50th AIAA Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition
09 - 12 January 2012, Nashville, Tennessee

AIAA 2012-0974

Ignition Evaluation of Monopropellant Blends of HAN and Imidazole-Based Ionic Liquid Fuels

Steven P. Berg[1] and Joshua L. Rovey[2]
Missouri University of Science and Technology, Rolla, Missouri, 65409

Potential dual-mode monopropellant/electrospray capable binary mixtures of hydroxyl ammonium nitrate with ionic liquid fuels [Bmim][NO$_3$] and [Emim][EtSO$_4$] are synthesized and tested for monopropellant ignition capability in a micro reactor setup. The setup is benchmarked using 30% hydrogen peroxide solution decomposed via silver catalyst. Results show similar trends, but variance in the quantitative data obtained in literature. A parametric study on the geometry of the sample holder that contains the catalyst material in the reactor shows a large variance leading to the conclusion that quantitative data may only be compared to the exact same geometry. Hydrazine decomposition was conducted on unsupported iridium catalyst. The same trends in terms of pressure rise rate during decomposition (~160 mbar/s) are obtained with unsupported catalyst, but at 100°C instead of room temperature for tests conducted on supported catalysts in literature. Two catalyst materials were tested with the novel propellants: rhenium and iridium. For the [Bmim][NO$_3$]/HAN propellant, rhenium preheated to 160°C yielded a pressure slope of 26 mbar/s, compared to 14 mbar/s for iridium and 12 mbar/s for no catalyst at the same temperature. [Emim][EtSO$_4$]/HAN propellant shows slightly less activity at 160°C preheat temperature, yielding a pressure slope of 20 mbar/s, 4 mbar/s, and 2.5 mbar/s for injection onto rhenium, iridium, and the thermal plate, respectively. Final results indicate that desirable ignition performance may potentially be obtained by using a supported rhenium catalyst, since the pressure slopes obtained with the new propellants on unsupported catalyst lie between that of hydrazine on iridium at 50°C and room temperature.

Nomenclature

MW_i	=	molecular weight of species i
m_i	=	mass of species i
N_i	=	number of moles of species i
P	=	pressure
R_u	=	universal gas constant
T	=	temperature
V	=	volume of reactor
V_{drop}	=	volume of droplet
Y_i	=	mass fraction of species i
ρ_p	=	propellant density

I. Introduction

DUAL-mode spacecraft propulsion utilizing a high-thrust chemical monopropellant thruster in combination with a high-specific impulse electric electrospray thruster has the potential to greatly improve spacecraft mission flexibility. The greatest gain in mission flexibility would be a system that utilizes a single propellant for both monopropellant and electrospray modes. The challenge is then to identify propellants that offer acceptable performance and successful operation in both modes. Previous research has identified several ionic liquids or mixtures of ionic liquids that theoretically can achieve high performance in both modes.[1,2] Work presented in this

---

[1] Graduate Research Assistant, Aerospace Plasma Laboratory, Mechanical and Aerospace Engineering, 160 Toomey Hall, 400 W. 13th Street, Rolla, Student Member AIAA
[2] Assistant Professor of Aerospace Engineering, Mechanical and Aerospace Engineering, 292D Toomey Hall, 400 W. 13th Street, Senior Member AIAA

paper evaluates the ignition performance of these ionic liquids through experimental analysis and further assesses their potential for use as spacecraft monopropellants.

The benefit of a dual-mode propulsion system is increased spacecraft mission flexibility through the availability of both high-thrust and high-specific impulse modes, enabling a large mission design space.[3] This technology has the potential to allow for greater changes to the mission plan during the mission as needs arise since a variety of maneuvers are available on the same propulsion system. A dual-mode system utilizing a single ionic liquid propellant for both chemical monopropellant or bipropellant propulsion and electric electrospray propulsion has been shown to be a potentially beneficial type of dual-mode system, as it would not only provide mission flexibility, but also save spacecraft mass through the use of a single propellant. Results have shown that a dual-mode system with shared hardware and propellant still provides better propellant utilization and enhanced mission flexibility even if each mode does not perform as well as the current state-of-the-art in each mode considered separately.[4-6] Furthermore, the most flexible configuration includes a monopropellant thruster, as utilization of a bipropellant thruster in this type of system would inherently lead to unused mass of stored oxidizer since some of the fuel is used for the electrical mode.[4-6]

Ionic liquids are essentially salts that maintain liquid state at room temperature or even well below room temperature. Ionic liquids have garnered more attention over the last decade due to their potential application as environmentally benign industrial solvents.[7] While they are considered environmentally benign, recent investigations have shown combustibility in certain ionic liquids as they approach decomposition temperature.[8] Furthermore, current research has aimed at synthesizing and investigating ionic liquids as potential propellants and explosives.[9,10] This opens the possibility of utilizing ionic liquids as a storable spacecraft chemical propellant.

Typically, hydrazine has been employed as a spacecraft monopropellant because it is storable and easily decomposed to give good propulsion performance.[11] Because it is also highly toxic, recent efforts have focused on finding an alternative "green" monopropellant. The energetic salts hydroxyl ammonium nitrate (HAN), ammonium dinitramide (ADN), and hydrazinium nitroformate (HNF) have been proposed as potential replacements.[12-16] Since all of these have melting points above room temperature, they are typically stored as an aqueous solution. A compatible fuel component such as methanol, glycerol, or triethanolammonium nitrate (TEAN) is typically also added to provide increased performance.

Imidazole-based ionic liquids are of particular interest to this study due to their already proven electrospray capabilities. The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][Im]) represents the only propellant used in colloid, or electrospray, thruster application to date.[17] Due to their favorable electrochemical properties, several other imidazole-based ionic liquids are currently the subject of research in the field of electrospray propulsion.[18] Previous research has shown that these types of ionic liquids will not perform well as monopropellants due to the large amount of carbon contained within their cation. However, considering the heavy ionic liquids as a fuel component in a binary mixture with an oxidizing salt, such as HAN, shows promise as a monopropellant. This may offer high performance as both a monopropellant and electrospray propellant if the favorable electrochemical properties are retained along with the high molecular weight of the mixture.[1,2]

Ignition is a transient process in which reactants are rapidly transitioned to self-sustained combustion via some external stimulus. Nonspontaneously ignitable propellants, such as monopropellants, must be heated by an external means before ignition can begin. For practical applications, the amount of energy needed to provide ignition must be minimal, and the ignition delay time should be small.[11] The most reliable methods of monopropellant ignition on spacecraft include thermal and catalytic ignition, in which the monopropellant is sprayed onto a heated surface or catalyst. Other ignition methods include spark or electrolyte ignition.[19,20] These have been investigated, but are less practical for spacecraft application as they require a high-voltage power source, further increasing the weight and cost of the spacecraft. Hydrazine monopropellant is typically ignited via the commercially manufactured iridium-based catalyst Shell 405. For optimum performance, the catalyst bed is typically heated up to 200 $^{\circ}$C, but can be 'cold-started' with no preheat in emergency situations.[11] The Swedish ADN-based monopropellant blends require a catalyst bed preheat of 200 $^{\circ}$C. They cannot be cold-started, which is a major limitation presently.[16]

The following sections present an experiment to assess the thermal or catalytic ignition feasibility of imidazole-based ionic liquid monopropellants. Section II describes the propellants used in this study and the catalysts employed in the ignition evaluation. Section III describes the experimental setup employed in this study. Section IV describes results of the experiments. Section V presents a discussion of the results. Section VI represents the conclusion of all work.

II. Propellants and Catalysts

The focus of this study is an ignition evaluation of three ionic liquids and their potential use as a fuel component in a binary, or ternary, mixture. The three ionic liquids selected for initial evaluation include the three identified in

the previous study[1,2] as having both favorable physical property and performance characteristics for both chemical and electrospray propulsion: 1-butyl-3-methylimidazolium dicyanamide ([Bmim][dca]), 1-butyl-3-methylimidazolium nitrate ([Bmim][NO₃]), and 1-ethyl-3-methylimidazolium ethyl sulfate ([Emim][EtSO₄]). Previous research shows that to attain high monopropellant performance these ionic liquids must be combusted with some form of oxidizer. The same research showed that mixtures of roughly 40% wt. ionic liquid fuel with hydroxyl ammonium nitrate (HAN) as the oxidizer component could theoretically achieve monopropellant performance in the range of 250 sec specific impulse.[1,2] The question remains, however, if the ionic liquid fuels can form a thermally stable binary mixture with HAN oxidizer. For [Bmim][dca] mixtures this may be possible due to favorable trends in the solvent capability of [Bmim][dca][21] and the solubility of HAN in organic solvents.[22] Additionally, hypergolicity tests of HAN and [Bmim][dca] showed no visible signs of reaction at room temperature.[23] However, literature also indicates that while these do not react violently, they may be incompatible and react to form a new liquid, most likely a mixture including ammonium dicyanamide.[24-26] The other two ionic liquids may be more promising due to the fact that they are both acidic and are unlikely to react with another acidic salt solution, as is the case with HAN. However, the solubility of HAN in these fuels remains an unknown. Water, or some other solvent or emulsifier, may also be beneficial in the formation of a stable ternary solution with an ionic liquid fuel and HAN, as is the case with other ADN and HAN based monopropellants mentioned previously. However, the previous study[1,2] emphasizes that water is detrimental to not only the chemical performance of these propellants, but also especially in the electrospray mode due to the volatility of water.

A. Propellants

Six chemicals are used in the course of this study: hydrogen peroxide solution (30% wt., Sigma Aldrich), hydrazine (anhydrous, 98%, Sigma Aldrich), [Bmim][dca] (≥ 97%, Santa Cruz Biotechnology), [Bmim][NO₃] (≥ 95% Sigma Aldrich), [Emim][EtSO₄] (≥ 95%, Sigma Aldrich), and HAN solution (24% wt., Sigma Aldrich). Hydrogen peroxide solution was used initially in the verification of the experimental setup, and hydrazine was used as a comparison to novel propellants. Solid HAN is produced by distillation at high vacuum (~10^{-5} torr) for 8h. All other chemicals are used as provided by the manufacturer without further purification.

Three propellant blends theorized in previous work[1,2] are synthesized in this study. The aforementioned ionic liquid fuels were combined with HAN oxidizer in an attempt to form binary monopropellant mixtures. The percent by weight of fuel and oxidizer in each mixture tested in this study is shown in Table 1. The mixture ratios are specifically chosen to provide an estimated 1900 K combustion temperature, and thus performance near that of some advanced "green" monopropellants, as shown in the previous work.[1,2] One gram

Table 1. Mass Percent of Fuel and Oxidizer in Binary HAN-IL Mixtures

Propellant	IL Fuel	%Fuel	%Oxidizer
A	[Bmim][dca]	31	69
B	[Bmim][NO₃]	39	61
C	[Emim][EtSO₄]	41	59

of each propellant was synthesized initially. Mass of HAN crystals was measured using a scale accurate to one milligram and added to a test tube according to the percentage given in Table 1. IL fuel was then injected until the total mass of propellant equaled one gram.

During the course of synthesizing the new propellants, several observations were made about which conclusions can be drawn as to whether or not these mixtures were indeed binary mixtures of HAN and an IL fuel. The [Bmim][dca] fuel in Propellant A was clear with a slight yellow coloration. HAN appeared to partly dissolve initially, but the mixture bubbled slowly and continuously for nearly 24 hours. After the 24 hour period, it had formed a much darker yellow liquid with a white precipitate beneath. Clearly [Bmim][dca] and HAN are incompatible, as was hypothesized by the literature describing synthesis of ammonium dicyanamide,[24-26] as no solution was formed and they likely reacted via ion exchange in a neutralization reaction. A check of the pH with an acid/base indicator revealed that [Bmim][dca] had a pH of roughly 8, while a 15M (~95% wt.) HAN solution in water had a pH of roughly 6.4. Propellant A is therefore dropped from consideration. Both Propellant B and C appeared to form a solution with HAN. [Bmim][NO₃] alone is a clear liquid, and [Emim][EtSO₄] is a clear liquid with a slight yellow coloration. When the fuels were added to HAN and stirred initially, they formed a cloudy substance; but after roughly one hour the solid HAN had mostly disappeared and the solution returned to the initial color of the fuels, and remained in that state thereafter. Propellants B and C are therefore retained for chemical ignition analysis, although some question marks remain that will be discussed in a later section.

B. Catalysts

The initial selection of catalysts is based on active metals that have shown reactivity with hydrazine, or are typically used in oxidation reactions, which may be favorable to the [Bmim][dca]-HAN blends described previously.

Active metals that have been found to decompose hydrazine include iridium, rhodium, nickel, platinum, cobalt, ruthenium, palladium, silver, and copper.[27] Other potential catalysts that may be favorable include iron, tungsten, manganese oxide, and rhenium.[28]

The list of catalysts described in the preceding paragraph is further narrowed by considering practical design limits of the catalyst bed in monopropellant thruster operation: specifically, the sintering phenomena. Sintering is defined as loss of active surface area on a catalyst due to exposure to high temperatures for an extended period of time. Two mechanisms cause the loss in surface area: closure of the pores in the support and migration and subsequent agglomerations of the active metal atoms on the support surface.[28] Hughes[29] suggests sintering is usually negligible at temperatures 40% below the melting temperature of the catalyst material. Since the 40% wt. IL fuel-HAN blends produce a theoretical chamber temperature of around 1900 K,[1,2] the catalysts in this study are narrowed to those whose melting temperature meets this criteria. Table 2 gives the melting temperature and the sintering temperature, defined as 40% below the melting temperature. Of the potential catalyst material listed, only rhenium and tungsten have sintering temperatures above the design chamber temperature of 1900 K; therefore, they will be retained for this study. Additionally, iridium will be retained since it has the next highest sintering temperature, recognizing that 40% may be a conservative estimate. For example, cobalt is sometimes used as a cheaper alternative to

Table 2. Melting and Sintering Temperatures of Select Catalyst Materials

Material	T_m (K)	T_s (K)
Iridium	2739	1643.4
Rhenium	3453	2071.8
Nickel	1728	1036.8
Cobalt	1768	1060.8
Platinum	2041	1224.6
Ruthenium	2523	1513.8
Palladium	1828	1096.8
Silver	1235	741
Copper	1358	814.8
Iron	1808	1084.8
Tungsten	3695	2217
Manganese Oxide	808	484.8

iridium in hydrazine thrusters, which typically have a chamber temperature around 1300 K.[11] From Table 2, this exceeds the expected sintering temperature of cobalt. Ruthenium is the next closest at just above 1500 K sintering temperature. However, since this study is focused on simply a proof-of-concept of ignitability, ruthenium is not included initially to limit the cost of this study.

III. Experimental Setup

The role of the igniter in operation of a monopropellant rocket engine is to provide an initial pressurization of the thrust chamber such that self-sustained combustion can begin. Ideally the igniter provides a short ignition delay with minimal preheat temperature so that less power is required of the on-board power systems. An experiment is designed to provide quantitative measurements of ignition delay and pressure rise characteristics for monopropellants injected onto a heated surface or catalyst acting as the igniter. A variety of setups have been employed in other studies,[30] but a micro-reactor is selected because it provides the most robust ignition analysis. This type of setup does not represent the actual ignition delay times and pressure rises that can be achieved through careful catalyst bed design in actual thrusters. Rather, this setup provides comparison to the ignition capabilities of already proven high-performance monopropellants, and represents the first step in verification of reaction initiation prior to more expensive thruster testing.
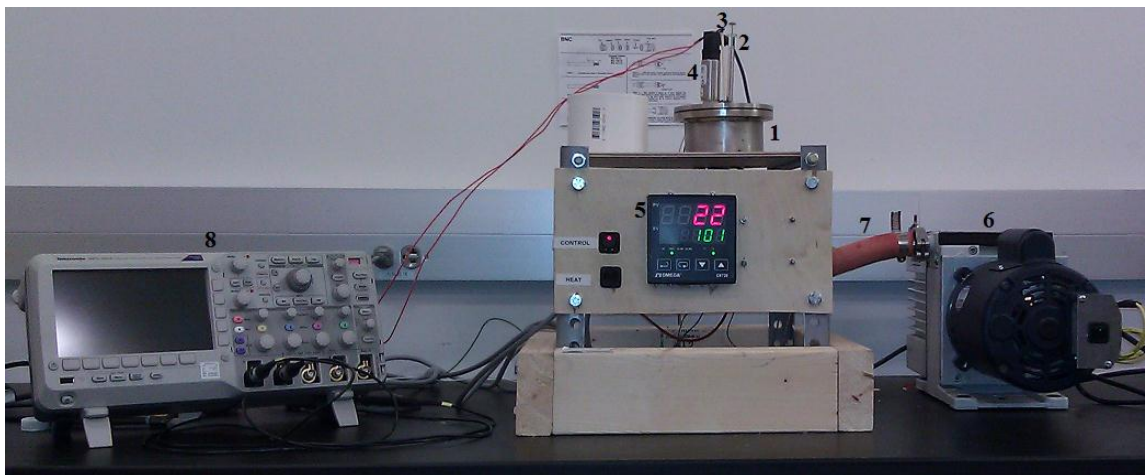
A. Experimental Setup

The experimental setup is a micro-reactor for thermal and catalytic ignition evaluation based on previous designs.[15,31] The reactor vessel itself consists of a stainless steel tube with stainless steel plates for the bottom and top plates of the reactor. The bottom plate has a 1" by 1" square machined to a depth of 1/4" to accommodate the thermal and
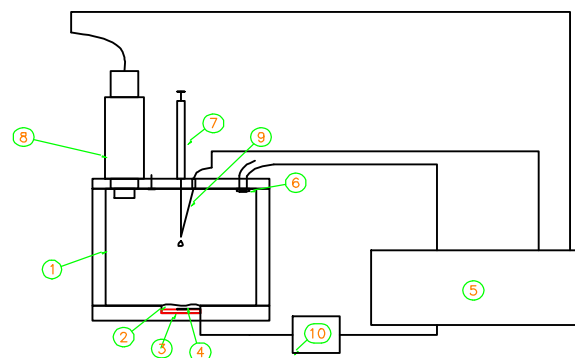
1 Reactor	5 Oscilloscope	8 Pressure transducer
2 Catalyst Bed	6 Photodiode	9 Liquid sensor
3 Resistance Heater	7 Microsyringe	10 Temperature controller
4 Thermocouple		

Figure 1. Instrumentation Schematic. *2D schematic of all instrumentation used in the micro-reactor.*

catalyst bed. The catalyst bed consists of a small stainless steel plate on top of a kapton heating element capable of reaching preheat temperatures up to 232 ^{o}C. A catalyst can be placed on the bed or left empty to evaluate thermal ignition. A type-K thermocouple is used to monitor the bed preheat temperature, as well as the catalyst bed temperature during the ignition process. A process controller is used to set preheat temperatures. The top plate is removable and contains the majority of the instrumentation. An o-ring groove accommodates a proper static seal when the top plate is bolted to the reactor. A stainless steel, fast response (2 ms typical) pressure transducer capable of 0-2.5 bar pressure measurements is located on the top plate. This is used to evaluate pressure rise and ignition delays for each propellant-catalyst combination. Additionally, a type-K thermocouple is secured to the top plate to monitor the internal atmosphere temperature. A photodiode of 400-1100 nm measurement range is also located on the top of the plate. It is used as redundancy in the ignition verification and delay measurement and may provide a measure of ignition delay more accurate than solely the pressure transducer. An oscilloscope is used to monitor all of the aforementioned instrumentation and record the data. Finally, a mechanical pump is used to create a vacuum in the reactor to a pressure of roughly 10^{-2} torr. The entire experimental setup is shown in Figs. 1, and 2.

1 Reactor	4 Pressure transducer	7 Vacuum hose
2 Microsyringe	5 Temperature controller	8 Oscilloscope
3 Liquid sensor	6 Vacuum pump	

Figure 2. Photograph of the Entire Experimental Setup with Numbered Components.

The feed system of the micro-reactor is a 100 μL Hamilton micro syringe. To evaluate ignition delay, the precise moment at which propellant is introduced into the reactor must be known. This is accomplished through a custom-designed liquid probe, shown in Fig. 3. The probe consists of a piece of copper wire and a separate electrical connection to the syringe needle. The copper wire is bent and carefully positioned so that when propellant is introduced through the syringe, its viscosity causes it to form a droplet between the tip of the syringe and the wire. When the propellant leaves the tip of the syringe, it opens a circuit between the syringe needle and the probe wire. The circuit is capable of activating a 5 V relay with liquids of conductivity at minimum equal to rain water. Since all of the propellants tested are ionic liquids that are highly conductive, this is more than adequate. Finally, since the distance from needle tip to catalyst bed is known, the propellant density and volume are known, and the propellant is in a vacuum environment, the fall time can be easily calculated and subtracted from the overall ignition delay.
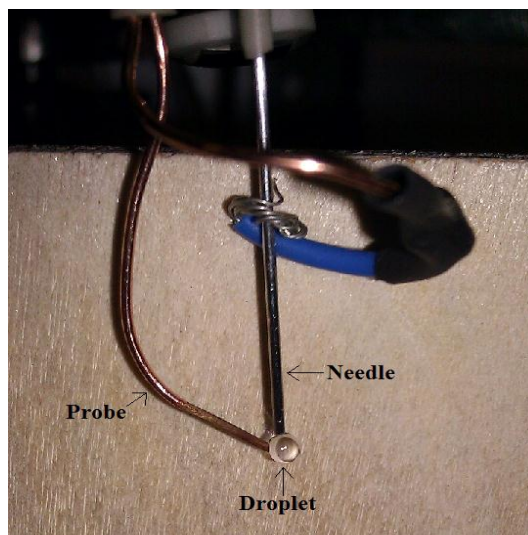

Figure 3. Liquid Probe. *Photograph of the liquid probe used to determine ignition delay time.*

IV. Results

Experiments are conducted first with hydrogen peroxide and hydrazine to verify that the reactor is functioning correctly. Additionally, hydrazine will serve as comparison to the novel propellants since it is the most utilized spacecraft monopropellant currently. Prior to full reactor testing, the novel propellants undergo spot plate testing in open atmosphere in order to gain qualitative understanding of the reactivity prior to more time consuming reactor tests. The novel propellants are spot plate tested, then reactor tested with each catalyst, both unsupported and supported.

A. Theoretical Pressure Rise Calculations

One of the important parameters when considering the ignition of monopropellants is the decomposition of the liquid into fully gaseous products. Therefore, it is necessary to calculate the theoretical pressure rise in the reactor, assuming decomposition into fully gaseous products. Eqs. (1) and (2) give the formulas for the chemical decomposition of hydrogen peroxide and hydrazine, respectively,

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \tag{1}$$

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \tag{2}$$

The general chemical reaction equation predicted for the IL-HAN blends in Table 1 is given by Eq. (3),

$$Fuel + aN_2H_4O_4 \rightarrow bCO_2 + cCO + dH_2O + eH_2 + fN_2 + gH_2S \tag{3}$$
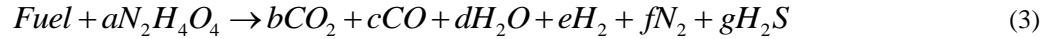
where the mole numbers a-g have been computed by using the NASA CEA chemical equilibrium code.[32] These are given in Table 3. The total pressure of the product gases for each reaction can then be computed through the following procedure. First, the mass and subsequent number of moles of each reactant species i in a given droplet volume is calculated from Eqs. (4) and (5),

$$m_{i,react} = Y_{i,reac} \rho_p V_{drop} \tag{4}$$

$$N_{i,react} = \frac{m_{i,react}}{MW_{i,react}} \tag{5}$$

Then, given the known molar ratios of products to reactants given in Eqs. (1)-(3), the pressure can be calculated by assuming the ideal gas law, Eq. (6),

$$PV = \sum N_{i,prod} R_u T \tag{6}$$

The results of the computation outlined by Eqs. (1)-(6) is given in Fig. 5 for droplet sizes from 10-100 μL. A temperature of 298 K is assumed for the gaseous product species, since it is expected they will cool to room temperature quickly due to the large thermal conductivity of the stainless steel reactor. Additionally, for the hydrogen peroxide decomposition, the partial pressure of water at 298 K is taken from steam tables rather than calculated by Eqs. (4)-(6) since most of the water will condense at this temperature. This figure is used to determine how much of the reactants are actually decomposed by the catalyst, providing a measure of ignition performance.

B. Hydrogen Peroxide

The first experiment conducted was room temperature decomposition of 30% wt. hydrogen peroxide on silver catalyst. The silver catalyst used is 10-20 mesh silver (Alfa Aesar), and each run consists of 100 μL hydrogen

Table 3. Mole Numbers Calculated in Eq. (3) for Each Propellant Blend.

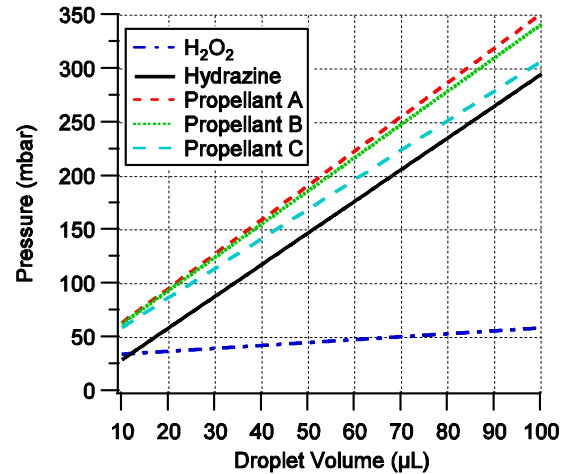| Propellant	A	B	C
Fuel	$C_{10}H_{15}N_5$	$C_8H_{15}N_3O_3$	$C_8H_{16}N_2O_4S$
a	4.75	3.28	3.54
b	1.55	1.39	1.87
c	8.45	6.58	6.10
d	7.47	6.69	8.12
e	9.52	7.36	6.46
f	7.25	4.78	4.54
g	0.00	0.00	0.47

Figure 5. Pressure Rise vs. Droplet Volume. *Theoretical pressure rise in reactor of propellants used in this study as a function of droplet volume.*

peroxide droplets on 200 mg silver catalyst. Room temperature was measured as 21°C prior to conducting the experiments. Results are shown in Fig. 6. Initially, the decomposition begins within 0.1 seconds and proceeds at a rapid rate at a pressure rise of 16 mbar/s. After the first second, the decomposition slows to a rate of 2.5 mbar/s until it begins to level off around 20 seconds. The total pressure rise in the reactor after 20 seconds is 43 mbar. From Fig. 5, the calculated theoretical maximum pressure rise is 60 mbar for a 100 µL droplet of hydrogen peroxide solution. After 20 seconds, the pressure in the reactor is therefore 72% of the maximum and is continuing to rise. After the initial rapid decomposition event, the pressure is 25% of the maximum.

Additional tests were conducted to show the dependence of the results on catalyst sample holder geometry. Four sample holder geometries were tested: 1/2" and 3/8" diameter with 0.5" and 1" lengths for each diameter. The size of the liquid probe prevented smaller geometries from being utilized. For each test 100 µL droplets of hydrogen peroxide were injected onto 200 mg silver at room temperature. The results are shown in Fig. 7. The figure shows wildly different results between the two diameters. The small diameter sample holder gives similar trends to those obtained by Eloirdi.[31] However, the 1/2" diameter sample holders have a much lower pressure rise rate at just 3 mbar/s. However, the 1/2" diameter sample holder achieves a higher pressure at the end of the 20 second interval: 58 mbar vs. 43 mbar for the 1" length, and 51 mbar vs. 38 mbar for the 1/2" length. Additionally, the pressure levels off prior to 20 seconds for both 1/2" length sample holders. From Fig. 5, the calculated theoretical pressure rise for a 100 µL droplet of hydrogen peroxide solution assuming complete decomposition of hydrogen peroxide is 60 mbar. The pressure rise using 1/2" diameter sample holders nears this value at 20 seconds, falling 5% and 8.5% below the theoretical maximum for the 1" and 1/2" lengths, respectively. The pressure rise obtained using the smaller diameter sample holders falls short after 20 seconds; however, after 2 seconds, the pressure is 25% of the maximum, compared to just 7% for the larger sample holder geometry. In the end, the 3/8" diameter, 1" length sample holder was chosen for the remainder of the study since it provides the trends closest to literature. The implications of this choice will be discussed in a later section.

Figure 6. Hydrogen Peroxide Decomposition. *Decomposition of 100 µL H_2O_2 droplet on 200 mg silver catalyst.*

Figure 7. Effect of Sample Holder Geometry. *Effect of varying sample holder geometry on test results.*

C. Hydrazine

For comparative purposes, microreactor experiments were conducted with hydrazine as a propellant. 30 µL droplets of hydrazine were injected onto 50 mg of pure iridium catalyst (22 mesh, Alfa Aesar) at various temperatures. Tests with iridium catalyst preheated to 100°C, 50°C, and 21°C are shown in Fig. 8. Fig. 8a shows that the 100°C preheat on iridium produces a significant ignition event. There is a 1.6 second period of some activity initially, followed by the main event from 1.6 to 1.9 seconds. The pressure rise rate during the main activity is 170 mbar/s. The pressure peaks at 64 mbar, then falls to a steady state value of 56 mbar after roughly one second. Comparison with the theoretical pressure calculated in Fig. 5, 88 mbar, shows that the steady state value falls at 64% of the maximum. The photodiode output clearly coincides with the ignition events seen in the pressure measurements, verifying that the ignition delay is correct. Figure 8b shows the same test except with a 50 °C catalyst preheat. A longer delay to the first event is seen, 1.9 seconds. The first event appears similar to the main event on
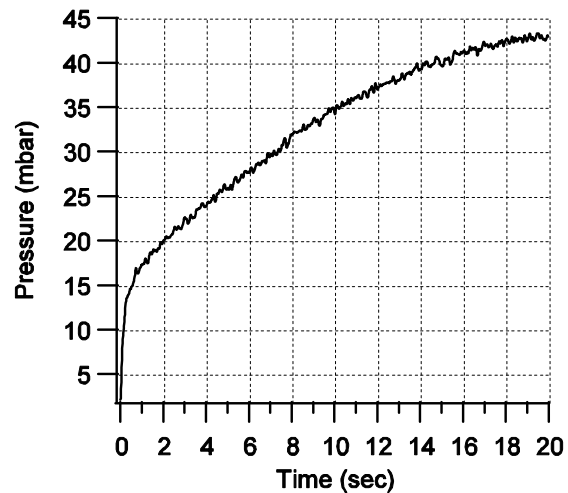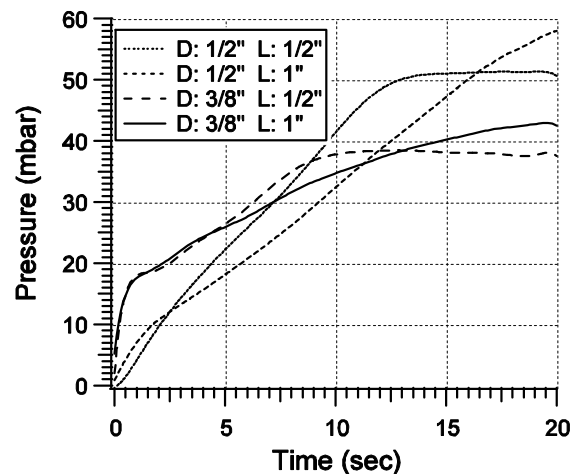
7

American Institute of Aeronautics and Astronautics

Fig. 8a, except the pressure rise is 70 mbar/s. The pressure actually decreases briefly followed by a second reaction that proceeds at roughly 10 mbar/s. The peak pressure in this time window is attained at 10 seconds and is 70 mbar, compared to 64 mbar for the 100°C case, and 79% of the maximum. After the first event, the pressure in the reactor is 28% of the maximum. The photodiode output is seen again, and lasts for a longer duration, as the reaction is seen to continue. Finally, Fig. 8c shows the same test, but at room temperature. The ignition delay is 3.2 seconds, and the reaction proceeds at a rate of 8 mbar/s. The reaction is clearly still proceeding after the initial ten second window, and reaches a pressure of 65% of the maximum during this interval.

D. Spot Plate Testing of Novel IL-HAN Propellants

Spot plate testing under atmospheric conditions is conducted to qualitatively determine ignition capability prior to reactor testing. For each test, a single droplet (~10 μL) was injected directly onto a preheated catalyst atop a preheated stainless steel plate. In each case, the mass of catalyst used was 10 mg. Propellant B decomposed at temperatures as low as 60°C, but after a delay of greater than 10 seconds, after which it appeared to decompose in less than one second. The rapid decomposition phase was characterized by smoke formation, but a visible flame was not observed. Additionally, the propellant left a yellowish residue on the stainless steel plate. As the temperature of the plate was increased, the delay time to the rapid decomposition phase decreased monotonically to the point which the entire process occurred in roughly less than one second at a temperature of 120°C. Adding iridium reduced the delay time at 60°C, while the tungsten catalyst showed no difference from the thermal case. The rhenium catalyst, however, showed significant reactivity by producing rapid decomposition almost instantaneously at 60°C. Temperatures below 55°C did not show any reactivity. Propellant C showed slightly different trends compared to Propellant B at low temperatures. Most notable is that at 80°C with no catalyst, the propellant bubbled and decomposed slowly over several minutes rather than almost instantaneously. Additionally, iridium appeared to be more effective at low temperatures, significantly reducing the decomposition time to less than 10 seconds at 80°C. Using rhenium catalyst at 80°C yielded an instantaneous decomposition, similar to the observations from Propellant B.

For comparison, each propellant ingredient was spot plate tested separately. A 15M (~95% wt. in H_2O) liquid HAN solution decomposed at 120°C in less than 10 seconds with smoke evolution, no flame, and no apparent residue left on the plate. Decomposition was not instantaneous as was the case with the IL-HAN mixtures, but lasted for a majority of the roughly ten
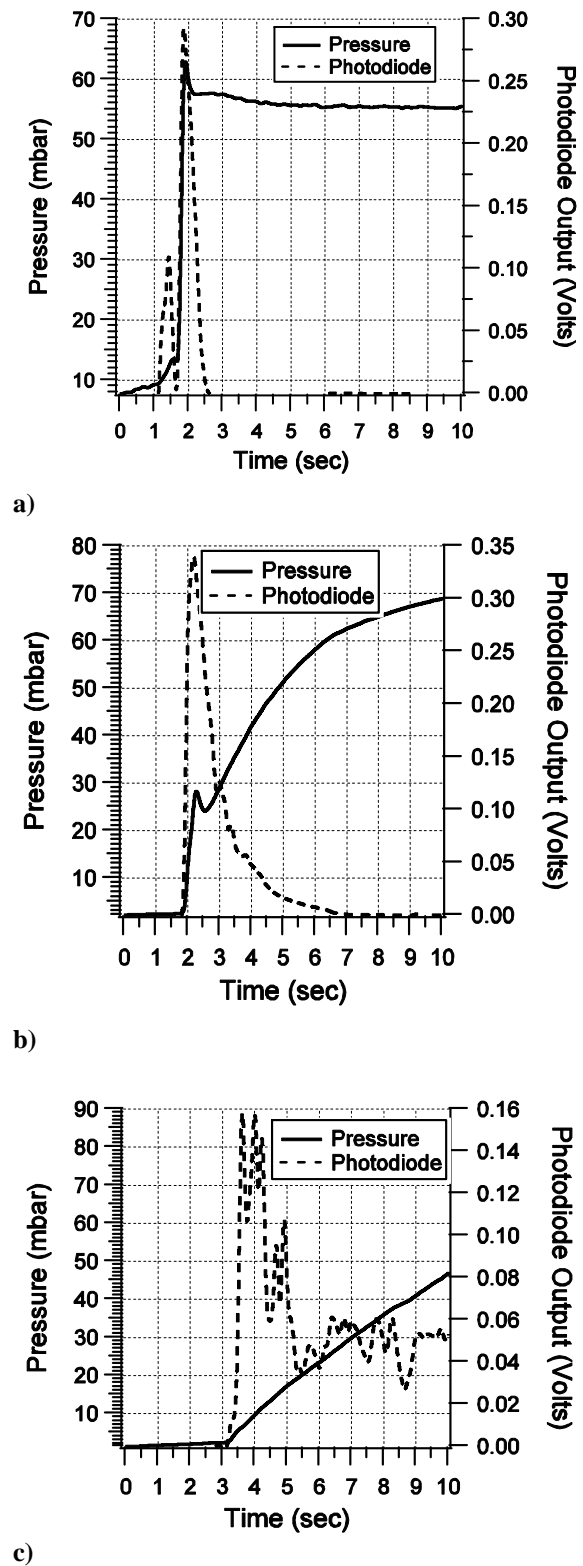

a)

b)

c)

Figure 8. Hydrazine on Iridium. *30 μL droplet of hydrazine on 50 mg iridium at catalyst preheat temperatures of (a) 100°C, (b) 50°C and (c)21°C.*

second interval. At 100 ^{o}C, the same trend was observed, but the decomposition event lasted much longer. At temperatures below 100°C, bubble formation was observed within the droplet, but no significant events occurred after several minutes. Adding rhenium, iridium, or tungsten catalyst at 100 ^{o}C showed roughly the same trend as the thermal test, and therefore determination of catalytic activity is inconclusive for the HAN solution. Testing [Bmim][NO$_3$] alone showed some activity in terms of bubble formation at 140°C, but quickly subsided and had no smoke formation. After several minutes the remaining liquid turned a yellow hue. The same trend was observed up to 200°C, but the time for duration of the bubble formation and subsequent formation of a yellowish liquid was shortened. Adding any catalyst did not show any significant changes than observed by thermal testing. [Emim][EtSO$_4$] showed no activity in thermal tests up to 200°C. Adding iridium or rhenium catalyst at 180°C yielded vigorous bubbling initially, which quickly subsided and left a yellowish residue. Tungsten showed no activity whatsoever up to 200°C.

E. Micro Reactor Testing of Novel IL-HAN Monopropellants

Experiments are conducted with the micro reactor setup described previously in order to qualitatively determine if the novel propellants can ignite by means typically used in spacecraft monopropellant thrusters, especially in comparison to monopropellant hydrazine. Both propellants showed almost instantaneous decomposition at 60°C on rhenium catalyst during spot plate testing. Fig. 9 shows the pressure during decomposition of a 30 μL droplet onto 50 mg of rhenium catalyst preheated to 60°C, 120°C, and 160°C in the vacuum environment of the micro reactor. Clearly, this is not the trend one would expect from the spot plate test results for either propellant. For both propellants, the reaction at 60°C occurs over a time period of more than 10 seconds, compared to the apparent instantaneous decomposition observed from the spot plate testing. The pressure at the 60°C condition for Propellant B rises at 2 mbar/s and continues at this constant rate throughout the duration of the test. The trend for Propellant C is similar, but the pressure slope is just 0.5 mbar/s. The final pressure after 10 seconds for Propellant B is 16 mbar, which is just 13% of the maximum of 125 mbar predicted in Fig. 5. Propellant C achieves just over 5 mbar after ten seconds, 4.5% of the predicted maximum. As the preheat temperature is increased, the pressure slope and total achieved pressure increase. At 120°C , the slope of the initial event is 7 mbar/s for Propellant B and 5 mbar/s for Propellant C. At 160°C the slope is nearly 26 mbar/s for Propellant B and 20 mbar/s for Propellant C. At 160°C, the first decomposition event shows a distinct peak in pressure for both propellants, but for Propellant B this is followed by a second peak 5.5 seconds after the first event. At 160°C, the pressure immediately following the initial event is 31 mbar for Propellant B and 30 mbar for Propellant C, which is 25% and 26% of the theoretical maximum for each propellant respectively.
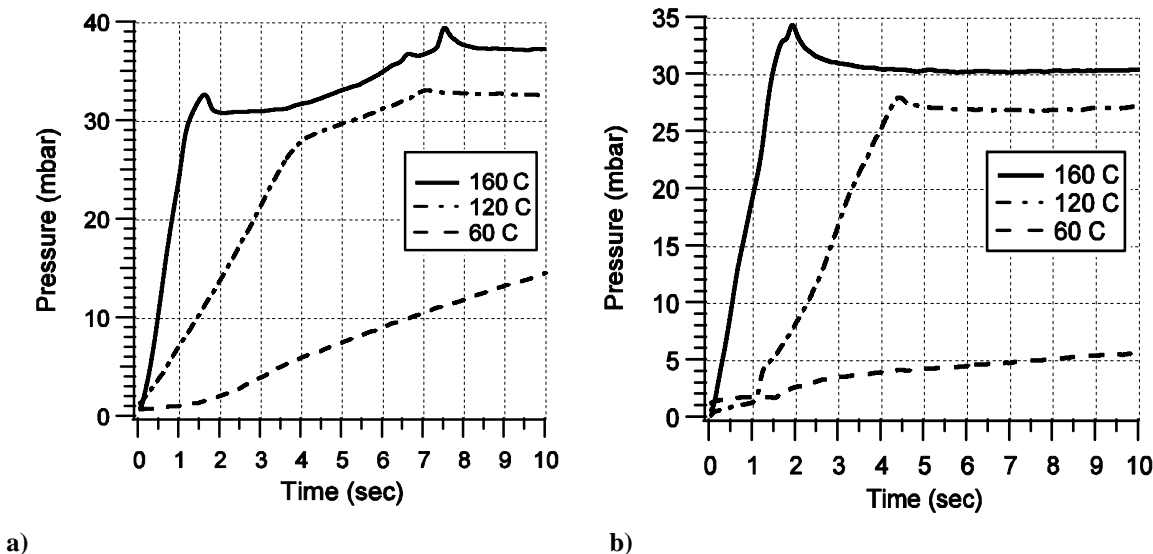

Figure 9. Novel Propellants on Rhenium Catalyst. *Pressure vs. time after injection of 30 μL of a) Propellant B and b) Propellant C onto 50 mg catalyst at preheat temperatures of 60, 120, and 160°C.*

In order to quantify the effect of the catalyst material on ignition of the novel propellants, tests are conducted at 160°C for both iridium and rhenium catalysts, as well as for the thermal case where no catalyst is present. The

results are shown in Fig. 10. Fig. 10a shows the decomposition of Propellant B at 160°C. The rhenium case is therefore the same as shown in Fig. 9. The iridium catalyst and thermal case show much less reactivity in comparison. The first significant event with iridium catalyst occurs at roughly one second after injection and has a pressure rise of roughly 10 mbar/s for an additional one second and then levels off. A second event of slightly greater slope, 14 mbar/s, occurs at 5.5 seconds after injection. This will be discussed further in the next section. The pressure during thermal ignition has a slope of roughly 12 mbar/s at 1.7 seconds after injection. The pressure slope then quickly levels off, but continues to rise at a much slower rate. Propellant C shows roughly the same trend as Propellant B for rhenium catalyst. From Fig. 10b, the slope of the major decomposition event is 20 mbar/s, and continues for nearly two seconds, followed by a sharp peak, and finally levels off at 30 mbar. Injection onto iridium catalyst shows a similar trend, except the slope is much less at 4 mbar/s. The greatest slope obtained during thermal decomposition is 2.5 mbar/s and occurs between two and three seconds after ignition. Both iridium and rhenium catalysts obtain a peak pressure of just over 30 mbar, which from Fig. 5 is only 26% of the calculated theoretical maximum.
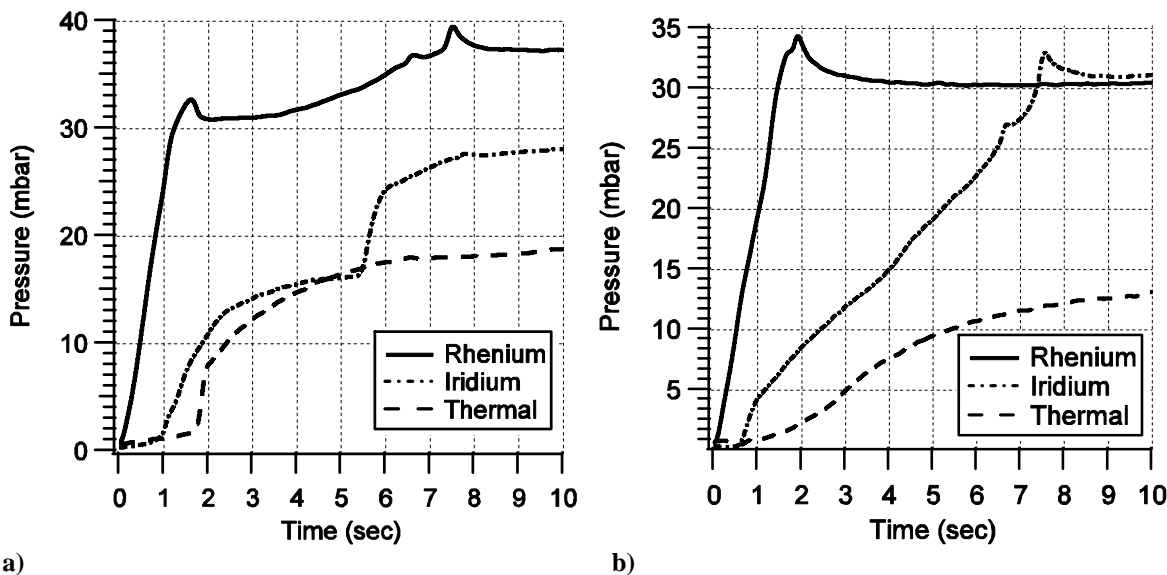

Figure 10. Catalytic Ignition of Propellants. *Pressure vs. time of 30 μL droplets of a) Propellant B and b) Propellant C injected onto thermal plate or 50 mg of catalyst at 160°C.*

V. Discussion

The results with the novel propellants show clear evidence of catalytic activity with rhenium. However, this fact alone is not adequate to assess their feasibility for use in a monopropellant thruster. In order to assess the ignition capabilities of the novel propellants, results from the micro-reactor testing can be compared to results from the same setup with state-of-the-art monopropellant and catalyst combinations, namely hydrazine and iridium. The results from the preceding section are discussed in an effort to determine the overall feasibility of the novel monopropellants to be ignited via catalyst and suggest the most appropriate route for further development.

A. Hydrogen Peroxide

The results from the parameter study on sample holder geometry clearly show that the results using this type of setup are highly dependent on geometry. The larger diameter sample holders produce a much slower reaction rate. This is largely due to the fact that the entire surface at the bottom of the sample holder is not covered by catalyst particles. Therefore, not all of the catalyst is accessible to propellant, reducing the reaction rate. The 3/8" sample holder accomplished complete coverage of the bottom plate, and actually visually contained two layers of particles. Since more catalytic surface area is covered by the propellant, the reaction rate increases, and gives similar trends to those found in the Eloirdi study.[31] Additionally, the smaller length sample holders produce a smaller pressure after an extended period of time, and actually appears to level off after just 20 seconds. This is due to atomization and ejection of smaller droplets away from the catalyst into the surrounding reactor during the initial ignition event. When the reactor was re-pressurized, several small droplets were seen throughout the inside of the reactor. These

droplets were also reactive upon placing a piece of silver catalyst on them, indicating that the hydrogen peroxide did not decompose completely in the catalyst bed. This issue was still present somewhat, but less droplets were seen with the longer sample holders.

While the hydrogen peroxide tests show results similar to those found in Eloirdi[31] with presumably the same propellant and catalyst, the results presented here differ somewhat, largely due to the geometric factors mentioned in the preceding paragraph. The actual dimensions of the Eloridi[31] sample holder are not given, therefore it may not be possible to replicate the results beyond qualitative trends. As a result, it is not prudent to compare quantitatively with the results from another setup of this type without knowledge of the exact geometric specifications. Therefore, measurements taken in this study will only be compared quantitatively with measurements from this study.

Despite the variance in the results due to the geometry, one must examine the situation this experiment is designed to replicate to adequately address the problem. The problems seen include incomplete coverage of the catalyst and atomization and subsequent ejection of smaller droplets away from the catalyst surface. In a typical monopropellant thruster design the catalyst bed is packed with several tens of layers of catalyst particles. Any portions of droplets not decomposed by the first two layers of catalyst, for example, will continue to traverse through the catalyst bed and eventually be decomposed by catalyst particles deeper into the catalyst bed. Therefore, atomization and complete decomposition of the propellant does not necessarily need to take place in the experimental setup presented in this study, as it only represents at most a few layers of a catalyst bed. The most important step in this type of setup is therefore the initial pressure rise because it is closest to actual monopropellant engine operation. The goal is to achieve as close to 100% decomposition into gaseous products within the first few seconds as possible. This means that the catalyst is more effective in absorbing and causing the propellant to react, and will therefore reduce the required catalyst bed length in an actual thruster. Since any secondary event seen in the experimental setup used in this study is highly dependent on the geometry of the experimental setup and will not affect monopropellant engine design, it should not be evaluated.

B. Hydrazine

The experiments conducted with hydrazine are mainly used as a comparison tool with the novel monopropellants. Figure 8a shows a similar trend to that found with hydrazine decomposition in Elordi.[31] The difference is that the Eloirdi[31] study uses a 36% iridium on alumina catalyst at room temperature, whereas Fig. 8a shows a 100°C preheat on pure iridium. This is the trend one would expect from a good ignition: a sharp peak followed by a roughly constant rate. The reason for the decrease in pressure after the peak is due to the fact that the gas temperature in the reactor is higher than room temperature initially, and then quickly cools as the particles collide with the high thermal conductivity stainless steel reactor walls. Figs. 8b and 8c show much less rapid activity, therefore an ignition similar to the Eloirdi results is not attained at room temperature. This is due to the active surface area of the supported catalyst being higher than pure iridium particles. However, at higher temperatures, a significant ignition event is attained; therefore, this type of experiment is valid for the selection of active material as it clearly shows catalytic ignition. This makes sense because although less propellant is absorbed by the lower surface area of pure iridium, it should still produce a reaction. Since the absorption rate and heat transfer is increased by increasing the temperature of the catalyst, it follows that the reaction rates seen at lower temperatures by large surface area supported catalysts can be mimicked by unsupported catalysts by increasing the preheat temperature. Therefore, pure active metal catalyst materials can be evaluated with novel propellants prior to manufacturing and testing more expensive supported catalysts.

C. Novel IL-HAN Propellants

Results from the experiments show that propellants with HAN oxidizer and either [Bmim][NO_3] or [Emim][$EtSO_4$] fuel show promise in terms of their ability to be readily ignited. Rhenium is clearly the best catalyst of the three tested in this study, providing the greatest pressure rise in the shortest amount of time at all temperatures. The ionic liquid propellants with rhenium catalyst do not compete with the ignition performance of the typical hydrazine and iridium combination. The pressure rise rate of hydrazine on iridium at 50°C is 70 mbar/s, compared to just 25 mbar/s for Propellant B on rhenium at 160°C. Additionally, hydrazine on iridium at 50°C and both IL-HAN propellants on rhenium at 160°C achieve 25-28% of the calculated theoretical maximum pressure after the main ignition event. Clearly, hydrazine when paired with iridium requires a much lower preheat temperature to achieve good ignition performance. Higher preheat temperatures should continue to increase the pressure slope and push the amount of gaseous products generated close to the maximum; however, limiting the preheat temperature as much as possible is desirable. In the preceding paragraph, the effect of catalytic surface area is discussed. By extension, the new propellants should perform better with large surface area supported catalysts, as shown with hydrazine. Since catalytic activity is clearly shown in this study, supported catalysts should be capable of improving

the ignition performance to desirable levels. However, it is unlikely ignition performance similar to hydrazine can be achieved since it performs much better than the ionic liquid propellants with unsupported catalysts. This may not be entirely detrimental, as ADN-based monopropellants typically require a catalyst preheat temperature of 200°C just to start the engine. Hydrazine, by contrast, can be cold-started with no preheat, but the catalyst is typically heated to provide improved performance.

Proof-of-concept on the ignitability of these propellants has been shown; however, in order to confirm the initial goal of designing a 'dual-mode' propellant, much more analyses must be conducted in terms of the synthesis and physical properties of the propellants. One of the important goals identified in the previous study[1,2] was to limit the amount of water contained in the propellants; therefore, HAN must be completely miscible in the ionic liquid fuel for this to be the case. This is not shown in this study. While the synthesis procedure described earlier may suggest that HAN is at least partly miscible, the hygroscopic nature of both the fuel and oxidizer might give a false indication. Although HAN was dried in vacuum just prior to testing, it is possible that it still contained at least 2% water.[33] Additionally, the total impurities for each fuel may have been as high as 95% and the fact that the HAN crystals took over an hour to disappear in solution means that the solution could have gained enough water from the atmosphere to form an aqueous ternary solution rather than a binary solution. In terms of the physical properties of the ionic liquids, it is unclear whether these new propellants retained favorable electrochemical properties required for minimum functionality in the electrospray mode. Therefore, the assertion that these new propellants are 'dual-mode' propellants is incomplete, but feasibility to function as a chemical monopropellant has been shown.

VI.   Conclusion

Novel propellants based on HAN oxidizer combined with ionic liquid fuels [Bmim][NO$_3$] and [Emim][EtSO$_4$] have been synthesized and tested for catalytic ignition capability. The propellants are selected because they have been specifically designed to provide performance near to or exceeding the state-of-the-art in chemical monopropellant and electrospray propulsion, making them candidates for a potential dual-mode spacecraft propulsion system. To determine their feasibility for use as a chemical mode, their ignition capabilities have been evaluated through the use of a micro reactor setup, which includes measurements of pressure rise and ignition delay.

Three catalyst active materials are selected based on their capability to handle high temperature associated with the predicted performance of these ionic liquid propellants: rhenium, iridium, and tungsten. Unsupported active material was used for the initial study in order to determine which catalysts are actually active in causing the decomposition reaction to proceed at a faster rate.

Hydrogen peroxide solution injected onto a silver catalyst is used as a comparison to values obtained in the literature. The trends obtained though this experiment are similar to the literature values, but differ somewhat in magnitude from the setup utilized in this study. Varying the geometry of the sample holder that contains the catalyst within the reactor shows greatly varying results obtained by this setup. The geometry that gave trends similar to those found in literature was selected. This leads to the conclusion that this experimental setup cannot be compared quantitatively to similar setups described in literature without specific knowledge of the entire geometry. Quantitative comparisons, then, can only be made by utilizing the exact same geometry.

Hydrazine is used as a direct comparison to novel propellants. Droplets were injected into the micro reactor onto unsupported iridium catalyst preheated to various temperatures. Pressure rise characteristics show a similar trend to those found in literature at 100°C; however, the literature results are for a supported iridium catalyst at room temperature. Similar results are therefore obtained for lower active surface area catalytic material compared to the supported catalyst, but at higher temperature. It is therefore concluded that unsupported catalytic material can be assessed for sufficient reactivity in relation to ignition properties.

The new propellants based on HAN with [Bmim][NO$_3$] and [Emim][EtSO$_4$] fuels show ignition properties significant enough for further evaluation. For both propellants, rhenium catalyst performs best of the three catalysts used in this study. In order to achieve performance similar to hydrazine, the new propellants require a much higher preheat temperature than hydrazine. Ignition of both propellants on rhenium at 160°C yields pressure slopes lower than hydrazine at 50°C, but the trends indicate that equal performance may be attained at higher temperature or increased catalytic surface area, as would be available in a supported catalyst. The new propellants therefore have the potential to be ignited via catalyst, and should be investigated further.

References

[1]Berg, S. P., Rovey, J. L., "Assessment of Imidazole-Based Energetic Ionic Liquids as Dual-Mode Spacecraft Propellants," *Journal of Propulsion and Power* (in review).

[2]Berg, S. P., Rovey, J. L. "Dual-Mode Propellant Properties and Performance Analysis of Energetic Ionic Liquids," *50th Aerospace Sciences Meeting,* 2012 (submitted for publication).

[3]Hass, J.M., Holmes, M.R., "Multi-Mode Propulsion System for the Expansion of Small Satellite Capabilities," NATO MP-AVT-171-05, 2010.

[4]Donius, B.R. "Investigation of Dual-Mode Spacecraft Propulsion by Means of Ionic Liquids," Masters Thesis, Department of Mechanical and Aerospace Engineering, Missouri University of Science & Technology, Rolla, MO., May 2010.

[5]Donius, B. R., Rovey, J. L., "Ionic Liquid Dual-Mode Spacecraft Propulsion Assessment," *Journal of Spacecraft and Rockets*, Vol. 48, No. 1, 2011, pp. 110-123.

[6]Donius, B. R., Rovey, J. L., "Analysis and Prediction of Dual-Mode Chemical and Electric Ionic Liquid Propulsion Performance," *48th Aerospace Sciences Meeting*, AIAA Paper 2010-1328, 2010.

[7]Wilkes, J.S., Wasserscheid, P., Welton, T., *Ionic Liquids in Synthesis*, 2nd ed., WILEY-VCH Verlag GmbH &Co., 2008, Ch.1.

[8]Smiglak, M., Reichert, M. W., Holbrey, J. D., Wilkes, J. S., Sun, L., Thrasher, J. S., Kirichenko, K., Singh, S., Katritzky, A. R., Rogers, R. D., "Combustible ionic liquids by design: is laboratory safety another ionic liquid myth?," Chemical Communications, Issue 24, 2006, pp. 2554-2556.

[9]Boatz, J., Gordon, M., Voth, G., Hammes-Schiffer, S., "Design of Energetic Ionic Liquids," *DoD HPCMP Users Group Conference*, IEEE Publ., Piscataway, NJ, Pittsburgh, 2008, pp. 196-200.

[10]Tao, G-H., Huang, Y., Boatz, J. A., Shreeve, J. M., "Energetic Ionic Liquids Based on Lanthanide Nitrate Complex Anions," *Chemical European Journal*, 2008.

[11]Sutton, G. P., Biblarz, O., *Rocket Propulsion Elements*, 7th ed., John Wiley & Sons, New York, 2001, Ch. 5, 7, 19.

[12]Zube, D., Wucherer, E., Reed, B., "Evaluation of HAN-Based Propellant Blends," 39th AIAA Joint Propulsion Conference, AIAA Paper 2003-4643, 2003.

[13]Amariei, D., Courtheoux, L., Rossignol, S., Batonneau, Y., Kappenstein, C., Ford, M., and Pillet, N., "Influence of the Fuel on the Thermal and Catalytic Decompositions of Ionic Liquid Monopropellants," 41st AIAA Joint Propulsion Conference, AIAA, Paper 2005-3980, 2005.

[14]Anflo, K., Grönland, T. A., Bergman, G., Johansson, M., Nedar, R., "Towards Green Propulsion for Spacecraft with ADN-Based Monopropellants," 38th AIAA Joint Propulsion Conference, AIAA Paper 2002-3847, 2002.

[15]Slettenhaar, B., Zevenbergen, J. F., Pasman, H. J., Maree, A. G. M., Moerel, J. L. P. A. "Study on Catalytic Ignition of HNF Based Non Toxic Monopropellants," 39th AIAA Joint Propulsion Conference. AIAA Paper 2003-4920, 2003.

[16]Anflo, K., Persson, S., Thormahlen, P., Bergman, G., Hasanof, T., "Flight Demonstration of an ADN-Based Propulsion System on the PRISMA Satellite," 42nd AIAA Joint Propulsion Conference, AIAA Paper 2006-5212, 2006.

[17]Gamero-Castano, M., "Characterization of a Six-Emitter Colloid Thruster Using a Torsional Balance," *Journal of Propulsion and Power*, Vol. 20, No. 4, 2004, pp. 736-741.

[18]Larriba, C., Garoz, D., Bueno, C., Romero-Sanz, I., Castro, S., Fernandez de la Mora, J., Yoshida, Y., Saito, G., Hagiwara, R., Masumoto, K., Wilkes, J., "Taylor Cones of Ionic Liquids as Ion Sources: The Role of Electrical Conductivity and Surface Tension," *Ionic Liquids IV: Not Just Solvents Anymore*, ACS Symposium Series, Vol. 975, American Chemical Society, Washington, DC, 2007, Ch. 21.

[19]Meng, H., Khare, P., Risha, G. A., Yetter, R. A., Yang, V., "Decomposition and Ignition of HAN-Based Monopropellants by Electrolysis," *47th AIAA Aerospace Sciences Meeting*, AIAA Paper 2009-451, 2009.

[20]Larsson, A., Wingborg, N., Elfsberg, M., Appelgren, P., "Characterization and Electrical Ignition of ADN-based Liquid Monopropellants," FOI-R-1639-SE, 2005.

[21]Yoshida, Y., Baba, O., Larriba, C., Saito, G., "Imidazolium-Based Ionic Liquids Formed with the Dicyanamide Anion: Influence of Cationic Structure on Ionic Conductivity," *Journal of Physical Chemistry B*, Vol. 111, 2007, pp. 12204-12210.

[22]Liggett, Thomas, "Hydroxylammonium Nitrate Process," Patent Application No. 662647, March 1976.

[23]Dambach, E., Heister, S., Ismail, I., Schneider, S., Hawkins, T., "An Investigation of Hypergolicity of Dicyanamide-Based Ionic Liquid Fuels with Common Oxidizers," TP-2008-371, 2008.

[24]Frankel, M. B., Burns, E. A., Butler, J. C., Wilson, E. R., "Derivatives of Dicyanamide," *Journal of Organic Chemistry*, Vol. 28, 1963, pp. 2428.

[25]Jurgens, B. A., Hoppe, H. A., Irran, E., Schnick, W., "Transformation of Ammonium Dicyanamide in the Solid," *Inorganic Chemistry*, Vol. 41, 2002, pp. 4849-4851.

[26]Lotsch, B. V., Schnick, W., "Towards Novel C-N Materials: Crystal Structures of Two Polymorphs of Guanidinium Dicyanamide and Their Thermal Conversion into Melamine," *New Journal of Chemistry*, Vol. 28, 2004, pp. 1129-1136.

[27]Maurel, R., Menezo, J., Barrault, J., "Decomposition De L'Hydrazine Sur Les Metaux Du Groupe VIII Et Du Groupe Ib," *Journal de Chimie Physique*, vol. 70, 1973, pp. 1221-1226.

[28]Fogler, H. S., *Elements of Chemical Reaction Engineering*, 3rd ed., Prentice Hall International, Upper Saddle River, New Jersey, 1999, Ch. 10.

[29]Hughes, R. *Deactivation of Catalysts*, Academic Press, San Diego, 1984.

[30]Christofferson, S., Wucherer, E. J., Zube, D. M., "Tools for Monopropellant Catalyst Development," *37th Joint Propulsion Conference,* AIAA Paper 2001-3941, 2001.

[31]Eloirdi, R., Rossignol, S., Kappenstein, C., Duprez, D., Pillet, N., "Design and Use of a Batch Reactor for Catalytic Decomposition of Propellants," *Journal of Propulsion and Power*, vol. 19, 2003, pp. 213–219.

[32]Gordon, S., "Computer Program for the Calculation of Complex Chemical Equilibrium Compositions and Applications," NASA RP-1311-P2, 1996.

[33]Klein, N., "Liquid Propellants for Use in Guns-A Review," BRL-TR-2641, 1985.

American Institute of Aeronautics and Astronautics