DESIGN AND DEVELOPMENT OF IONIC LIQUID DUAL-MODE SPACECRAFT PROPELLANTS

by

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A THESIS

Presented to the Faculty of the Graduate School of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN AEROSPACE ENGINEERING

2012

Approved by

Joshua L. Rovey, Advisor
David W. Riggins
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PUBLICATION THESIS OPTION

This thesis consists of the following articles that have been submitted for publication as follows:

Pages 8-54 have been submitted to the AIAA Journal of Propulsion and Power. Submitted 5/15/2011, revision submitted 3/7/2012, in review.

Pages 55-88 have been submitted to the AIAA Journal of Propulsion and Power. Submitted 2/6/2012, in review.

ABSTRACT

Energetic ionic liquids capable of dual-mode chemical monopropellant or bipropellant and electric electrospray rocket propulsion are investigated. Following an extensive literature review, ionic liquids [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$] are selected for study since their physical properties align well with the current state-of-the-art in chemical and electrospray propellants. Simulations show that these liquids will not be useful for monopropellant propulsion due to the prediction of solid carbon formation in the exhaust and performance 13-23% below that of hydrazine. Considering these ionic liquids as a fuel component in a binary monopropellant mixture with hydroxyl ammonium nitrate shows 1-4% improved specific impulse over some ‘green’ monopropellants, while avoiding volatility issues and reducing the number of electrospray emitters by 18-27% and power required by 9-16%, with oxidizing ionic liquid fuels providing the greatest savings.

Mixtures of HAN with ionic liquid fuels [Bmim][NO3] and [Emim][EtSO4] are synthesized and tested for catalytic decomposition in a micro-reactor to investigate their potential for use as monopropellants. Two unsupported catalyst materials were tested with the novel propellants: rhenium and iridium. For the [Bmim][NO3]/HAN propellant, 30 µL droplets on rhenium preheated to 160^{o}C yielded a pressure rise rate of 26 mbar/s, compared to 14 mbar/s for iridium and 12 mbar/s for no catalyst. [Emim][EtSO4]/HAN propellant shows slightly less activity at 160^{o}C preheat temperature, yielding a pressure rise rate of 20 mbar/s, 4 mbar/s, and 2.5 mbar/s for injection onto rhenium, iridium, and the thermal plate, respectively.

ACKNOWLEDGMENTS

I would first like to acknowledge and thank my advisor, Dr. Joshua Rovey. His support and motivation have been instrumental in not only this work, but my growth as a professional researcher in general. I also thank the members of my committee for agreeing to serve on my committee and also for their advice during my two years spent compiling this work. The Missouri Space Grant Consortium is especially recognized for providing funding for this project.

I would like to recognize the following for their assistance on this project without asking anything in return. The authors would like to thank Dr. Jason Baird and Phillip Mulligan of the Missouri S&T Explosives Engineering Department for their assistance and advice on the handling of energetic materials. The authors also thank Dr. S. Maddela of Missouri S&T Materials Research Center for graciously lending us the hydrogen peroxide solution required to complete these experiments. Dr. K. Chandrashekhara and J. Nicholas of Missouri S&T Mechanical and Aerospace Engineering department are especially thanked for allowing us use of their fume hood. Members of the Aerospace Plasma Laboratory at Missouri S&T are also acknowledged for their contributions in terms of fruitful discussions and moral support in the lab.

As is APLab tradition (starting now), the following paragraph is tongue-in-cheek acknowledgements. My advisor spent an entire paragraph of his dissertation thanking Kapton™ tape. I also thank Kapton™ tape, although to a less extreme extent. In the APLab, we have found that the simplest solution to ANY experimental hardware issue is “More Kapton.” What were most instrumental in the development of this project were Dr. Rovey’s sometimes unconventional motivational techniques. For example, if members of APLab left early on a Friday, say 4:45 PM, sure enough by 4:47 PM we would receive an e-mail from Dr. Rovey wondering where his “top grad students” had gone because “surely they haven’t left for the weekend.” (I had to immortalize that one.)

Lastly, as is tradition, I would like to thank all of my family and friends. Without their support and encouragement this work would have been an impossible task.

TABLE OF CONTENTS

Page

SECTION

PAPER

SECTION

LIST OF ILLUSTRATIONS

Figure Page

PAPER I

PAPER II

LIST OF TABLES

Table Page

PAPER I

PAPER II

1. INTRODUCTION

This thesis presents work on development of dual-mode specific spacecraft propellants. Specifically, this work attempts to realize a single propellant capable of both chemical monopropellant and electric electrospray rocket propulsion. Previous attempts at realizing a dual-mode propulsion system have focused on utilizing available monopropellants in some electrical propulsion mode, results of which have thus far been mixed as the monopropellants tend to be unsuitable for use, or have very low performance in electric propulsion devices. The approach taken in this study is to quantify traits of the propellant necessary to achieve functionality and high performance in both chemical and electric modes. Thus, a novel dual-mode specific propellant can be selected, synthesized, and tested.

In this thesis, two papers intended for publication are presented which describe the methods and results of research on dual-mode spacecraft propellants. Paper I provides a roadmap to dual-mode propellant design by describing the physical properties and performance that can be attained within the class of ionic liquids selected for study. Paper II presents experimental work on the synthesis and catalytic decomposition of two novel propellants designed from the results of Paper I. Evidence of catalytic decomposition provides initial proof-of-concept for use in monopropellant systems, and represents the first step on the development path. These papers are preceded by an introduction which describes the motivation for pursuing the research and the basic concepts of both dual-mode spacecraft propulsion and ionic liquids.

1.1. DUAL-MODE SPACECRAFT PROPULSION

The main benefit of a dual-mode system is increased mission flexibility through the use of both a high-thrust chemical thruster and a high-specific impulse electric thruster. By utilizing both thrust modes, the mission design space is much larger [1]. Missions not normally accessible by a single type of thruster are possible since both are available. The result is the capability to launch a satellite with a flexible mission plan that allows for changes to the mission as needs arise. Since a variety of high specific impulse and high thrust maneuvers are available in this type of system, this may also be viewed as a technology enabling launch of a satellite without necessarily determining its thrust history beforehand. Research has shown that a dual mode system utilizing a single ionic liquid propellant in a chemical bipropellant or monopropellant and electrical electrospray mode has the potential to achieve the goal of improved spacecraft mission flexibility [2-4]. Furthermore, utilizing a single ionic liquid propellant for both modes would save system mass and volume to the point where it becomes beneficial when compared to the performance of a system utilizing a state-of-the-art chemical and electric thruster with separate propellants, despite the performance of the ionic liquid being less than that of each thruster separately. While a bipropellant thruster would provide higher chemical performance, a monopropellant thruster provides the most benefit because the utilization of a bipropellant thruster in this type of system could inherently lead to unused mass of oxidizer since some of the fuel is used for the electrical mode [3].

1.1.1. Monopropellant Propulsion. Monopropellant propulsion is a combustion-based propulsive method that consists of a single propellant being ignited through some external stimulus in order to produce an energy release, and therefore a temperature and pressure increase in a combustion chamber. The pressurized gas is then expanded through a nozzle to produce thrust. High thrust can be attained with monopropellant devices, but specific impulse is limited due to energy being lost to random thermal collisions which reduces the exhaust velocity. A schematic of a typical monopropellant thruster is shown in Figure 1.1.

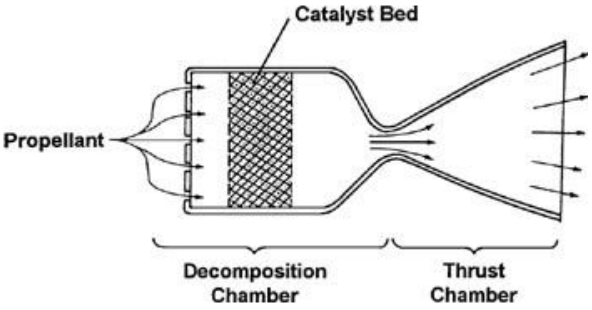

Figure 1.1. Simplified Schematic of Monopropellant Thruster.

A monopropellant must be thermally stable under storage conditions, but also readily ignitable. Typically, hydrazine has been employed as a spacecraft monopropellant because it is storable and easily decomposed to give good propulsion performance [5]. Because it is also highly toxic, recent efforts have focused on finding an alternative “green” monopropellant. Binary or ternary mixtures including the energetic salts hydroxyl ammonium nitrate (HAN), ammonium dinitramide (ADN), or hydrazinium nitroformate (HNF) have been proposed as potential replacements [6-10]. These are not true monopropellants in the traditional sense, but rather essentially premixed bipropellants with separate oxidizer and fuel components in the mixture. 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.

Nonspontaneously ignitable propellants, such as monopropellants, must be decomposed by some external means before ignition can begin. Ignition is a transient process in which reactants are rapidly transitioned to self-sustained combustion via some external stimulus. For practical applications, the amount of energy needed to provide ignition must be minimal, and the ignition delay time should be small [5]. 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 [11, 12]. 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 decomposition by the commercially manufactured iridium-based catalyst Shell 405. For optimum performance, the catalyst bed is typically heated up to 200^{o}C, but can be ‘cold-started’ with no preheat in emergency situations [5]. The Swedish ADN-based monopropellant blends require a catalyst bed preheat of 200^{o}C. They cannot be cold-started, which is a major limitation presently [10].

1.1.2. Electrospray Propulsion. Electrospray, or colloid, propulsion utilizes and electrostatic-type device to extract ions or charged droplets from a liquid meniscus, which in turn are accelerated through an intense electric field to produce a high exhaust velocity. As with most electric propulsion devices, the mass flow rates that can be attained in this type of device are low. Electrospray devices are therefore high-specific impulse, low-thrust type devices. A typical electrospray thruster consists of an emitter, which is essentially a needle, an extraction grid, and a power supply. The propellant may be either externally wetted or injected through a capillary tube. A potential is applied between the extraction grid and the needle, which causes the formation of a Taylor cone on the surface of the propellant meniscus. If the electric field on the meniscus is sufficiently high, ions or charged droplets are extracted and accelerated by the grid. A typical electrospray thruster is shown in Figure 1.2.

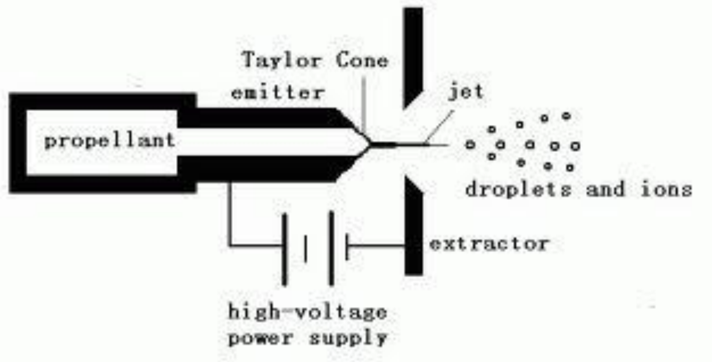

Figure 1.2. Simplified Schematic of Electrospray Thruster.

1.2. IONIC LIQUIDS

An ionic liquid is essentially a molten, or liquid, salt. All salts obtain this state when heated to high enough temperature; however, a special class of ionic liquids is known as room temperature ionic liquids (RTIL's) that remain liquid well below room temperature. These differ from traditional aqueous ionic solutions, such as salt water, in that a solute is not required to dissolve the ionic portion, but rather the ionic substance is liquid in and of itself. Ionic liquids have been known since the early 20th century; research in the field, however, has only currently begun to increase, with the number of papers published annually increasing from around 120 to over 2000 in just the last decade [13]. As a result, many of the ionic liquids that have been synthesized are still being researched, and data on their properties is not yet available. Current research has aimed at synthesizing and investigating energetic ionic liquids for propellants and explosives, and current work has highlighted the combustibility of certain ionic liquids as they approach decomposition temperature [14, 15]. This leads to the possibility of using an ionic liquid as a storable spacecraft propellant.

Ionic liquids have been investigated as electrospray propellants. Electrospray liquids with relatively high vapor pressure boil off the emitter and produce an uncontrolled, low performance emission. Ionic liquids are candidates for electrospray propulsion due to their negligible vapor pressure and high electrical conductivity [16]. Ionic liquid emissions can range from charged droplets to a purely ionic regime (PIR) similar to that of field emission electric propulsion with specific impulses in the range of 200-3000 seconds for current propellants [17]. The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][Im]) was selected as the propellant for the ST7 Disturbance Reduction System mission, and represents the only application of electrospray, or colloid, thrusters to date [18]. Several other imidazole-based ionic liquids have been suggested for research in electrospray propulsion due to their favorable physical properties [19].

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PAPER

I. Assessment of Imidazole-Based Ionic Liquids as Dual-Mode Spacecraft Propellants

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ABSTRACT

Imidazole-based ionic liquids are investigated in terms of dual-mode chemical monopropellant and electrospray rocket propulsion capability. A literature review of ionic liquid physical properties is conducted to determine an initial, representative set of ionic liquids that show favorable physical properties for both modes, followed by numerical and analytical performance simulations. Ionic liquids [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$] meet or exceed the storability properties of hydrazine and their electrochemical properties indicate that they may be capable of emission in the purely ionic regime. These liquids will not be useful for monopropellant propulsion due to the prediction of solid carbon formation in the exhaust and performance 13-23% below that of hydrazine. Considering these ionic liquids as a fuel component in a binary monopropellant mixture with hydroxyl ammonium nitrate shows 1-4% improved specific impulse over some ‘green’ monopropellants, while avoiding volatility issues and reducing the number of electrospray emitters by 18-27% and power required by 9-16%, with oxidizing ionic liquid fuels providing the greatest savings. A fully oxygen balanced ionic liquid will perform close to the state-of-the-art in both modes, but will require more power in the electrospray mode and will be unsuitable if the required emitter preheat temperature is above its decomposition temperature.

NOMENCLATURE

$E_{\max}$ = Maximum electric field

e = Fundamental charge

F = Thrust

g_0 = Acceleration of gravity

I_d = Density specific impulse

I_{emit} = Current flow per emitter

I_i = Output current associated with charged particle *i*

I_{sp} = Specific impulse

K = Electrical conductivity

MW = Molecular weight

m_i = Mass of particle *i*

$\dot{m}_{emit}$ = Mass flow rate per emitter

$\dot{m}_{tot}$ = Total mass flow rate

N_{emit} = Number of emitters

P_c = Chamber pressure

P_e = Nozzle exit pressure

P_{sys} = Power of electric propulsion system

Q = Volume flow rate

q = Particle charge

R = Gas constant

R_A = Ion fraction

T_c = Combustion temperature

T_m = Melting temperature

V_{acc} = Electrostatic acceleration potential

$V_{e,N=0}$ = Exit velocity of pure ions

$V_{e,N=1}$ = Exit velocity of ions in $N=1$ solvated state

x_i = Mass fraction of species *i*

ΔH_f^0 = Heat of formation

δ_{av} = Average specific gravity

ε = Dielectric constant, or nozzle expansion ratio

ε_0 = Permittivity of free space

η = Viscosity

η_{sys} = Efficiency of power conditioning system

γ = Specific heat ratio, or surface tension

$\varphi(\varepsilon)$ = Proportionality coefficient

ρ = Density

ρ_i = Density of species *i*

ρ_n = Density of mixture *n*

1. INTRODUCTION

The purpose of a dual-mode spacecraft propulsion system is to improve spacecraft mission flexibility by utilizing both high-thrust chemical and high-specific impulse electric propulsion modes on a single spacecraft. A dual-mode system utilizing a single propellant, and therefore a single propellant tank, for both modes would reduce system mass and volume and provide maximum mission flexibility. The goal of this paper is to examine typical ionic liquids in terms of their capability for use in a dual-mode propulsion system utilizing a single propellant. Since the list of available ionic liquids is enormous, and most liquids are not yet well characterized, this study will also attempt to identify trends favorable toward dual-mode propulsion in order to provide guidelines for the selection of ionic liquids for future use in dual-mode propulsion research. This paper describes and examines requirements on the physical properties of various ionic liquids to assess their potential for use as propellants in a potential dual-mode system. Chemical and electrical propulsion performance of sample ionic liquids that have shown favorable properties toward feasible operation in both modes is then computed and compared to the current state-of-the-art in both chemical monopropellant and electrospray propulsion.

The main benefit of a dual-mode system is increased mission flexibility through the use of both a high-thrust chemical thruster and a high-specific impulse electric thruster. By utilizing both thrust modes, the mission design space is much larger [1]. Missions not normally accessible by a single type of thruster are possible since both are available. The result is the capability to launch a satellite with a flexible mission plan that allows for changes to the mission as needs arise. Since a variety of high specific impulse and high thrust maneuvers are available in this type of system, this may also be viewed as a technology enabling launch of a satellite without necessarily determining its thrust history beforehand. Research has shown that a dual mode system utilizing a single ionic liquid propellant in a chemical bipropellant or monopropellant and electrical electrospray mode has the potential to achieve the goal of improved spacecraft mission flexibility [2-4]. Furthermore, utilizing a single ionic liquid propellant for both modes would save system mass and volume to the point where it becomes beneficial when compared to the performance of a system utilizing a state-of-the-art chemical and electric thruster with separate propellants, despite the performance of the ionic liquid being less than that of each thruster separately. While a bipropellant thruster would provide higher chemical performance, a monopropellant thruster provides the most benefit because the utilization of a bipropellant thruster in this type of system could inherently lead to unused mass of oxidizer since some of the fuel is used for the electrical mode [3].

An ionic liquid is essentially a molten, or liquid, salt. All salts obtain this state when heated to high enough temperature; however, a special class of ionic liquids is known as room temperature ionic liquids (RTIL’s) that remain liquid well below room temperature. Ionic liquids have been known since the early 20th century; research in the field, however, has only currently begun to increase, with the number of papers published annually increasing from around 120 to over 2000 in just the last decade [5]. As a result, many of the ionic liquids that have been synthesized are still being researched, and data on their properties is not yet available. Additionally, the number of ionic liquids theorized, but not yet synthesized has been estimated in the millions [6] and the estimated number of possible ionic liquids is on the order of ~10^{18} [7]. Current research has aimed at synthesizing and investigating energetic ionic liquids for propellants and explosives, and current work has highlighted the combustibility of certain ionic liquids as they approach decomposition temperature [8, 9]. This leads to the possibility of using an ionic liquid as a storable spacecraft monopropellant.

Hydrazine has been the monopropellant of choice for spacecraft and gas generators because it is storable and easily decomposed to give good combustion properties [10]. However, hydrazine is also highly toxic and recent efforts have been aimed at replacing hydrazine with a high-performance, non-toxic monopropellant. The energetic salts hydroxyl ammonium nitrate (HAN), ammonium dinitramide (ADN), and hydrazinium nitroformate (HNF) have received attention as potential replacements [10-14]. All of these have melting points above room temperature, and it is therefore necessary to use them in an aqueous solution to create a storable liquid propellant. Typically, these are also mixed with a compatible fuel component to provide improved performance. The main limitation to the development of these as monopropellants has been excessive combustion temperatures [14, 15]. Engineers in Sweden, however, have recently flight tested an ADN-based thruster capable of handling combustion temperatures exceeding 1900 K [14].

Electrospray is a propulsion technology in which charged liquid droplets or ions are extracted from an emitter via an applied electric field [16]. Electrospray liquids with relatively high vapor pressure boil off the emitter and produce an uncontrolled, low performance emission. Ionic liquids are candidates for electrospray propulsion due to their negligible vapor pressure and high electrical conductivity [17]. Ionic liquid emissions can range from charged droplets to a purely ionic regime (PIR) similar to that of field emission electric propulsion with specific impulses in the range of 200-3000 seconds for current propellants [16]. The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][Im], or [Emim][Tf_2N]) was selected as the propellant for the ST7 Disturbance Reduction System mission, and represents the only flight application of electrospray, or colloid, thrusters to date [18]. Several other imidazole-based ionic liquids have been suggested for research in electrospray propulsion due to their favorable physical properties [19].

The following sections analyze the potential of ionic liquids to be used as spacecraft propellants in a dual-mode system and develops criterion for selection or design of true dual-mode propellants. Section II identifies the physical properties required for acceptable performance in both modes. Sample ionic liquids are then selected for performance analysis. Section III investigates the expected chemical performance of these ionic liquids as both monopropellants. Section IV examines the electrospray performance of the ionic liquid propellants. The results of the preceding sections are discussed, and criteria for future dual-mode propellant selection and developments are presented in Section V. Section VI presents conclusions based on the entirety of analyses.

2. IONIC LIQUID PHYSICAL PROPERTIES

Fundamental physical properties required of ionic liquids to perform as both monopropellants and electrospray propellants in a spacecraft environment are identified. These properties are compared to those of the current state-of-the-art propellants to develop tools and criterion to assess the feasibility of using these ionic liquids for the intended application.

2.1. THERMOCHEMICAL PROPERTIES

The fundamental thermochemical properties required to initially analyze the ability of ionic liquids to perform as spacecraft propellants include the following: melting temperature, density, viscosity, and heat of formation [10]. High density, low melting temperature, and low viscosity are desired traits common to both propulsive modes in the dual-mode system because they do not have a significant effect on the operation of each thruster, but represent the storability of propellants only. A low viscosity aids in transporting the propellant from the tank and its subsequent injection into either type of thruster. A low melting temperature is desired so that the power required to keep the propellant in liquid form is minimal. Monopropellant grade hydrazine has a melting temperature of 2°C, so it is reasonable to assume that new propellants must fall near or below this value. Density is an additional storability consideration. A high density is desired to accommodate a large amount of propellant in a given volume on a spacecraft. The chemical propellant must also be easily ignitable and give good combustion properties. The heat of formation of the compound is required to estimate the equilibrium composition, and subsequently compute the estimated chemical performance, namely specific impulse. A high heat of formation results in a greater energy release upon combustion, therefore a higher combustion temperature, and subsequently a higher specific impulse for a given species and number of combustion products.

2.2. ELECTROCHEMICAL PROPERTIES

The electrochemical properties important for electrospray propulsion include both surface tension and electrical conductivity. The highest performance in terms of specific impulse is attained for emissions in the purely ionic regime (PIR). Emission of charged droplets, rather than clusters of ions, greatly reduces the efficiency of the emission. [Emim][Im], for example, operates in the purely ionic regime with a specific impulse of around 3500 seconds [20], but in the droplet regime, this drops to lower than 200 seconds [21]. Liquids with sufficiently high surface tension and electrical conductivity have been shown to be capable of operating in the purely ionic regime. This has been shown both theoretically and experimentally [19, 22, 23], and is related to the maximum electric field on the meniscus of the liquid on the emitter [18, 19]

$$E_{\max} = \varphi(\varepsilon)\gamma^{1/2}\varepsilon_0^{-2/3}(K/Q)^{1/6} \tag{1}$$

Additionally, De La Mora [19, 23] has shown that the smallest flow rate that can form a stable Taylor cone scales as γ/K, hence [19]

$$E_{\max} \sim (\gamma K)^{1/3} \tag{2}$$

It should be noted that Eqs. (1) and (2) do not accurately predict the meniscus electric field for PIR emissions. Instead, because PIR emission experimental results indicate the same trend for ionic liquids that can attain PIR, Eq. (2) will be used as a comparison tool. This relation is a measure of the ability of an ionic liquid to form a Taylor cone with emission in the purely ionic regime, and does not necessarily translate to thruster performance. The thrust and specific impulse for an electric propulsion system by an individual particle are calculated as [10, 16]

$$F = I_i \sqrt{2V_{acc}(m_i / q)} \tag{3}$$

$$I_{sp} = (1/g_0)\sqrt{2V_{acc}(q / m_i)} \tag{4}$$

A high charge per mass is desired for high specific impulse, but is inversely proportional to thrust. Previous research has shown that an excessively high specific impulse for electrospray propulsion is not practical for typical satellite maneuvering operations [3]. Higher molecular weight propellants are desirable due to the higher thrust produced by emission of heavier ions. Therefore, ionic liquids with electrical conductivity and surface tension close to the current state-of-the-art electrospray propellants that have achieved PIR operation and high molecular weight are of utmost importance.

2.3. PHYSICAL PROPERTIES OF IONIC LIQUIDS USED IN THIS STUDY

The number of ionic liquids available for study is numerous; therefore, this study has initially been restricted to only imidazole-based ionic liquids. The main reason for selecting imidazole-based ionic liquids is their capability as electrospray propellants, particularly those based on the $[\mathrm{Emim}]^+$ cation [19]. A recent patent on this particular type of dual-mode system lists several potential ionic liquid propellants, most of which are imidazole-based [24]. These are used in the initial screening for chemicals of interest; however, many ionic liquids do not have enough published physical property data to make reasonable estimates of initial system feasibility. In particular, heat of formation is not available for many of the ionic liquids considered initially. It is therefore necessary and useful to consider trends in the physical properties of ionic liquids. This will be discussed in further detail in a later section, but for the sake of this study and to discern performance trends, three ionic liquids are selected for further study based on availability of property data: 1-butyl-3-methylimidazolium nitrate ([Bmim][NO3]), 1-butyl-3-methylimidazolium dicyanamide [Bmim][dca], and 1-ethyl-3-methylimidazolium ethyl sulfate ([Emim][EtSO4]). Representative physical property data for these ionic liquids are shown in Table 2.1; variance in this data will be addressed in the next section. The properties of hydrazine and [Emim][Im] are shown for comparison of thermochemical and electrochemical properties, respectively. The density, viscosity, electrical conductivity, and surface tension reported in the table are at a temperature of 298 K for all liquids listed, except for the electrical conductivity of [Bmim][NO3], where the only data point given in literature is at a temperature of 379 K.

Table 2.1. Physical Properties of Ionic Liquids.

Propellant	Formula	ρ [g/cm^3]	T$_m$ [^{o}C]	ΔH_f^o [kJ/mol]	K [S/m]	γ [dyn/cm]	η [cP]
[Bmim][NO$_3$]	$C_8H_{15}N_3O_3$	1.157 [25]	<10 [25]	-261.4 [26]	0.820 [27]		165 [28]
[Bmim][dca]	$C_{10}H_{15}N_5$	1.058 [29]	-10 [29]	206.2 [30]	1.052 [31]	46.6 [32]	32 [33]
[Emim][EtSO$_4$]	$C_8H_{16}N_2O_4S_1$	1.236 [34]	-37 [35]	-579.1 [36]	0.382 [37]	45.4 [38]	100 [39]
[Emim][Im]	$C_8H_{11}F_6N_3O_4S_2$	1.519 [40]	-18 [41]		0.910 [42]	36.9 [43]	32 [40]
Hydrazine	N_2H_4	1.005 [10]	2 [10]	109.3 [44]	0.016 [45]	66.4 [45]	0.9 [45]

All of the ionic liquids have density greater than that of hydrazine. The melting temperature of [Bmim][dca] and [Emim][EtSO$_4$] is less than that of hydrazine. [Bmim][NO$_3$] has a slightly higher melting temperature, but the exact melting temperature is not reported. The value shown in Table 2.1 represents the fact that liquid viscosity measurements are reported for as low as 10^{o}C in literature [26, 28]. The final consideration is the viscosity of the ionic liquids, which is much higher than typical chemical propellants, such as hydrazine, and is even still an order of magnitude higher than ADN-based monopropellant blends [ADN]. This could lead to difficulties in engine calibration and injector performance, but likely can be mitigated through clever design. In terms of electrospray considerations, the viscosity of [Bmim][dca] is roughly the same as [Emim][Im], which has been successfully sprayed through a capillary emitter [46]. The viscosity of the other two ionic liquids is higher than [Emim][Im], but not unlike some higher molecular weight propellants that have been electrosprayed successfully, but only by heating the emitter [46]. Similarly, heating [Bmim][NO_3] to 60^oC [28] and [Emim][$EtSO_4$] to 50^oC [39] lowers the viscosity to levels equal to [Emim][Im].

The electrochemical properties should first and foremost be assessed in terms of the likelihood of the candidate ionic liquid to attain PIR emission since, as mentioned, operation in the mixed, or droplet, regime causes the efficiency of the thruster, and consequently specific impulse, to drop drastically. Therefore, this assessment should be one of the first considerations when considering new candidate propellants for dual-mode systems. Since electrical conductivity of ionic liquids increases greatly with temperature, the emitter can be heated to attain PIR emission. Using Eq. (2) as an estimate and comparison tool to assess the combined effects of surface tension and electric field, the estimated maximum electric field parameter in Eq. (2) is computed and shown as a function of temperature in Fig. 2.1. The surface tension and electrical conductivity of [Emim][Im], [Bmim][dca], and [Emim][$EtSO_4$] as a function of temperature were obtained from literature [31, 40, 47]. [Emim][Im] has been shown experimentally to achieve PIR emission at an emitter preheat temperature of 80^oC [46]. From Fig. 2.1, the electric field on the surface of the meniscus for [Bmim][dca] and [Emim][$EtSO_4$] is comparable at temperatures of 45^oC and 80^oC, respectively. This is not surprising as these liquids were selected specifically due to their electrospray potential. The same data for [Bmim][NO_3] is not available, and it can therefore not be fully assessed in the same manner. As stated, the electrical conductivity reported for [Bmim][NO_3] is at a temperature of 379 K, making it slightly less feasible to use as an electrospray propellant since it will have to be heated to well over 100^oC to achieve an electrical conductivity nearly equal to that of [Emim][Im] at 80^oC. Surface tension for [Bmim][NO_3] is not reported; however, it can be reasonably inferred based on trends reported in literature. A longer alkyl chain in imidazole-based ionic liquids has been reported to result in decreased surface tension [48]. [Emim][NO_3], the lower alkyl chain derivative of [Bmim][NO_3] has a surface tension of 82.7 [dyne/cm] [49]. The value reported for the lower alkyl chain derivative of [Bmim][dca] is 1-ethyl-3-methylimidazolium dicyanamide, [Emim][dca] is 64 [dyne/cm] [50]. Following these trends, the surface tension for [Bmim][NO_3] should fall below that of [Emim][NO_3], but above that of [Bmim][dca]; therefore, the surface tension of [Bmim][NO_3] should be higher than that of [Emim][Im], and may allow for a slightly lower electrical conductivity.

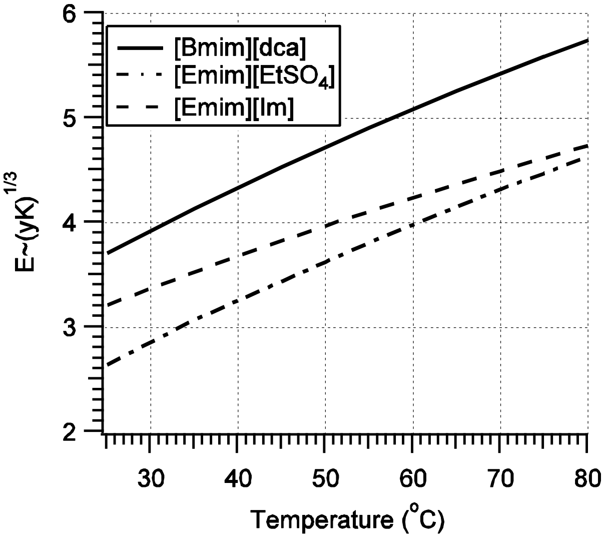

Figure 2.1. Electric Field on Meniscus Parameter, Eq. (2), as a Function of Temperature.

It should also be noted that the numbers computed in Fig. 2.1 provide an estimate only and are predictions based on the minimal number of ionic liquids that have experimentally exhibited PIR emission. Of the PIR capable ionic liquids listed in Garoz et al. [46], only the ionic liquid 1-butyl-3-methylimidazolium bis(perfluoroethylsulfonyl)imide, [Bmim][Beti], had the requisite physical property data available to test the validity of the use of Eq. (2) as a predictor for PIR capability [41]. In comparison to [Emim][Im], Eq. (2) predicts that this ionic liquid will achieve PIR near a 180°C preheat temperature. This ionic liquid has been observed to emit in the PIR regime with a preheat of 204°C [46]. So, while the type of data presented in Fig. 2.1 should be used with heed, it can be used to screen out obviously poor candidates and provide a reasonable means of comparison to ionic liquids that have attained PIR emission.

2.4. VARIANCE OF PROPERTY DATA IN LITERATURE

Representative physical property data for candidate ionic liquid propellants has been shown and analyzed in the previous section; however, the multiple values reported in literature are found to deviate slightly from the values listed in Table 2.1. Therefore, a full literature review is presented to determine how this affects the conclusions in this study.

Of the ionic liquids presented in this study, [Bmim][NO_3] has the least, and also the most questionable, published physical property data currently available. The densities reported in literature are in good agreement, with reported values ranging from 1.157-1.159 [g/cc] [25, 28, 51]. This 0.2% difference is not significant for this study. The reported value for electrical conductivity is the result of molecular dynamics simulations [27]. Currently, there are no data available for experimental conductivity measurements of [Bmim][NO_3]; however, Kowsari [27] reports that their simulated conductivity results are less than obtained from experimental results of ionic liquids they studied which had published experimental results available.

[Bmim][dca] has more experimental data available in literature. Density measurements range from 1.058-1.063 [g/cc] [29, 31, 33 52, 53]. This is a 0.3% difference, but again is not significant for the purposes of this study. Electrical conductivity measurements show a slight variance, ranging from 1.052-1.139 [S/m] [31, 52, 54]. Zech [31] suspects halide impurities result in a higher measured electrical conductivity for this ionic liquid, and expects the value of pure [Bmim][dca] to be even lower than his measured value of 1.052 [S/m]. Values obtained for surface tension also show a slight variance: 45.81-48.6 [dyne/cm] [32, 55]. Klomfar [32] measured surface tension using both the Wilhelmy plate and du Nuoy ring methods and found values of 45.81 and 45.88 [dyne/cm], respectively, suggesting that the variance in surface tension is likely also due to impurities. Since the lowest values for surface tension and electrical conductivity found in literature are still above that of [Emim][Im], the conclusion that [Bmim][dca] is a good candidate for electrospray propulsion remains unchanged.

For a variety of reasons, [Emim][EtSO$_4$] has been intensely studied over the past five years.; as such, a plethora of published data is available. Density, as with the other two ionic liquids, shows good agreement: 1.236-1.242 [g/cc] [34, 56]. Since over 30 sources that have experimentally measured density were found over the course of this study, only the highest and lowest values obtained are included. Again, this amounts to only 0.5% difference between the highest and lowest values, and is therefore not significant for purposes of this study. Surface tension, like [Bmim][dca], has a slight variance amongst published data. Values range from 45.43-48.79 [dyne/cm] [38, 47, 57], but again do not affect the conclusions because these values are still well above that of [Emim][Im]. Other than the value listed in the table, an electrical conductivity of 0.398 [S/m] is published in literature [47], which does not affect the conclusions significantly.

3. CHEMICAL PERFORMANCE ANALYSIS

The three aforementioned liquids are feasible candidates for both chemical and electrical propulsion purely based on their reported physical properties. Although initially selected mainly because of electrospray considerations, a chemical rocket performance analysis is conducted to determine if they have potential as chemical monopropellants with the understanding that they may perform below state-of-the-art, but have dual-mode capability. Equilibrium combustion analysis is conducted using the NASA Chemical Equilibrium with Applications (CEA) computer code [44]. In each case, the temperature of the reactants is assumed to be 298 K. Where applicable, specific impulse is calculated by assuming frozen flow at the throat [10]

$$I_{sp} = \sqrt{\left(\frac{2\gamma}{\gamma-1}\right)\left(\frac{RT_c}{MW}\right)\left(1-\left(\frac{P_e}{P_c}\right)^{\frac{(\gamma-1)}{\gamma}}\right)} \qquad (5)$$

$$\frac{1}{\varepsilon}=\left(\frac{\gamma+1}{2}\right)^{\frac{1}{\gamma-1}}\left(\frac{P_e}{P_c}\right)^{\frac{1}{\gamma}}\sqrt{\frac{\gamma+1}{\gamma-1}\left(1-\frac{P_e}{P_c}\right)^{\frac{\gamma-1}{\gamma}}} \tag{6}$$

Given a combustion pressure and nozzle expansion ratio, Eqs. (5) and (6) are then only functions of the combustion gas temperature and products, which are given in the CEA output. When condensed species are found to be present in the equilibrium combustion products, a shifting equilibrium assumption through the nozzle must be applied instead to account for the multi-phase flow. For each simulation hereafter a chamber pressure of 300 psi and nozzle expansion ratio of 50 are assumed. These represent typical values for on-orbit engines [58]. The ambient pressure is taken as vacuum, therefore the specific impulse computed is the absolute maximum for the given design conditions. As an additional measure of chemical performance, the density specific impulse, is computed simply from [10]

$$I_d=\delta_{av}I_{sp} \tag{7}$$

3.1. MONOPROPELLANT PERFORMANCE

The CEA computer code is utilized to determine the expected performance of the ionic liquids as monopropellants with the assumptions and conditions described above. The reaction is then decomposition of the ionic liquid into gaseous products. The computed specific impulse and density impulse values are shown in Table 3.1. CEA predicts condensed carbon in the exhaust species for the ionic liquids; therefore, the specific impulse shown in the table is for shifting equilibrium. For comparison, the performance of ADN-based monopropellant FLP-103 (63.4% ADN, 25.4% water, 11.2% methanol) is also computed. The specific impulse computed in this analysis for FLP-103 agrees precisely with the theoretical calculations performed by Wingborg, et al. [59] at the same design conditions and a frozen flow assumption, as CEA was also utilized in that study for performance prediction. The maximum specific impulse for hydrazine is 257 sec [45] and is where the catalyst bed has been designed to allow for no ammonia to dissociate. Typically, however, hydrazine monopropellant thrusters operate around 243 sec since the catalyst bed cannot handle the high combustion temperature [10]. None of the ionic liquids show performance comparable to that of hydrazine, with [Bmim][NO_3] coming closest at a value of 13.2% lower specific impulse. The performance of the ionic liquids is slightly more promising in terms of density specific impulse. [Bmim][dca], and [Emim][$EtSO_4$] fall 18% and 5.3%, respectively, below that of hydrazine, while [Bmim][NO_3] has a density specific impulse equal to that of hydrazine. None of the ionic liquids compete with the theoretical density specific impulse of advanced monopropellant FLP-103, which is predicted to be 35% higher than hydrazine.

Table 3.1. Chemical Performance of Ionic Liquids.

Propellant	I_{sp} [s]	I_d [kg-s/m^3]
[Bmim][NO_3]	211	244000
[Bmim][dca]	189	200000
[Emim][$EtSO_4$]	186	231000
FLP-103	254 (Equilibrum)	333000
	251 (Frozen)	329000
Hydrazine	243	244000

Analysis of the equilibrium combustion products, Table 3.2, indicates a large amount of solid carbon in the theoretical exhaust gases, indicating incomplete combustion, and leading to the poor performance of the ionic liquids. [Bmim][dca] has no oxidizing components in its anion and as expected it has the highest mole fraction of carbon of the three ionic liquids. The other two liquids have 15% less carbon in the exhaust due to the oxygen present in their anions, which tends to form the oxidized species CO, H_2O, and CO_2. Decomposition of [Emim][$EtSO_4$] shows a higher mole fraction of H_2O and CO_2 compared to that of [Bmim][NO_3] due to the additional oxygen atom in the anion with the same carbon content. Each of the ionic liquids is predicted to form roughly 10% CH_4, a product that could be combusted further with additional oxidizer. Additionally, some of the hydrogen is used to form H_2S due to the presence of the sulfur atom in the anion, another product that with additional oxidizer will combust further.

Table 3.2. Equilibrium Decomposition Products of Ionic Liquids.

Product	Mole Fraction		
Species	[Bmim][NO_3]	[Bmim][dca]	[Emim][$EtSO_4$]
C	0.35	0.50	0.35
N_2	0.10	0.15	0.07
H_2	0.27	0.24	0.19
H_2O	0.07	0.00	0.11
CO	0.09	0.00	0.07
CO_2	0.02	0.00	0.05
CH_4	0.09	0.11	0.09
H_2S	0.00	0.00	0.07

3.2. IONIC LIQUIDS IN BINARY MIXTURES AS MONOPROPELLANTS

The possibility of using ionic liquids as fuel components in a binary monopropellant mixture is considered. This may, in fact, be possible due to the ionic liquids capability as solvents, particularly [Bmim][dca] and [Bmim][NO_3], as their anions have H-bond accepting functionality [54, 60]. Furthermore, many imidazole-based ionic liquids tend to have solubility properties close to those of methanol and ethanol [6]. HAN, also, is noted for its solubility in water and fuels such as methanol, which led to its initial application as a liquid gun propellant [61]. Additionally, these are the ingredients to FLP-103, and the solubility of ADN in both water and methanol was a key to the development of the monopropellant [12, 59]. [Bmim][dca] has been tested for hypergolicity with HAN oxidizer, and, notably, it showed no visible signs of reactivity at room temperature [62]. A monopropellant mixture of the ionic liquids with HAN, or another oxidizer salt, may be created which would be thermally stable at room temperature, and ignited thermally or catalytically.

CEA is again employed with the same conditions applied previously, and with shifting equilibrium assumption. Specific impulse is calculated as a function of percent HAN oxidizer by weight in the binary mixture. This is shown in Fig. 3.1. The highest performance is seen at mixture ratios near the stoichiometric value, around 80%, and represents values nearer to bipropellant performance. However, this performance is not feasible when considering current monopropellant thruster technology. The main issue facing monopropellant development is the fabrication of catalyst material that can withstand the high combustion temperatures. A typical hydrazine thruster may operate at temperatures exceeding 1200 K [10]; however, after a painstaking trial and error process lasting more than a decade, engineers in Sweden have developed a monopropellant thruster capable of operation with ADN-based propellant at combustion temperatures exceeding 1900 K [14]. Considering 1900 K to be the current technology limit on monopropellant combustion temperature, the ionic liquids [Bmim][dca], [Bmim][NO3], and [Emim][EtSO4] exceed this value at roughly a 69%, 61%, and 59% binary mixture with HAN by weight, respectively, as shown in Fig. 3.2. From Fig. 3.1, these mixture ratios correspond to a specific impulse of 263, 263, and 255 seconds for [Bmim][dca], [Bmim][NO3], and [Emim][EtSO4], respectively. This is promising as the specific impulse of the binary mixtures is higher than the ADN-based FLP-103 (Table 3.1) at the same design conditions.

Additional conclusions can be made by further consideration of the equilibrium combustion products associated with the ionic liquid binary mixtures in Fig. 3.3. For [Bmim][dca], as the percent by weight of HAN oxidizer is increased, the solid carbon species decreases as both CO and H_2 increase and reach a maximum at 58% oxidizer. Further HAN addition leads to formation of complete combustion products CO_2 and H_2O at the highest combustion temperatures. The same trend is observed in the other ionic liquids, with the exception of the solid carbon disappearing at 44% oxidizer for [Bmim][NO_3] and at 41% oxidizer for [Emim][$EtSO_4$]. The sulfur atom in the

[Emim][EtSO$_4$] fuel functions to form oxidized sulfur species SO$_2$, which peaks at roughly 2% near the stoichiometric mixture ratio.

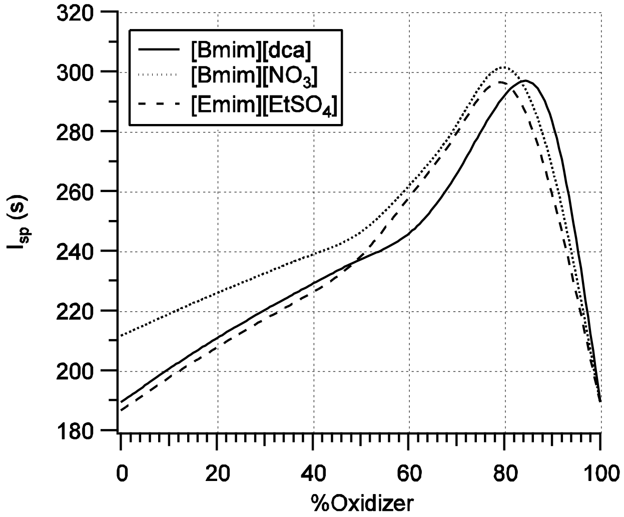

Figure 3.1. Specific Impulse of Binary Mixture of Ionic Liquid with HAN Oxidizer.

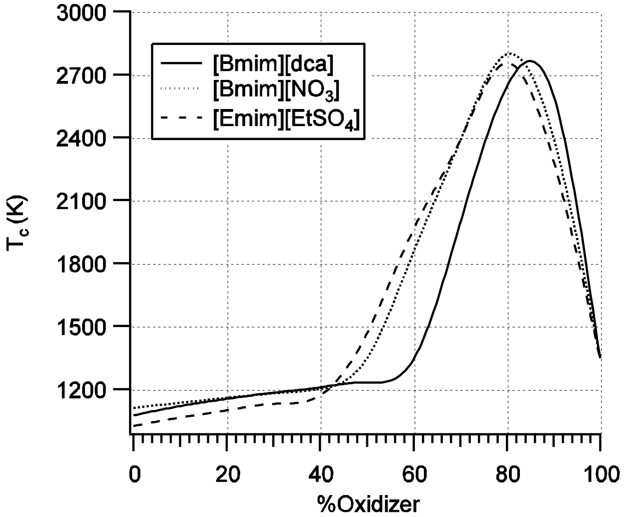

Figure 3.2. Combustion Temperature of Binary Mixture of Ionic Liquid with HAN Oxidizer.

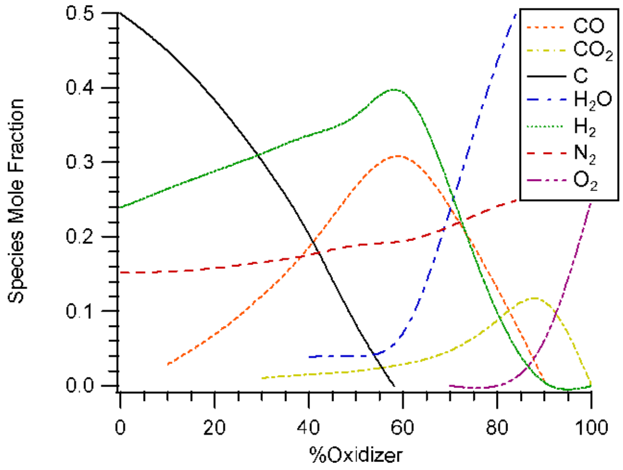

Figure 3.3. Major Combustion Products of Binary Mixture of [Bmim][dca] and HAN.

For further comparison, the specific impulse of the binary mixtures of ionic liquids as a function of percent HAN oxidizer is computed assuming frozen flow; therefore, only mixture ratios that do not yield solid carbon are included. This is shown in Fig. 3.4. At the aforementioned mixture ratios yielding a 1900 K combustion temperature, the specific impulse is now 251 seconds for [Bmim][dca] and [Bmim][NO_3], and 249 seconds for [Emim][$EtSO_4$] which are roughly equal to that of FLP-103. As mentioned, a [Bmim][dca] mixture requires at least 58% HAN to form completely gaseous products. At this mixture ratio, the specific impulse is 213 seconds, 15% below that of FLP-103. For [Bmim][NO_3], the specific impulse at a 44% mixture of HAN oxidizer is 212 seconds, and for [Emim][$EtSO_4$] at a 41% mixture of HAN the specific impulse is 200 seconds. So, at the minimum oxidizer amount required for conversion of the predicted solid carbon to gaseous combustion products, the specific impulse of a mixture with an ionic liquid fuel is 15-20% below that of advanced monopropellant FLP-103, but at a much lower combustion temperature of roughly 1300 K in each case.

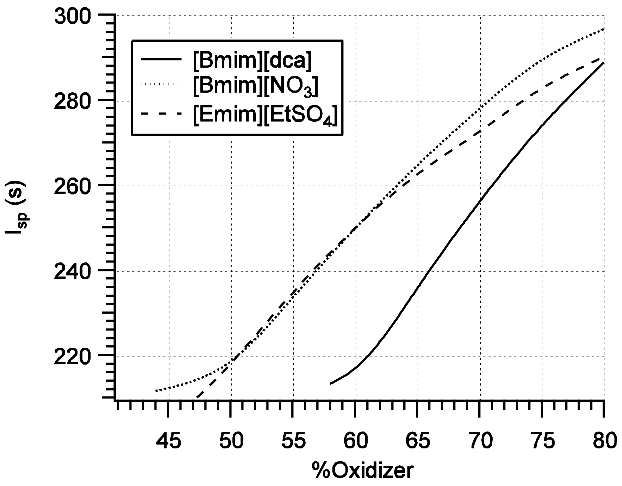

Figure 3.4. Specific Impulse of IL/HAN Binary Mixture Under Frozen Flow Assumption.

The greatest performance gain in the current generation of proposed ‘green’ monopropellants is their superior density to traditional hydrazine monopropellant. As mentioned, ADN-based propellant FLP-103 is predicted to have a density specific impulse 35% higher than that of hydrazine, as calculated by Eq. (7). The density of a mixture of liquids can be estimated by assuming volume is additive,

$$\frac{1}{\rho_n} = \sum\left(\frac{x_i}{\rho_i}\right) \tag{8}$$

Eq. (8) is a conservative estimate since it does not take into account intermolecular attraction between the constituent liquids. The density specific impulse can then be computed for a desired mixture ratio using Eq. (7). The results for each ionic liquid fuel as a function of percent HAN oxidizer are shown in Fig. 3.5. Again looking at the mixture ratio that produces a 1900 K combustion temperature, the density specific impulse is 358000, 362000, and 362000 [kg-s/m^3] for [Bmim][dca], [Bmim][dca], and [Emim][EtSO$_4$], respectively. This corresponds to an improvement in density specific impulse of 8-9% over FLP-103 advanced monopropellant. Considering the minimum oxidizer amount required to form completely gaseous products, the density specific impulse for [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$] binary mixtures is 287000, 284000, and 277000 [kg-s/m^3], a 13-18% improvement over hydrazine.

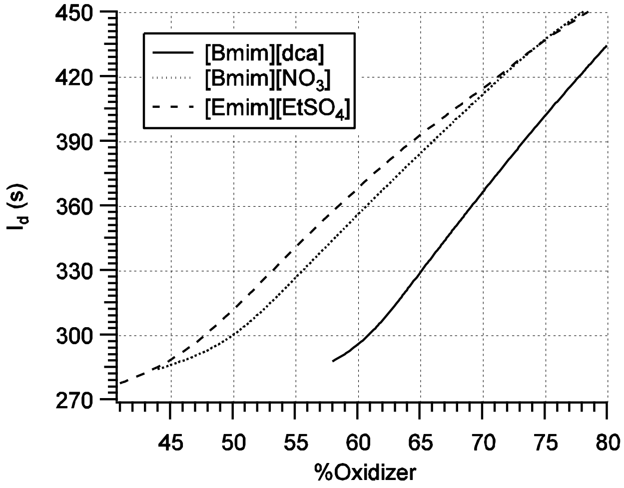

Figure 3.5. Density Specific Impulse of IL/HAN Binary Mixture.

4. ELECTROSPRAY PERFORMANCE ANALYSIS

The three candidate ionic liquids selected may exceed the performance of state-of-the-art monopropellants when considered as a fuel component in a binary mixture with HAN oxidizer. To fully assess the dual-mode capability of each ionic liquid, the electrospray performance must also be considered. Electrospray performance can be estimated by considering emission in the desired purely ionic regime (PIR) [2-4, 16]. For ionic liquids, PIR emission consists of both pure ions and clusters with ions attached to N number of neutral pairs. Typically, ionic liquids that achieve PIR emit mostly ions (N=0) and ions attached to a single neutral pair (N=1), although small amounts of the third ion state (N=2) are also detected [16]. The actual ratio of N=0 to N=1 states in an electrospray emission is determined experimentally. Furthermore, experiments have shown that this ratio cannot be controlled, but rather for a stable emission a single ratio is preferred and may be related to the thermal stability of the ion clusters [63]. Of the few ionic liquids that have achieved emission in the PIR regime, the ratio of pure ions (N=0) to ions in the first solvated state (N=1) generally lies between 0.5 and 0.7 [20]. The number of N=2 states or greater is typically less than 5% of the total emission current. Additionally, for a single ionic liquid, this ratio may also vary depending on the polarity of the extractor, but again the ratio falls within the same bounds.

Electrospray performance in the PIR regime can be estimated by the following methods. First, since the number of N=2 states is typically small, it is ignored. The specific impulse for an emission consisting of the first two ion states is given by [2-4]

$$I_{sp} = \frac{V_{e,N=0}R_A + V_{e,N=1}(1-R_A)}{g_0} \tag{9}$$

where R_A is the fraction of the flow that is pure ions. For an electrostatic device, the following relations hold [10]. The velocity of a charged particle accelerated through a net potential is given by

$$V_e = \sqrt{\frac{2e\Delta\phi}{m}} \tag{10}$$

The power supplied to the system is related to thrust and specific impulse by

$$\eta_{sys}P_{sys} = \frac{1}{2}FI_{sp}g_0 \tag{11}$$

Thrust is therefore inversely proportional to specific impulse for an electrostatic thruster regardless of the ionization method. The total mass flow rate required to produce the given thrust is calculated by

$$F = \dot{m}_{tot}I_{sp}g_0 \tag{12}$$

where the total mass flow rate is the sum of the mass flow from all electrospray emitters

$$\dot{m}_{tot} = N_{emit}\dot{m}_{emit} \tag{13}$$

The mass flow produced by a single emitter is related to the current produced by a single emitter by

$$\dot{m}_{emit} = \frac{I_{emit}m}{e} \tag{14}$$

4.1. ELECTROSPRAY SYSTEM PARAMETERS

The relations described in Eqs. (9)-(14) are used to estimate the electrospray propulsion performance of the three ionic liquid fuels analyzed in the previous sections. In terms of electrospray operation, two parameters govern the performance of the thruster: current per emitter and extraction voltage. For this analysis, these parameters are held constant in order to discern the effect of the propellant on total system performance and mass. Improvements in the current electrospray technology level will affect all propellants the same [2-4], provided it is not the physical properties of the propellant that drive the technology improvement; therefore, for this analysis it is prudent to use constant system parameters with respect to estimated current technology levels. The possibility of the physical properties affecting the current and extraction voltage will be discussed in a later section. Emitters being investigated for PIR electrospray devices can emit a current on the order of 1 μA per emitter [20]. Also, typical extraction voltages range from 1.5 to 2.5 kV [16, 20]. Therefore, in this analysis, a current of 1 μA per emitter and an extraction voltage of 2000 V will be used for all calculations. The final consideration made is with respect to the operation mode of the thruster. An alternating polarity (AC) mode has been selected because both positive and negative ions are extracted. This is most likely the mode in which future electrospray systems will operate because all of the propellant is extracted, it provides a net neutral beam, and it generally avoids the problem of electrochemical fouling. The result of AC operation is an averaged thrust and specific impulse of the emitted cations and anions. Finally, although the actual ratio of ions to clusters of ions is not constant with respect to polarity, for simplification and because these ratios are not known for new ionic liquids it is assumed to be the same for either cation or anion emission.

4.2. ELECTROSPRAY PERFORMANCE OF SINGLE IONIC LIQUIDS

The electrospray performance of the three ionic liquid fuels alone is computed through the aforementioned analysis techniques and conditions. Throughout the analysis, the ionic liquids [Emim][Im] and HAN have been shown for comparison. From Eqs. (9)-(14), it is seen that the electrospray performance when all system parameters are held constant is a function of the propellant mass alone. The cation and anion masses for each propellant used in this study are given in Table 4.1.

The specific impulse of each propellant is calculated for a net accelerating voltage of 2000 V and for ion fractions of 0.5 and 0.7. The results are shown in Table 4.2. From the table, it is clear that the specific impulse increases as ion fraction increases because more massive clusters are emitted in the first solvated state at lower ion fraction. The thrust per unit power is inversely proportional to specific impulse and increases as the ionic liquid molecular weight increases. The variation in specific impulse and thrust calculated between ion fractions of 0.5 and 0.7 varies by roughly 10 percent for all propellants. The remainder of this analysis will be restricted to the 0.5 ion fraction case. Based on current knowledge of ionic liquid electrosprays in the PIR regime, all subsequent calculations could therefore overestimate thrust and underestimate specific impulse by roughly 10 percent. This becomes important when considering ionic liquid propellants of similar molecular weight and could be a difference maker when choosing between ionic liquids such as [Bmim][dca] and [Bmim][NO_3]. But, as seen in Table 4.2, with a modest 13% difference in molecular weight, even if [Emim][$EtSO_4$] were to emit only at an ion fraction of 0.7, it would still have more thrust per unit power than the 0.5 ion fraction case for [Bmim][dca].

Table 4.1. Mass Data for Ionic Liquid Propellants.

Propellant	Chemical Formula		MW [g/mol]	
	Cation	Anion	Cation	Anion
[Bmim][dca]	$C_8H_{15}N_2$	C_2N_3	139	66
[Bmim][NO_3]	$C_8H_{15}N_2$	NO_3	139	62
[Emim][$EtSO_4$]	$C_6H_{11}N_2$	$C_2H_5SO_4$	111	125
[Emim][Im]	$C_6H_{11}N_2$	$C_2NF_6S_2O_4$	111	280
HAN	NH_3OH	NO_3	34	62

One of the major limitations on electrospray propulsion currently is the number of emitters required to produce thrust levels high enough to be useful in actual satellite operations. At a constant extraction voltage, and therefore a constant specific impulse, lighter ionic liquids will require a larger total current to produce thrust equal to that of heavier ionic liquids. Fig. 4.1 shows the number of emitters required to produce a given thrust level for each propellant. As expected, for a constant current per emitter, the heavier propellants require less emitters to produce a given thrust due to heavier species being extracted. At every thrust level, [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$] require 40 %, 41%, and 35% more emitters, respectively, than [Emim][Im]; however, the number of emitters required is 33%, 32%, and 35% less than HAN, respectively. If the required thrust is 10 mN, the sheer number of emitters required is enormous: 140000 for HAN and roughly 90000 for [Bmim][dca]. Reduction in the number of emitters will require an increase in the current processed per emitter, or a reduction in the net accelerating voltage. How this may be achieved and how it relates to the overall goals of dual-mode propellant design will be discussed further in a later section.

Perhaps the most important drawback in any electric propulsion device is the mass of the power processing unit. The power required to produce a given thrust can be calculated from Eq. (11). Since an extraction voltage has been specified, and the corresponding specific impulse, Eqs. (9) and (10), is therefore constant across every thrust level, the power required is then not a function of current per emitter. In other words, the emitter design does not affect the requirements for the power system provided the required extraction voltage is not affected greatly by emitter design or propellant selection. The required power as a function of thrust for each propellant is shown in Fig. 4.2. Fig. 4.2 appears similar to that of Fig. 4.1. [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$] require 36%, 38%, and 22% more power than [Emim][Im] at any given thrust level, respectively. In comparison to HAN, the same ILs require 31%, 30%, and 38% less power, respectively. The effect of utilizing higher molecular weight electrospray propellants is therefore twofold: higher molecular weight requires less emitters and lower power. It should also be noted that the required power in Fig. 4.2 is the power input required and does not take into account the efficiency of the power processing unit. The actual efficiency is likely to be less than 50%, which is the efficiency of hall thruster PPUs [64], and therefore the power required of the PPU will be at least double that of Fig. 4.2.

Table 4.2. Specific Impulse and Thrust per Unit Power.

	I_{sp} (s)		F/P (μN/W)	
Ion Fraction	0.5	0.7	0.5	0.7
[Bmim][dca]	5100	5700	40.0	35.8
[Bmim][NO_3]	5200	5800	39.2	35.2
[Emim][$EtSO_4$]	4600	5000	44.3	40.8
[Emim][Im]	3800	4200	53.7	48.5
HAN	7400	8200	27.6	24.9

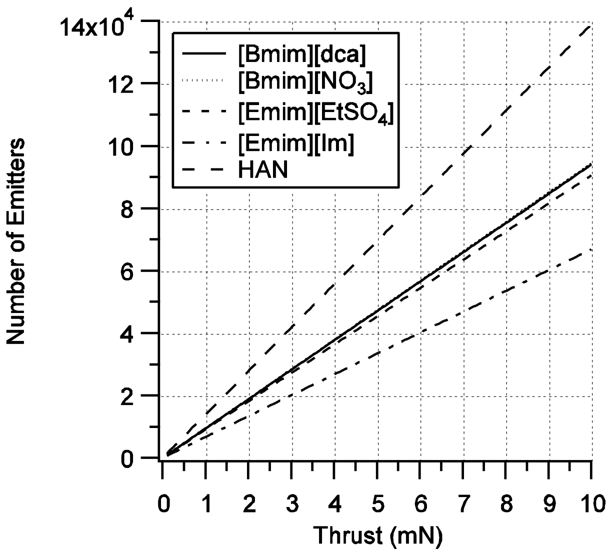

Figure 4.1. Number of Emitters as a Function of Thrust for IL Propellants for R_A=0.5.

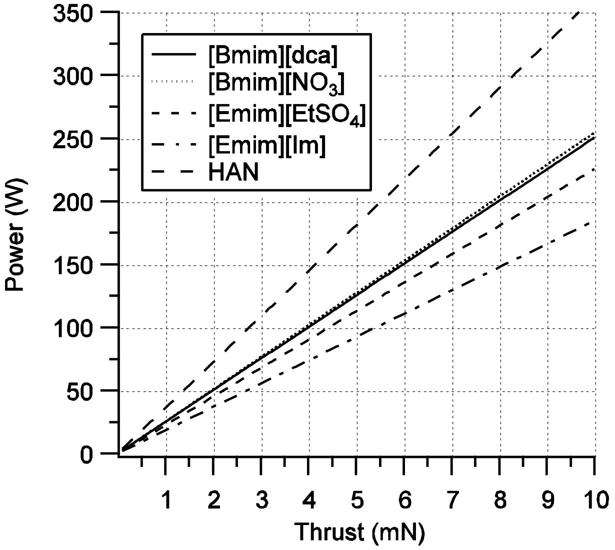

Figure 4.2. Power as a Function of Thrust for IL Propellants for R_A=0.5.

4.3. ELECTROSPRAY PERFORMANCE OF IONIC LIQUIDS IN BINARY MIXTURES

In the preceding sections, ionic liquid binary mixtures have been suggested as a potential route toward development of a true dual-mode propellant. It was shown that the chemical performance of these propellants may theoretically exceed that of some state-of-the-art monopropellants. The electrospray performance is more difficult to analyze because electrospray research on ionic liquids has focused on single ionic liquids. Mixtures of liquids have been studied as electrospray propellants, but most were simply solutions consisting of a salt and an electrically insulating solvent [16]. Garoz [46] studied a mixture of two ionic liquids, but did not study the composition of the droplets in the plume. A mixture of two ionic liquids may yield emissions more complicated than a single liquid since field emission of additional ion masses occurs. Extraction of pure ions would yield four possible emitted species: two cations and two anions. Extraction of higher solvated states may yield many more possible emitted species since the two salts essentially dissociate in solution and remain in chemical equilibrium, although the solution remains neutral. For example, the only *N=1* solvated state of the cation of [Bmim][dca] is $[\mathrm{Bmim}]^+$-[Bmim][dca]; however, extraction of the $[\mathrm{Bmim}]^+$ cation in an *N=1* solvated state from a mixture of HAN and [Bmim][dca] could yield $[\mathrm{Bmim}]^+$-[Bmim][dca], $[\mathrm{Bmim}]^+$-HAN, or even $[\mathrm{Bmim}]^+$-$[\mathrm{Bmim}]^+$-$[\mathrm{NO3}]^-$. Although this poses an interesting research question, analysis of binary mixtures as electrospray propellants for this study is restricted to the extraction of pure ions only. As shown in the preceding section, the comparisons between various propellants should still hold somewhat, but the calculated thrust will be much lower than what will be attained in actuality; therefore power and number of emitters will be higher.

The number of emitters required and power required to produce an electrospray thrust level of 5 mN is computed as a function of percent oxidizer in the binary monopropellant mixture. The same conditions of 1 μA current per emitter and 2000 V extraction voltage are also applied. The results are shown in Figs. 4.3 and 4.4. The same trends are shown as with the single ionic liquids: higher molecular weight mixtures require less emitters and less power to produce a given thrust. For emission of pure ions, [Emim][Im] requires 51000 emitters to produce 5 mN of thrust, and HAN requires 109000. From the chemical performance analysis, the binary mixture of fuels

[Bmim][dca], [Bmim][NO3], and [Emim][EtSO4] with HAN oxidizer reached a combustion temperature, and thus performance, roughly equal to ADN-based monopropellant FLP-103 at 69%, 61%, and 59% oxidizer. From Fig. 4.3, this equates to 18%, 21%, and 27% less emitters than required for pure HAN, but pure [Emim][Im] requires 43%, 40%, and 36% less emitters than the ionic liquid fuels, respectively. From Figure 4.4, the required power is 9.5%, 12%, and 16% lower than for pure HAN, but 75%, 70%, and 63% higher than [Emim][Im], respectively. From the chemical performance analysis, the minimum amount of oxidizer required for elimination of solid exhaust species is 58%, 44%, and 41% for each fuel, respectively. At these mixture ratios, the required number of emitters is now 24%, 27%, and 31% less than required for pure HAN. The power required is 13%, 16%, and 23% lower than for pure HAN.

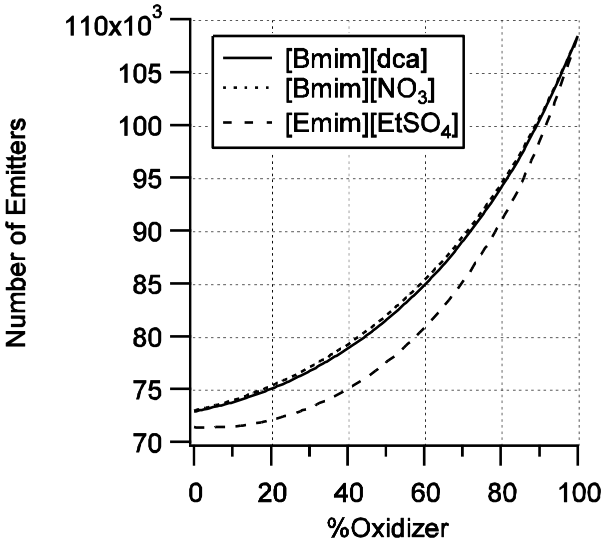

Figure 4.3. Number of Emitters Required to Produce 5 mN of Thrust as a Function of Percent HAN Oxidizer for IL Binary Mixtures.

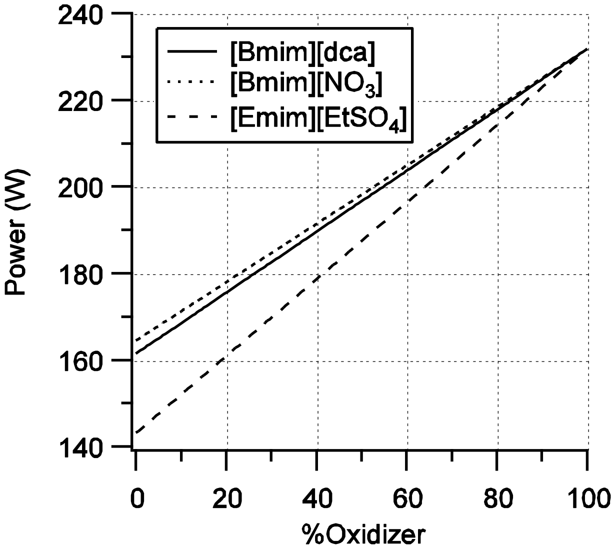

Figure 4.4. Required Power to Produce 5 mN of Thrust as a Function of Percent HAN Oxidizer for IL Binary Mixtures.

5. DISCUSSION

The results of the chemical performance analysis are promising for dual-mode propulsion since the performance of high-molecular weight ionic liquids as fuel components in a binary monopropellant mixture theoretically exceeds the performance of some state-of-the-art advanced monopropellants. The electrospray performance of these ionic liquids is promising and may yield higher performance than the current state of the art, but also may be limited by current technology levels. The results of the preceding sections are discussed and overall feasibility of imidazole-based ionic liquids as dual-mode propellants is assessed. Finally, using the results of this paper, trends are discussed and extrapolated into a selection guide for future dual-mode propellant development.

5.1. IMIDAZOLE-BASED IONIC LIQUIDS AS MONOPROPELLANTS

Although these ionic liquids have favorable physical properties toward electrospray propulsion, considering solely a thermal decomposition of the ionic liquids as monopropellants shows poor performance in terms of specific impulse, but slightly more acceptable performance in terms of density specific impulse as all of the ionic liquids in the study have greater density than hydrazine. However, this must be re-examined considering the fact that a shifting equilibrium assumption was employed due to the solid carbon present in the exhaust. Typically, shifting equilibrium specific impulse is an over-estimate of actual specific impulse. Sutton [10] suggests that this is a 1-4% over-estimate. If this is taken as 4%, the highest performing ionic liquid, [Bmim][NO_3], now falls 9% below hydrazine in terms of density specific impulse and 22% below hydrazine in terms of specific impulse. The solid carbon formation in the exhaust gases leads to the poor performance directly. Furthermore, solid exhaust particles are also objectionable in many spacecraft applications because they degrade functional surfaces such as lenses and solar cells [10], and could cause a cloud of orbital debris. And, for monopropellant thrusters, solid particles may agglomerate on the catalyst bed, rendering it unusable. The solid carbon formation in decomposition of the ionic liquids is a direct result of the lack of oxidizer present in the anion compared to the large organic alkyl substituted chains in the cation for the imidazole-based ionic liquids. While these high molecular weight organic chains are favorable for electrospray propulsion application, they are detrimental to the chemical aspect of a dual mode system. The highest performing ionic liquid is [Bmim][NO_3], which contains three oxygen atoms that form small amounts of water and carbon monoxide that lead to its higher performance. Despite having an additional oxygen atom, the large negative heat of formation of [Emim][$EtSO_4$] produces a lower overall energy release, and therefore leads to its poor performance. [Bmim][dca] performs slightly better than [Emim][$EtSO_4$] because it has a large, positive heat of formation despite containing zero oxidizing components. In order for a single imidazole-based ionic liquid to achieve even acceptable chemical performance, it must have enough oxygen to eliminate the solid carbon species in the exhaust. Ideally, in terms of performance, this type of ionic liquid will also contain a high number of nitrogen bonds, and therefore higher heat of formation [65].

5.2. BINARY MIXTURES OF IMIDAZOLE-BASED IONIC LIQUIDS AS MONOPROPELLANTS

Imidazole-based ionic liquids as fuel components in a binary mixture with HAN oxidizer may be a viable option for dual-mode monopropellants. The specific impulse computed via the shifting equilibrium assumption at a combustion temperature of roughly 1900 K for the ionic liquid monopropellant blends is 1-4% higher than that of FLP-103, and roughly equal to that of FLP-103 with a frozen flow assumption. This is a feat considering the predicted combustion temperature for FLP-103 is actually 2000 K. The reason for the improved performance of the ionic liquid monopropellant blends is the combustion products that are formed. At the conditions producing a 1900 K chamber temperature, the binary ionic liquid mixtures form incompletely oxidized species CO, H2, and N2, as shown in Fig. 3.3. By contrast, the ADN-based monopropellants such as FLP-103 have been specifically designed to provide a complete combustion with major products CO2, H2O, and N2 [12]. Examination of Eq. (5) shows that lower molecular weight exhaust products yield higher specific impulses. The lower molecular weight combustion products of the binary ionic liquid mixtures lead to higher specific impulse despite slightly lower combustion temperature compared to FLP-103. In terms of density specific impulse, the binary mixtures of ionic liquids have 8-9% greater than that of FLP-103 for the frozen flow assumption, which yielded roughly equal specific impulse. The main consideration here is the ingredients in each mixture. The density of the fuel component, methanol, in FLP-103 is 0.79 [g/cc] [59]. The ionic liquid fuels have a much higher density, making their use as fuel components in a monopropellant mixture attractive. Additionally, FLP-103 contains a large amount of water, which also lowers the density of the mixture.

These types of binary mixtures have been shown to be advantageous in terms of performance, but practically they must be chemically compatible and also be thermally stable and readily ignitable. As mentioned previously, mixtures of [Bmim][dca] with HAN have notably shown no visible reactivity, leading to the possibility that they may indeed be thermally stable at room temperature. However, this represents somewhat of an unknown presently as this has not been measured quantitatively. Literature suggests that mixtures of ammonium salts with dicyanamide anions may not be compatible [66-68]. [Bmim][NO3] or [Emim][EtSO4] may be compatible with HAN, but HAN may not be miscible in either liquid, requiring a third liquid solvent which may be undesirable. Furthermore, it is also unknown whether these mixtures will ignite either thermally or catalytically at reasonable temperatures (typically < 200^{o}C). These ignition methods represent the most common and reliable means of igniting a monopropellant and verification of this is a major milestone in any monopropellant development effort.

5.3. BINARY MIXTURES OF IMIDAZOLE-BASED IONIC LIQUIDS AS ELECTROSPRAY PROPELLANTS

In terms of electrospray performance, the ionic liquid fuels investigated show potential to be higher performing than the current state-of-the-art in electrospray propellants; however, they may present a challenge in terms of the current technology levels. The ionic liquid fuels investigated in this study have the potential to have higher performance, and also greater flexibility, than the current state-of-art electrospray propellant [Emim][Im]. This is a direct result from the lower molecular weight of the investigated ionic liquids compared to [Emim][Im]. However, low molecular weight may be a detriment to electrospray propulsion. Considering the number of emitters required to produce thrust levels typical of electric propulsion missions shows this effect. To produce 10 mN of thrust with emission of half $N=0$ ions and half $N=1$ ion clusters, [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$] require 90000-95000 emitters compared to 67000 for [Emim][Im]. If the current technology limit is taken as 13000 emitters per cm^2 [69], this equates to a total area of 7-7.3 cm^2 for the ionic liquid fuels compared to 5.2 cm^2 for [Emim][Im]. The 200 W SPT-35 Hall thruster has an area of 9.6 cm^2 and produces a comparable thrust of 11 mN [70]. Purely ionic emission of HAN at an ion fraction of 0.5 requires a total area of 10.8 cm^2 to produce 10 mN of thrust.

While the thruster geometry in terms of area is roughly comparable to a hall thruster producing roughly equal thrust, it is the power required that will ultimately be the strongest influence on design of electrospray systems. From Figs. 4.1 and 4.2, it is seen that lower molecular weight propellants require not only more emitters, but also more power to produce the same thrust as those with higher molecular weight. To produce 10 mN of thrust [Bmim][dca], [Bmim][NO_3] and [Emim][$EtSO_4$] require 225-250 W of power compared to 185 for [Emim][Im]. Even if the PPU for these thrusters is of equal efficiency to that of typical hall thrusters (~50%), the power required from the PPU is 450-500 W, more than double that required for a hall thruster that produces the same thrust and is of roughly the same size. Additionally, at the same conditions, pure HAN will require a 730 W power supply, nearly four times that of the BHT-200 hall thruster. The limitation here is the required extraction voltage, which as mentioned is typically in the range of 1.5-2.5 kV [16, 20]. The net accelerating voltage with just a single extraction grid is therefore 1.5-2.5 kV, which produces a specific impulse of roughly 5000 seconds. The specific impulse can be lowered by addition of a deceleration grid [71]. This requires additional complexity and power, but can reduce the number of emitters required since the thrust per emitter is increased. Improvements in electrospray technology will help reduce the required number of emitters to produce a given thrust level; however, the heavier ionic liquid propellants will always require less emitters and power, and therefore less massive electrospray systems as a whole.

One of the assumptions made in this analysis was that all propellants could emit at the same current per emitter. In reality, with current state-of-the-art emitter technology considered, this may not be entirely the case. In perhaps the most promising advancement in emitter technology for dual-mode purpose, Legge and Lozano [20] use a porous metal emitter geometry to produce PIR electrospray emission. What was most intriguing was that with this geometry, the same heavier, less electrically conductive ionic liquids that required a preheat of over 200^{o}C were able to emit in the purely ionic regime at room temperature. However, the current emitted was much less at the same extraction voltage in comparison to ligher molecular weight propellants such as [Emim][BF_4]. The higher molecular weight propellants will therefore require either higher extraction voltage or heating of the emitter to produce the same current per emitter as lighter, less viscous and more electrically conductive propellants. Each propellant, however, still required roughly 1.5 kV extraction voltage to begin emission. So, while the number of emitters could be reduced if the propellant is less viscous and also more electrically conductive, the power requirements should remain roughly the same even without heating the emitter. However, emitter technology, especially the novel porous metal emitter described here, is still very much in its infancy and these conclusions could eventually change.

5.4. BINARY MIXTURES OF IONIC LIQUIDS AS ELECTROSPRAY PROPELLANTS

The chemical performance of ionic liquids in binary mixtures is promising; however achieving good performance with current technology in the electrospray mode may present more of a challenge than for a single ionic liquid. The reason is the same as discussed above: the low molecular weight of the propellants. This issue is compounded by adding ionic oxidizers, such as HAN or ADN, which have a much lower molecular weight than even the ionic liquid fuels investigated in this paper. To achieve chemical performance equal to ADN-based FLP-103, the number of emitters required to produce 5 mN of thrust is 88000, 82000, and 79000 emitters when using [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$] as fuels, respectively, but assuming only ions are emitted. Therefore, to achieve equal chemical and electrospray performance, [Emim][$EtSO_4$] requires 10% less emitters than [Bmim][dca], thereby saving roughly 10% mass in terms of the emitter hardware. Additionally, considering the minimum amount of oxidizer to achieve no solid carbon in the theoretical exhaust species, [Emim][$EtSO_4$] will require nearly 15% less emitters than [Bmim][dca]. In terms of power requirements, at the condition where chemical performance is greater than FLP-103, [Emim][$EtSO_4$] requires 7% less power than [Bmim][dca]. At the minimum oxidizer amount, [Emim][$EtSO_4$] requires 15% less power than [Bmim][dca]. It is therefore more ideal for dual-mode propellants to use fuels with high molecular weight, but that have a higher oxygen balance, as equal performance may be obtained in both modes, but with a reduction in electrospray hardware.

5.5. CONSIDERATIONS FOR DUAL-MODE PROPELLANT DESIGN

Based on the results presented in this paper there are two logical methods to achieving a workable dual-mode propellant: a single, oxygen-balanced, task specific ionic liquid or a mixture of two or more ionic liquids. While this may seem to not depart from conventional wisdom in energetic ionic liquid monopropellant design, when viewed as a dual-mode propellant the requirements will have to change somewhat.

In terms of pure performance, the ultimate in dual-mode propellants may be a single liquid which would provide enough oxidizer in the anion to combust to gaseous products CO, H_2, and N_2, while still retaining reasonable electrospray properties. This would not only provide good chemical performance, but inherently this would also be a high-molecular weight propellant assuming $[\text{Emim}]^+$ or higher cations were used. This idea of an oxygen-balanced ionic liquid is not new, as attempts have been made to synthesize such a liquid for energetic use [72, 73]. The ionic liquids in [72] were based on lanthanide nitrate complex anions and either triazole- or tetrazole-based cations. The ionic liquids in [73] were imidazole-based. Many of the liquids in these efforts were not thermally stable, but a few of these ionic liquids were reportedly stable at room temperature, for example 1-ethyl-3-methylimidazolium tetranitratoaluminate ($C_6H_{11}N_6AlO_{12}$). These are not ideal spacecraft monopropellants as their combustion forms a significant amount of solid products, such as Al_2O_3, which are objectionable in many spacecraft applications, as mentioned previously [10]. Furthermore, it is unknown to this point whether these propellants have the electrochemical properties required for electrospray propulsion. However, based on trends reported for many imidazole-based ionic liquids these can be reasonably inferred qualitatively and commented upon. In general, ionic liquids with large, bulky anions have both lower electrical conductivity and lower surface tension [5, 6]. Additionally, increasing the size of the cation for imidazole-based liquids always decreases the surface tension and electrical conductivity. This is in an almost direct contradiction to what is typically preferred in energetic ionic liquid design. Making use of an increased alkyl chain size in the cation or increased number of N-N bonds in the anion, therefore raising the heat of formation of the liquid combined with the requirement for oxygen balance is actually detrimental to the minimum performance requirements to achieve PIR for electrospray propulsion: high surface tension and high electrical conductivity.

Perhaps the most important consideration to be made in the early stages of dual-mode propellant design is actually the thermal stability of ionic liquids. The high thermal stability of ionic liquids compared to more traditional energetic materials is usually viewed as a benefit rather than a strict requirement. For dual-mode propellants, this will be a requirement. The reason is that larger molecular weight propellants will inevitably require the emitter to be preheated due to their inherently low surface tension and electrical conductivity. As mentioned, in some cases this has been found to be greater than 200°C, which actually is above or near the decomposition temperature of many energetic ionic liquids that have been synthesized [74]. As mentioned, with porous metal emitters this could be avoided, but at the cost of lower current. If the emitter preheat temperature is limited due to the thermal stability consideration when spraying an energetic ionic liquid rather than a much more stable fluorinated ionic liquid, then either the extraction voltage or the number of emitters will have to be increased to compensate. Higher power requirements compared to state-of-the-art electrospray propellants may therefore be inevitable for a dual-mode monopropellant/electrospray system if performance near the state-of-the art in each mode individually is desired. For future design considerations of dual-mode monopropellants, the effect of adding oxidizing species to the anion on the surface tension and electrical conductivity of ionic liquids must be quantified, and elimination of metallic elements in the anion must be achieved.

In this paper, the method of combining a fuel-rich ionic liquid with an ionic oxidizer such as HAN or ADN as means of obtaining a workable dual-mode propellant is presented. This may be a much simpler method than developing a task-specific ionic liquid, but may ultimately have lower performance than the ideal oxygen balanced ionic liquid. It was shown that in order to obtain performance closer to state-of-the-art more power and emitters will be necessary given the low molecular weight of the oxidizer. The main challenge for this method will be the chemical compatibility and also the miscibility of the oxidizer in the ionic liquid fuel. To be even usable in the electrospray mode, it is absolutely paramount that no portion of the mixture be volatile, which departs from conventional ‘green’ monopropellants which make use of both water and a volatile fuel. While it may be possible that the addition of water to a certain ionic liquid system may show azeotropic behavior, this is difficult to assess and even in the best case scenario will be detrimental to electrospray performance as a whole. When selecting candidate ionic liquid fuels, liquids that have a higher oxygen balance will be more promising when considering the dual-mode system as a whole. The main reason, as discussed is the fact that a smaller amount of the lower molecular weight oxidizer is required. However, an interesting point can be made when considering the minimum amount of oxidizer required. Although the chemical performance drops, mass can be saved on the electrospray system and therefore the potential for increased flexibility in the design choices exists.

6. CONCLUSIONS

Imidazole based ionic liquids have been examined as potential candidates for dual-mode chemical monopropellant and electrospray propulsion. Physical properties required of ionic liquids for dual-mode spacecraft propulsion are high density, low melting temperature, high electrical conductivity, high surface tension, and high molecular weight. These properties should be comparable to current state-of-the-art propellants hydrazine and [Emim][Im] for the chemical and electrical modes, respectively. Three generic, sample ionic liquids were identified that exceed or are close to meeting the physical property criteria: [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$].

Theoretical chemical performance was calculated for these ionic liquids using the NASA CEA computer code and performance equations. Considering these ionic liquids as monopropellants shows that they do not perform well compared to hydrazine and will be essentially unusable due to the large amounts of solid carbon predicted in the exhaust species. Considering the ionic liquids as fuel components in a binary monopropellant mixture with 60-70% HAN oxidizer shows performance exceeding that of ADN-based monopropellants. Ionic liquid fuel components with more oxidizing elements in the anion require less additional HAN oxidizer to form gaseous CO, and thus achieve an acceptable level of performance.

Examination of the electrospray performance of these ionic liquids shows that they may compete with current state-of-the-art propellants with improvements in technology. High molecular weight propellants reduce the number of required electrospray emitters, while also requiring higher power. The addition of a lower molecular weight oxidizer to an imidazole-based ionic liquid fuel increases the number of emitters required, but is necessary to obtain good chemical performance. Ionic liquid fuel components with oxidizing components in the anion require less additional oxidizer to achieve similar chemical performance, thereby reducing the number of required emitters for electrospray propulsion. By extension, in terms of pure performance oxygen-balanced ionic liquids may be the ultimate in dual mode propulsion as they have the required oxidizer to combust into complete products, while most likely retaining high molecular weight favorable to electrospray propulsion.

Two methods typical of design of energetic ionic liquids for monopropellant applications were discussed: design of a task-specific, oxygen balanced ionic liquid or design of a mixture of multiple ionic liquids. In terms of performance, a task-specific ionic liquid will likely outperform any mixture in a dual-mode system. However, this may be a much more difficult task due to the inherently low surface tension and electrical conductivity, which may require an electrospray emitter to be heated to near or above the propellant decomposition temperature to even achieve minimum functionality. Overall, for dual-mode propellants, in order to obtain even minimum chemical performance, the electrospray propulsion system will require more power compared to a state-of-the-art electrospray propellant.

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PAPER

II. Decomposition of Monopropellant Blends of HAN and Imidazole-based Ionic Liquid Fuels

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ABSTRACT

Potential dual-mode monopropellant/electrospray capable mixtures of hydroxyl ammonium nitrate with ionic liquid fuels [Bmim][NO_3] and [Emim][$EtSO_4$] are synthesized and tested for catalytic decomposition 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. This was found to be direct result of the sample holder 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^{o}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^{o}C yielded a pressure rise rate 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^{o}C preheat temperature, yielding a pressure rise rate 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 supported rhenium catalyst.

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

1. 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 paper evaluates the potential of these mixtures to be decomposed readily via catalyst 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. 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. Binary or ternary mixtures including the energetic salts hydroxyl ammonium nitrate (HAN), ammonium dinitramide (ADN), or 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 flight 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 decomposed by some 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 decomposition by the commercially manufactured iridium-based catalyst Shell 405. For optimum performance, the catalyst bed is typically heated up to 200^{o}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^{o}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. This is done by studying the decomposition of propellants injected onto preheated catalyst material. 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.

2. PROPELLANTS AND CATALYSTS

The focus of this study is experimental determination of the catalytic decomposition rates of three ionic liquids and their potential use as a fuel component in a binary, or ternary, mixture with hydroxyl ammonium nitrate (HAN) oxidizer. 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][NO_3]), and 1-ethyl-3-methylimidazolium ethyl sulfate ([Emim][$EtSO_4$]). 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 HAN as the oxidizer component could theoretically achieve monopropellant performance in the range near 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 in vacuum.

2.1. 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][NO_3] (≥ 95% Sigma Aldrich), [Emim][$EtSO_4$] (≥ 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 suggested 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 2.1. 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]. For safety reasons, only one gram of each propellant was synthesized initially and utilized in this study. 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 2.1. 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, from 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][NO_3] alone is a clear liquid, and [Emim][$EtSO_4$] 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 questions remain that will be discussed in a later section.

Table 2.1. Mass Percent of Fuel and Oxidizer in Binary HAN-IL Mixtures

Propellant	IL Fuel	%Fuel	%Oxidizer
A	[Bmim][dca]	31	69
B	[Bmim][NO_3]	39	61
C	[Emim][$EtSO_4$]	41	59

2.2. 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 2.2 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 was 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 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 catalytic decomposition, ruthenium is not included initially to limit the cost of this study.

Table 2.2. 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

3. 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 from on-board power systems. Our 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 was selected because it provides the most robust 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, nor does it determine if the decomposition results in self-sustained combustion. The goal of these experiments is to determine if the novel propellants can be decomposed readily and which catalyst materials are most effective in doing so. This setup provides means of 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 and time consuming thruster testing.

3.1. EXPERIMENTAL SETUP

The experimental setup is a micro-reactor for study of thermal and catalytic decomposition 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 total internal volume of the reactor is 440 Ml. The bottom plate has a 1” by 1” square machined to a depth of 1/4” to accommodate the thermal and 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. 3.1 and 3.2.

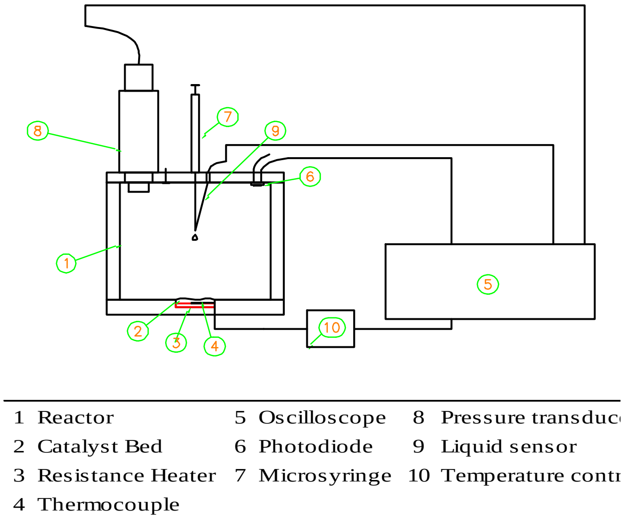
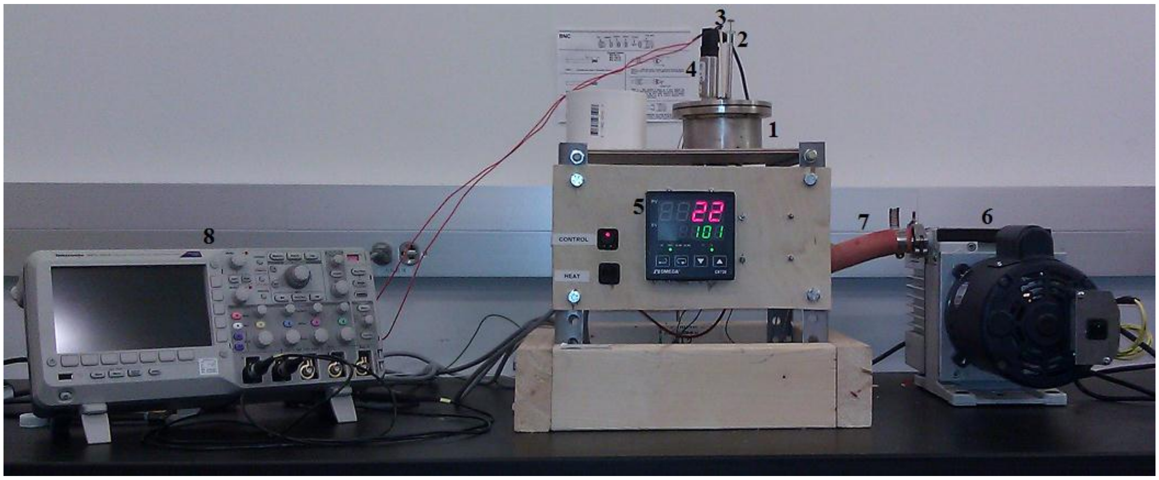


Figure 3.1. Instrumentation Schematic.



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

Figure 3.2. 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. 3.3. 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.

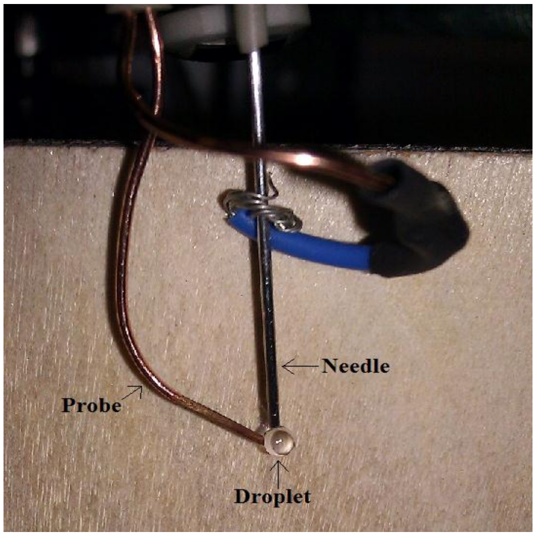


Figure 3.3. Liquid Probe.

3.2. UNCERTAINTY QUANTIFICATION

Uncertainty in the pressure measurements analyzed hereafter can be traced to two instruments: the pressure transducer and the microsyringe. According to the manufacturer’s calibration data, the total uncertainty in the pressure measured by the transducer is ±3 mbar. In terms of the microsyringe, the actual volume injected may vary from the intended value due to the fact that measurements are read directly from physical markings on the syringe. The smallest graduation is 1 µl, and it is therefore reasonable to assume a worst case scenario of ± 1 µL. This uncertainty is important in terms of the theoretical pressure rise calculations, since an exact volume is assumed. This translates into an error of ±3 mbar in the theoretical calculations. The effect of both uncertainties on the conclusions will be discussed in a later section. Additional uncertainties concerning the repeatability of measurements exist in terms of the geometry of the reactor and the inherently heterogeneous nature of the catalyst particles. This is an integral part of the analysis and will be discussed in detail in a later section.

4. 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 underwent 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 unsupported catalyst material.

4.1. THEORETICAL PRESSURE RISE CALCULATIONS

One of the important parameters when considering the decomposition of monopropellants in reference to ignitability 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 4.1. 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),

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

Table 4.1. 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

The results of the computation outlined by Eqs. (1)-(6) is given in Fig. 4.1 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.

4.2. 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 peroxide droplets on 200 mg silver catalyst. Room temperature was measured as 21^{o}C prior to conducting the experiments. Results are shown in Fig. 4.2. Decomposition begins within 0.1 seconds and proceeds at a rapid rate at a pressure rise of 16 mbar/s. After the initial rapid decomposition event, the pressure is 25% of the maximum, as calculated from Fig. 4.1. 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. 4.1, the calculated theoretical maximum pressure rise is 60 mbar for a 100 Ml droplet of hydrogen peroxide solution. After 20 seconds, the pressure in the reactor is therefore 72% of the maximum and is continuing to rise.

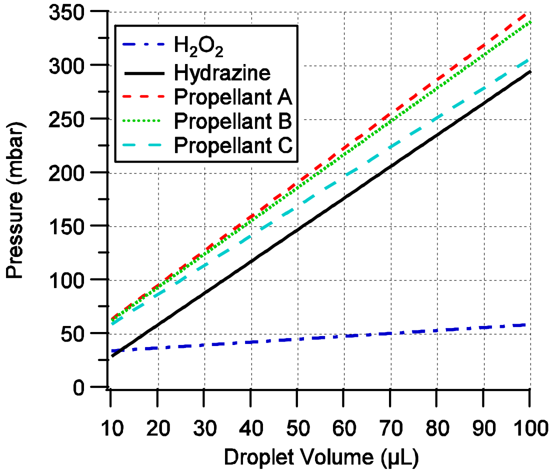


Figure 4.1. Theoretical Pressure Rise vs. Droplet Volume.

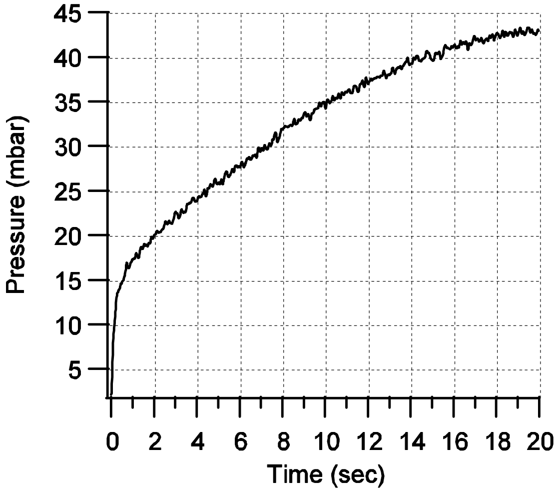


Figure 4.2. Hydrogen Peroxide Decomposition on Silver Catalyst.

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. 4.3. 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. 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. 4.1, the calculated theoretical pressure rise for a 100 Ml 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.

4.3. HYDRAZINE

For comparative purposes, micro reactor 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^{o}C, 50^{o}C, and 21^{o}C are shown in Fig. 4.4. Fig. 4.4a shows that a 100^{o}C preheat on iridium produces a significant decomposition 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. 4.1, 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 4.4b 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 Fig. 4.4a, 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. 4.4c 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.

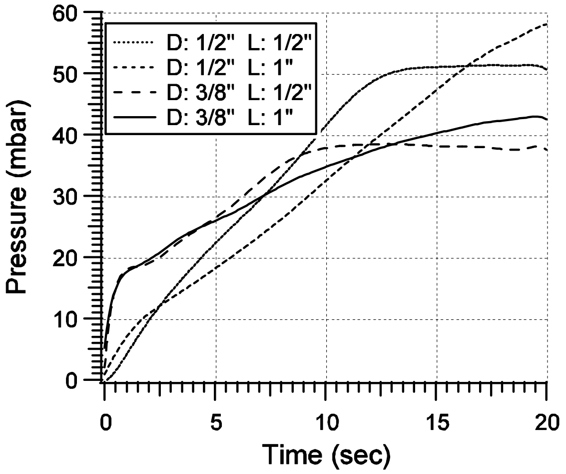
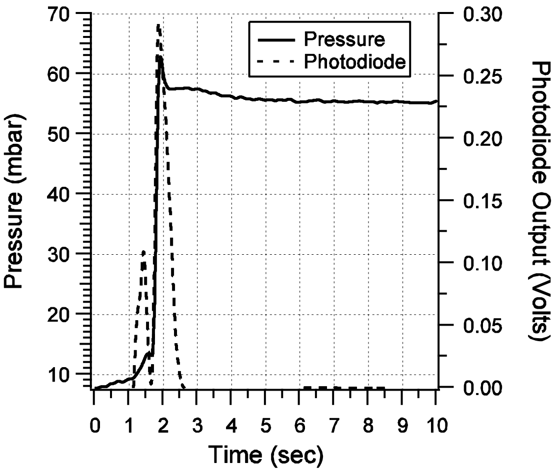
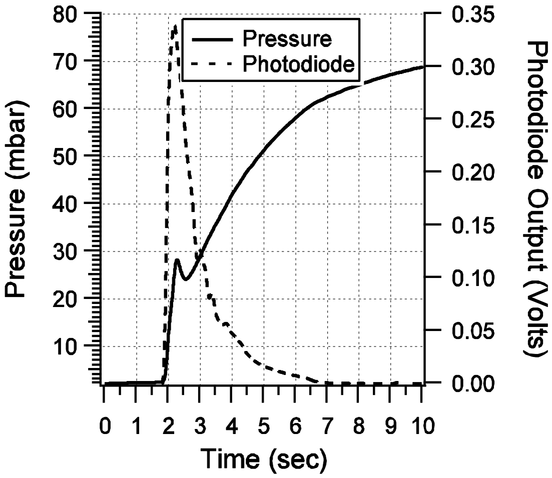


Figure 4.3. Effect of Sample Holder Geometry on Test Results.

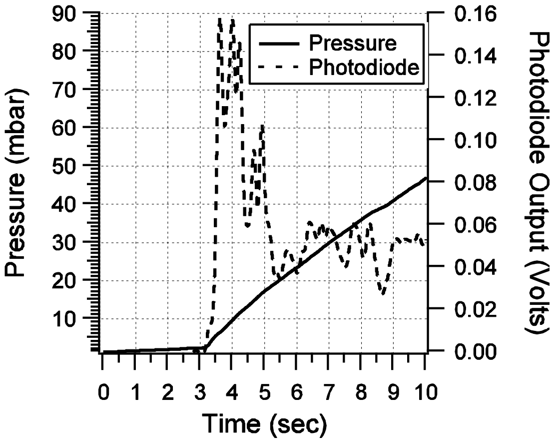


(a) 100°C



(b) 50°C

Figure 4.4. Hydrazine on Iridium Catalyst at Preheated Temperature.



(c) 21°C

Figure 4.4. Hydrazine on Iridium Catalyst at Preheated Temperature (cont.).

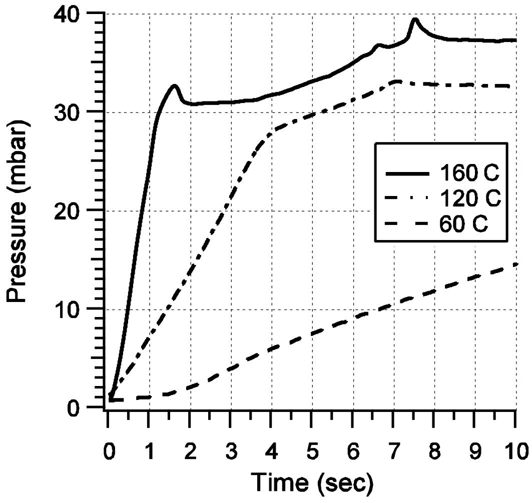
4.4. SPOT PLATE TESTING OF NOVEL IL-HAN PROPELLANTS

Spot plate testing under atmospheric conditions is conducted to qualitatively describe the decomposition event prior to reactor testing, and narrow the range of preheat temperatures of interest. For each test, a single droplet (~10 Ml) 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. 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^{o}C. Using rhenium catalyst at 80^{o}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^{o}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 second interval. At 100^{o}C, the same trend was observed, but the decomposition event lasted much longer. At temperatures below 100^{o}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^{o}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^{o}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^{o}C. Adding iridium or rhenium catalyst at 180^{o}C yielded vigorous bubbling initially, which quickly subsided and left a yellowish residue. Tungsten yielded no activity whatsoever up to 200^{o}C.

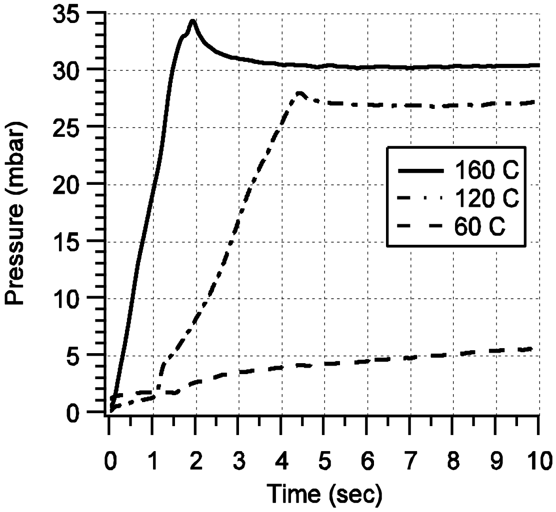
4.5. MICRO REACTOR TESTING OF NOVEL HAN-IL PROPELLANTS

Experiments are conducted with the micro reactor setup described previously in order to qualitatively determine if the novel propellants can be rapidly decomposed by means typically used in spacecraft monopropellant thrusters, especially in comparison to monopropellant hydrazine. Testing began at 60^{o}C preheat on rhenium catalyst material since both propellants showed almost instantaneous decomposition at 60^{o}C on rhenium during spot plate testing. Fig. 4.5 shows the pressure during decomposition of a 30 Ml droplet onto 50 mg of rhenium catalyst preheated to 60^{o}C, 120^{o}C, and 160^{o}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. 4.1. 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.



(a) Propellant B

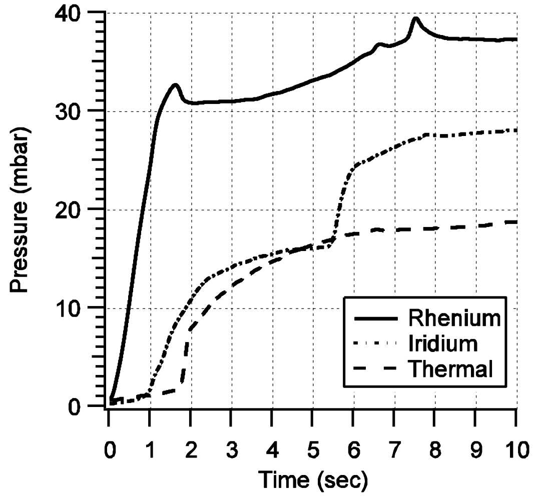
Figure 4.5. Decomposition of Novel Propellant on Rhenium Catalyst.



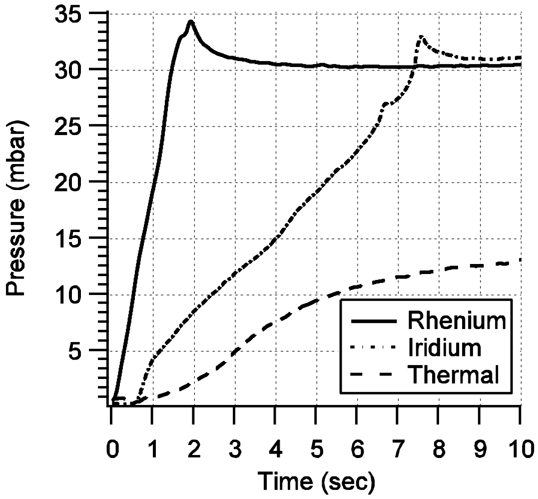
(b) Propellant C

Figure 4.5. Decomposition of Novel Propellant on Rhenium Catalyst (cont.).

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. 4.6. Fig. 4.6a shows the decomposition of Propellant B at 160°C. The rhenium case is therefore the same as shown in Fig. 4.5a. 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. 4.6b, 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. 4.1 is only 26% of the calculated theoretical maximum.



(a) Propellant B



(b) Propellant C

Figure 4.6b. Catalytic Decomposition at 160°C of Novel Propellant.

5. 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 potential of the novel propellants to ignite readily, 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.

5.1. 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. Additionally, this causes the position of the reaction centers to become more heterogeneous, thus leading to the inconsistencies in the slope. 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 as quickly 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.

5.2. HYDRAZINE

The experiments conducted with hydrazine are mainly used as a comparison tool with the novel monopropellants. Figure 4.4a 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. 4.4a 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. 4.4b and 4.4c show much less rapid activity, therefore an ignition similar to the Eloirdi [31] results is not attained at room temperature. This is due to the active surface area of the supported catalyst being much 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 desirable catalytic activity. This makes sense because although less propellant is absorbed by the lower surface area of pure iridium, it should still produce a similar 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.

5.3. NOVEL HAN-IL PROPELLANTS

The observations made during spot plate testing, while entirely qualitative, serve as clear evidence of the reactivity of these propellants. Both ionic liquid fuels alone do not show significant decomposition activity up to 200°C. Furthermore, the HAN solution did not show any significant decomposition below 100°C. When the ionic liquid fuels are combined with HAN oxidizer in the manner described in this paper, decomposition occurs in a rapid manner at temperatures of 80°C. Because this observation was so stark in comparison to each constituent fuel and oxidizer alone, qualitative comparison was included to show that these propellant blends are sufficiently more reactive than their constituent ingredients.

Results from the experiments show that propellants with HAN oxidizer and either [Bmim][NO3] or [Emim][EtSO4] 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 $50^{o}C$ is 70 mbar/s, compared to just 25 mbar/s for Propellant B on rhenium at $160^{o}C$. Additionally, hydrazine on iridium at $50^{o}C$ and both IL-HAN propellants on rhenium at $160^{o}C$ achieve 25-28% of the calculated theoretical maximum pressure after the main decomposition event. Clearly, hydrazine when paired with iridium requires a much lower preheat temperature to achieve good ignition performance compared to the novel propellants. Higher preheat temperatures should continue to increase the pressure slope and push the amount of gaseous products generated closer to 100% with the same amount of catalyst particles; 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 $200^{o}C$ just to start the engine [16]. 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 catalytic decomposition 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 investigated 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.

6. 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 decomposition. 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 or at lower temperature.

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^{o}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 clear evidence that they may be decomposed readily via catalyst, leading to the assertion that they may potentially be readily ignited in a monopropellant thruster. 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. Decomposition of both propellants on rhenium at 160^{o}C yields pressure slopes lower than hydrazine at 50^{o}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 for both monopropellant and electrospray propulsion.

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SECTION

2. CONCLUSIONS

Imidazole based ionic liquids have been examined as potential candidates for dual-mode chemical monopropellant and electrospray propulsion. Physical properties required of ionic liquids for dual-mode spacecraft propulsion are high density, low melting temperature, high electrical conductivity, high surface tension, and high molecular weight. These properties should be comparable to current state-of-the-art propellants hydrazine and [Emim][Im] for the chemical and electrical modes, respectively. Three generic, sample ionic liquids were identified that exceed or are close to meeting the physical property criteria: [Bmim][dca], [Bmim][NO_3], and [Emim][$EtSO_4$].

Theoretical chemical performance was calculated for these ionic liquids using the NASA CEA computer code and performance equations. Considering these ionic liquids as monopropellants shows that they do not perform well compared to hydrazine and will be essentially unusable due to the large amounts of solid carbon predicted in the exhaust species. Considering the ionic liquids as fuel components in a binary monopropellant mixture with 60-70% HAN oxidizer shows performance exceeding that of ADN-based monopropellants. Ionic liquid fuel components with more oxidizing elements in the anion require less additional HAN oxidizer to form gaseous CO, and thus achieve an acceptable level of performance.

Examination of the electrospray performance of these ionic liquids shows that they may compete with current state-of-the-art propellants with improvements in technology. High molecular weight propellants reduce the number of required electrospray emitters, while also requiring higher power. The addition of a lower molecular weight oxidizer to an imidazole-based ionic liquid fuel increases the number of emitters required, but is necessary to obtain good chemical performance. Ionic liquid fuel components with oxidizing components in the anion require less additional oxidizer to achieve similar chemical performance, thereby reducing the number of required emitters for electrospray propulsion. By extension, in terms of pure performance oxygen-balanced ionic liquids may be the ultimate in dual mode propulsion as they have the required oxidizer to combust into complete products, while most likely retaining high molecular weight favorable to electrospray propulsion.

Novel propellants based on HAN oxidizer combined with ionic liquid fuels [Bmim][NO_3] and [Emim][$EtSO_4$] were then synthesized and tested for catalytic decomposition. 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 or at lower temperature.

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VITA

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