Cold-Infusion of Catalytic Materials into 3-D Printed Fuels for In-Space Hybrid Propulsion Performance Enhancement

Ryan Thibaudeau, Stephen A. Whitmore
Department of Mechanical and Aerospace Engineering, Utah State University
Logan, Utah 84322; 651-278-9756
ryan.j.thibaudeau@gmail.com

ABSTRACT

A recent study by the ESA Space Research and Technology Center has identified that "reducing toxicity of propellants" offers the highest potential for reducing commercial space operating costs. Developing a “green” alternative for hydrazine, the most commonly used space propellant, was highly recommended. Hybrid propulsion offers an emerging, low-cost solution, especially for SmallSat propulsion.

Historically, a primary drawback of hybrid systems was a lack of reliable multiple-use ignition methods. Recently, restartability issues were overcome by leveraging unique dielectric breakdown properties of 3-D printed acrylonitrile butadiene styrene (ABS). Additive printing significantly changes thermoelectric properties, and when ABS is subjected to an electrostatic potential, the layered structure allows "arc-tracks" to be carved between the electrodes. Associated Joule-heating pyrolyzes fuel, allowing ignition to spontaneously occur when oxidizer flows.

Arc-ignition has been harnessed to develop a High-Performance Green Hybrid Propulsion (HGHP) family that has capability for reliable on-demand start, stop, and re-ignition. In its most mature form, HPGHP uses gaseous oxygen (GOX). However, unless stored at very high pressures, GOX has low-density, and it is highly desirable to employ higher density, long-term storable oxidizers, such as high-test hydrogen peroxide (HTP), nitrous oxide (N2O), or N2O/GOX blends (Nytrox) to improve volumetric efficiency. Unfortunately, when these oxidizers are "dropped-in" to replace GOX, HPGHP systems have experienced ignition reliability and latency issues resulting from decomposition energy barriers found in both HTP and N2O.

Previously published studies have demonstrated catalytic-assist, using high-atomic-weight metals to decompose the incoming oxidizer and release free oxygen, as effective in increasing ignition reliability. In a typical configuration, catalytic materials are supported by a substrate housed in an external pressure vessel placed in-line with the oxidizer flow-path. Unfortunately, in-line catbeds pose a series of technical issues. First, catbeds are heavy and add significantly to the spacecraft dry-mass without increasing propulsive efficiency. Second, in order to be effective, catalysts must be externally heated to high temperatures, often exceeding 300ºC. The required pre-heat energy has a significant impact on the total spacecraft energy budget. Finally, catbeds often self-consume at the high temperatures necessary for efficient decomposition action. There exists a universally limited operating lifetime for the expensive catalyst materials.

The presented research solves this problem. As described, external catalysts are replaced by an internal fuel-blend that mixes catalyst directly into the combustible material. The simple, inexpensive process works by cold-diffusion of 3D-printed ABS fuels with appropriate catalytic materials. The infused catalyst allows for near-instantaneous oxidizer decomposition, releasing gaseous oxygen that, when combined with "spark" energy, provides quick and reliable ignition. No system preheating is required, and the infused catalyst does not reduce the overall system performance. Design options and test results are presented for a 150-N Nytrox/ABS prototype using Ruthenium as the catalyst. "Drop-in" performance and reliability are demonstrated for both systems.

INTRODUCTION

Significant advances in the miniaturization of electronic components have emerged during the first two decades of the 21st century and have allowed spacecraft bus sizes to shrink by nearly an order of magnitude. Spacecraft as small as 25 kg now offer the sensing and computational capability of a spacecraft weighing more than several hundred kilograms from just a generation ago. As a result, global interests in very small spacecraft (SmallSats) have grown dramatically, and a competitive commercial market has emerged during the last decade.

To date, SmallSats have primarily been used for educational, technology demonstration, or other novelty purposes. SmallSats are currently launched using a limited number of "ride-share" options that rely on the excess launch vehicle payload capacity. These ride-share options offer secondary payload satellite customers little or no control over the launch schedule and the achieved final orbit. To support the expending capability of SmallSats, a cheap, reliable, high-performing, safe, and preferably, "green" propulsion unit is required in order to re-position the spacecraft properly; and once-inserted, maintain the required orbit. Figure 1 shows the current state of CubeSat propulsion systems with flight heritage. Unfortunately, SmallSat technology development has primarily centered on spacecraft bus design and miniaturization of sensor components. Generally, the propulsion industry has not kept pace with the bus avionics growth trend. With the current state of the art only a few space propulsion options are available to the systems designer.

This lack of options is insufficient to support the emerging growth demands of the "NewSpace" economy.

The cost associated with these propulsion systems has led to many small satellites launching with no propulsion: often restricting the capability of the mission. In support of the SmallSat market demands, the hybrid propulsion system discussed in this paper aims to address two key issues in filling the technology gap shown in Figure 1, handling safety and the prohibitive cost requirements that often impede SmallSat developers from incorporating propulsion into their design.

BACKGROUND

This section describes the properties of hydrazine and the hazards and environmental issues associated with its use. Next the emerging class of green propellants based on ionic-liquids is described, and the associated environmental and operational issues are described. Finally, hybrid rocket systems using environmentally friendly propellants are offered as a potential solution. Issues associated with their operational use are presented.

Hydrazine as the Current Operational Standard for In-Space Propulsion.

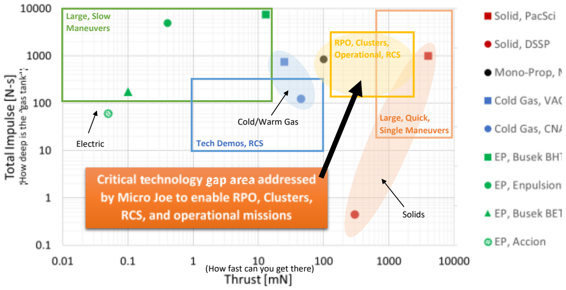

Figure 1. Current SmallSat Propulsion Trade space.

Hydrazine is a very effective and reliable monopropellant. Hydrazine thrusters are simple, versatile, and dependable. Hydrazine technology has been under development since the late 1950's and has a very high technology readiness level (TRL) level.

Unfortunately, hydrazine-based systems bring a wide range of objective and environmental hazard issues. Hydrazine is a highly toxic and dangerously unstable substance. The United States Environmental Protection Agency classifies hydrazine as “highly toxic.” Hydrazine is destructive to living tissues and is a known carcinogen.[1] Hydrazine possesses a high vapor pressure and boils readily at room temperature. Thus, there exists significant risks of respiratory contamination, and special servicing procedures that employ full-pressure self- contained atmospheric protective ensemble suits are required. The toxicity and explosion potential of hydrazine requires extreme handling precautions.

On the Need for a "Green" Replacement for Hydrazine as a Spacecraft Propellant.

With a growing regulatory burden, the associated infrastructure requirements for hydrazine transport, storage, servicing, and clean up resulting from accidental releases, are rapidly making the use of hydrazine cost prohibitive. A recent study by the European Space Agency Space Research and Technology Center (ESTEC)[2,3] identified *"reduced production, operational, and transport costs associated with lower propellant toxicity/explosion hazards...,"* as an essential operations change required for achieving low-cost commercial space access developing a non-toxic, stable “green” alternative for hydrazine was highly recommended.

In response to this recommendation, The USAF,[4] NASA,[5] and the Swedish Space Corporation Ecological Advanced Propulsion Systems (ECAPS) [6] are actively involved in the development of green alternatives to hydrazine. A useful "green" replacement for hydrazine must be sufficiently chemically and thermally stable to allow technicians and engineers to safely work with the propellant in a normal "shirt-sleeve" commercial environment; but must reliably combust and have good performance properties. Cryogenic or high freezing point propellants requiring temperature control are not appropriate for space propulsion applications. Although mass-specific impulse is important, volume-specific impulse *(density impulse)* is an even more important consideration, and a high propellant storage density is preferred.

Ionic Liquids as an Alternative to Hydrazine

Although some low-TRL electrical-chemical systems in SmallSat scales have been tested[7], currently the only operational green chemical-propellant options are associated with the ionic-liquids (ILs)[8] Ammonium Dinitramide (ADN),[9,10,11,12] and Hydroxyl Ammonium Nitrate (HAN).[13,4 ,14] Both propellants have achieved at least one spaceflight, with the ADN-based propellant LMP-103S flying on the PRISMA Spacecraft,[15] and the HAN-based propellant AFM-315E flying on NASA's Green Propellant Infusion Mission (GPIM)[16,17] The PRISMA flight report[18] states that LMP-103S delivered equivalent–to-superior performance to hydrazine, with a vacuum specific impulse of 230 seconds. The GPIM flight report does not specifically report the achieved in-flight specific impulse (I_{sp}) for AFM-315E, but extrapolations from ground tests show that I_{sp} values between 220 and 230 seconds are achievable[17].

Environmental and Operational Issues Associated with Ionic Liquid Propellants

In spite of being called “green,” by their manufacturers, IL-based propellants are generally not environmentally-friendly. Both of the above-mentioned IL-propellants are toxic to organic tissue, for example AF-M315E contains hydroxyethyl hydrazine (HEHN) as an ignition enhancer and burn stabilizer. In high concentrations IL-based propellants are prone to energetic uncontrolled decomposition events. Thus, special handling precautions are required for processing and storage. The major advantage of both propellants is a low-vapor pressure at room temperature, allowing handling and servicing without the use of Self Contained Atmospheric Protective Ensemble (SCAPE) suits.

Because of these properties, the USAF has recently begun to refer to such IL-formulations more properly as having “reduced toxicity” instead of being "green." In addition to potential toxicity and objective hazards, there exist several key developmental issues that make IL-based propellants unsuitable for some small spacecraft applications.

The high water content makes *IL*-propellants notoriously hard to ignite,[19] and LMP-103S and AFM-315E propellants cannot be cold-started. Multiple catalyst systems have been developed to augment IL ignitability; however, the associated catalyst beds must be preheated from 350-400°C before and during ignition. This pre-heat cycle pre-heat consumes a significant amount of energy. For example, on the Prisma[15] demonstration flight the pre-heat time was 30 min, requiring 16.7 kJ of total energy input. This input was required for every cold-cycle of the LMP-103S thruster. Thus, it can be concluded that the ionic liquid catalyst beds and associated heating systems add significantly to the inert mass of the spacecraft and the high-wattage preheat requirement presents a significant disadvantage for small spacecraft where power budgets are extremely limited.

Also, due to the very slow reaction kinetics demonstrated by Hori and Katsumi[20] for HAN, and Whitmore and Burnside[21] for ADN at the moderate pressures levels required for SmallSat Thruster systems (1000–2000 kPa), ignition latencies can be significant, up to several seconds, and may limit the usefulness of IL-propellants for spacecraft maneuvering and control systems. Below 1000 kPa chamber pressure the IL liquid propellants will not ignite, and this issue limits the ability to scale these systems for thrusters below the 1-N thrust level.

Clearly, significant technology improvements must occur before IL-based systems can be employed as a primary propulsion unit or as part of the reaction control system for small spacecraft. With the current state of propulsion technology, the only proven non-hazardous propulsion alternative to hydrazine, and available for small ride-share payloads, is based on low-performing cold-gas thrusters.

Even under ideal operating conditions, when compared to conventional solid, hybrid, or bi-propellant options, the performances of ionic liquid propellants are generally quite low — with achieved vacuum I_{sp} values at or less than 230 seconds. The combination of these middling performance characteristics and lack of truly “green” advantages have led some in the industry to question whether ionic liquids as propellants have been “oversold”.[22] Clearly, significant technological issues exist and must be overcome before the ionic-liquid propellants are used routinely as a hydrazine replacement.

Hybrid Rockets as Green Alternative for In-Space Propulsion.

In response to this emerging need for environmentally-sustainable in-space propulsion systems, hybrid rocket systems have emerged as a potential alternative to traditional toxic-propellants. When compared to conventional liquid- and solid- propelled rocket systems, hybrid rockets possess well-known operational safety and handling-advantages. A study by the U.S.

Department of Transportation concluded that hybrid rocket motors can be safely stored and operated without a significant risk of explosion or detonation and offer the potential to significantly reduce operating costs for commercial launch vehicles.[23] Finally, Hybrid rocket systems offer higher performance than hydrazine-based systems; and their inherent-design safety offers a significant potential for ride-share spacecraft applications.

Operational Issues Associated with Hybrid Rockets

However, in spite of these well- known safety and handling advantages; conventionally-designed hybrid rocket systems have not seen widespread commercial use due to two key technical challenges. The first technical challenge is the current lack of an operational method reliable multiple-use ignition, allowing on-demand start, stop, and re-start. The second technical challenge is low fuel regression rates associated with hybrid combustion.

Because of the relative propellant stability, hybrid rocket systems can be difficult to ignite; and a substantial ignition enthalpy source is required. The ignition source must provide sufficient heat to pyrolyze the solid fuel grain at the head end of the motor, while simultaneously providing sufficient residual energy to overcome the activation energy of the propellants. Such high-energy devices often come with a suite of environmental and objectives risks, and operational challenges.

Most conventional hybrid rocket applications have used high output pyrotechnic or “squib” charges to initiate combustion. Pyrotechnic charges are extremely susceptible to inadvertent detonation due to with electromagnetic radiation,[24,25] and present significant explosion hazards that are incompatible with rideshare opportunities. Most importantly, for nearly all applications pyrotechnic ignitors are designed as "one-shot" devices that do not allow a multiple restart capability. Thus, the great potential for restartable upper stages or in-space maneuvering systems using hybrid propulsion has remained largely unrealized. An operational hybrid system with multiple restart capability does not currently exist.

The second disadvantage is that the internal motor ballistics of hybrid combustion produce regression rates that are typically between 30 and 40% of the regression rates of solid fuel motors of the same thrust and impulse class.[26,27] To make up for the lower regression rate, a higher oxidizer mass flow rate is required to maintain the same thrust level. This increases the system’s oxidizer-to-fuel (O/F) ratio and ultimately results in poor mass impulse performance, erosive fuel burning, nozzle erosion, reduced motor duty cycles, potential combustion instability, and poorer overall performance of the system. To overcome this O/F problem, hybrid rockets are traditionally designed with cylindrical fuel ports that have high length-to-diameter ratios. This high aspect ratio can result in poor volumetric efficiency, and thus limits a hybrid motor application to a customarily volume-constrained small satellite.[28]

High Performance Green Hybrid Propulsion Systems

In order to fill the technology gaps as described in the previous section, over the past decade Space Dynamics Laboratory (SDL) and the Propulsion Research Laboratory at Utah State University (PRL-USU) have actively teamed to develop a High-Performance Green Hybrid Propulsion (HPGHP) technology as a safe and environmentally-sustainable replacement for hydrazine across a wide range of applications.

HPGHP is enabled by recent advances in 3D printing and leverages unique electrical breakdown characteristics of certain 3D-printed plastics, the most effective being acrylonitrile butadiene styrene (ABS). Additive manufacturing changes the electrical breakdown properties, and when printed materials are presented with an inductive electrical potential, electrical-arcing along the layered surface pyrolyzes material and seeds combustion when an oxidizing flow is introduced.[29] This "sparking" property has been developed into a proprietary, power-efficient system that can be cold-started and restarted with a high degree of reliability. Multiple prototype units with thrust levels varying from less than 1 N to greater than 900 N have been developed and tested.[30,31,32]

Although there may appear to be some similarities, the arc-ignition method described in this paper is distinctly different from the action of a pulse plasma thruster[7]. Pulse plasma thruster designs use a high alternating current source to pyrolyze the surface of a Teflon block. The high current in the plasma arc induces a magnetic field. The action of the current and the magnetic field causes the plasma to accelerate. When the current is stopped, pyrolysis ceases. A typical ignition cycle requires up to 1 kW of power. The arc-ignition method used in this work requires a low direct current source to pyrolyze the fuel material. Additive printing of the fuel changes the material dielectric proper ties; when ABS is subjected to the electro-static potential between embedded electrodes, the layered structure allows an “arc track” to be carved between the electrodes. Associated joule heating pyrolyzes the fuel; and as oxidizing flow is introduced, ignition spontaneously occurs. Combustion continues even after the current source is terminated. A typical ignition cycle requires less than 5 W of power applied for a second or two, and consumes less than 10 joules of total ignition energy. Once started, the system can be sequentially fired with no additional energy inputs required. Figure 2 shows a schematic of the HPGHP Ignition System Electronics, and Figure 3 shows the head-end of a 3D-printed ABS fuel grain with embedded electrodes.

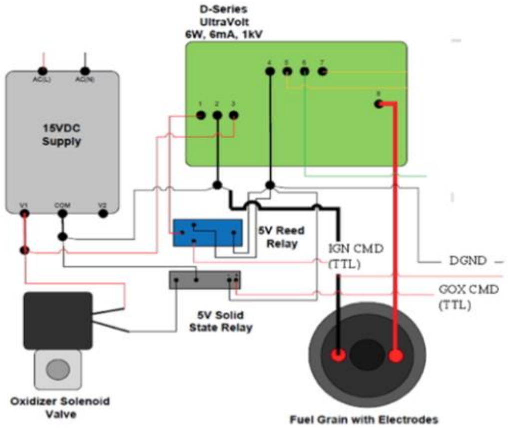

Figure 2. Ignition System Electronic Schematic.

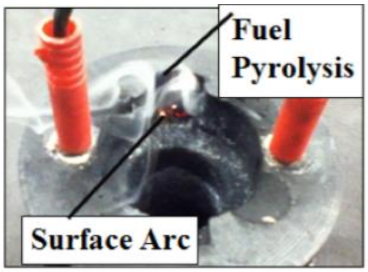

Figure 3. 3D Printed Fuel Grain with ESC-Terminated Electrodes.

The patented system[33] has been scaled over a large range with successful prototypes with thrust levels varying from 1 to 900 N having been tested.[7] Multiple oxidizers including gaseous oxygen (GOX), nitrous oxide (N_2O), hydrogen peroxide (H_2O_2), enriched air (EAN40), and Nytrox have been successfully tested with the HPGHP system. Nytrox is a "green" blend GOX and N_2O and is similar to the laughing gas used for medial anesthesia applications. A flight-weight 25 N thruster system was extensively vacuum tested.[34]

On 25 March 2018, a flight experiment containing a 10 N prototype of this thruster system was launched aboard a two-stage Terrier-Improved Malemute sounding rocket from Wallops Flight Facility. The launch achieved apogee of 172 km, allowing more than 6 min in a hard-vacuum environment above the Von-Karman line. The thruster was successfully fired five times Whitmore and Bulcher[35] report the results of this flight test experiment.

On the Need for Higher-Density Hybrid Oxidizers

In its most mature form, the HPGHP system uses GOX as the oxidizer with 3D-printed ABS as the fuel. The GOX/ABS propellants are highly mass efficient system, with a flight weight 25 N thruster system achieving vacuum I_{sp} greater than 300 seconds. Unfortunately, unless stored at very high pressures, GOX has a low specific gravity and is a volumetrically inefficient propellant.

Due to its higher density, hydrogen peroxide and Nytrox – a blend of nitrous oxide and GOX – were considered to be very promising alternative oxidizers for this application. In order to achieve comparable density, GOX would need to be stored at pressures above 10,000 psi. Table 1 compares the performance of a hypothetical 90% peroxide/ABS and Nytrox/ABS system to hydrazine, LMP-103S and AFM315-E. This work has investigated using these hybrid oxidizers as a "drop-in" replacement for GOX in the HPGHP system. Data for hydrazine, LMP-103S and AFM315-E were taken from Ref. [4].

Issues Associated with Catalytic Ignition of H_2O_2 and Nytrox in Hybrid Motors

Although HPGHP ignition works quite reliably using GOX as the oxidizer; HPGHP has experienced reliability and ignition latency issues when replaced by hydrogen peroxide and Nytrox. The reasons for these issues will be described in the following sections. High concentrations of 90% or greater of hydrogen peroxide, referred to as high-test peroxide (HTP), and Nytrox have been used extensively for propulsion applications, both as a monopropellant and in combinations with fuels. Figure 4 shows the associated end-to-end reaction for peroxide. In this reaction both oxidation and reduction occur at the same time. This reaction is very energetic and exothermic. Both oxidizers are relatively stable and require a certain amount of activation energy to begin decomposition. Figure 5 shows this transition process.

Figure 4. Hydrogen Peroxide Decomposition Reaction.

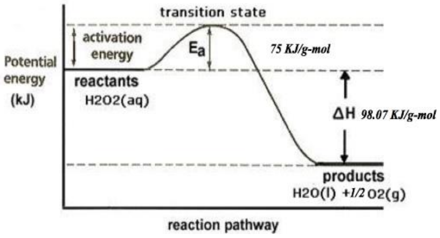

Figure 5. Peroxide Decomposition Energy State.

In typical rocket applications with H_2O_2 or N2O as a monopropellant, a heated catalyst bed is used to initiate decomposition. The catbed lowers the activation energy

Table 1: Comparison of Propulsion Systems

Propellant	LOX/LH2 (Cryogenic Bi-Propellant)	N_2O_4/MMH (Bi-Propellant)	AP Composite Solid Propellant	Hydrazine (Mono-Prop)	LMP-103S (Mono-Prop)	AF-M315E (Mono-Prop)	Nytrox/ABS (Hybrid Bi-Propellant)	H2O2/ABS (Hybrid Bi-Propellant)
Flame Temperature, °C	3200 °C	3350 °C	2800 °C	1300 °C	1600 °C	1900 °C	3150 °C	2900 °C
Characteristic Velocity	2350	1765	1500	1300	1380	1380	1650	1600
Vacuum, I_{sp}, s	440	335	260-285	225	252 (theory) 235 (delivered)	266 (theory) 245 (delivered)	320 (theory) 305 (extrap.)	324 (theory) 302 (delivered)
Optimal O/F Ratio	6.0:1	2.16:1	7.5:1	N/A	N/A	N/A	4:1	6:1
Storage Specific Gravity @ 0°C	0.36	1.20	1.52	1.01	1.24	1.465	0.82 (85% N_2O)	1.392 (90% H_2O_2)
Propellant Freezing Temperature	-219 0°C (LOX) -259°C (LH2)	-11 0°C (N_2O_4) -52 °C (MMH)	N/A	2 °C	−7 °C	< 0 °C (forms glass, no freezing point)	−70 °C (Nytrox)	−10 °C (90% H_2O_2)
Impulse density, N:s/L	1600	4000	4100	2270	3125 (theory) 2915 (delivered)	3900 (theory) 3650 (delivered)	2500 (vacuum, extrap.) 1850 (ambient, delivered)	4450 (theory) 4002 (delivered)
Cold-Storability	Low	High	Moderate	High	Moderate	Moderate	High	Moderate-High
Preheat Temperature, °C	N/A none-required	N/A none-required	N/A none-required	315 °C Nominal, cold-start capable	300 °C	370 °C	N/A none-required	N/A none-required
Required Ignition Input Energy, Joules	10 kJ	Hypergolic	<1 kJ	2500-5000 J Nominal, cold-start capable	12,000 J (10 Watts @ 1200 s)	27,000 J (15 Watts @ 1800 s)	2.5 J (5 Watts for 500 ms)	2.5 J (5 Watts for 500 ms)
Ignition Reliability	High	High	High	High	Low-to-Moderate	Low-to-Moderate	Moderate	Moderate
Restart Capable	Yes	Yes	No	Yes	Yes	Yes	Yes	Yes
Throttleability	Yes, 65-100%	Yes, 50-100%	Not Throttleable	Yes, 0-100%	Likely	Likely	Yes, 10-100%	Yes, 10-100%
System Complexity	High	Moderate	Low	Low-to-Moderate	Moderate	Moderate	Moderate	Moderate
Cost	$$$$	$$$	$ (Hobby Grade) $$$ (Military Grade)	$$	$$$	$$$$	$	$
Availability	Widely Available	Limited, Restricted Access	Widely Available (Hobby Grade), Restricted Access (Military Grade)	Limited, Restricted Access	Limited, Restricted Access	Limited, Restricted Access	Very Widely Available	Very Widely Available
Objective Hazard Risk	Moderate	High	Moderate-to-High	High	Moderate	Moderate	Low	Low
Toxicity	Low	High	High	High	Moderate	Moderate	Low	Low
NFPA 704 Hazard Class [67]								

to the point where a moderate amount of heat can initiate decomposition. Noble metal catalysts like platinum or ruthenium can lower the activation energy to less than 50 kJ/mol. Although catalytic decomposition of monopropellant HTP has been successfully used for a variety of applications, this method typically requires very high concentrations of peroxide, greater than 90%. Even then, "wet" partially decomposed burns are very typical. As shown by Figure 4, even in fully decomposed HTP plumes, water is an inherent by-product.

When catalytic decomposition is applied to hybrid rocket systems, the results are less satisfactory. As the oxidizer plume exits the injector and enters the hybrid combustion chamber, it rapidly expands and super-cools to well below the evaporation temperature of water. As a result, liquid water re-condenses and the "soaked" fuel grain will simply not ignite. This problem appears to be endemic to all hybrid rockets but is especially problematic when lower concentration peroxides (<90%) are used.

The ESA-funded Nammo Raufoss Project[36] has been ongoing since 2003 and is currently the most accomplished of the existing peroxide-hybrid programs. The Nammo design used HTPB as the accompanying fuel. For this design the peroxide solution was decomposed using SAAB's proprietary catalyst bed design, with the resulting hot gases injected into the combustion chamber through a vortex injector. The catalyst bed hybrid was able to work with peroxide concentrations as low as 87.5%, but the catbed was quite large and made up a considerable fraction of the overall inert motor weight.

For the typical Nammo motor ignition sequence, after peroxide flow is initiated the chamber pressure gradual builds up from ambient to a plateau at approximately 1500 kPa (220 psia). This "smoldering" buildup of chamber pressure takes slightly more than 2 seconds, followed by a sharp rise in chamber pressure to approximately 2500 kPa bars (360 psia). NAMMO refers to the initial pressure buildup as the "*mono-propellant combustion mode*." and the sharp rise and subsequent plateau as "*hybrid combustion mode*."

As reported by Whitmore and Merkley (2017)[37] no matter the concentration level, the initial expansion from the catbed exit to ambient will always super-cool the water vapor in the decomposition products and result in a "wet motor." This expansion and adiabatic cooling phenomenon are very likely the reason for the large ignition latencies and the self-described "*monopropellant*" combustion modes, smoldering burns, and large ignition latencies experienced by the NAMMO hybrid motors. In any case, the resulting enthalpy levels are often too low to achieve full combustion, and ignition is highly unreliable.

It must be noted that, in addition to the previously-described ignition reliability issues, catalyst beds also pose a series of operational issues:

- Catbeds are heavy and volumetrically inefficient. They contribute nothing to the propulsive mass of the system.
- In order to be effective, catalysts must be externally heated to high temperatures, often exceeding 300ºC. As described previously, this pre-heat presents a serious problem for SmallSats that have limited energy budgets.
- Catbeds often self-consume at the high temperatures necessary for efficient decomposition action,
- Catalyst beds can be "poisoned" and rendered ineffective in the presence of stabilizers in HTP.

Because H_2O_2 and N_2O catbeds tend to rely on noble metals like platinum or ruthenium as the active agent, they are extremely expensive, and the final two events in the above list can significantly increase programmatic development costs.

Catalytic Assist for Arc-Ignition of H_2O_2 and Nytrox in Hybrid Motors.

Previous studies by Whitmore and Martinez[38,39] have demonstrated that a catalytic-assist, where a catalyst bed is placed in line with the system, significantly increases ignition reliability and reduces ignition latency. Catalytic-assist works by partially decomposing the incoming oxidizer to release free oxygen before entering the combustion chamber. Because catalytic-assist is only intended to assist the arc ignition system, and not fully decompose the incoming HTP; pre-heat is not required, and far less expensive materials like potassium permanganate, manganese dioxide, manganese (III) oxide, and potassium nitrate can be used in lieu of silver and platinum.

Similar approaches have been done for Nytrox testing, with mixed results[47].

Thermal Decomposition of H_2O_2 and Nytrox Using GOX Pre-Lead and Pre-Ignition

Even with the success of the previously described catalytic-assist methods, considering the issues associated with catbeds, including weight and volume, it is desirable to remove the catalytic system entirely from the design. An alternative method initiates combustion using a gaseous oxygen pre-lead and then introduces HTP to the hot combustion chamber. Residual energy from the GOX/ABS combustion thermally decomposes the HTP flow, with the freed oxygen allowing full hybrid combustion to initiate.

Previously, this thermal ignition method was applied by Whitmore[40] for ignition of a larger-76 mm, 140 N thrust hybrid system. Thermal decomposition for an HTP-hybrid on the proposed 1 N to 5 N thrust level required for SmallSat propulsion was investigated by Smith[46]. Similar approaches have been done for Nytrox testing[47]. While he saw success with this method, there are still drawbacks for this system; 1) System architecture doubles in complexity because separate plumbing, valves, and sensors are needed for the GOX lines. 2) Spacecraft volume is sacrificed because transitioning from a ground-based developmental unit to a space-ready flight unit requires a high pressure GOX tank and its associated plumbing and controls, which don't directly contribute to the propulsion system's power or efficiency. The smaller the spacecraft is, the greater the percent volume increase, making the drawback more significant. For a spacecraft classified as a Small Satellite, this approach is not viable to allow for enough HTP or Nytrox propellant to be stored onboard to achieve a delta-V that's useful for most space missions.

THEORETICAL CONSIDERATIONS

This section discusses three key considerations that were investigated during this preliminary testing campaign. These considerations are 1) the effects of Oxidizer-to-Fuel Ratio (O/F) and fuel grain geometry on motor performance, 2) assessing the potential for motor feed-coupling instability, and 3) the effect of infusing catalyst material into the fuel grain and igniter to improve ignition latency and reliability.

Effects of O/F Ratio and Fuel Grain Geometry on Motor Performance.

Hybrid Rocket systems generally favor a narrow range of O/F ratios where the system performance is near optimal. Figure 6 illustrates this point where the characteristic velocity c_* and Vacuum I_{sp} of ABS burned with 90% aqueous H_2O_2 and Nytrox are plotted as a function of O/F ratio for 5 different chamber pressures, 50, 100, 150, 200 and 250 psi. These calculations were performed using the NASA industry-standard chemical equilibrium code CEA,[41] and assume a 25:1 nozzle expansion ratio for the specific impulse calculation.

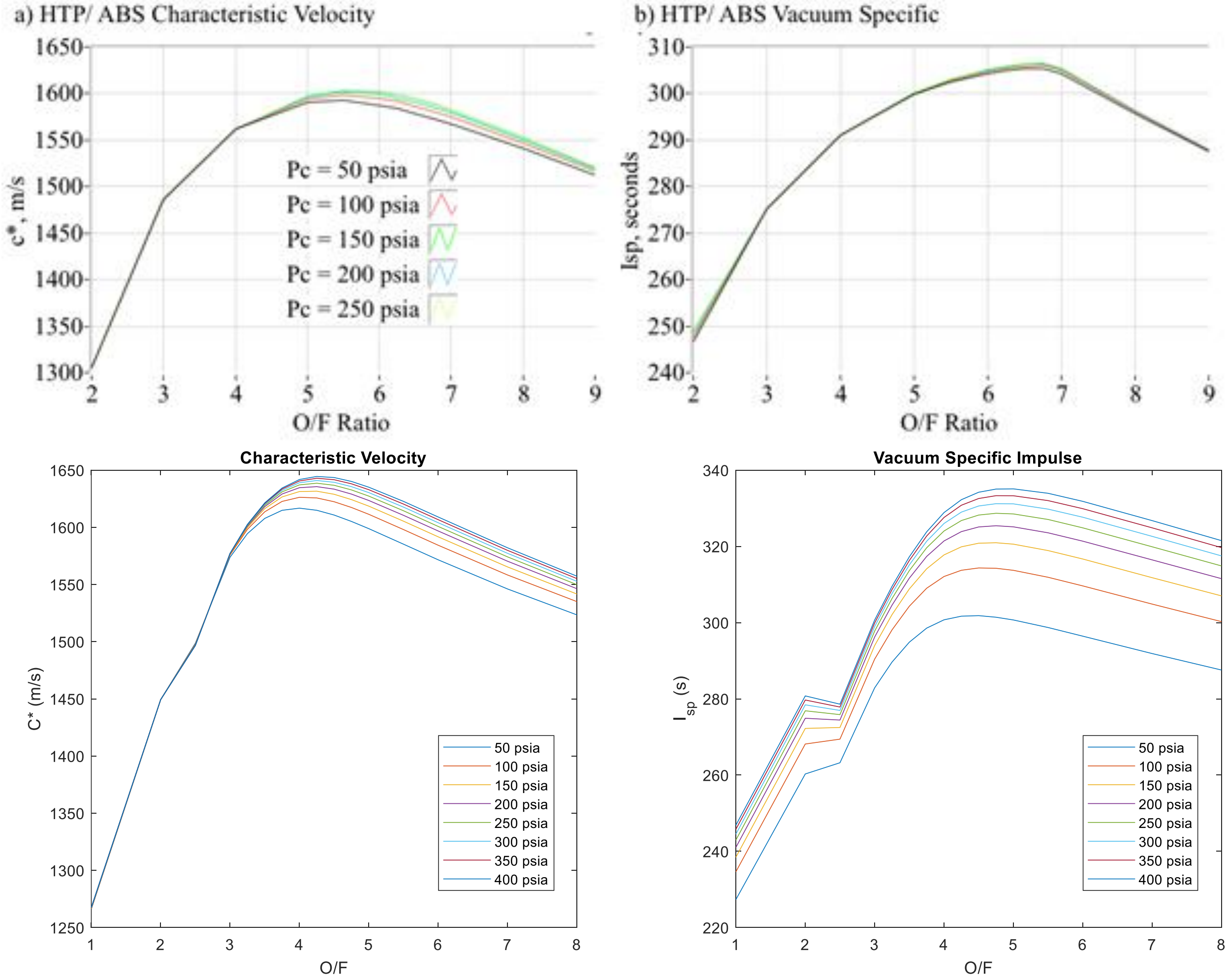

Figure 6: Theoretical Performance of 90% HTP (top) and Nytrox (bottom) with 3D Printed ABS using CEA

Generally, it is observed that the primary heat-transfer mechanism for fuel pyrolysis in larger-scale hybrid rocket systems forced convection within the boundary layer, Sutton and Biblarz (Ref. [26, Chapt. 11]). As the fuel port opens, greater burn area is exposed and this growth in burn area is greater than the drop-off in fuel regression rate resulting from the drop in oxidizer massflux. The result is that the large majority of hybrid rockets tested to date tend to experience oxidizer-to-fuel ratios that shift from fuel-rich to lean during the burn lifetime. Fuel regression rates are only weakly dependent on motor size.

In contrast, at small scales, i.e., 5 N thrust levels and lower, oxidizer massflux is sufficiently small that the rate of convective heat transfer is significantly reduced. For this combustion regime, radiative heat transfer dominates fuel pyrolysis. Whitmore and Merkley[42] have shown that unlike massflux-driven fuel regression for larger hybrid systems, the radiation-driven fuel regression rates of small-scale hybrids tend to grow with time. As a result, small-scale hybrids tend to burn with a reverse behavior, from shifting from lean to fuel-rich over the burn lifetime.

Thus, at small scales low hybrid fuel-regression rates are not an issue. In fact, the reverse behavior is experienced. In order to keep fuel regression rates near the optimal points one must anticipate this O/F shift and design the system to initially burn very lean, with the O/F shift crossing over the optimal point.

Although Figure 6 shows that both propellant sets achieve above 300 seconds theoretical vacuum I_{sp}, this range is rather narrow and drops off rapidly as the motor burns rich. Due to the tendency of small-scale hybrids to burn richer with time, this result has significant ramifications with respect to the real-world motor performance.

Assessing the Potential for Injector Feed Coupling

Because Nytrox exists as a two-phase fluid, there exists a potential for injector-feed coupling during hybrid combustion. As described by Karabeyoglu et al.,[43] the underlying dynamics of the injector system is governed by the inertia of the fluid mass in the injector orifice and the pressure difference between the injector manifold and the combustion chamber.

Since Nytrox is a two-phase fluid, the dynamics of understanding and balancing the incompressible liquid and compressible gas phases at the same time can be quite complicated, and multiple methods have been developed to calculate the flows using only pressure and temperature data[43]. For this research at this stage, oxidizer massflow was measured directly by resting the oxidizer tank on a load cell scale that is monitored by the LabVIEW DAQ and VI.

Injector feed coupling results in a low-frequency instability, that generally lies between 10 and 25 hertz. This oscillation results when the burn process is perturbed, resulting in a transient increase on chamber pressure, this increase subsequently drops the massflow rate into the chamber, resulting in a lowered fuel burn rate, and a subsequent drop in chamber pressure. The chamber pressure drop increases the massflow, and the cycle repeats. Depending on the motor geometry and the combustion rates of the propellants, feed-coupling instability can be mild or severe. A key driver of severe instability is combustion delay caused by slow vaporization of the incoming oxidizer.

To mitigate the potential coupling instability, a commercial atomizing 45° cone-spray nozzle was used. It was considered that a straight-port injector, which shoots a stream of oxidizer directly into the fuel port and the flame zone, offered the highest potential for injector-feed coupling. The atomizing cone-spray nozzle was intended to break up and spread the liquid Nytrox, resulting in faster evaporation, thereby buffering any potential feed coupling instabilities.

Catalyst-Infused Fuel Grain Solution

Previous testing conducted by Thibaudeau[48] has shown that infusing the fuel grain with a catalytic material significantly improves the ignition issues with HTP. The infusion technique relies on heterogeneous diffusion of a solution containing a powdered catalyst – for HTP, the catalyst used was potassium permanganate (KMnO4). This diffusion ensures that catalytic materials are directly exposed to the injected oxidizer, allowing for in-situ catalytic decomposition to release GOX for ignition. This eliminates the need for external catalyst beds or GOX prelead burns. There is always exposed catalyst as the fuel burns away. Ignition latencies were reduced from 4 seconds to 0.6 seconds. Reliability improved from 50% ignition success to 100%. Additionally, the several performance metrics of the motor also improved, including chamber pressure, thrust, specific impulse, and combustion efficiency.

Preliminary tests, shown later in this paper, indicate that this infusion technique can be applied for Nytrox. Initial tests confirm that ruthenium powder can be heterogeneously infused into the 3D printed ABS fuel grain and significantly reduce ignition latency and enhance ignition reliability while improving system performance. Test data for this catalyst-infused fuel grain (CatGrain) is presented later.

DATA ANALYSIS METHODS

This section details the analytical methods that were used to calculate key derived parameters from the raw test data. These mass-flow based calculations include 1) oxidizer massflow, 2) total massflow exiting the nozzle, 3) fuel massflow, 4) oxidizer-to-fuel ratio. Key performance parameters calculated from the raw data include 1) combustion efficiency, 2) thrust coefficient, 3) specific impulse, 4) characteristic velocity, and 5) impulse density. The following section details how these calculations were performed.

Calculating the Fuel Massflow Rate.

Although the inline Venturi measures the oxidizer massflow in real-time, the test stand was not configured to directly measure the fuel massflow. Instead, before and after each hot-firing the fuel grains were weighed to give the total fuel mass consumed during the test. As will be described later in this section, these mass measurements were used to anchor the "instantaneous" fuel massflow rates, calculated as the difference between the nozzle exit and oxidizer massflows,

$$\dot{m}_{fuel} = \dot{m}_{total} - \dot{m}_{ox} . \tag{2}$$

Knowing the nozzle throat area A^* and the plume exhaust gas properties, the nozzle exit (total) massflow at each time point was calculated from the measured chamber pressure time history P_0, using the 1-dimensional choking massflow equation, [Anderson[44] Chapter 4.]

$$\dot{m}_{total} = A^* \cdot P_0 \cdot \sqrt{\frac{\gamma}{R_g \cdot T_0} \cdot \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{\gamma-1}}} \quad . \tag{3}$$

The calculation of Eq. (2) assumes the flow composition is frozen at the nozzle entrance, (Anderson, [44], pp 659-661) and nozzle erosion during the burn.

A table of thermodynamic and transport equilibrium properties of the GOX/ABS, HTP/ABS and Nytrox/ABS exhaust plumes were calculated using the previously described CEA code[41] with chamber pressure P_0 and mean O/F ratio as independent look up variables for the tables. For each data point in the burn time history, the two-dimensional tables of thermodynamic and transport properties were interpolated using chamber pressure P_0 and mean O/F ratio as lookup variables. Calculated parameters included the gas constant R_g, ratio of specific heats γ, and flame temperature T_0. Defining the combustion efficiency as

$$\eta^* = \frac{c^*_{actual}}{c^*_{ideal}} = \frac{\sqrt{\left(\frac{\gamma+1}{2\cdot\gamma}\right)^{\frac{\gamma+1}{(\gamma-1)}} R_g \cdot T_{0_{actual}}}}{\sqrt{\left(\frac{\gamma+1}{2\cdot\gamma}\right)^{\frac{\gamma+1}{(\gamma-1)}} R_g \cdot T_{0_{ideal}}}} \approx \sqrt{\frac{T_{0_{actual}}}{T_{0_{ideal}}}} \quad , \tag{4}$$

the theoretical flame temperature $T0_{ideal}$ was scaled by adjusting the combustion efficiency

$$T_{0_{actual}} = \eta^{*2} \times T_{0_{ideal}} \quad , \tag{5}$$

such that the calculated fuel mass consumption

$$\Delta M_{fuel} = \int_0^t \left(\dot{m}_{total} - \dot{m}_{ox}\right) dt \tag{6}$$

matched the measured value from differences of the pre- and post-test weight measurements. As described earlier, the consumed fuel mass anchored the thermodynamic calculations.

Adjusting input combustion efficiency upwards has the effect of increasing the calculated fuel mass consumption, and downwards decreases the calculated fuel mass consumption. The calculations of Equations (3-6) were iterated, adjusting η^* after each iteration, until the calculated fuel mass matched the measured mass within a prescribed level of accuracy, in this case 0.5%. For each iteration, the time-averaged *oxidizer-to-fuel* ratio was calculated as integrated oxidizer massflow divided by the consumed fuel mass,

$$\overline{O/F} = \frac{\int_0^{t_{burn}} \dot{m}_{ox}(t) \cdot dt}{\Delta M_{fuel}} = \frac{\int_0^{t_{burn}} \dot{m}_{ox}(t) \cdot dt}{\int_0^{t_{burn}} \left[\dot{m}_{total}(t) - \dot{m}_{ox}(t)\right] \cdot dt} \quad . \tag{7}$$

Calculating the Motor Performance Parameters

The 1-dimensional de Laval flow equations (Anderson [44], Chapter 4) were used to calculate the thruster performance parameters. Thrust and thrust coefficient were calculated from chamber pressure as

$$F_{thrust} = P_0 A^* \cdot \left(\sqrt{\frac{2}{\gamma-1} \cdot \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{\gamma-1}}} \left(1 - \frac{p_{exit}}{P_0}\right)^{\frac{\gamma-1}{\gamma}} + \left(\frac{A_{exit}}{A^*}\right)\left(\frac{p_{exit} - p_\infty}{P_0}\right) \right) , \tag{8}$$

$$C_F = \frac{F_{thrust}}{P_0 A^*} = \gamma \sqrt{\frac{2}{\gamma-1} \cdot \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{\gamma-1}}} \left(1 - \frac{p_{exit}}{P_0}\right)^{\frac{\gamma-1}{\gamma}} + \left(\frac{A_{exit}}{A^*}\right)\left(\frac{p_{exit} - p_\infty}{P_0}\right) \tag{9}$$

Specific Impulse, Characteristic Velocity, and Impulse density were calculated as

$$I_{sp} = \frac{F_{thrust}}{g_0 \dot{m}_{total}} \quad ,$$

$$c^* = \frac{P_0 \cdot A^*}{\dot{m}_{total}} \quad ,$$

$$\rho I_{sp} = s_g \cdot g_0 \cdot I_{sp} \tag{10}$$

In Eq. (10) g_0 is normal acceleration of gravity at sea level, *9.8067 m/s²*. The thrust coefficient C_F and specific impulse I_{sp} were also calculated directly from the thrust sensed by the test stand load cell. Values calculated from both sources will be presented later in order to support the verisimilitude of the collected test data.

EXPERIMENT SETUP

The test apparatus and motor configuration for the tests presented in this paper are portrayed in this section.

Test Article

Figure 7 shows the motor configuration, which includes the injector cap containing a COTS spray injector nozzle, 75mm motor casing, ignition cap, fuel grain, and 150N nozzle retainer assembly. The injector cap, which

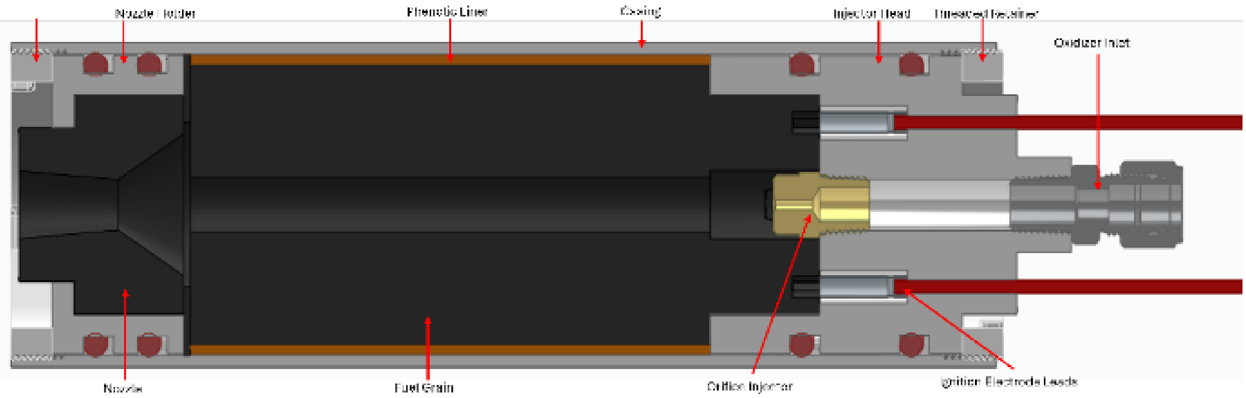

Figure 7: 75mm Nytrox Motor Assembly

includes ports for the injector, ignition electrodes and chamber pressure fitting, was machined from 6061-T6 grade aluminum. A phenolic liner insulates the case from the fuel. The nozzle was machined from a single piece of graphite with a 3:1 expansion ratio.

Test Apparatus

Figure 8 shows the system Piping and Instrumentation diagrams for the Nytrox system. A separate path for CO_2 or N_2 leads directly to motor injection to provide a fire suppression and purge function in the case of a misfire.

Fire control and data acquisition are managed from outside the test cell using laptop computer that communicates with the instrumentation system via a single Ethernet Bus. The ignition system has a physical switch for arming/disarming, adding an additional layer of safety. Motor performance measurements include motor injector and chamber pressure, and thrust level is sensed by a load cell mounted to the test sled.

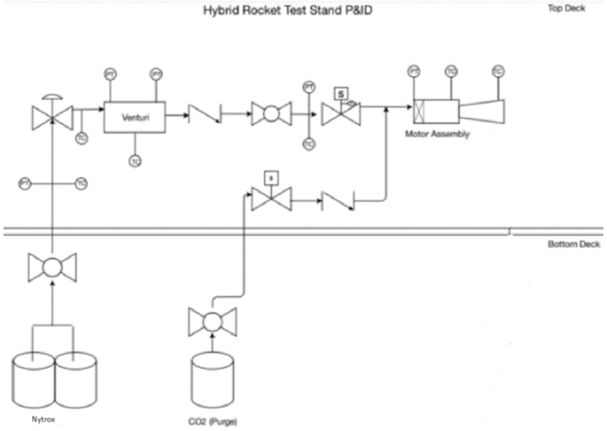

Figure 8: Nytrox Hybrid Thruster Test System Piping and Instrumentation Diagram.

The thruster chamber is mounted on an inverted pendulum thrust stand, shown in Figure 9. This consists of an aluminum T-slot railing supported by three thin aluminum flexures. These flexures allow the structure to move in the direction of the thrust axis when the motor fires, resulting in load cell measurements. Figure 9 shows this mounting configuration. The motor fires to the right of the test sled in this image.

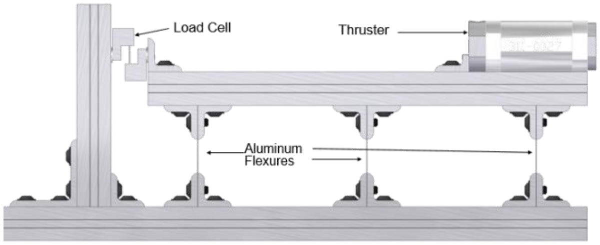

Figure 9: Motor Sled with Mounted Thrust Chamber and Load Cell.

CatGrain Fabrication

The catalyst-infused fuel grain (CatGrain) is critical to the development of an HTP or N2O propulsion system that can be a simple drop-in replacement of a GOX propulsion system without ignition latency or increased ignition energy.

The CatGrain is created by making an aqueous solution of a powdered catalytic material, then diffusing the solution into a fuel grain. To achieve sufficient diffusion, the fuel grain material must be porous. Most fuel grains used for hybrid rocket motors are plastic, which are not porous enough – if at all – as extruded or cast material. Plastic filament used for FDM 3D printing is porous, and the layering in printed parts provides additional locations for diffusion. Printed ABS is the best choice for this application because of the porosity and burn characteristics. Figure 10 shows the ABS fuel grain before and after KMnO4 infusion for the HTP application.

Figure 10: ABS Fuel Grain Before (left) and After (right) Catalyst Infusion

The process for infusing Ruthenium for Nytrox CatGrain is very similar. Since ruthenium isn't soluble, a very fine powder is required to keep the powder suspended in the solution. With constant agitation, non-soluble powders can still be infused using this method. Ruthenium alumina (Ru/Alumina) and ruthenium on carbon powder (Ru/C) were tested and shown to work well with this method.

RESULTS AND DISCUSSION

This section presents preliminary results from the Nytrox initial testing campaign. Test data for the HTP configuration can be found in Thibaudeau's paper[48]. To date, a total of 6 successful full-combustion Nytrox CatGrain hot firings have been performed.

Ignition Validation Tests

From the initial validation tests conducted, the Nytrox CatGrain shows strong promise, with some initial test data shown in Figure 11. Ruthenium on alumina pellets were used for the initial validation test by grinding them into a fine powder and infusing them into the fuel grain. About 0.1% of the total fuel grain mass was the ground Ru/Alumina. An ignition latency of 1.4 seconds is observed, with average steady-state ambient and vacuum Isp at 250 and 310 seconds, respectively. Vacuum Isp is extrapolated using a 25:1 expansion ratio into vacuum conditions. The O/F ratio averages right at the stoichiometric point, about 4.1. The combustion efficiency reached 98%.

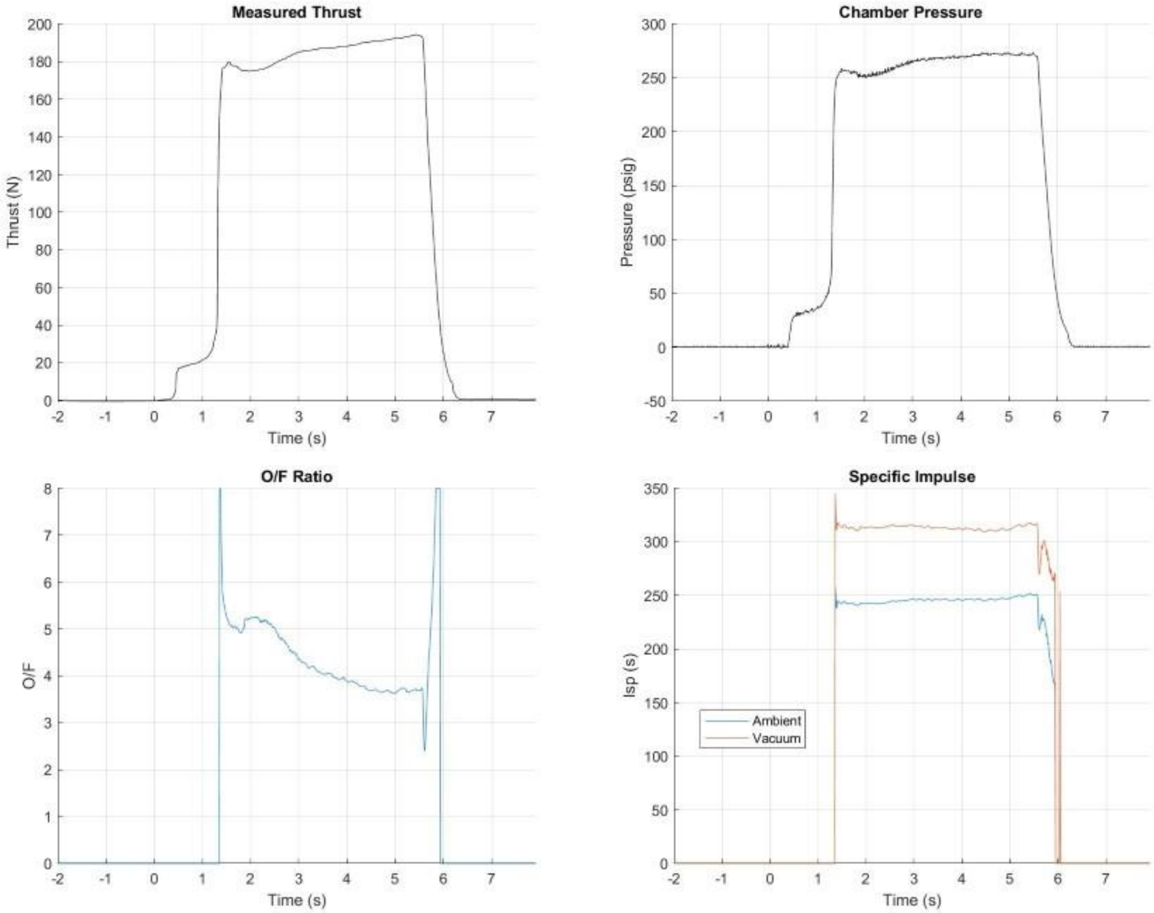

Figure 11: Test Data of Initial Ignition Test of Ru/Alumina CatGrain

Previous work[48] has shown that 3D printed ABS can hold as much as 2% by weight of the catalyst powder. The results of the 0.1% Ru/Alumina infusion lends itself to skepticism of how well the alumina can be carried by the solvent into the printed ABS. The ability to carry more catalyst is expected to correlate to faster ignition and higher performance. For this reason, it was decided to switch to Ru/C, which proved very successful – the fuel grain was able to absorb 1% of the Ru/C catalyst.

Results from the Ru/C CatGrain are shown in Figure 12. Ignition latency was significantly reduced to only 130 milliseconds, nearly an order of magnitude faster than with the Ru/Alumina. Combustion efficiency remained high, nearly 99%. However, there was lower thrust observed, with a pretty significant shift throughout the burn. This is likely driven by increased the regression rate of the fuel as a result of the increased amount of catalyst, as shown in Table 2. A more drastic shift in O/F ratio is also observed, adding evidence to the increase in regression rate of the fuel.

Table 2: Fuel Consumed Comparison Between ABS neat and CatGrain

Date	Burn Number	Fuel Burned (g)	Configuration
7/15/2024	1	50	ABS neat, GOX Prelead
7/15/2024	2	53	ABS neat, GOX Prelead
7/15/2024	3	41	ABS neat, GOX Prelead
7/19/2024	1	58	Ru/C CatGrain, Direct Ignition
7/19/2024	2	67	Ru/C CatGrain, Direct Ignition
7/19/2024	3	65	Ru/C CatGrain, Direct Ignition

For comparison, a test with a normal ABS fuel grain – not a CatGrain – was conducted without a GOX prelead. Of six attempts conducted, only one actually ignited – the results are shown in Figure 13. A significant rise time is seen, about 4.3 seconds. Because there was so short of time of actual combustion, there was very little mass burned. As such, the calculations presented in Data Analysis Methods Section to calculate the fuel massflow

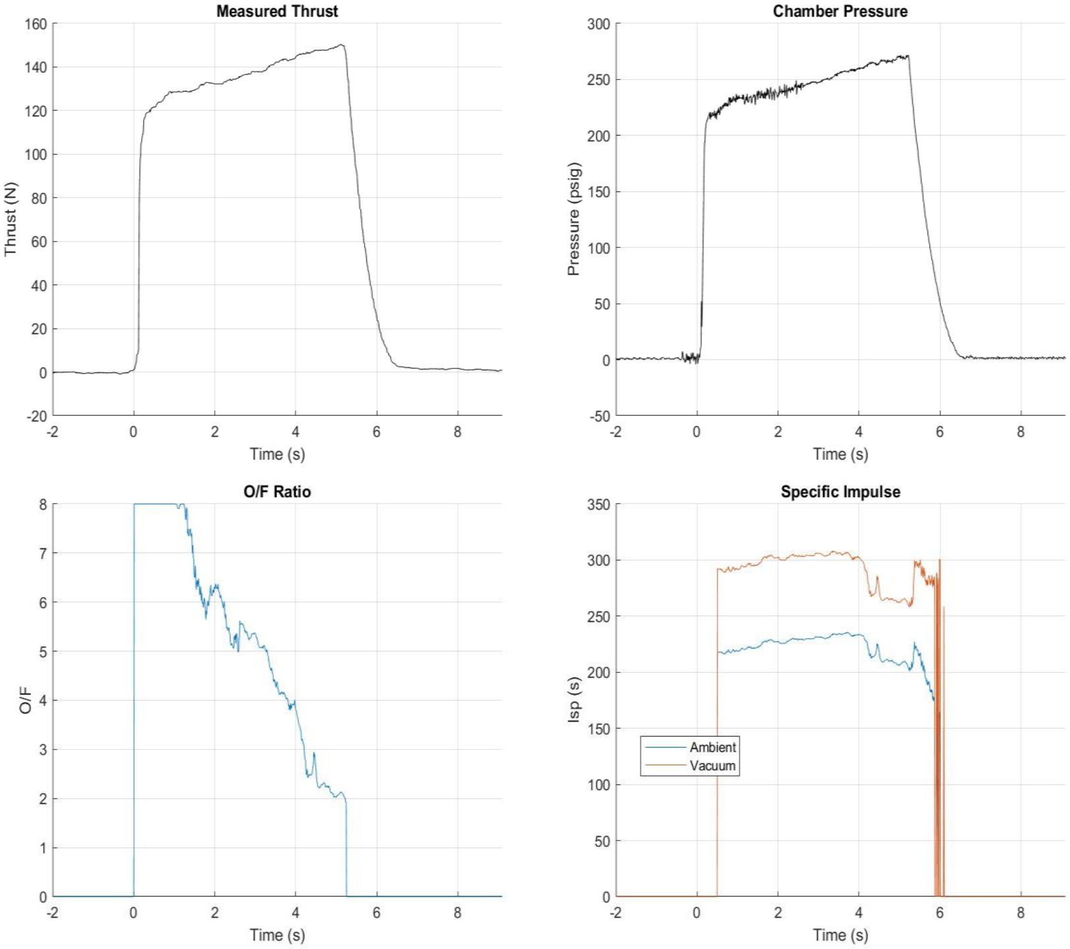

Figure 12: Test Data of Initial Ignition Test of Ru/C CatGrain

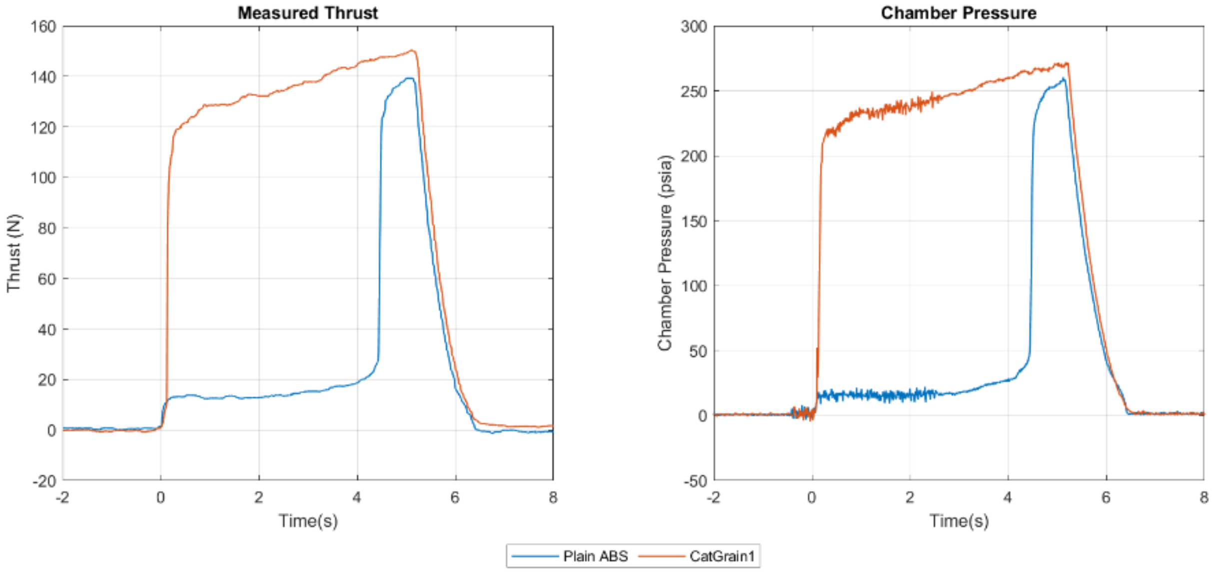

Figure 13: Comparison with ABS Neat and CatGrain

and subsequent performance data could not be sufficiently anchored by the measured fuel burned. Thus, performance data is not presented, only the measured thrust and chamber pressure readings.

This comparison highlights the drastic ignition improvement the CatGrain has over an ABS neat fuel grain.

Initial Performance Observations

Oxidizer to Fuel Ratio

Core burning hybrid motors are susceptible to an O/F ratio shift during the burn, especially the first several seconds of the initial burn when the combustion port area changes most rapidly. This effect is shown in Figure 14. The CatGrain has an even larger effect on this, evident in the data shown in Figure 15. The O/F ratio starts at very high (maxed out at 8 due to the code referencing CEA) but decays down to about 2 over the 5 second hot-fire. Throughout the rest of the burn, there is significantly less shift.

Specific Impulse

Despite this large shift in O/F ratio, the performance attained from this initial test shows the potential for this system to outperform hydrazine and its newer "green" derivatives. Extrapolating the specific impulse values to vacuum conditions exceeds 300 seconds, a 36% increase over hydrazine. Additionally, 300 seconds is the threshold that begins to make it competitive with liquid bi-propellant rocket engines.

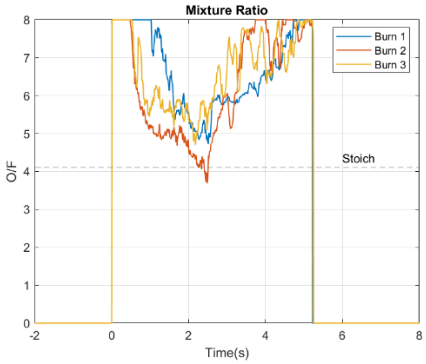

Figure 14: Shift in O/F Ratio Between Multiple Burns of ABS Neat Fuel Grain

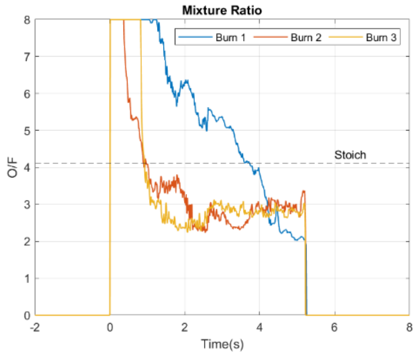

Figure 15: Shift in O/F Ratio Between Multiple Burns of Ru/C CatGrain

Alternative Catalysts

Due to the high cost of Ruthenium, a copper catalyst was also attempted. Initial research indicated the potential for copper to work as a catalyst, though most of required a preheat temperature of 300C. Direct ignition of Nytrox copper CatGrain without preheat was attempted without success. More research and development will be spent on searching for a less expensive catalyst that does not require a preheat.

Future Work

This research is ongoing, with future work focusing on the following:

- Consistency in ignition latency through the life of the fuel grain while maintaining latency values at or below 200 ms,
- Catalyst investigation to reduce cost and avoid preheating,
- Detailed evaluation of regression behaviors,
- Development to maintain more consistent O/F ratios,
- Exploration of throttling capability,
- Characterization of minimum impulse bit,
- Flight system optimization.

SUMMARY AND CONCLUSION

In support of the emerging SmallSat market, there does not currently exist a Commercial Off the Shelf (COTS) "green" propulsion system that offers both intermediate thrust and specific impulse levels in the 240-300 second range. The only available options are associated with gold-gas flow or monopropellant hydrazine. Cold-gas systems are volumetrically inefficient and produce very low I_{sp}. Hydrazine-based systems bring a wide range of objective and environmental hazard issues, and their use can significantly increase operating costs of the total spacecraft system.

To fill this technology gap, SDL and PRL-USU have partnered to develop a non-toxic hybrid prototype propulsion system based on Utah State's HPGHP. HPGHP technology leverages the unique dielectric breakdown properties of 3D printed ABS to develop family of hybrid propulsion systems with capability for reliable start, stop, and re-ignition.

In its most mature form, the HPGHP system uses GOX as the oxidizer. Unfortunately, unless stored at very high pressures, GOX has a low specific gravity and is a volumetrically inefficient propellant. Due to its high density and excellent oxidizing performance, Nytrox was considered to be very promising alternative "drop-in" oxidizer for this application.

Although HPGHP ignition works quite reliably with GOX as the oxidizer, the technology has experienced reliability and ignition latency issues when GOX is replaced by Nytrox. Ignition augmentation using external catalyst beds or GOX preleads have been explored but ultimately are prohibitive for flight configurations.

An alternative method, as tested in this study, replaces the external catalyst by diffusion-blending ABS fuel with Ruthenium supported on activated carbon. The embedded catalyst allows for near-instantaneous decomposition as Nytrox enters the combustion chamber, releasing gaseous oxygen that, when combined with the arc-ignition energy, provides quick and reliable ignition. No preheat is required, and the infused fuel does not reduce the overall system performance. A patent has been applied for this fabrication method and products presented.

The "CatGrain" system was used as a true “drop-in” replacement, allowing Nytrox to be burned directly in a legacy 150-N GOX/ABS HPGHP thruster with no hardware modifications. The GatGrain configuration out-performs monopropellant hydrazine and the ionic-liquid “green” hydrazine alternatives and is also within a competitive threshold for liquid bi-propellant rocket engines.

Acknowledgments

The authors want to thank Hybird Space Systems and the NASA Small Spacecraft Technology Program (SSTP) for partially funding this work through the Cooperative Agreement (CA) Partnerships with Universities and NASA Centers, Grant No. 80NSSC20M0083.

REFERENCES

1. Choudhary, G., Hansen, H., Donkin, S., and Kirman, C., "Toxicological Profile for Hydrazines," Vol. 21, U.S. *Dept. of Health and Human Services*, Public Health Service, Agency for Toxic Substances and Disease Registry, 1997, pp. 1–224. https://www.atsdr.cdc.gov/toxprofiles/tp100.pdf

2. Bombelli, V., "Economic Benefits for the Use of Non-toxic Monopropellants for Spacecraft Applications, AIAA-2003-4783, [39th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, Huntsville, AL, July 2003.] https://doi.org/10.2514/6.2003-4783

3. Haeseler, D., Bombelli, V., Vuillermoz, P., Lo, R., Marée, T., & Caramelli, F., "Green Propellant Propulsion Concepts for Space Transportation and Technology Development Needs," ESA SP-557, [Proceedings of the 2nd International Conference on Green Propellants for Space Propulsion, Cagliari, Sardinia, Italy, 7-8 June 2004.] https://adsabs.harvard.edu/full/2004ESASP.557E...4H

4. Hawkins, T. W., Brand, A. J., McKay, M. B., and Tinnirello, M., "Reduced Toxicity, High Performance Monopropellant at the U.S. Air Force Research Laboratory," AFRL-RZ-ED-TP-2010-219, [4th International Association for the Advancement of Space Safety Conference, Huntsville, AL, 19-21 May 2010.] https://ui.adsabs.harvard.edu/abs/2010ESASP.680E..10H/abstract

5. Goldstein, Edward, "The Greening of Satellite Propulsion," *Aerospace America*, February, 2012, pp. 26-28. https://www.researchgate.net/publication/293560444_The_greening_of_rocket_propulsion

6. Larsson, A., and Wingborg, N., "Green Propellants Based on Ammonium Dinitramide (ADN)," *Adv. in Spacecraft Tech.*, Vol. 2, Intech Open, London, U.K., 2011, Chap. 7. https://doi.org/10.5772/13640

7. Patel, A., Zhang, Y., and Shashurin, A., "Liquid-Fed Pulsed Plasma Thruster with Low-Energy Surface Flashover Igniter for Propelling Nanosatellites," *J. of Prop. and Power*, Vol. 36, No. 5, Sept. 2020, pp. 715–720. https://doi.org/10.2514/1.B37800.

8. Amrousse, R., Katsumi, T., Azuma, N., Hatai, K., Ikeda, H., and Hon, K., "Development of Green Propellants for Future Space Applications," *Sci. and Tech. of Eng. Mat.*, Vol. 77, Nos. 5–6, 2016, pp. 105–110. http://www.jes.or.jp/mag/stem/Vol.77/documents/Vol.77,No.5,p.105-110.pdf

9. Pokrupa, N., Anglo, K., and Svensson, O., "Spacecraft System Level Design with Regards to Incorporation of a New Green Propulsion System," AIAA-2011-6129, [46th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, San Diego, CA, July 31-Aug 3, 2011.] https://doi.org/10.2514/6.2011-6129

10. Nagamachi, M. Y., Oliveira, J. I., Kawamoto, A. M., and Dutra, R., C., "ADN – The new oxidizer around the corner for an environmentally friendly smokeless propellant," *J. of Aerospace Technology Management*, Vol. 1, No. 2., December 2009, pp. 153-160. http://dx.doi.org/10.5028/jatm.2009.0102153160

11. Persson, M., Anflo, K., and Dinardi, A., "A Family of Thrusters For ADN-Based Monopropellant LMP-103S," AIAA-2012-3815, [48th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit 30 July - 01 August 2012, Atlanta, Georgia, 2012.] https://doi.org/10.2514/6.2012-3815.

12. Ide, Y., Takahashi, T., Iwai, K., Nozoe, K., Habu, H., and Tokudome, S., "Potential of ADN-Based Ionic Liquid Propellant for Spacecraft Propulsion," *Procedia Engineering*, Vol. 99, 2015, pp. 332–337. https://doi.org/10.1016/j.proeng.2014.12.543

13. Dennis Meinhardt, D., Brewster, G., Christofferson, S., and Wucherer, E., "Development and testing of new, HAN-based monopropellants in small rocket thrusters, AIAA 90-4006. [34th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, 13 July 1998 - 15 July 1998, Cleveland,OH,U.S.A.] https://doi.org/10.2514/6.1998-4006

14. Spores, R. A., Masse, R., and Kimbrel, S., "GPIM AF-M315E Propulsion System," [AIAA_2013-3849, [49th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, San Jose CA, 15-17 July 2013.] https://doi.org/10.2514/6.2013-3849

15. Anflo, K.; Crowe, B. In-Space Demonstration of an ADN-based Propulsion System, [AIAA-2011-5832. [47th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, San Diego, CA, USA, 31 July–03 August 2011]. https://doi.org/10.2514/6.2011-5832

16. Masse, R., Spores, R. A., Allen, M., Lorimer, E., Meyers, P, and McLean, C., "GPIM AF-M315E Propulsion System," [AIAA 2015-3753. [51st AIAA/SAE/ASEE Joint Propulsion Conference. July 2015.] https://doi.org/10.2514/6.2015-3753

17. McLean, C.; Marotta, B.; Porter, B. Flight performance of the propulsion subsystem on the green propellant infusion mission, AAS 20-062. [30th AIAA/AAS Space Flight Mechanics Meeting, Orlando, FL, USA, 6–10 January 2020]; http://www.univelt.com/AASPapers.html (Accessed on 25 May 2022).

18. Anflo, K.; Crowe, B. "In-Space Demonstration of an ADN-based Propulsion System," [AIAA-2011-5832.

[47th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, San Diego, CA, USA, 31 July–03 August 2011.] https://doi.org/10.2514/6.2011-5832

19. Kang, S., and Kwon, S., “Difficulties of Catalytic Reactor for Hydroxylammonium Nitrate Hybrid Rocket,” *Journal of Spacecraft and Rockets*, Vol. 52, No. 5, Sept.–Oct. 2015, pp. 1508–1510. https://doi.org/10.2514/1.A33255

20. Katsumi, T.; Hori, K. "Combustion Wave Structure of Hydroxylammonium Nitrate Aqueous Solutions," AIAA 2010-6900. [46th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, Nashville, TN, USA, 25–28 July 2010.] https://arc.aiaa.org/doi/10.2514/6.2010-6900

21. Whitmore, S.A.; Burnside, C.G. Performance Analysis of a High Performance Green Propellant Thruster. NASA Marshall Space Flight Center Faculty Program, NASA TM-2015-218216. December 2015; pp. 125–151. Available online: https://ntrs.nasa.gov/search.jsp?R=20160000456 (Accessed on 1 December 2019).

22. Lowe, D. The Overselling of Ionic Liquids. Science Magazine, In The Pipeline, 11 June 2013. http://blogs.sciencemag.org/pipeline/archives/2013/06/11/the_overselling_of_ionic_liquids (Accessed on 24 May 2022).

23. Anon., “Hazard Analysis of Commercial Space Transportation; Vol. 1: Operations, Vol. 2: Hazards, vol. 3: Risk Analysis,” U.S. Dept. of Transportation, PB93-199040, Accession No. 00620693, May 1988. https://rosap.ntl.bts.gov/view/dot/35788.

24. Anon., “Department of Defense Interface Standard, Electromagnetic Environmental Effects requirements for Systems, MIL-STD-464, http:// http://www.tscm.com/MIL-STD-464.pdf, [Accessed 24 May 2022].

25. “Electromagnetic Environmental Effects Requirements for Systems,” United Sates Dept. of Commerce National Technical Information Service, Vol. MIL-STD-46, Springfield, VA, 2010. https://absolute-emc.com/article/MIL-STD-464

26. Sutton, G., and Biblarz, O., *Rocket Propulsion Elements, 9th ed*., Wiley, New York, 2016, Chaps. 15, 19. ISBN-13: 978-1118753651, ISBN-10: 1118753658.

27. Cheng, G., Farmer, R., Jones, H., and McFarlane, J., “Numerical Simulation of the Internal Ballistics of a Hybrid Rocket Motor,” AIAA 1994-0554. [32nd Aerospace Sciences Meeting and Exhibit, , Jan. 1994.] https://doi.org/10.2514/6.1994-554

28. Whitmore, S. A., “Three-Dimensional Printing of “Green” Fuels for Low-Cost Small Spacecraft Propulsion Systems,” Journal of Spacecraft and Rockets, Vol. 55, No. 1, 2018, pp. 13–26. https://doi.org/10.2514/1.A33782

29. Mathias, S. D., Whitmore, S. A., and Harvey, R., "High Voltage Breakdown and Arc-Tracking Mechanism of Thermoplastics with Applications to Hybrid Rocket Arc- Ignition," *AIAA 2017-4601, 53rd AIAA/SAE/ASEE Joint Propulsion Conference*, 10-12 July 2017, Atlanta, GA. https://doi.org/10.2514/6.2017-4601

30. Whitmore, Stephen A., “Additive Manufacturing as an Enabling Technology for "Green" Hybrid Spacecraft Propulsion," RAST-1039, *Conference on Recent Advances in Space Technology 2015*, Istanbul Turkey, June 16-19 2015. https://ieeexplore.ieee.org/document/7208305

31. Whitmore, S. A., Merkley, Stephen L., Zachary S., Walker, Sean D., “Development of a Power Efficient, Restartable, "Green" Propellant Thruster for Small Spacecraft and Satellites,” SSC15-P-34, *29th AIAA/USU Conference on Small Satellites*, Logan UT, 8-13 August, 2015. https://digitalcommons.usu.edu/smallsat/2015/all2015/90/

32. Whitmore S. A., "Three-Dimensional Printing of “Green” Fuels for Low-Cost Small Spacecraft Propulsion Systems," *Journal of Spacecraft and Rockets*, Vol. 54, No. 6 (2017), https://doi.org/10.2514/1.A33782

33. Whitmore, S. A., Bulcher, A. M., Lewis, Z., and Inkley, N. “Methods and Systems for Restartable Hybrid Rockets,” United States Patent 10,774,789 B2, September 15, 2020. https://patents.google.com/patent/US20150322892A1/en.

34. Whitmore, S. A., and Anthony M. Bulcher, A. M., "Vacuum Test of a Novel Green-Propellant Thruster for Small Spacecraft", AIAA 2017-5044. [*53rd AIAA/SAE/ASEE Joint Propulsion Conference*, *AIAA Propulsion and Energy Forum*, 2017.] https://doi.org/10.2514/6.2017-5044

35. Whitmore, S. A., and Bulcher, A. M., "A Green Hybrid Thruster Using Moderately Enriched Compressed Air as the Oxidizer", AIAA 2018-4841, [*2018 Joint Propulsion Conference*, *AIAA Propulsion and Energy Forum*,] https://doi.org/10.2514/6.2018-4841

36. Rommingen, J. E., AND Husdal J., *"Nammo Hybrid Rocket Propulsion TRL Improvement Program,"* AIAA-2012-4311 [48th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit; 2012.] https://doi.org/10.2514/6.2012-4311

37. Whitmore S. A., Merkley D. P., "Arc-Ignition of an 80% Hydrogen Peroxide/ ABS Hybrid Rocket System," AIAA-2017-5047. [53rd AIAA/SAE/ASEE Joint

Propulsion 53rd AIAA/SAE/ASEE Joint Propulsion Conference, AIAA Propulsion and Energy Forum, Salt Lake City UT, July 10-14 2017.] https://doi.org/10.2514/6.2017-5047

38. Whitmore, S. A., and Martinez, C J., " Novel Catalyst Materials for Reducing Combustion Latency of a Thermally-Ignited Peroxide/ABS Hybrid Rocket," AIAA-2018-4445. [2018 AIAA Propulsion and Energy Forum Duke Energy Center Cincinnati Oh, 8-11 July, 2018.] https://doi.org/10.2514/6.2018-4445

39. Whitmore, S. A., and Martinez, C J., "Catalyst Development for an Arc-ignited Hydrogen Peroxide/ABS Hybrid Rocket System," Aeronautics and Aerospace Open Access Journal, MedCrave International, Vol. 2. No. 6, 2018, pp.356-388. https://medcraveonline.com/AAOAJ/catalyst-development-for-an-arc-ignited-hydrogen-peroxideabs-hybrid-rocket-system.html

40. Whitmore, S. A. "Direct Ignition of a High Performance Hydrogen Peroxide Hybrid Rocket with 3-D Printed Fuel," *Int. J. Astronaut. Aeronautical. Eng*., Vol. 4, No. 021, 2019). https://www.vibgyorpublishers.org/content/ijaae/fulltext.php?aid=ijaae-4-021

41. Gordon, S.; McBride, B.J., "Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications," *NASA Technical Report RP-1311*; 1994. Available online: https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/19950013764.pdf. (Retrieved on 22 May 2022).

42. Whitmore, S. A., and Merkley, S., "Radiation Heating Effects on Oxidizer-to-Fuel Ratio of Additively Manufactured Hybrid Rocket Fuels," *J. of Prop. and Power*, Vol.35, No. 4, 2019, pp. 863-878, https://arc.aiaa.org/doi/abs/10.2514/1.B37037

43. Karabeyoglu, A., Stevens, S., and Cantwell, B., "Investigation of Feed System Coupled Low Frequency Combustion Instabilities in Hybrid Rockets," AIAA 2007-5366. [43rd AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit 8 - 11 July 2007, Cincinnati, OH.] https://doi.org/10.2514/6.2007-5366

44. Anderson, J. D. Jr., *Modern Compressible Flow with Historical Perspective, 4th ed*., McGraw-Hill, New York, 2003, pp. 127–187. ISBN-13: 978-1260588767, ISBN-10: 1260588769.

46. Smith, T. K., Lewis, Z., Olsen, K., Thibaudeau, R., Whitmore, S.A., "A Miniaturized Hydrogen Peroxide/ABS Based Hybrid Propulsion Systems for CubeSats," AIAA/Utah State University Conference on Small Satellites, Logan, UT, 2022. https://digitalcommons.usu.edu/smallsat/2022/all2022/116/

47. Olsen, Kurt C., "Fabrication and Testing of Catalyst-Infused Filament for 3D Printing of Ignition-Augmented Hybrid Rocket Fuels" (2022). All Graduate Theses and Dissertations, Spring 1920 to Summer 2023. 8563. https://digitalcommons.usu.edu/etd/8563

48. Thibaudeau, Ryan J., "Development of a Potassium Permanganate Catalyst-Infused Fuel Grain for Hydrogen Peroxide Hybrid Thruster Ignition Enhancement" (2023). All Graduate Theses and Dissertations, Fall 2023 to Present. 47. https://digitalcommons.usu.edu/etd2023/47