][11]. Swirl injectors are able to reduce both thickness and growth of the boundary layer, thus enhancing heat transfer. The heat transfer variation is reduced and regression rate is more uniform. Some effects of swirling must still be addressed, including induced torque and effects of non-axial flow in the nozzle (effective throat area and divergence losses). No swirl or vortex injection hybrid motor has ever been flighttested. The effects of motor acceleration upon the swirl effectiveness also have yet to be assessed.

Karabeyoglu, et al. [12] have investigated a class of hybrid fuel materials based on paraffin wax formulations. These paraffin-based fuels melt before vaporizing, and a properly formulated wax mix produces a melt layer with a low viscosity and high surface tension. When the oxidizer flows at high speed over the upper side of the melting fuel surface, the liquid layer becomes unstable and minute surface waves are formed. The resulting fluid boundary layer is hydro-dynamically unstable and allows fuel droplets to be entrained into the core flow. The entrained fluid droplets significantly increase the massflow generated by the ablating fuel, but does not increase the "blowing-effect" that suppresses regression rate due to the ablating radial massflow. For stable oxidizer flux levels, droplet entrainment massflow is significantly greater than massflow resulting from direct gasification. Paraffin-based fuels have been developed that burn at surface regression rates three to four times that of conventional hybrid fuels [13]. The high regression rate hybrid removes the need for a complex multiport grain, and most applications up to large boosters can be designed with a single port configuration. Karabeyoglu et al. have ground-tested paraffin fuel hybrid rocket motors large as 60 cm in diameter [14].

However, due to the fuel drop entrainment, significant unburned materials are ejected from the nozzle, and combustion efficiencies for paraffin-based fuels are inherently lower. More significantly, the properties that allow the fuel droplet entrainment in paraffin-based fuels introduce mechanical and structural problems that reduce the fuel grain integrity as the propellant burns. Solid phase paraffin is rather brittle and is easily cracked when subjected to launch vibration loads. As the paraffin melts the material softens and tends to flow and “sluff” under axial launch loads. Thus, paraffin based fuels require either special additives or a support lattice to keep the grain structure intact under launch loads.

Several strengthening materials have been tested in hybrid motors [15]. Polyurethane foam (PUF) strengthening structure shows promising results, but leads to heterogeneous fuel formulations that are difficult to manufacture with any degree of consistency. To avoid this problem and ensure paraffin-based formulations with sufficient elasticity to survive launch vibration levels, a miscible thermoplastic elastomer Styrene-Ethylene-Butylene-Styrene (SEBS) was tested as a strengthening alternative to PUF. Mixing SEBS into the paraffin fuel produces a homogenous fuel grain and offers significantly lower manufacturing costs. During the combustion of the homogeneous material, the material melts; when using heterogeneous materials, only the paraffin melts. Unfortunately, both the SEBS fuel additive and PUF structural support materials reduced the burn effectiveness and performance of the hybrid motor.

C. Proposed Alternative Solution

As an alternative to the above methods based on increasing heat transfer efficiency from the flame zone to the fuel gain, this research investigates the effectiveness of mixing a solid oxidizing material into the fuel material, thereby achieving fuel ablation in two ways 1) heat transfer from the flame zone to the fuel grain, and 2) surface burning due to the added oxidizer. This concept is known as a mixed hybrid system. George et al [16] have demonstrated an increased regression rate in HTPB fuel with the addition of 8% ammonium perchlorate (AP). Knox et al [17] have increased regression rates by 50-90% using 25% AP with HTPB.

These added oxidizers also have the effect of reducing the optimal O/F ratio for the system; O/F being defined here as the mass ratio of fluid oxidizer to solid propellant. This reduces the amount of fluid oxidizer required for efficient combustion, decreases oxidizer tank size, and increases the volumetric efficiency of the system.

However, ammonium perchlorate has proven to be a hazardous material for both humans and for the environment. Hydrochloric acid is a substance formed when ammonium perchlorate based rockets burn, which is poisonous to plants and wildlife. Leftover ammonium perchlorate can also contaminate waters sources and affects thyroid function in humans.

Ammonium nitrate is a much more environmentally friendly alternative to ammonium perchlorate and is often used in agriculture as a fertilizer. While much work has been done to document the effect of AP in hybrid systems, little work has been done to study the effects of ammonium nitrate (AN). Ammonium nitrate, like AP, is a strong oxidizer, and its safety features could make it a valuable alternative to ammonium perchlorate. This study proposes the use of AN to increase volumetric specific impulse and regression rate in mixed hybrid applications.

Introducing oxidizing materials into the fuel grain creates a quasi-solid propellant design and introduces the potential for pressure-coupling during the motor burn. Pressure coupling causes a significant increase in the fuel regression rate as the motor chamber pressure increases. Hybrid rocket combustion can frequently display a sudden amplification of combustion pressures leading into low frequency instability that typically occurs in the 10-20 Hz range [18][19]. Thus, introducing pressure coupling can result in a significantly increased explosion risk. These hazards are mitigated by incorporating subcritical amounts of solid oxidizer in the fuel grain, and by ensuring that the fuel grain isn't susceptible to cracking which can create pressure spikes. Operating at low chamber pressures also helps to dampen out pressure coupled oscillations. Care should be taken when testing fuel compositions or geometries that could potentially obstruct the nozzle throat, which could lead to pressure spikes and potential explosion risks.

CHAPTER III

TEST OBJECTIVES AND EXPECTED OUTCOMES

This test objectives for this study include 1) demonstrate the usefulness of ammonium nitrate in mixed hybrid applications and confirm its ability to replace ammonium perchlorate as an environmentally friendly oxidizer; 2) quantify the effect of ammonium nitrate on regression rate, characteristic velocity, specific impulse, and volumetric specific impulse; 3) use regression rate data to model and predict regression rate in ammonium nitrate mixed hybrids as a function of ammonium nitrate content, fluid oxidizer mass flux, and chamber pressure.

Results are expected to show that ammonium nitrate mixed hybrids perform in accordance with CEA predictions and that ammonium nitrate is a competitive alternative to ammonium perchlorate. Regression rates are expected to increase with higher concentrations of ammonium nitrate and show coupling effects with the chamber pressure of the rocket. Characteristic velocity and specific impulse are expected to increase in low O/F ratio regimes with the addition of ammonium nitrate, and overall volumetric I_{sp} is expected to rise with the addition of solid oxidizer to the fuel grain.

With these outcomes, models can be made to better understand the regression rates of AN/HTPB mixed hybrids and predict the regression rates of new compositions. These models could also help predict critical concentrations of AN and determine at what pressures mixed hybrid grains begin to behave as solid rocket propellant. Quantifying the effects of ammonium nitrate on I_{sp} and volumetric I_{sp} allows for more advanced and efficient mixed hybrids to be designed and tested in the future.

CHAPTER IV

EXPERIMENT DESCRIPTION

This study sets out to test and compare fuel grains made from hydroxyl-terminated poly butadiene (HTPB) with two different (10% and 20%) ammonium nitrate concentrations against control grains made entirely from HTPB. Two identical fuel grains of each composition were cast and each was fired multiple times, for a total of 6 fuel grains and 17 burns. For convenience gaseous oxygen (GOX) was selected as the matching fluid oxidizer. Table 1 lists the fuel grain ingredients and relative mass concentrations.

Table 1 Propellant Ingredients and Mass Concentrations

Propellant Ingredient	**Type**	**Compositions**		
		A	**B**	**C**
Hydroxyl Terminated Poly-butadiene (HTPB) $(C_4H_6(OH)_2)_n$	Polymeric binder/fuel	89.6%	80.6%	71.6%
Ammonium Nitrate (AN) (NH_4NO_3)	Oxidizer	0%	10%	20%
Diphenylmethane Diisocyanate (Isonate 143L)	Curative	9.9%	8.9%	7.9%
Graphite (5 μm) (C)	Opaquifier	.5%	.5%	.5%

Fuel grains of identical composition were cast simultaneously from the same batch of propellant to ensure uniformity across identical fuel grains.

The experimental setup used for conducting experiments is shown in figure 1. Oxidizer feed pressure is set using a regulator on the oxygen bottle. Oxidizer mass flow rate is measured using a differential pressure transducer in a venturi, and also using the differential pressure across the injector and applying compressible fluid equations for choked injector flow. A nitrogen tank is used to purge the port after motor shutdown. Valves are powered pneumatically with compressed air, and are controlled through a laptop. Data is collected and stored on a laptop at a rate of 1 kHz. Recorded measurements include valve conditions, igniter condition, venturi differential pressure, injected pressure, chamber pressure, motor thrust, injected oxidizer temperature, and rocket case temperature. Fuel grain weights are collected before and after each burn as well as nozzle throat diameter to record any nozzle erosion.

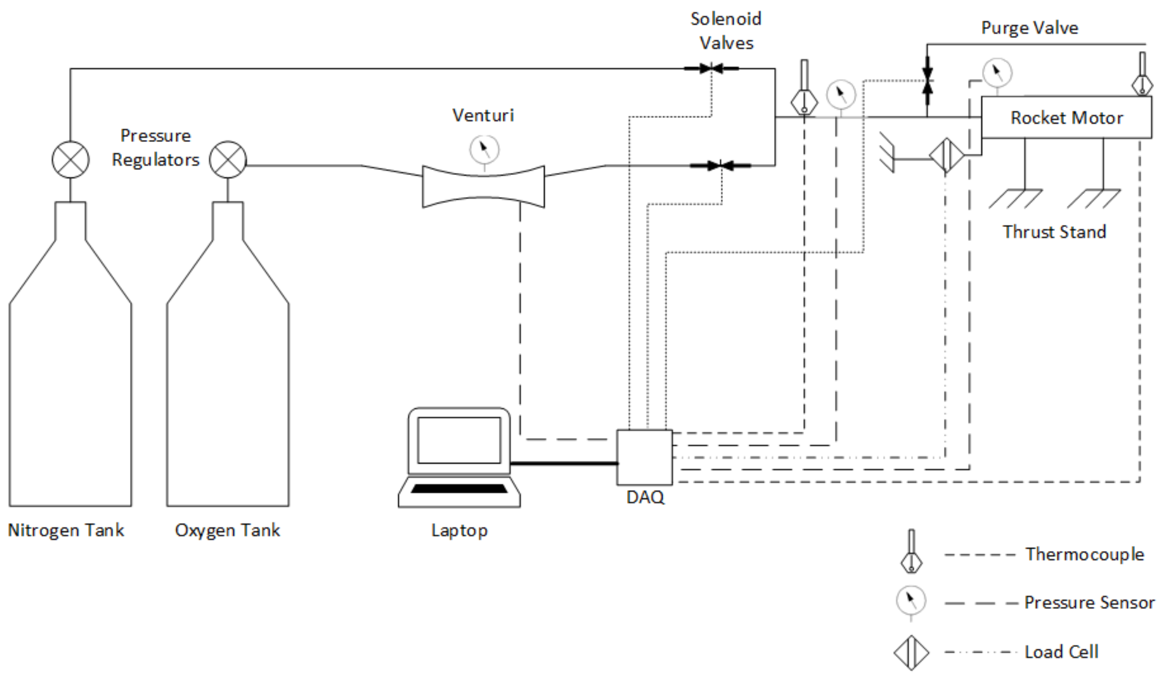

Figure 1 Test Apparatus

Because short burns typically have higher reported errors in regression rate, test burn durations were 3 or 5 seconds. Burn start time was defined to be midway through the startup transient, and burn end time was defined as being midway through the burn down transient. Instantaneous fuel grain mass was calculated by assigning a polynomial curve fit to pre and post burn weights as a function of burn start time and burn end time.

Fuel mass flow rate was taken from the derivative of fuel grain mass. Port diameter and regression rate were calculated as a function of grain weight, density, and fuel grain geometry.

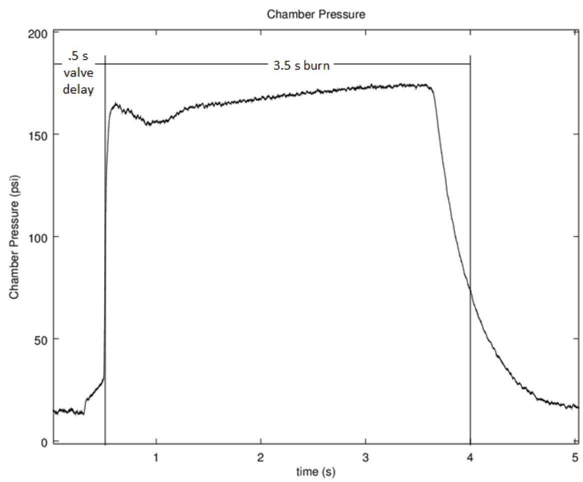

Figure 2 Example Chamber Pressure Data

The lab scale fuel grain has a length of 6.25 inches, an initial port diameter of .5 inches, and an outer diameter of 2 inches. Motor geometry is displayed in figure 3. The injector has a diameter of .059 inches. A graphite nozzle with a throat diameter of .238 inches and an expansion ratio of 2.2 is used. To ensure a choked inlet, tests were performed with an oxidizer feed pressure of 500 psi, and a chamber pressure of 180-200 psi.

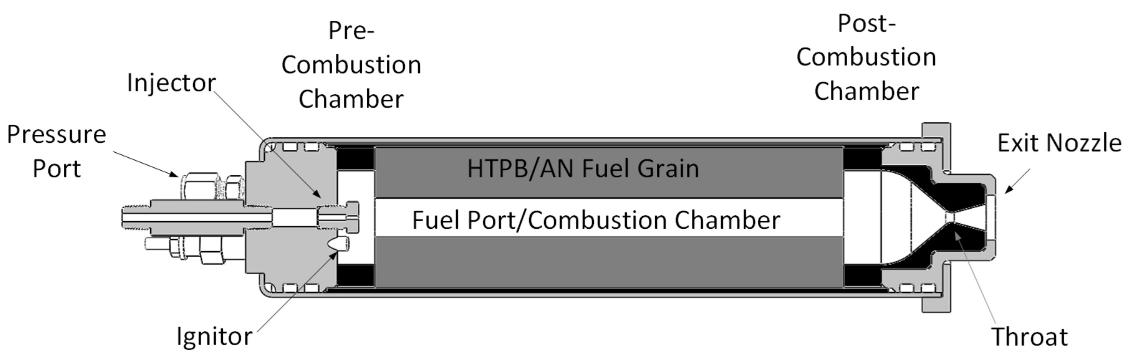

Figure 3 Test Motor Geometry

CHAPTER V

RESULTS AND DISCUSSION

During the course of testing, 17 test burns were conducted on the 6 grains that were cast. Results appear to align well with predictions made with the NASA Chemical Equilibrium with Applications tool (CEA). Changes in regression rate, characteristic velocity, I_{sp}, and volumetric I_{sp} are discussed in the sections below.

A. Regression Rate

Regression rate in solid propellants is most closely tied to chamber pressure. The most commonly used empirical equation to describe regression rate in solid propellants is the Saint Robert's Law correlation,

$$\dot{r} = ap_1^n$$

where $\dot{r}$, the regression rate, is usually in mm/s and the chamber pressure, p_1, is typically in MPa. a is an empirical constant which is often influenced by initial grain temperature, and n is the burn rate exponent [6].

Regression rate in hybrid propellants is not closely tied to chamber pressure, but rather oxidizer mass flux, G. The most commonly used empirical equation to describe regression rate in hybrid rockets is

$$\dot{r} = aG^n$$

Where $\dot{r}$ is the regression rate, G is the oxidizer mass flux, and a and n are empirically fitted constants [6].

Fuel regression rate in the mixed hybrids is a function of both chamber pressure and oxidizer mass flux. This study expected to see an increase in regression rate with the addition of ammonium nitrate to the fuel grain due to the pressure effects which are found in oxidized rocket motors. However, these pressure effects were not clearly witnessed in testing. The reasons that pressure effects on regression rate were not obvious may include: (1) temperature sensitivity of burn rate; (2) small sample size; (3) scale effects from using a small motor where regression rate is influenced by other factors such as radiation; or (4) chamber pressure was not high enough to see noticeable effects of pressure on regression rate.

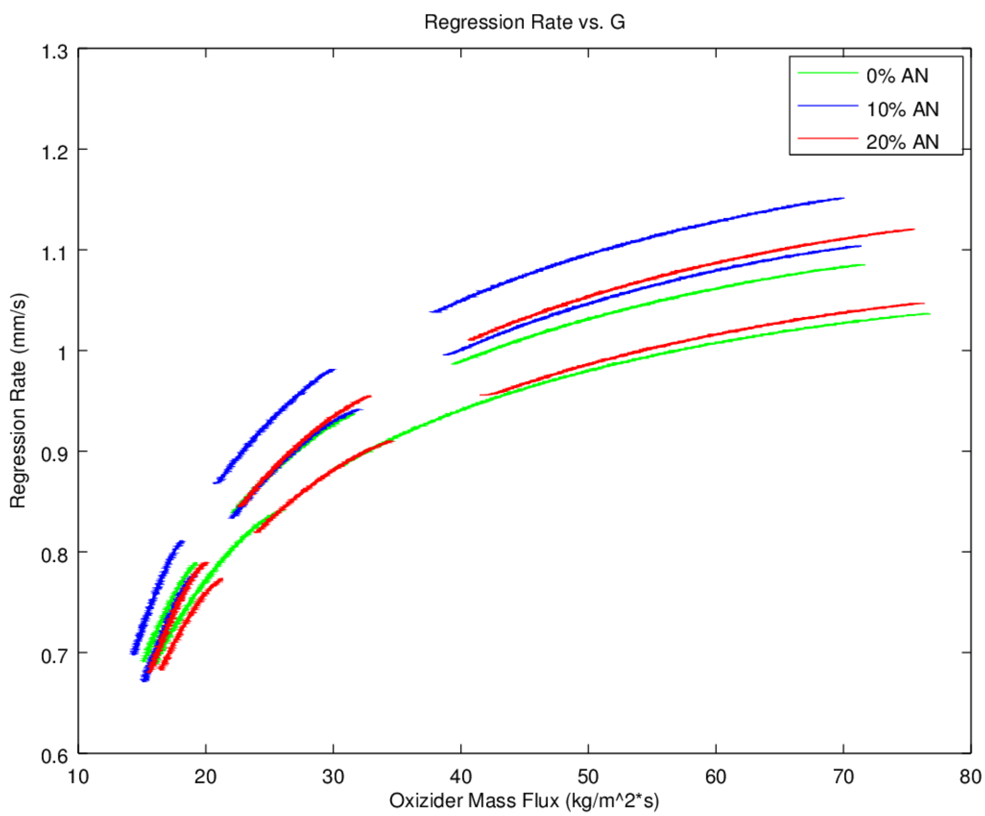

Figure 4 Regression Rate as a Function of Oxidizer Mass Flux

B. Characteristic Velocity

Characteristic velocity, C*, is used in comparing the relative performance of different chemical rocket propulsion system designs and propellants; it is easily determined from measured data of mass flow rate, chamber pressure, and nozzle throat area.

CEA shows in figure 5 that ammonium nitrate and ammonium perchlorate have very similar performance. Mixed hybrids are shown to have better performance than traditional hybrids at low O/F ratios.

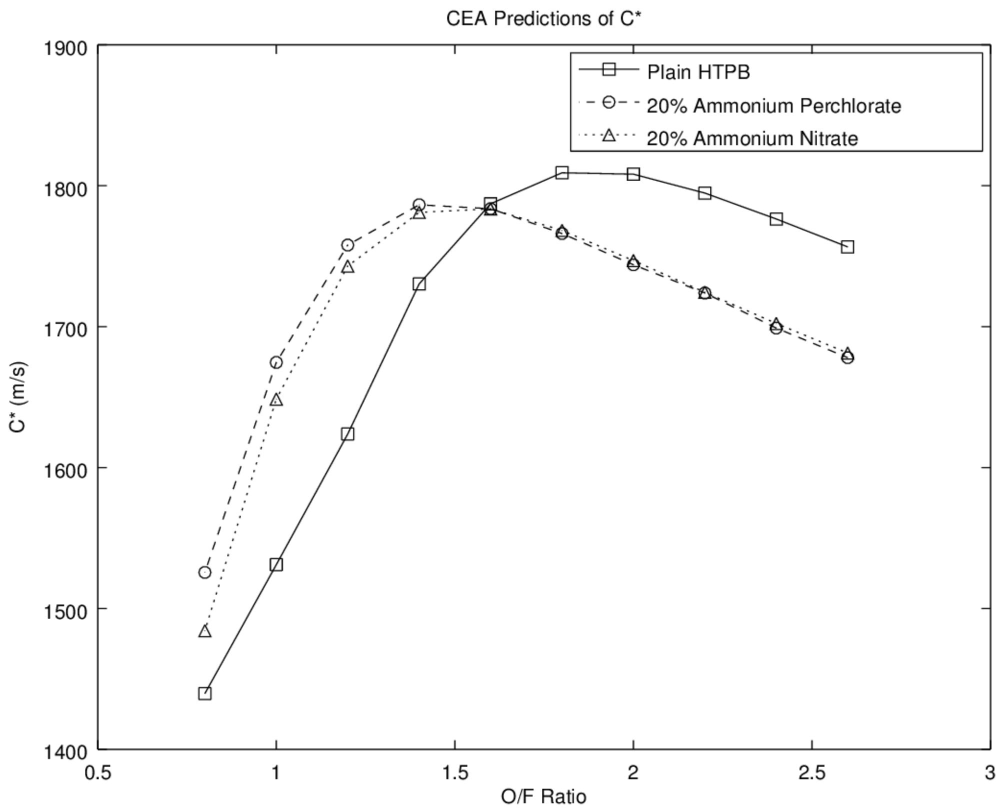

Figure 5 CEA Predictions for Ammonium Nitrate and Ammonium Perchlorate Mixed Hybrid Fuel Grains

Experimental results confirmed the CEA predictions that ammonium nitrate mixed hybrids have enhanced chemical performance at low O/F ratios as shown in figures 6 and 7.

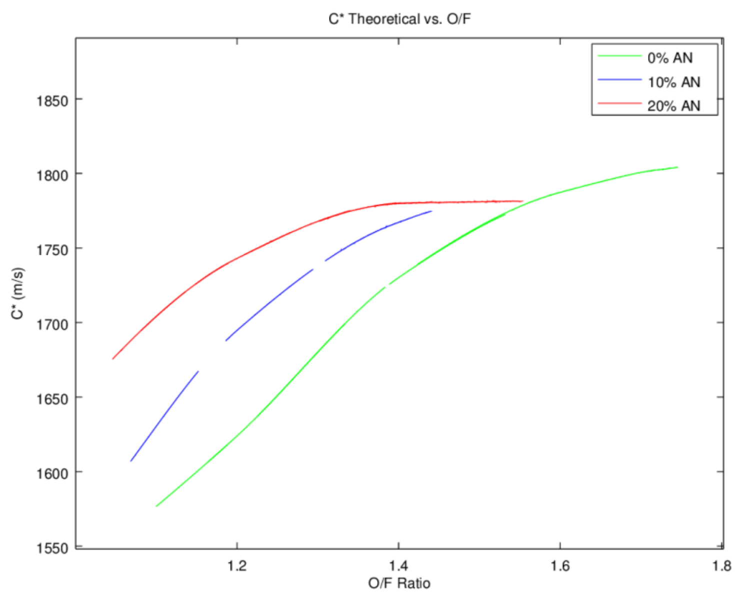

Figure 6 Theoretical C* with respect to O/F Ratio

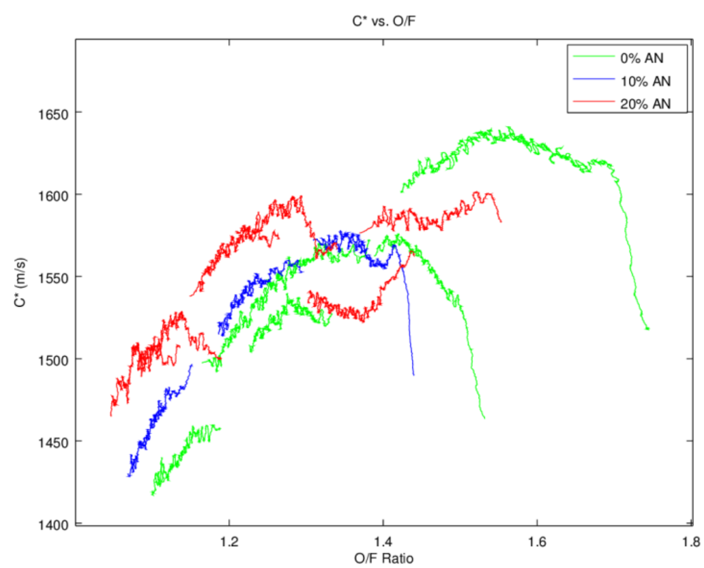

Figure 7 Experimental C* with respect to O/F Ratio

C. Specific Impulse

Specific Impulse, I_{sp}, is the total impulse per unit weight of propellant [6]. Specific impulse is a measure of the overall efficiency of a propellant, and takes into account the chemical performance of fuels, as well as the molecular weights of exhaust gasses and exit nozzle geometry.

CEA in figure 8 shows that mixed hybrids have slightly lower maximum specific impulses than true hybrids. This is because O2 performs much better as an oxidizer than ammonium nitrate or ammonium perchlorate. However, at low O/F ratios, when traditional hybrids become fuel rich and lose performance, mixed hybrids perform better because of the oxidizer stored within their fuel grains. Because of this effect, mixed hybrids with 20% oxidized fuel grains require roughly 20% less fluid oxidizer than their traditional hybrid counterparts. Less fluid oxidizer means that oxidizer tanks can be smaller and lighter weight, and can be used at lower pressures, potentially increasing the overall system delta v capability of the rocket.

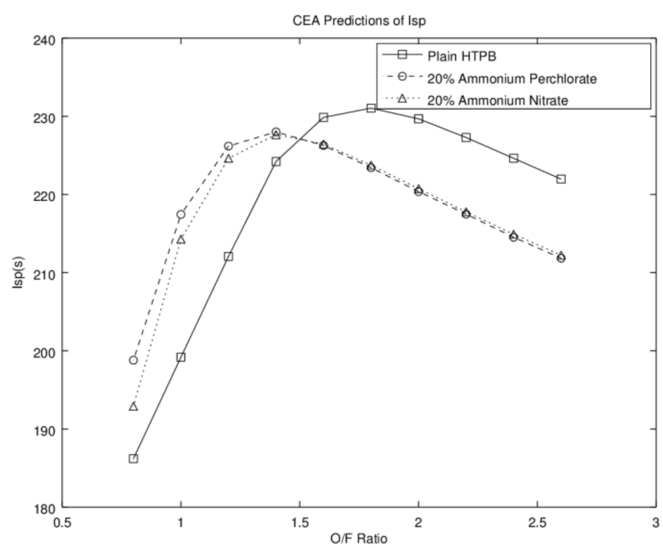

Figure 8 CEA Predictions of I_{sp} for Ammonium Nitrate and Ammonium Perchlorate Mixed Grains calculated with a 200 psi chamber pressure and an expansion ratio of 2.2.

Experimental results verify that grains oxidized with ammonium nitrate have better specific impulse than plain HTPB grains at low O/F ratios, and that oxidizer tank sizes can indeed be reduced as a result of adding ammonium nitrate to the fuel grain.

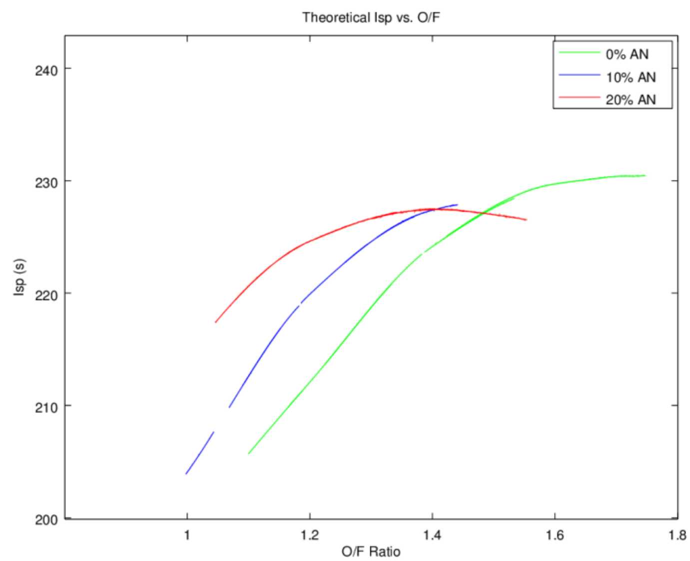

Figure 9 Theoretical I_{sp} as a Function of O/F Ratio calculated with experimental chamber pressure and an expansion ratio of 2.2.

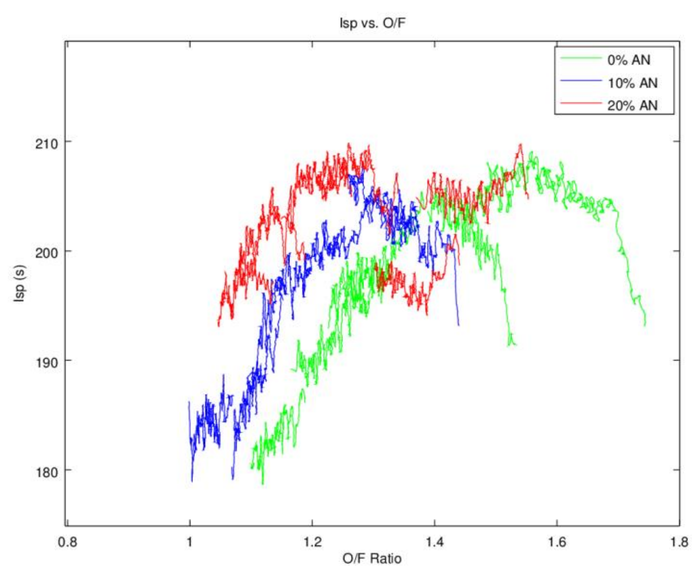

Figure 10 Experimental I_{sp} as a function of O/F Ratio

D. Volumetric Specific Impulse

Volumetric specific impulse, VI_{sp} is the total impulse of a rocket per unit volume. For example the VI_{sp} of the augmented HTPB/NH_4NO_3/GOX propellant mix is calculated as

$$Volumetric\ I_{sp} = \frac{\int_0^{T_{burn}} Thrust \cdot dt}{\frac{M_{GOX}}{\rho_{\substack{initial\\GOX}}} + \frac{M_{NH_4NO_3}}{\rho_{NH_4NO_3}} + \frac{M_{HTPB}}{\rho_{HTPB}}}$$

where the integral in the numerator represents the total impulse delivered by the thruster during the burn, $(M_{GOX}, M_{NH_4NO_3}, M_{HTPB})$ are the mass quantities of each propellant consumed during the burn, and $(\rho_{GOX}, \rho_{NH_4NO_3}, \rho_{HTPB})$ are the initial densities of the propellants at the start of the burn. In the case of the GOX portion of the oxidizer, the density is calculated at the initial storage pressure, approximately 2200 psig.

As the O/F ratio decreases in a hybrid rocket, an increased portion of the propellant comes from the solid fuel than from the fluid oxidizer. This causes the pre-combustion density the propellant mixture to increase as the O/F ratio decreases. Because ammonium nitrate is denser than HTPB, it has the added benefit of increasing the fuel grain density of mixed hybrids. Collected data indicates that at an O/F ratio of 1, a 20% AN mixed hybrid will have a 10% higher volume I_{sp} than a plain HTPB motor.

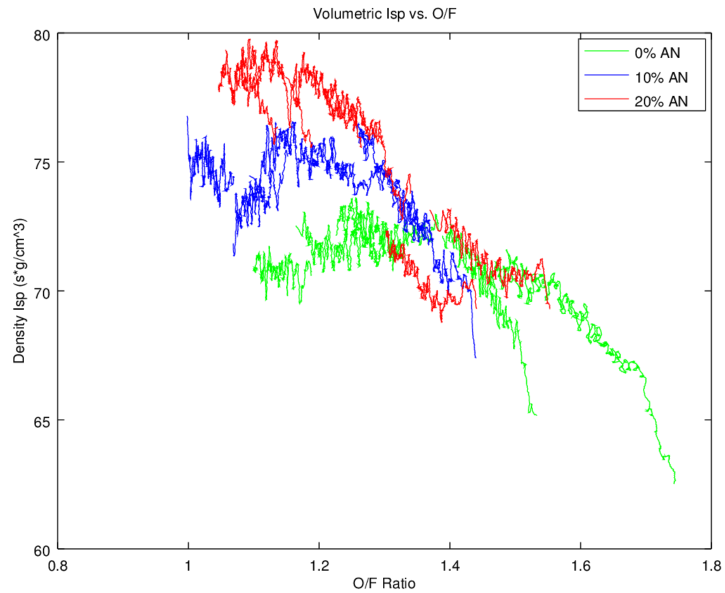

Figure 11 Experimental Volumetric I_{sp} as a function of O/F Ratio

These results are significant because they indicate that an HTPB/GOX motor with 20% ammonium nitrate could deliver the same amount of impulse as a plain HTPB/GOX motor, but occupy 10% less space. This could open up possibilities for hybrid rockets to be used more frequently in SmallSat launches, air-launch to orbit, or other applications where propulsion system size may be a concern.

CHAPTER IV

CONCLUSIONS AND FUTURE WORK

Hybrid rocket systems have many advantages when compared to other rocket systems, including safety, high performance, stop/start/re-light capabilities and throttleability. However, drawbacks of hybrid systems include low fuel regression rates and poor volumetric efficiency. Ammonium perchlorate has been shown to increase regression rates and volumetric efficiency in mixed hybrid motors, but ammonium perchlorate is dangerous to humans and to the environment. This study proposed that ammonium nitrate could be a key alternative to ammonium perchlorate in helping to improve the regression rate and volumetric efficiency of hybrid rocket systems in an environmentally friendly way.

This study set out to 1) demonstrate the usefulness of ammonium nitrate in mixed hybrid applications and confirm its ability to replace ammonium perchlorate as an environmentally friendly oxidizer; 2) quantify the effect of ammonium nitrate on regression rate, characteristic velocity, specific impulse, and volumetric specific impulse; 3) use regression rate data to model and predict regression rate in ammonium nitrate mixed hybrids as a function of ammonium nitrate content, fluid oxidizer mass flux, and chamber pressure.

Through successful testing of AN/HTPB fuel grains, this study has verified the advantages of using ammonium nitrate in mixed hybrids and demonstrated the ability of ammonium nitrate to replace ammonium perchlorate as an environmentally friendly oxidizer. Experimental burns have quantified the effects of ammonium nitrate in the characteristic velocity, specific impulse, and volumetric specific impulse of lab scale motors. Results confirm that addition of 20% ammonium nitrate to HTPB fuel grains can decrease O2 tank sizes by up to 20%, and increase the volumetric I_{sp} of a mixed hybrid system by up to 10%.

This study was unable to accurately model the regression rates of ammonium nitrate mixed hybrids as a function of oxidizer massflux, chamber pressure, and AN concentration. To obtain this objective, future work must be done with larger sample sizes, and varying chamber pressures. With a larger, more accurate collection of regression rate data, trends will be revealed which will associate changes in regression rate to chamber pressure and AN concentration.

There is still more work that can be done to better understand and characterize the effects of AN in mixed hybrid applications. Further work may also be done to better understand the relationship ammonium nitrate has to other fuel additives that are typically used in mixed hybrids, including, aluminum, iron oxide, and copper chromite. Similar tests have been carried out on ammonium perchlorate mixed hybrids [20][21], but few if any have been done using ammonium nitrate. With further experimentation and development, ammonium nitrate mixed hybrid motors may one day become competitive propellant systems for SmallSat, air-launch to orbit, or many other applications where rocket size and safety are high priorities.

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