Application of Ionic Liquids to Space Propulsion

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1. Introduction

1.1 Propellants and ignition systems

A propellant is an energetic compound or a mixture in gas, liquid or solid state, which undergoes a rapid and predictable combustion resulting in a large volume of hot gas used to thrust a projectile (rocket, missile, launcher). Liquid propellants are subdivided into monopropellants and bipropellants. Monopropellants are liquids which decompose in the absence of external oxygen. They have comparatively low energy content and display lower performance by comparison with bipropellants. They need an ignition system and are used in small missiles and engines which require low thrust. Hydrazine is currently the most widely used monopropellant for orbit and attitude control of satellites or for roll control of launcher (Schmidt, 2001). Bipropellants consist of two components, a fuel (or reducer) and an oxidizer, which are stored in separate tanks and are injected simultaneously into a combustion chamber where they come into contact and burn. They display higher energetic content and higher thrust and are used on the most demanding missions. Current fuels include hydrogen, methanol, kerosene, hydrazine, monomethylhydrazine (MMH), unsymmetrical dimethylhydrazine (UDMH). Common oxidizers are nitric acid and dinitrogen tetroxide (NTO).

The ignition systems can be sorted into three types:

- Spontaneous reaction between oxidizer and fuel as it is the case for the MMH-NTO mixture ($CH_3N_2H_3$ - N_2O_4); such mixtures are called *hypergolic*. The reaction can be restarted several times and enable launcher upper stage to reach precisely the expected satellite orbit.
- Energy supply using thermal, electrical or photochemical procedures. It is applied to non-hypergolic bipropellants (i.e. hydrogen–oxygen) and to monopropellants. The main drawback is the ability to enable restarts which depend on the ignition mode.
- Catalytic ignition of bipropellant or catalytic decomposition of monopropellant, using an adequate catalyst. This is a very simple and convenient ignition system, which enables numerous restarts. The major hurdle is the long term stability of the catalyst which suffers very severe conditions: high pressure and temperature increases in very short time.

1.2 Propulsion parameters and propulsion types

The critical parameters of space propulsion engines are:

- The thrust F (unit N) given by the 2nd Newton's law: $F = (dm/dt).V_e$, where dm/dt (unit kg s^{-1}) is the mass flow rate of the exhaust propellant and V_e (unit m s^{-1}), the average velocity of the exhaust gas;
- The specific impulse I_{sp} (unit s) and the volumetric impulse I_{vol} (unit s kg L^{-1}) which characterize the propellant, and are defined by the relation: $I_{sp} = V_e/g = F/(dm/dt).g$ (g is the gravitational constant, 9.807 m s^{-2}) and $I_{vol} = I_{sp}*\rho$ where ρ is the density of the propellant;
- The efficiency η given in percentage and corresponding to the ratio (power associated with propulsive force)/(power input); it depends on the propulsion type and system.

From the kinetic theory of gases, the exit velocity is proportional to $(T_c/M)^{1/2}$ where M is the average molecular weight of gas mixture (in kg mol^{-1}) and T_c the gas temperature in the chamber (in K). Therefore, to increase the thrust, we have to increase the chamber temperature and/or decrease the average molar weight of the exit gas. This can be obtained using more energetic propellant, adding electric energy through heating elements or using an electric field and charged particles.

The simplest and cheapest propulsion system is the *cold gas system* where a gas under pressure is released through a remote-controlled valve (Fig. 1). Chemical propulsion uses (i) *liquid monopropellant system* with catalytic decomposition of an energetic liquid (Fig. 1); (ii) *bipropellant system* that provides higher performances for launchers; and (iii) *solid propellant system* best represented by the huge boosters of launchers, that contain mainly ammonium perchlorate (Fig. 2). For electric propulsion systems, three families have been developed, depending on the force used: (i) Coulomb force for *electrostatic system,* i.e. an electric field is applied to accelerate ions or charged droplets, (ii) electromagnetic field to generate plasma for *electrothermal systems*, and (iii) Lorentz force for *electromagnetic systems*. Concerning micropropulsion applications, the first family was developed as ion electrospray (Lozano, 2011). The characteristics of the propulsion types are compared in Table 1.

	Cold gas	Chemical monopropellant	Chemical bipropellant	Electric Ion electrospray
Isp	Low (60 s)	Medium (200 s)	Medium (320 s)	High (5000 s)
Miniaturization	Yes	Yes	No	Yes
Safe materials	Yes	No	No	Yes
Power needed	No	No	No	Yes
Simplicity	Yes	No	No	Yes

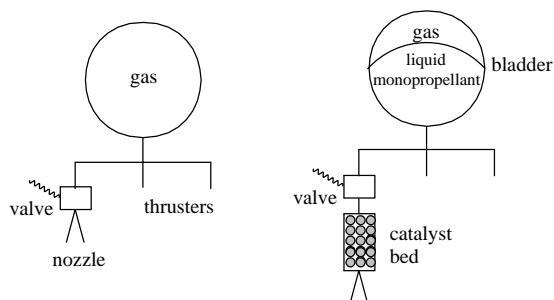Table 1. Comparison of the propulsion types; adapted from (Lozano, 2011).

Fig. 1. Cold gas engine and monopropellant engine, from (Batonneau et al., 2008).
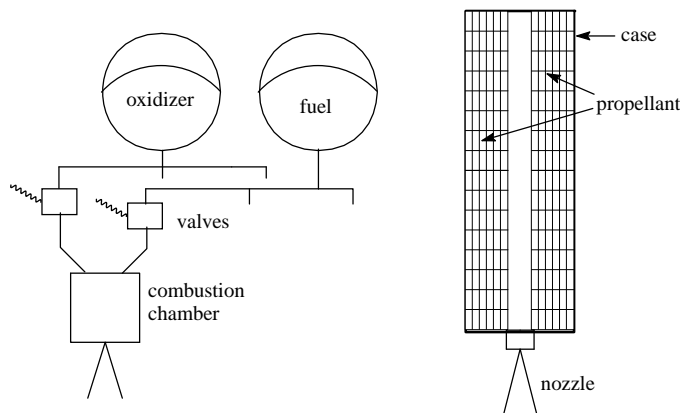
Fig. 2. Bipropellant system and solid motor, from (Batonneau et al., 2008).

1.3 Oxygen balance

When using propellants containing an oxidizer and a fuel in the same chemical (as in NH_4NO_3) or in two independent species, the best performances are obtained when the oxidizer to fuel ratio is close to the value corresponding to a complete combustion giving nitrogen, steam, carbon dioxide and the most stable metal oxides (if metals are present) as sole products. In this case, the oxygen balance is zero. The oxygen balance corresponds to the mass percentage of released or consumed oxygen by the theoretical decomposition of the oxidizer or the fuel. Oxidizers present a positive oxygen balance whereas fuels display negative oxygen balance. Recently, it was proposed to take the formation of CO instead of CO_2 at high temperatures, into account to calculate the oxygen balance (Jones et al., 2006). In the case of monopropellants composed of single energetic species, the oxygen balance is an important parameter linked to the performance.

1.4 Replacement of hydrazine and hydrazine derivatives: toward "green propellants"

Liquid hydrazine as monopropellant and its derivatives (MMH and UDMH) for bipropellant systems have been the most used propellants for space propulsion since the fifties. But they display several drawbacks that lead to increasing handling and storage costs: (i) high crystallization point (1.4 °C for hydrazine); (ii) poisonous and carcinogenic properties; (iii) high vapor pressure at room temperature; and (iv) sensitivity to adiabatic compression (risk of detonation). These drawbacks have prompted, in the last years, the search for possible "green monopropellants" which would be cheaper, and less toxic. Different substitutes have been proposed and can be sorted into three main types: energetic ionic liquids, hydrogen peroxide, and nitrous oxide (Batonneau et al., 2008).

1.5 Previous review papers

Energetic ionic liquids have been previously studied in the late seventies as LGP (Liquid Gun Propellants), but due to development problems, they have been finally discarded for this peculiar application (Klingenberg et al., 1997). More recently, they have been proposed as space monopropellants to replace hydrazine and numerous research papers appeared in this field. A general review focusing on the catalytic decomposition of propellants, including

ionic liquids, is presented in (Batonneau et al., 2008). Two recent reviews concerning new energetic ILs appeared in (Smiglak et al., 2007) and (Singh et al., 2006), whereas (Chiu & Dressler, 2007) presented a review paper entitled *Ionic liquids for space propulsion* focusing mainly on ion electrospray electric propulsion (vide infra).

2. Monopropellants

2.1 HAN, ADN and HNF-based propellants

The first family of EILs (energetic ionic liquids) used as monopropellant component is represented by ionic compounds used; they are used in concentrated aqueous solutions, in order to control the performance and the maximum reached temperature in steady state flow. The propellant contains an IL as an ionic oxidizer associated to a fuel (or reductant) to have a zero oxygen balance. The most promising oxidizers are (the indicated temperatures correspond to the melting point and the percentage to the oxygen balance):

HAN, hydroxylammonium nitrate	$[NH_3OH]^+[NO_3]^-$	44 °C	33.3 %
ADN, ammonium dinitramide	$[NH_4]^+[N(NO_2)_2]^-$	92 °C	25.8 %
HNF, hydrazinium nitroformate	$[N_2H_5]^+[C(NO_2)_3]^-$	118 °C	13.1 %
AN, ammonium nitrate	$[NH_4]^+[NO_3]^-$	170 °C	20.0 %
HN, hydrazinium nitrate	$[N_2H_5]^+[NO_3]^-$	70 °C	8.4 %

Different ionic or molecular fuels have been associated to these oxidizers:

TEAN, tris(ethanol)ammonium nitrate	$[NH(C_2H_4OH)_3]^+[NO_3]^-$	81 °C	-105.6 %
AA, ammonium azide	$[NH_4]^+[N_3]^-$	160 °C	-53.3 %
HA, hydrazinium azide	$[N_2H_5]^+[N_3]^-$	75 °C	-53.3 %
HEHN, 2-hydroxyethylhydrazinium nitrate	$[HO-C_2H_4-N_2H_4]^+[NO_3]^-$	57 °C	-51.8 %
Methanol, ethanol, glycerol, glycine, urea			

Kinetics of the thermal decomposition of ADN, HAN, HNF and HAN-TEAN-H$_2$O mixture, have been intensively studied in the past, but the results concerning catalytic ignition remain scarce. The major merit of the catalytic decomposition versus the thermal decomposition is to strongly decrease the ignition temperature needed to trigger the decomposition and, at the same time, to increase the decomposition rate. This is obtained by a complete change in the reaction pathway, with lower activation energies due to the surface active centers of the catalyst. However, this introduces limitations coming from the thermal stability of the catalyst bed as the decomposition temperature rises. Electric ignition has also been used with success for HAN-water solution (Meng et al., 2009), HAN-TEAN-water propellant (Risha et al., 2007) and ADN-based monopropellant (Wingborg et al., 2005). The effects of electric current, voltage, volume, temperature and propellant concentration on the ignition delay time were investigated. For the HAN-TEAN-water mixture, the time delay to peak power decayed exponentially from 160 s to 2-3 s with an increase in the input voltage from 7 to 12 V; beyond 12 V, the time delay dependency became less significant and appeared to remain constant. Resonant laser ignition was also demonstrated for HAN and HEHN mixtures which were successfully and reliably ignited with single laser pulses in the IR, whereas UV did not lead to ignition (Alfano et al., 2009).

2.1.1 Results on HAN-based propellants

HAN-based aqueous blends have been investigated mainly by US (Meinhardt et al., 1999; Wucherer et al., 2000), French (Courthéoux et al., 2002) and Japanese groups (Katsumi et al.,

2010). The percentage of water controls the maximum adiabatic temperature, and several mixtures have been proposed, depending on the adiabatic temperature that can be reached in steady state conditions: low temperature propellants (up to about 1300 °C) or high temperature propellants (up to about 1800 °C); examples of weight composition are given below:

- 55 % HAN + 12 % CH_3OH + 33 % H_2O 1090 °C
- 59 % HAN + 26 % glycine + 15 % H_2O 1720 °C

Another example is given by HAN-TEAN-H_2O mixture, previously known as LGP (liquid gun propellant) (Klingenberg et al., 1997; Hisatsune et al., 2004). The mass composition HAN 60.8 %-TEAN 19.2 %-H_2O 20 % corresponds to the balanced equation:

$$7 \ NH_3OHNO_3 + NH(C_2H_4OH)_3NO_3 \rightarrow 22 \ H_2O(g) + 8 \ N_2(g) + 6 \ CO_2(g)$$
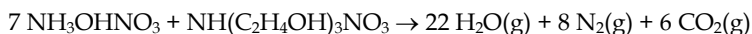
Different catalysts for HAN decomposition have been previously patented (Schmidt & Gavin, 1996): unsupported platinum group metals (wire mesh and sponge) and supported catalysts (32 % Ir, 10 % Pt, 12 % Rh) were proposed to start ignition between 80 and 120 °C. Decomposition of HAN-glycine-water mixtures on Shell 405 (Ir/Al_2O_3 catalyst developed for the decomposition of hydrazine) and other home made catalysts was studied for application in small thrusters (Meinhardt et al., 1999).

Catalysts prepared more recently by a French team are able to decompose HAN catalytically at room temperature with an ignition delay of around 1 s. Successive injections of the propellant (80 wt.-% HAN, 40 °C) decompose easily on such catalysts, thus displaying a very good catalytic activity (Courthéoux et al., 2005a). Fig. 3 shows the mass spectrum of the gas phase during 5 successive injections of 100 µL aliquots on a catalyst preheated at 85 °C (Farhat et al., 2007). The catalysts consist of 10 wt.-% platinum supported on a silicon-doped alumina prepared using sol-gel process (Nguéfack et al., 2003). The impact of drying procedure (xerogel Vs. aerogel) and active phase introduction way (impregnation or one-step addition before sol formation) on catalytic activity are compared (Courthéoux et al., 2004, 2005), showing that aerogel based catalysts display always a better activity and stability. The thermal and catalytic decomposition using the optimized catalyst were followed for different HAN concentrations (20, 40 and 79 wt.-% HAN) (Courthéoux et al., 2006).
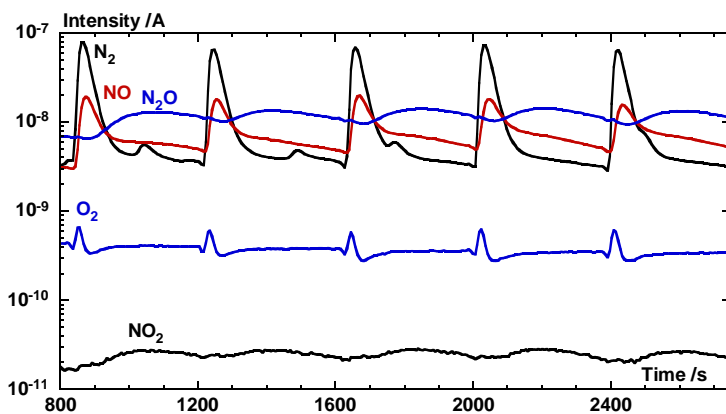

Fig. 3. Catalytic decomposition of HAN(80 wt.-%)-water mixture at 85 °C. Mass spectrometer data versus time after successive HAN injections (Farhat et al., 2007).

The analysis of the products during the decomposition of HAN-based propellants was performed using a dynamic reactor with on-line mass spectrometer analysis of the gas phase and acid-base titration of the trapped aqueous solution, associated with Raman spectroscopy (Amariei et al., 2007; Farhat et al., 2007). For thermal as well as catalytic decomposition, the gaseous primary products are nitrogen N_2 (major, thermodynamic product) and nitrogen oxide NO (medium, kinetic product) (Fig. 4), whereas nitric acid is the major product in the trapped solution, associated with ammonium nitrate (Farhat et al., 2007). The amount of oxygen species (second expected thermodynamic product) is about two orders of magnitude lower than nitrogen and corresponds to oxygen impurities introduced during the injection.
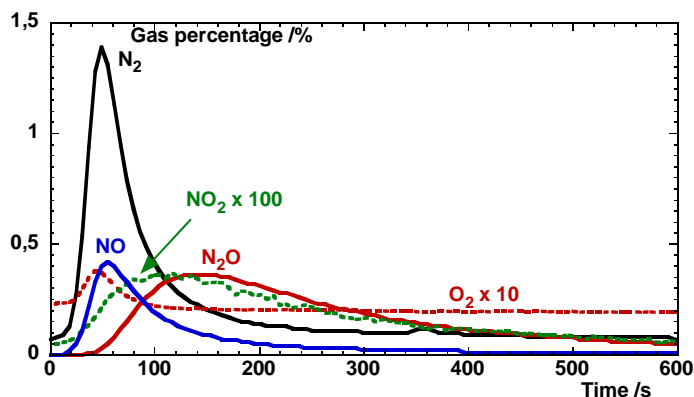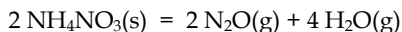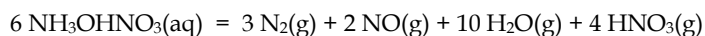

Fig. 4. Thermal decomposition of HAN (80 wt.-%)-water mixture at 200 °C. Gas percentage versus time after the HAN injection (100 µL).

Secondary products are nitrous oxide N_2O (medium) and nitrogen dioxide NO_2 (traces). The formation of NO_2 traces can be the result of NO oxidation by oxygen impurities. The rise of NO_2 follows the drop of oxygen. The concentration difference between oxygen and NO_2 (about one order of magnitude) is related to the solubility of nitrogen dioxide in water.
The simultaneous formation of nitrogen, nitrogen oxide and nitric oxide (primary products) are described by parallel competitive redox reactions between hydroxylammonium and nitrate ions; then, the delayed formation of N_2O is the result of the decomposition of intermediate ammonium nitrate:

$$6\ NH_3OHNO_3(aq)\ =\ 3\ N_2(g) + 2\ NO(g) + 10\ H_2O(g) + 4\ HNO_3(g)$$

$$6\ NH_3OHNO_3(aq)\ =\ 2\ N_2(g) + 2\ NH_4NO_3(s\ or\ l) + 6\ H_2O(g) + 4\ HNO_3(g)$$

$$2\ NH_4NO_3(s)\ =\ 2\ N_2O(g) + 4\ H_2O(g)$$

These results have been supplemented by a study of the decomposition of ammonium nitrate (AN) (Farhat et al., 2009a). The heating of small amounts of aqueous AN (50-55 wt-%) shows only the quantitative endothermic vaporization of water and AN, with no evidence of thermal decomposition even at high temperature. In the presence of various mono- and bimetallic catalysts, we can observe a true decomposition, but only Pt-based

catalysts were able to trigger the decomposition at low temperature (210 °C). The addition of Cu or Zn to platinum leads to an improvement of the catalytic activity and a reduction of the decomposition temperature (close to the melting point 170 °C). The product analysis reveals the presence of the same gaseous and condensed products as observed with HAN e.g. major nitrogen and nitric acid.

The influence of the fuel (methanol and glycerol) added in stoichiometric proportions, or in excess, to HAN, ADN, or HNF was evaluated (Amariei et al., 2005). Fig. 5 displays the thermogravimetric results obtained for binary (no fuel) and ternary HAN-based propellants. Obviously, the presence of the fuel increases the ignition temperature for both thermal and catalytic decomposition, disclosing an inhibiting behavior.
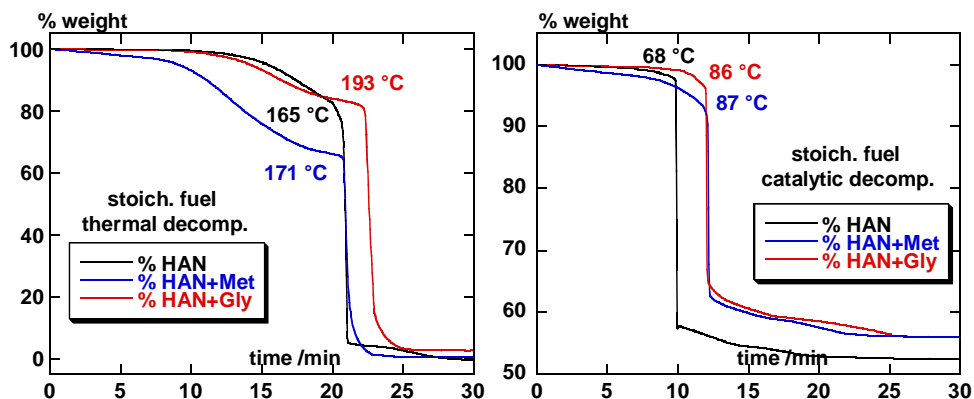

Fig. 5. Comparison of thermal and catalytic decomposition of HAN-based propellants. "Met" = methanol, "Gly" = glycine (Amariei et al., 2005).

To overcome this problem, azides have been proposed as ionic fuels (Farhat et al., 2009b). But the first results were disappointing: for binary ammonium azide (AA)-water mixture, no azide decomposition occurred even in the presence of the catalyst and only endothermic processes corresponding to water and azide vaporization have been recorded. For ternary mixtures HAN-azide-water, no redox reaction has been observed; when using AA, the predominant step is linked to acido-basic reactions. In the case of ammonium nitrate-azide-water ternary mixtures, no reaction between reactants has been observed, but the presence of azide compounds influences strongly the decomposition of ammonium nitrate and the onset temperature decreases enough to enter the solid domain of AN.

Using strand burner technique, it was showed that for binary HAN-water solutions (50-95 wt.-%), the combustion mode is very complex as the linear burning rate increases up to 80 % and decreases from 80 to 95 %. The role of the two-phase region is very important and the boiling of water caused by superheat is responsible for the high burning rate (Katsumi et al., 2010). The combustion mechanism of HAN-based propellant containing ammonium nitrate and methanol shows that the instability of the liquid interface may trigger a sudden increase in the burning rate to a violently high region; methanol was found to reduce the bubble growth rate in the solution. S405 catalyst (which replaces Shell 405 catalyst) showed the best performance (Katsumi et al., 2008, Matsuo et al., 2008). Strand burner investigation of HAN

60 %-glycine 14 %-water 26 % showed that the burning rate exhibited four burning rate regimes for pressures ranging from 1.5 to 18.2 MPa. The temperatures of combustion products were found to be near the water boiling point at pressures lower than 8.8 MPa and under at pressures larger than 8.8 MPa. The observed slope breaks in burning rates are shown to be associated with the reaction mechanism changes between adjacent pressure regimes. Major species detected are nitrogen, nitric oxide, carbon dioxide, and formaldehyde (Chang & Kuo, 2002).

2.1.2 Results on ADN-based propellants

Aqueous ammonium dinitramide (ADN) based mixtures, using as a fuel, glycerol (defining the LMP 101 propellant) or methanol (LMP 103), have been developed by Swedish groups (Wingborg, 2004; Wingborg et al., 2006; Groenland et al. 2004; Anflo & Möllerberg, 2009) with promising results. A new thruster with propellant LMP-103-S (ADN-methanol-water-ammonia) is currently under flight demonstration on-board the Prisma satellite (ESA, 2010). This group has patented catalysts for ADN decomposition and tested them on mixtures comprising Ca 65 %ADN + 10 %CH$_3$OH + 25 % H$_2$O and stabilized with weak base (urea and hexamine). Catalysts are supported Pt, Rh or Ir onto hexaaluminates (LaAl$_{11}$O$_{18}$) which are prepared by a combined sol-gel and microemulsion technique. The so-obtained catalysts are heat resistant above 1000 °C (Groenland et al., 2002). Such catalysts have been investigated and developed in combination with the preparation of other ADN-based ternary mixtures for the propulsion of rocket engines. ADN-based mixtures have been also tested using catalysts developed for HAN (Kappenstein et al., 2004; Farhat et al., 2008). Fig. 6 compares thermal and catalytic decomposition of aqueous ADN (50 wt.-%) and we can observe a full decomposition at lower temperature in the presence of the catalyst. The products are similar to the ones observed during the decomposition of HAN and again ammonium nitrate was found as an intermediate product.
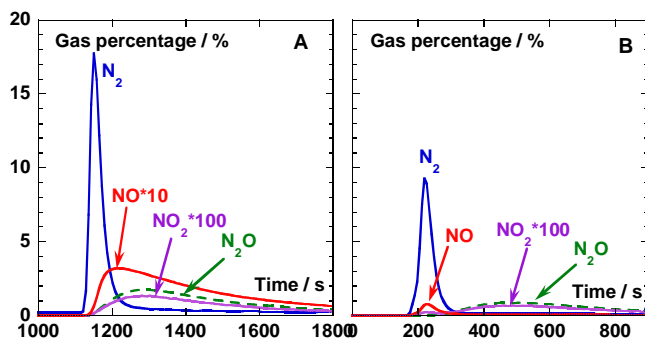

Fig. 6. Gas analysis after thermal (A, 320 °C) and catalytic (B, 250 °C) decomposition of ADN.

2.1.3 Results on hydrazinium-based propellants (HNF, HEHN)

Hydrazinium NitroFormate (HNF), was mainly developed as a substitute for ammonium perchlorate for solid propulsion, but has been also proposed as a more energetic oxidizer than HAN for monopropellant, when combined with reductants (Fick et al., 2001;

Slettenhaar et al., 2003). 44 wt.-% HNF in water (maximum solubility is about 50 wt.-% at 20 °C) was catalytically decomposed with the catalyst Pt/Al_2O_3Si previously described for HAN (Farhat et al., 2008). The gaseous products formed during the catalytic decomposition are major N_2, medium NO, N_2O and CO_2, minor CO and traces of NO_2. Raman analysis of the trapped solution evidenced the complete disappearance of hydrazinium cation, the formation of nitric acid and ammonium, whereas nitroformate anion remains in the solution. Pt, Rh and Pd catalysts supported on doped alumina were used for HNF decomposition (Courthéoux et al., 2004b).

The use of 2-hydroxyethylhydrazinium nitrate (HEHN) was proposed recently as hydrazine substitute (Shamshina et al., 2010). HEHN is more stable than HAN and displays a glass transition temperature of -57 °C. The catalytic decomposition in contact with iridium supported on alumina (Shell 405) was demonstrated when the catalyst is preheated at 150 °C, but with the formation of soot most probably linked to a negative oxygen balance:

$$[HO\text{-}C_2H_4\text{-}N_2H_4]^+[NO_3]^- + 2.25\ O_2 = 2\ CO_2 + 1.5\ N_2 + 4.5\ H_2O$$
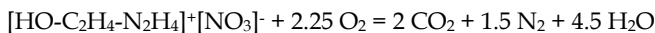
2.2 New energetic ionic liquids for space propulsion

Energetic ionic liquids (EILs) are now numerous and fully described in several papers (Singh et al., 2006; Smiglak et al., 2007). New EILs have been recently prepared and characterized, mainly by the research groups of R. D. Rogers in Alabama and J. M. Shreeve in Idaho. The required properties of a possible propellant are: melting point < -40 °C, density > 1.4 g cm^{-3}, surface tension < 100 dyne cm^{-1}, viscosity as low as possible, long term stability; the development of an IL toolbar is proposed (Smiglak et al., 2007). Imidazolium, triazolium, and tetrazolium families, with different N- and C-substituents (alkyl, amino, azido…) are presented and discussed (Fig. 7). Azolates are surprisingly stable (Smiglak et al., 2010) and the most promising anion for liquid propellant is 3,5-dinitro-1,2,4-triazolate (Fig. 7, species 7). But few EILs have been experimentally investigated as monopropellants. The compound 4-amino-1-methyl-1,2,4-triazolium nitrate (2, Fig.7) displays a glass transition point of -55 °C, shows low sensitivity against impact and friction, and a burn rates with low pressure dependence (Schaller et al., 2009). The decomposition of triazolium (2, Fig. 7) (Chowdhury & Thynell, 2010a) and tetrazolium-based EILs (3, Fig. 7) has been followed by confined rapid thermolysis using FTIR spectroscopy and time-of-flight mass spectroscopy to identify the products. The primary formation of nitrogen and methylisocyanide was evidenced (Chowdhury et al., 2009a). For triazolium EILs, the processes governing the decomposition were found to be autocatalytic in nature and the catalytic species were strong acids generated by the initial decomposition step, with an activation energy of 167-188 kJ mol^{-1} (Chowdhury & Thynell, 2010b).

As an oxygen balance close to zero remains a strong requirement for new propellants, the search for such compounds has been fruitful and new EILs have been proposed (Christe & Drake, 2003; Jones et al., 2006; Tao et al., 2008) and some examples are presented in Fig. 8. Table 2 presents the corresponding oxygen balance values for the formation of CO_2 and CO. As an example, the oxygen balance equation for 1 (Fig. 8), based on CO formation is:
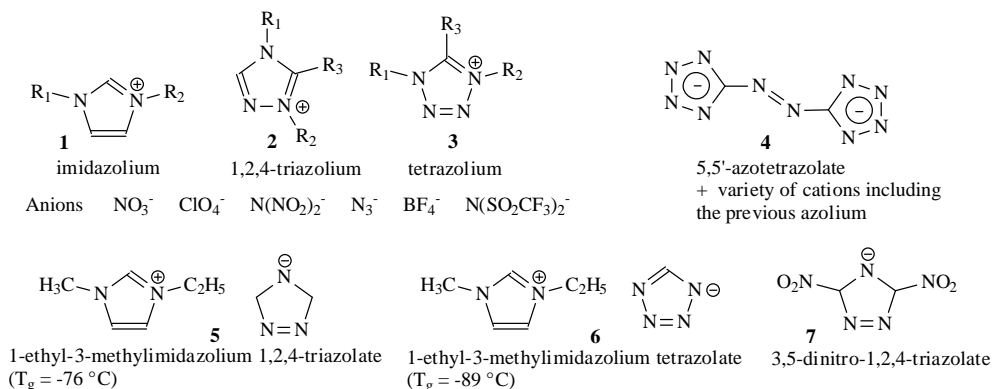
$$2\ [N_4C_5H_{11}]^+[Al(NO_3)_4]^- \ = \ Al_2O_3 + 8\ N_2 + 11\ H_2O + 10\ CO$$

Fig. 7. Representative EILs based on rich nitrogen anions and cations.
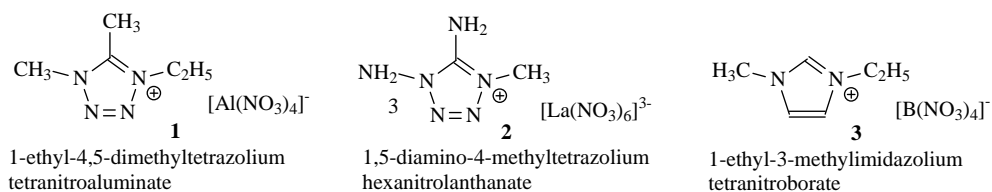
Fig. 8. New EILs with reduced oxygen balance.

Sample (Fig. 8)	Formula	Tm/Tg	OB, CO2	OB, CO
1	$[N_4C_5H_{11}]^+[Al(NO_3)_4$	- 46 °C	-39.8 %	0 %
2	$3[N_6C_2H_7]^+[La(NO_3)_6]^-$	88 °C	-22.4 %	0 %
3	$[N_2C_6H_{11}]^+[B(NO_3)_4]^-$	-25 °C	-60.5 %	-8.6 %

Table 2. Examples of ILs with low oxygen balance (OB).

3. Hypergolic bipropellants

3.1 New hypergolic IL fuels for bipropellant systems

Hypergolic fuel-oxidizer systems hypergolic systems have been widely used in bipropellants engines, mainly for upper stage of launchers because they afford restart of the engine, leading to a better accuracy of the trajectory and finally the satellite orbit. The most used fuels are hydrazine, monomethylhydrazine (MMH) or dimethylhydrazine (UDMH), with oxidizing agents such as white fuming nitric acid (WFNA, 100 % HNO_3), red fuming nitric acid (RFNA, HNO_3 plus NO_2) or nitrogen tetroxide (NTO, N_2O_4). The main drawback of these systems is linked to the toxicity of hydrazines associated with high vapor pressures, which increase strongly the handling and storage costs. The need for non-toxic "green" hydrazine substitutes appeared recently and new hypergolic liquid fuels must present low vapor pressures, high energy densities, low viscosities to enhance ease of mixing, as well as short ignition delays to preclude accumulation of fuel and oxidizer that could lead to an explosion. EILs are the candidates of choice for this application and have been proposed by different research groups in the US.

The first family or ILs fuels exhibiting hypergolic activity toward WFNA was reported by the research group at AFRL Edwards. It corresponds to dicyanamide-based ILs (Chambreau et al., 2008); it must be quoted that the same group prepared also azide-based ILs which show high reactivity with nitric acid, but do not ignite (Schneider et al., 2008a). Then other IL families have been more recently proposed, mainly by the Idaho group, like nitrocyanamide-based (He et al., 2010), or dicyanoborate-based fuels (Zhang & Shreeve, 2011).

3.2 Composition and properties of hypergolic IL fuels

The composition of the different hypergolic IL families is presented in Fig. 9 and some of the properties in Table 3. The borate and cyanoborate ILs are water sensitive, whereas the DCB-based ILs remain water-stable. From Table 3, we can sort the three hypergolic families for ignition delay and viscosity that decrease in the order: NCA > DCA > DCB. Table 3 shows that the DCB-based ILs present much shorter ID than the DCA or NCA, associated with these ILs meet all the important criteria to be selected as hypergolic hydrazine substitutes, with ignition delay close to the ID of the current MMH-NTO bipropellant (2 ms).

cation	anion	T_m/T_g /°C	T_d /°C	Density ρ /g cm^{-3}	Viscosity η /mPa s	ID /ms	Ref.
1	DCB	< -80	307	0.96	17.3	28	a
1	DCA					47	b
1	NCA	-90	256	1.13	57	81	c
2	DCB	< -80	222	0.91	39.4	6	a
2	DCA	20	263	1.01	113.9	46	d
2	NCA	9	286	1.11	119.5	228	d
3	DCB	< -80	189	0.93	35.0	4	a
3	DCA		199	1.05	78.6	30	d
3	NCA		208	1.16	84.9	130	d
4	DCB	< -80	266	0.99	12.4	8	a
4	DCA	-85	207		42	43	b
4	NCA	-91	220	1.11	44	46	c
5	DCB	< -80	252	0.96	19.8	18	a
6	DCB	< -80	203	1.00	13.5	6	a
7	DCB	< -80	220	0.99	29.9	32	a
8	DCB	< -80	217	1.03	21.0	6	a

T_m/T_g: phase-transition temperature, T_d: decomposition temperature (onset), ρ: density (25 °C), η: viscosity (25 °C), ID: ignition delay time with WFNA. Ref: [a] (Zhang & Shreeve, 2011), [b] (Schneider et al., 2008b), [c] (He et al., 2010), [d] (Zhang et al., 2010).

Table 3. Properties of the dicyanoborate-based (DCB) ILs and the corresponding dicyanamide- (DCA) and nitrocyanamide- (NCA) based Ils.
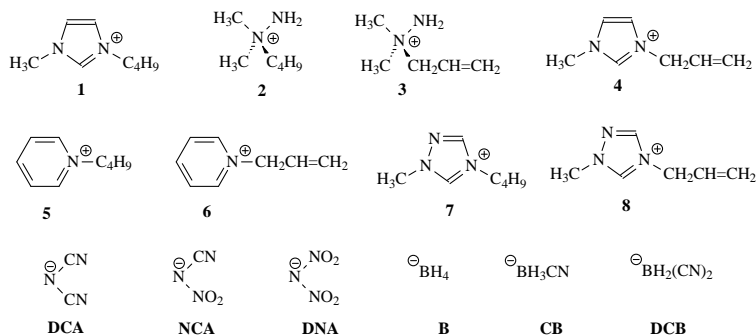
Fig. 9. Constituents of the new hypergolic IL families. DCA = dicyanamide, NCA = nitrocyanamide, DNA = dinitramide, B = tetrahydroborate, CB = cyanoborate, DCB = dicyanoborate.

3.3 Reactivity of hypergolic IL fuels

One example of hypergolic drop test followed by high speed camera is given in Fig. 10 (cation **1** + DCB). The fuel sample is dropped into a beaker containing an excess of WFNA. The ignition delay is defined as the elapsed time between the fuel-oxidizer contact and the appearance of a luminous flame.

New azide-functionalized IL associated with DCA or NCA have been demonstrated to be hypergolic, whereas azide-based ILs display non hypergolic behavior (Joo et al., 2010).

The hypergolic reaction of sodium dicyanamide with nitric acid was followed to investigate the ignition and reaction mechanism (Litzinger & Iyer, 2011). Gas phase products were analyzed by mass spectrometry, and the proposed balanced equation is:

$$Na^+N(CN)_2^- + 4\ HNO_3 \rightarrow 2\ CO_2 + 3\ N_2O + 2\ H_2O + NaNO_3$$

The major products are CO_2 and N_2O. Traces of NO_2, HNO_3 and carbamic acid H_2NCOOH (i.e. $HNCO + H_2O$) have been detected. No nitrogen, ammonia and hydrogen cyanide has been evidenced.
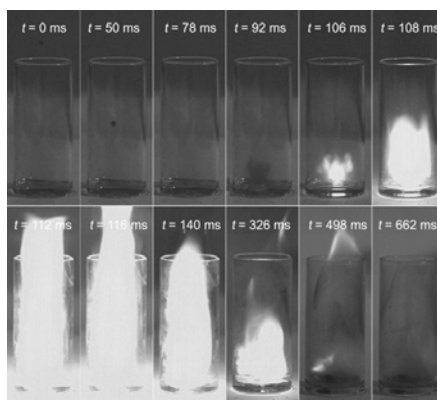

Fig. 10. Ignition delay test shown with a series of high-speed camera photos. A droplet of IL contacting WFNA (Zhang & Shreeve, 2011).

The reaction of 1-ethyl-3-methyl imidazolium dicyanamide (EmimDCA) with WFNA was followed by IR spectroscopy and the presence of CO_2, N_2O, H_2O and isocyanic acid HNCO was evidenced whereas HCN, HONO, NO and CO do not form (Chowdhury at al. 2009b). The use of labeled nitric acid ($H^{15}NO_3$) leads to the formation of $^{14}N^{15}NO$ and $H^{14}NCO$, proving that the NO functionality of nitrous oxide derived from nitric acid and the isocyanic acid nitrogen atom comes from DCA anion only.

Propellant gels can bring safety and insensitivity to tactical systems fueled by storable hypergolic propellants. The unique rheological behavior of gel phase can curtail leakage from damaged tanks and can reduce the volatility of the propellants. Drop ignition tests have been followed used gelled fuel – liquid oxidizer or liquid fuel – gelled oxidizer combination. The ignition of liquid and gelled methyl ethyl imidazolium DCA have been demonstrated (Coil, 2010).

4. Electric propulsion

Among the different propulsion options for small satellites (from micro to nano), ion electrospray propulsion system (iEPS) is a good candidate for high precision applications (Table 1) and with the possibility of miniaturization. Ions are emitted from a conducting liquid in contact with a metallic tip (tungsten, nickel) and accelerated by a static electric field (Fig. 11, left). The tip can be externally wetted in the case of a bulk metal or internally in the case of a porous metal. The liquid is a liquid metal (e.g. indium) or an ionic liquid. The advantages of ILs over liquid metals are: (i) very low vapor pressure, (ii) low surface tension, (iii) possibility to emit positive and negative ions; they are thus described as "a plasma in a bottle" (Lozano, 2011). To scale up the thrust, iEPS can be arranged in the form of arrays of densely packed porous metal emitters; the delivery of the IL propellant uses the passive capillary force (Fig. 11, right). The meniscus of the propellant, when under the influence of an electric field exceeding a critical value will deform into a cone (known as Taylor cone) where the surface tension is balanced by the electrostatic force. An alternating polarity of 1 Hz suppresses the electro-chemical effects.
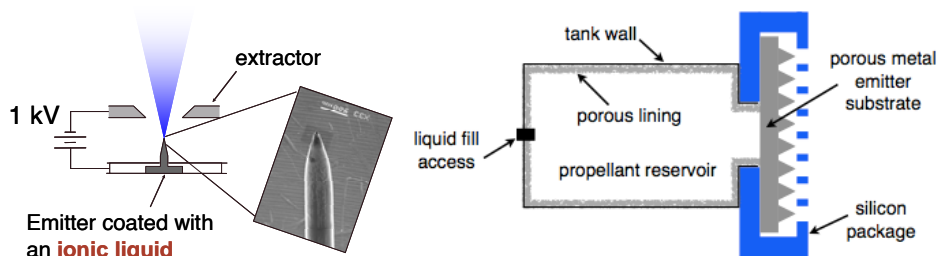
If the electric field

Fig. 11. Scheme of an ion electrospray propulsion system (left); propellant storage and delivery for an array of emitters (right) (Lozano, 2011).

Ionic liquids used as propellants for iEPS do not need to be energetic as it was the case previously, but they must satisfy the requirement to change the classical operation mode from a droplet dominated emission mode (as it is the case for colloid thrusters) to a pure ion emission regime. ILs classically used for iEPS comprise EMIM-BF4, EMIM-Im and EMIM-Beti (Fig. 12) (Daily, 2008; Ticknor et al., 2010; Legge & Lozano, 2011).

$H_3C-N\overset{\oplus}{\diagup}N-C_2H_5$ $[BF_4]^-$

1

EMIM-BF4
1-ethyl-3-methylimidazolium
tetranfluoroborate

$H_3C-N\overset{\oplus}{\diagup}N-C_2H_5$ $[(CF_3SO_2)_2N]^-$

2

EMIM-Im
1-ethyl-3-methylimidazolium
bis(trifluoromethylsulfonyl)imide

$H_3C-N\overset{\oplus}{\diagup}N-C_2H_5$ $[(C_2F_5SO_2)_2N]^-$

3

EMIM-Beti
1-ethyl-3-methylimidazolium
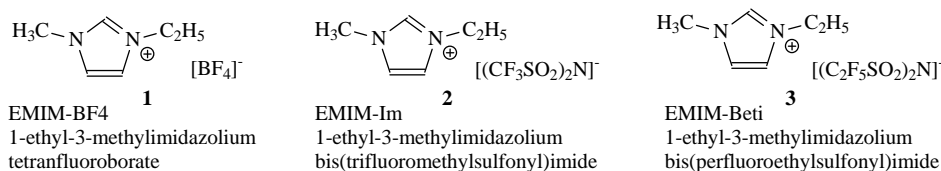bis(perfluoroethylsulfonyl)imide

Fig. 12. Some ILs used for electrospray propulsion.

5. Other propulsion applications

5.1 Hybrid engines

To improve the performances of a monopropellant engine and reduce the risk linked to the simultaneous presence of an oxidizer and a fuel for the long term storage, the oxidizer can be use alone and after decomposition, the hot gaseous oxygen can burn a solid fuel grain in a hybrid solid/liquid engine (Fig. 13). The proposed IL oxidizers can be concentrated aqueous solution of HAN (hydroxylammonium nitrate) or HAN plus AN (ammonium nitrate) and the fuel polyethylene or HTPB (hydroxy-terminated polybutadiene) (Biddle & Sutton, 1985; Ramohalli & Dowler, 1995).
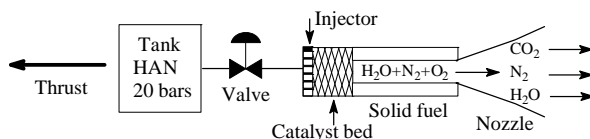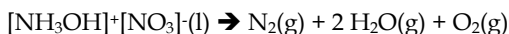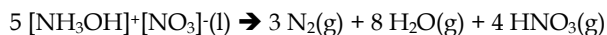
Fig. 13. Scheme of a HAN-based hybrid engine.

Despite the interest of such energetic IL-based hybrid engine, the current development replaced EIL by hydrogen peroxide; this is most probably due to the formation of major nitric acid (kinetic product) instead of expected oxygen (thermodynamic product) during thermal or catalytic decomposition of HAN:

$$5\ [NH_3OH]^+[NO_3]^-(l) \rightarrow 3\ N_2(g) + 8\ H_2O(g) + 4\ HNO_3(g)$$

$$[NH_3OH]^+[NO_3]^-(l) \rightarrow N_2(g) + 2\ H_2O(g) + O_2(g)$$

5.2 Solid propellant stabilizers

Double base (DB) propellants are composed primarily of nitroglycerin (NG) and nitrocellulose (NC). The decomposition reaction is complex, depends on the temperature, but also on the storage history when exposed to conditions in excess of the qualified limit; this last point needs the use of inert stabilizers with a performance decrement (specific impulse, burn rate, energy release…). One solution is to introduce energetic stabilizers that do not carry a performance penalty and ILs are proposed for the next stabilizer generation because they offer the possibility to choose ions that provide task-specific performance: one ion has stabilization capability (generally linked to an affinity for NO_x species) whereas the counterion displays an energetic nature. The feasibility of creating such ILs has been recently demonstrated from NDPA (nitrodiphenylamine) and choline (Fig. 14) (Forton et al., 2010). The use of simpler tetra-alkyl ammonium cations was not successful.
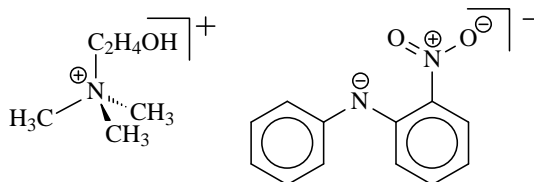
Fig. 14. Example of double base propellant stabilizer: cholinium nitrodiphenylamide.

6. Conclusion

We have seen that different ionic liquids are proposed for the different propulsion systems (monopropellants, hypergolic bipropellants, ion electrospray, hydrid engines). The current and future challenges that can be drawn from this review are summarized as follows: (i) to find new and safe EILs whose thermal or catalytic decomposition avoid the formation of nitric acid as a primary product; (ii) to develop new catalysts able to decompose EILs at low temperature and stable at high temperature; (iii) to find new fuels associated to IL oxidizers but with no inhibiting properties for the catalysts; and (iv) to develop cheaper and safer synthetic method to prepare ILs.

Currently, ionic liquids are part of the GRASP project (GReen Advanced Space Propulsion) of the seven framework program of the European Community (GRASP, FP7).

7. Acknowledgment

8. References

Alfano, A. J., Mills, J. D. & Vaghjiani, G. L. (2009). Resonant laser ignition study of HAN-HEHN propellant mixture, *Combust. Sci. Technol.*, Vol. 181, No. 6, pp. 902-913, ISSN 0010-2202

Amariei, D., Courthéoux, L., Rossignol, S., Batonneau, Y., Kappenstein, C., Ford, M. & Pillet, N. (2005). Influence of Fuel on Thermal and Catalytic Decompositions of Ionic Liquid Monopropellants. *AIAA paper* 2005-3980, ISSN: 0146-3705. Available from http://www.aiaa.org/content.cfm?pageid=320

Amariei, D., Courthéoux, L., Rossignol, S. & Kappenstein, C. (2007). Catalytic and thermal decomposition of ionic liquid monopropellants using a dynamic reactor, *Chem. Eng. Process.*, Vol. 46, No. 2, pp. 165-174

Anflo, K. & Möllerberg, R. (2009). Flight demonstration of new thruster and green propellant technology on the PRISMA satellite, *Acta Astronaut.*, Vol.65, No.9-10, pp. 1238-1249, ISSN 0094-5765

Batonneau, Y.; Kappenstein, C. & Keim, W. (2008). Catalytic decomposition of energetic compounds: gas generator, propulsion. In: *Handbook of Heterogeneous Catalysis,* Ertl,

G.; Knözinger, H.; Schüth, F. & Weitkamp J., Eds., 2nd edition, Vol. 5, Chapter 12.7. pp 2647-2680, VCh-Wiley, ISBN 978-3-527-31241-2, Weinheim, Germany

Biddle, R. A. & Sutton, E. S. (1985). Highly soluble, non-hazardous hydroxylammonium salt solutions for use in hybrid rocket motors, *US Patent* N° 4527389, July 9, 1985

Chambreau, S. D., Schneider, S., Rosander, M., Hawkins, T., Gallegos, C. J., Pastewait, M. F., & Vaghjiani, G. L. (2008). Fourier Transform Infrared Studies in Hypergolic Ignition of Ionic Liquids, *J. Phys. Chem. A*, Vol. 112, No. 34, pp. 7816-7824, ISSN 0022-3654

Chang, Y.-P. & Kuo, K. K. (2002). Assessment of combustion characteristics and mechanism of hydroxylammonium nitrate-based liquid monopropellant, *J. Propul. Power*, Vol. 18, No. 5, pp. 1076-1085, ISSN 0748-4658

Chiu, Y. H. & Dressler, R. A. (2007). Ionic liquids for space propulsion, in *ACS Symp. Ser., No. Ionic Liquids IV*, Vol. 975, pp. 138-160

Chowdhury, A., Thynell, S. T. & Lin, P. (2009a). Confined rapid thermolysis/FTIR/ToF studies of tetrazolium-based energetic ionic liquids, *Thermochim. Acta*, Vol. 485, No. 1-2, pp. 1-13, ISSN 0040-6031

Chowdhury, A., Thynell, S. T. & Wang, S. (2009b). Ignition Behavior of Novel Hypergolic Materials, *AIAA Paper* 2009-5352, ISSN: 0146-3705

Chowdhury, A. & Thynell, S. T. (2010a). Confined rapid thermolysis/FTIR/ToF studies of methyl-amino-triazolium-based energetic ionic liquids, *Thermochim. Acta*, Vol. 505, No. 1-2, pp. 33-40, ISSN 0040-6031

Chowdhury, A. & Thynell, S. T. (2010b). Kinetics of Decomposition of Energetic Ionic Liquids, *Propell. Explos. Pyrot.*, Vol. 35, No. 6, pp. 572-581, ISSN 0721-3115

Christe, K. O. & Drake, G. W. (2003). Energetic ionic liquids, Patent US N° 2003-681502

Coil, M. A. (2010). Hypergolic Ignition of a Gelled Ionic Liquid Fuel, *AIAA Paper* 2010-6901, ISSN: 0146-3705

Courthéoux, L.; Eloirdi, R.; Rossignol, S.; Kappenstein, C.; Duprez, D. & Pillet, N. (2002). Catalytic decomposition of HAN-water binary mixtures, *AIAA Paper* 2002-4027, ISSN: 0146-3705

Courthéoux, L., Rossignol, S., Kappenstein, C., Duprez, D. & Pillet, N. (2003). Improvement of catalyst for the decomposition of HAN-based monopropellant - comparison between aerogel and xerogel, *AIAA Papers*, 2003-4645, ISSN: 0146-3705

Courthéoux, L., Popa, F., Gautron, E., Rossignol, S. & Kappenstein, C. (2004a). Platinum supported on doped alumina catalysts for propulsion applications. Xerogels versus aerogels, *J. Non-Cryst. Solids*, Vol. 350, pp. 113-119, ISSN 0022-3093

Courthéoux, L., Amariei, D., Rossignol, S., Kappenstein, C., Pillet, N. & Ford, M. (2004b). Thermal and catalytic decomposition of HNF and HAN-based propellants, *European Space Agency,* SP-557, ISBN 978-92-909286-6-9, pp. 106-111

Courthéoux, L., Amariei, D., Rossignol, S. & Kappenstein, C. (2005a). Facile catalytic decomposition at low temperature of energetic ionic liquid as hydrazine substitute, *Eur. J. Inorg. Chem.*, No. 12, pp. 2293-2295, ISSN 1434-1948

Courthéoux, L.; Gautron, E.; Rossignol, S. & Kappenstein, C. (2005b). Transformation of platinum supported on silicon-doped alumina during the catalytic decomposition of energetic ionic liquid, *J. Catal.*, Vol .232, No.1, pp. 10-18, ISSN: 00219517

Courthéoux, L., Amariei, D., Rossignol, S. & Kappenstein, C. (2006). Thermal and catalytic decomposition of HNF and HAN liquid ionic as propellants, *Appl. Catal. B-Environ.*, Vol. 62, No. 3-4, pp. 217-225, ISSN 0926-3373

Daily, J. W. (2008), Molecular dynamics simulation of ion emission from nanodroplets of ionic liquids, *J. Propul. Power*, Vol. 24, No. 5, pp. 981-986, ISSN 0748-4658

ESA. 2010. 'Green' satellite fuel designed to make space safer, in *ESA news*, available from: http://www.esa.int/esaCP/SEMPJQ9KF6G_index_0.html

Farhat, K., Batonneau, Y.; Florea, O. & Kappenstein, C. (2006). Preparation and use of ammonium and sodium azide as a fuel additive to ionic oxidizer. European Space Agency, SP-635, ISBN 978-92-909294-6-8

Farhat, K., Amariei, D.; Batonneau, Y.; Kappenstein, C. & Ford, M. (2007). Reaction balance of thermal and catalytic decomposition of nitrogen-based ionic monopropellants. *AIAA Paper* 2007-5642, ISSN: 0146-3705

Farhat, K., Batonneau, Y. & Kappenstein, C. (2008). Thermal and Catalytic Decomposition of AN-, ADN and HNF-Based Ionic Monopropellants, *AIAA Paper* 2008-4938, ISSN 0146-3705

Farhat, K., Cong, W., Batonneau, Y. & Kappenstein, C. (2009a). Improvement of catalytic decomposition of ammonium nitrate with new bimetallic catalysts, *AIAA Paper* 2009-4963, ISSN 0146-3705

Farhat, K., Batonneau, Y. & Kappenstein, C. (2009b). Azide-based fuel additives for ionic monopropellants, *AIAA Paper* 2009-4876, ISSN 0146-3705

Fick, M.; Schiebener, P.; Moerel, J. L. P. A.; van den Berg, R. P.; Sanders, H. M. & Welland-Veltmans, W. H. M. (2001). Industrial benefits of applying HNF in monopropellant satellite propulsion, *European Space Agency*, SP-484, pp. 138-147

Forton, M. S.; Sims, J. D.; Askins, R. E.; Stevenson, W. H.; Shamshina, J.; Smiglak, M.; Rogers, R. D.; and Barrow, R. (2010). An Ionic Liquid-Based Next Generation Double Base Propellant Stabilizer, *AIAA Paper* 2010-6587, ISSN 0146-3705

Grasp, FP7. GReen Advanced Space Propulsion. 7th Framework Program of the European Community. Available from https://www.grasp-fp7.eu/grasp/

Grönland, T.-A., Westerberg, B., Bergman, G., Anflo, K., Brandt, J., Lyckfeldt, O., Agrell, J., Ersson, A., Jaeras, S., Buotonnet, M. & Wingborg, N. (2002). Reactor and hexaaluminate-based catalysts for thermal decomposition of ammonium dinitramide single-base monopropellants, Patent N° 2002095207

Grönland, T. A., Anflo, K., Bergman, G. & Nedar, R. (2004). ADN-based propulsion for spacecraft-Key requirements and experimental verification, *AIAA Paper* 2004-4145, ISSN 0146-3705

He, L., Tao, G.-H., Parrish, D. A. & Shreeve, J. n. M. (2010). Nitrocyanamide-Based Ionic Liquids and Their Potential Applications as Hypergolic Fuels, *Chem.-Eur. J.*, Vol. 16, No. 19, pp. 5736-5743, ISSN 0947-6539

Hisatsune, K.; Izumi, J.; Tsutaya, H. & Furukawa, K. (2004). Development of HAN-based liquid propellant thruster. *Proceeding of 2nd Intl Conf. on Green Propellants for Space*

Propulsion, European Space Agency, ESA SP-557, pp. 153-157, ISBN 978-92-909286-6-9

Jones, C. B., Haiges, R., Schroer, T. & Christe, K. O. (2006). Oxygen-balanced energetic ionic liquid, *Angew. Chem., Int. Ed.,* Vol. 45, No. 30, pp. 4981-4984, ISSN 1433-7851

Joo, Y.-H., Gao, H., Zhang, Y. & Shreeve, J. n. M. (2010). Inorganic or Organic Azide-Containing Hypergolic Ionic Liquids, *Inorg. Chem.,* Vol. 49, No. 7, pp. 3282-3288, ISSN 0020-1669

Kappenstein, C., Batonneau, Y., Perianu, E.-A. & Wingborg, N. (2004). Non toxic ionic liquids as hydrazine substitutes. Comparison of physico-chemical properties and evaluation of ADN and HAN, *European Space Agency, [Special Publication]*, Vol. SP-557, pp. 112-117, ISBN 978-92-909286-6-9

Katsumi, T., Kodama, H., Shibamoto, H., Nakatsuka, J., Hasegawa, K., Kobayashi, K., Ogawa, H., Tsuboi, N., Sawai, S. & Hori, K. (2008). Combustion characteristics of HAN-based liquid monopropellant, *International Journal of Energetic Materials & Chemical Propulsion,* Vol. 7, No. 2, pp. 123-137, ISSN 2150-766X

Katsumi, T; Matsuda, R.; Inoue, T.; Tsuboi, N.; Ogawa, H.; Sawai, S. & Hori, K. (2010). Combustion characteristics of hydroxylammonium nitrate aqueous solutions. *Int. J. Energetic Materials Chem. Prop.,* Vol.9, No.3, pp. 219-231, ISSN 2150-766X

Klingenberg, G.; Knapton, J. D.; Morrison, W. F. & Wren, G. P. Eds. (1998). *Liquid Propellant Gun Technology.* Progress in Astronautics and Aeronautics Series, V-175, AIAA (American Institute of Aeronautics & Astronautics), ISBN-10 1-56347-196-5, Reston, Virginia, USA

Legge, R. S., Jr. & Lozano, P. C. (2011). Electrospray propulsion based on emitters microfabricated in porous metals, *J. Propul. Power,* Vol. 27, No. 2, pp. 485-495, ISSN 0748-4658

Litzinger, T. & Iyer, S. (2011). Hypergolic Reaction of Dicyanamide-Based Fuels with Nitric Acid, *Energ. Fuels,* Vol. 25, No. 1, pp. 72-76, ISSN 0887-0624

Lozano, P. (2011). Miniaturizing Electric Propulsion: the ion Electrospray Propulsion System (iEPS), Desktop Delta-V Workshop, Brown University, February 17, available from www.engin.brown.edu/ddv/ppt/Paulo_Lozano.ppt

Matsuo, T., Mishima, H., Hisatsune, K., Katsumi, T., Sawai, S. & Hori, K. (2008). Development of HAN-based liquid propellant thruster,*International Journal of Energetic Materials & Chemical Propulsion*, Vol. 7, No. 2, pp. 139-152, ISSN 2150-766X

Meinhardt, D.; Christofferson, S.; Wucherer, E. & Reed, B. (1999). Performance and life testing of small HAN thrusters. *AIAA Paper* 1999-2881, ISSN: 0146-3705.

Meng, H., Khare, P., Risha, G. A., Yetter, R. A. & Yang, V. (2009). Decomposition and Ignition of HAN-Based Monopropellants by Electrolysis, *AIAA Paper* 2009-451, ISSN 0146-3705

Nguéfack, M., Popa, A. F., Rossignol, S. & Kappenstein, C. (2003). Preparation of alumina through a sol-gel process. Synthesis, characterization, thermal evolution and model of intermediate boehmite, Phys. Chem. Chem. Phys., Vol. 5, No. 19, pp. 4279-4289, ISSN 1463-9076

Ramohalli, K. & Dowler, W. (1995). Helping HAN for hybrid rockets, *Aerospace America*, Vol. 33, No. 1, pp. 20-21, ISSN 0740-722X

Risha, G. A., Yetter, R. A. & Yang, V. (2007). Electrolytic-induced decomposition and ignition of HAN-based liquid monopropellants," *International Journal of Energetic Materials & Chemical Propulsion*, Vol. 6, No. 5, pp. 575-588, ISSN 2150-766X

Schaller, U., Weiser, V., Roth, E., Keicher, T. & Krause, H. (2009). Synthesis and first combustion studies of a nitrate based ionic liquid, *40th International Annual Conference of ICT,* Energetic Materials, pp. 91/1-91/9

Schmidt, E. W. & Gavin, D. F. (1996). Catalytic decomposition of hydroxylammonium nitrate-based monopropellants, US Patent N° 5485722

Schmidt, E. W. (2001). *Hydrazine and its derivatives. Preparation, Properties, Applications.* (2nd edition), John Wiley & Sons, Inc., ISBN 978-0-471-41553-4, New York

Schneider, S., Hawkins, T., Rosander, M., Mills, J., Vaghjiani, G. & Chambreau, S. (2008a). Liquid Azide Salts and Their Reactions with Common Oxidizers IRFNA and N2O4, *Inorg. Chem.*, Vol. 47, No. 13, pp. 6082-6089, ISSN 0020-1669

Schneider, S., Hawkins, T., Rosander, M., Vaghjiani, G., Chambreau, S. & Drake, G. (2008b). Ionic Liquids as Hypergolic Fuels, *Energ. Fuels,* Vol. 22, No. 4, pp. 2871-2872, ISSN 0887-0624

Shamshina, J. L., Smiglak, M., Drab, D. M., Parker, T. G., Dykes, H. W. H., Jr., Di Salvo, R., Reich, A. J. & Rogers, R. D.(2010). Catalytic ignition of ionic liquids for propellant applications, *Chem. Commun.*, Vol. 46, No. 47, pp. 8965-8967, ISSN 1359-7345

Singh, R. P., Verma, R. D., Meshri, D. T. & Shreeve, J. n. M. (2006). Energetic nitrogen-rich salts and ionic liquids, *Angew. Chem., Int. Ed.*, Vol. 45, No. 22, pp. 3584-3601, ISSN 1433-7851

Slettenhaar, B., Zevenbergen, J. F., Pasman, H. J., Maree, A. G. M. & Moerel, J. L. P. A. (2003). Study on catalytic ignition of HNF based non toxic monopropellants, *AIAA Paper* 2003-4920, ISSN 0146-3705

Smiglak, M., Metlen, A. & Rogers, R. D. (2007). The Second Evolution of Ionic Liquids: From Solvents and Separations to Advanced Materials-Energetic Examples from the Ionic Liquid Cookbook, *Accounts Chem. Res.*, Vol. 40, No. 11, pp. 1182-1192, ISSN 0001-4842

Smiglak, M., Hines, C. C., Wilson, T. B., Singh, S., Vincek, A. S., Kirichenko, K., Katritzky, A. R. & Rogers, R. D. (2010). Ionic Liquids Based on Azolate Anions, *Chem.-Eur. J.*, Vol. 16, No. 5, pp. 1572-1584, ISSN 0947-6539

Tao, G.-H., Huang, Y., Boatz, J. A. & Shreeve, J. M. (2008). Energetic ionic liquids based on lanthanide nitrate complex anions, *Chem.--Eur. J.*, Vol. 14, No. 35, pp. 11167-11173, ISSN 0947-6539

Ticknor, B. W., Anderson, J. K., Fritz, B. A. & Chiu, Y.-H. (2010). Effect of Aspect Ratio on the Wettability and Electrospray Properties of Porous Tungsten Emitters with the Ionic Liquid [Emim][Im], *AIAA-Paper* 2010-6618, ISSN 0146-3705

Wingborg, N., Eldsäter, C. & Henrik, S. (2004). Formulation and characterization of ADN-based liquid monopropellants, *European Space Agency*, SP-557, ISBN 978-92-909286-6-9, pp. 101-106

Wingborg, N., Larsson, A., Elfsberg, M. & Appelgren, P. (2005). Characterization and Ignition of ADN-Based Liquid Monopropellants, *AIAA Paper* 2005-4468, ISSN 0146-3705

Wingborg, N. (2006). Ammonium Dinitramide-Water: Interaction and Properties, *J. Chem. Eng. Data*, Vol. 51, No. 5, pp. 1582-1586, ISSN 0021-9568

Wucherer, E. J., Christofferson, S. & Reed, B. (2000). Assessment of high performance HAN-monopropellants, *AIAA Paper* 2000-3872, ISSN 0146-3705

Zhang, Y., Gao, H., Guo, Y., Joo, Y.-H. & Shreeve, J. M. (2010). Hypergolic N,N-Dimethylhydrazinium Ionic Liquids, *Chem.-Eur. J.*, Vol. 16, No. 10, pp. 3114-3120, ISSN 0947-6539

Zhang, Y., and Shreeve, J. M. (2011). Dicyanoborate-Based Ionic Liquids as Hypergolic Fluids, *Angew. Chem., Int. Ed.*, Vol. 50, No. 4, pp. 935-937, ISSN 1433-7851