Study on hypergolic ignition of ionic liquid solutions

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Abstract

In recent investigations at DLR Lampoldshausen a highly active catalytically promoted ionic liquid fuel with hydrogen peroxide was found. This fuel is based on an ionic liquid and a dissolved metal salt as catalytic promoter. But due to high viscosity of this fuel and bad mixing behaviour between hydrogen peroxide and fuel reliable ignition was not achieved. This investigation introduced different amounts of an organic solvent to the fuel and drop test were conducted to evaluate hypergolic performance. Repeatable ignition was achieved and the ignition delay times were around 28 ms.

1. Introduction

1.1 Motivation

Hypergolic propellants are the baseline for space propulsion systems of large spacecraft since the 1960s. For example, they have been the choice for orbital propulsion systems of the Apollo program, which celebrates the 50th anniversary of the first moon landing this year. Also today's spacecraft e.g. European Automated Transfer Vehicle (ATV) or its successor, the European Service Module of the Orion vessel still use those propellants. Hypergolic fuel-oxidizer combinations ignite spontaneously when coming into contact. This property assures reliable ignition and supersede an external ignition system. These conventional hypergolic propellants are based on hydrazine (N_2H_4) or one of its derivatives and dinitrogen tetraoxide (N_2O_4 or NTO).

Hydrazine and its derivates are highly toxic and carcinogenic. Because of the latter health effect hydrazine was put on the candidate list as substance of very high concern of the European REACH (Registration, Evaluation, Authorization of Chemicals) regulation by the European chemicals agency [1]. As a next step, it is possible that the use of hydrazine is banned in Europe. In addition, use of hydrazine derivates such as unsymmetrical dimethyl hydrazine (UDMH) or monomethyl hydrazine (MMH), which are also highly toxic, could be restricted in future.

NTO is a liquid which is toxic and highly corrosive. The vapor phase contains NO_2. The boiling point of NTO is at 21.1° C [2], which leads to contamination of the atmosphere with toxic vapor if spilled or accidently leaked. NTO is used as oxidizer in solutions with nitric oxide (NO), which lowers the corrosive effects. Those mixtures are referred as mixed oxides of nitrogen or MON-x, where x indicates the percentage of NO.

Because of its toxicity, those propellants come along with excessive safety procedures during handling. For example it is required to wear SCAPE (Self Contained Atmospheric Protective Ensemble) suits. Because of this, handling is very time consuming and costly. Research for alternative so-called green propellants is conducted due to the possibility that hydrazine is banned in Europe and the costly handing of conventional propellants. The main requirements for green propellants compared to the conventional propellants are the lower toxicity for personnel and environment [3]. Moreover green propellants should have a comparable performance and be storable on earth and space. By fulfilling these requirements, green propellants could offer a cost and time reduction potential due to simpler handling [4].

Alternative storable, less toxic oxidizers compared to NTO are limited. A promising alternative to NTO is highly concentrated hydrogen peroxide. Hydrogen Peroxide (H_2O_2) is a widely used substance in several industry sectors and available in different concentration with water as diluent. For the use as propellant H_2O_2 with concentrations of more than 70% come into consideration. Those solutions are also referred as High Test Peroxide or HTP. Highly concentrated H_2O_2 is able to decompose exothermically into water vapor and oxygen. Consequently, HTP can be used as monopropellant [5, 6]. Furthermore the generated oxygen can be used to burn a fuel. The toxicity of hydrogen peroxide is lower compared to NTO and the decomposition products are non-toxic. On the downside hydrogen peroxide is subject to self-decomposition during storage. The decomposition rate is a function of storage temperature, concentration, purity and material compatibility [7]. Nevertheless, decomposition rates below 1% per year have been demonstrated [7]. HTP has space flight heritage from the early days of space flight and was used as

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monopropellant for the orbital control system of the mercury capsule [8]. HTP is still in use as monopropellant of the reaction control system of the Soyuz re-entry module [9].

In contrast to alternative oxidizers there is a wide variety of fuels which are regarded as green. An interesting group of new green fuels are room temperature ionic liquids (ILs). Room temperature ILs are salts which have a melting point below 100°C [10]. As potential fuel candidate, the melting point should be at least below 0°C. Furthermore, physical and thermodynamic properties of ionic liquids can be directly influenced by changing the composition of the ionic liquid. The composition can be changed by modifying the anion or cation. In general, ILs have a very low vapor pressure at ambient conditions due to their ionic composition. This allows open handling of fuels without the risk of contaminating the atmosphere with vapor.

New propellant combinations should also be hypergolic to be competitive with conventional toxic propellants. There are only a few substances, which are hypergolic with hydrogen peroxide. For example hydrazine is hypergolic with hydrogen peroxide but it is not suited, because of the reasons discussed earlier. Since the 1990s efforts are made to find a hypergolic fuel to highly concentrated hydrogen peroxide. But until today pure substances which are hypergolic with HTP are very rare. Therefore several fuels with additives which initiate the ignition were developed. The fuels are distinguished in the type of additive used. The first group of fuels are catalytic fuels which have a catalytic additive dissolved. These additives are transition metal salts for instance with Co^{2+}, Co^{3+}, Cu^{1+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+} or Mn^{3+} cations which catalyse the decomposition of hydrogen peroxide [11]. After contact of fuel and oxidator, mixing takes place and the decomposition reaction heats up the propellant. Gaseous oxygen is generated, fuel is vaporized and when the auto ignition temperature is reached the mixture finally ignites. One early development in the mid-1990s by the US Navy is called Block 0, which is a mixture of methanol and manganese acetate tetrahydrate [12]. The second group are reactive fuels, which have an additive, which directly reduces the hydrogen peroxide. This reaction generates more energy than the decomposition reaction and ignition delay can be shorter [12]. Typical additives are strong reducing agents. Currently, several groups in Korea [13, 14], USA [15] and Poland [16] investigate reactive fuels. Reactive fuels can consist of a high performing fuel, a reducing agent and a suitable solvent for the reducing agent which is blended with the fuel. The investigated reducing agents are sodium borohydride or lithium borohydride. Handling of such strong reducing agents is challenging due to their high sensitivity to air and moisture. Propellants with dissolved additives can be subject to segregation of the additive during storage. Beside hypergolic liquid fuels, gelation of fuels could help to prevent sedimentation of additives [17] and offers the possibility introducing nano-sized additives [18].

Ionic Liquids came into attention as fuels due to their low volatility and high versatility. Various ILs have been found to be hypergolic with different oxidizers such as white or red fuming nitric acid, NTO and hydrogen peroxide [19, 20]. Hypergolic behaviour is mainly driven by the anion of an ionic liquid. The selection of the cation may influence the thermodynamic or physical properties and ignition delay time [21].

Hypergolic ionic liquids with hydrogen peroxide have been investigated by AFRL, USA [22, 23], Hannam University, South Korea [24], Tel Aviv University, Israel [25, 26] and ICT Germany [27]. Schneider et al. synthesized an IL with an aluminium boron hydride ($Al(BH_4)_4^-$) anion. This IL was hypergolic with hydrogen peroxide with concentrations of 90 % and 98 %. The ignition delay time was below 30 ms [23]. Also ILs with an iodide or tetrachloroferrate anion can react as a catalytic additive dissolved in another fuel IL [22]. Kim et al. investigated solutions of a fuel with a dissolved additive. They found that azide (N_3^-), cyanide (CN^-), iodide (I^-) and tetrachloroaluminate ($AlCl_4^-$) anions introduce hypergolic behaviour with hydrogen peroxide. Ignition delay time between 8 and 33 ms were reached [24]. Chinnam et al. investigated hypergolic ignition between 70% hydrogen peroxide and 3-Ethyl-1-methyl imidazolium cyanotrihydroborate (H_3BCN^-). This IL proved not to be hypergolic, but by introducing boron and iodine rich compounds ($B_{12}I_{12}^{2-}$) ignition was achieved with a minimum delay time of 17ms. [26]. Wang et al. prepared different boron containing fuels. To introduce hypergolicy with highly concentrated hydrogen peroxide different catalytic ILs with iodocuprate ($Cu_xI_y^{z-}$) anion were dissolved in the fuel. The most promising promoted fuel reached an ignition delay time of 14 ms [25]. Weiser et al. investigated an IL which proved not to be hypergolic with hydrogen peroxide. By dissolving a copper salt, hypergolic ignition was achieved [27].

Hypergolic propellants should have a short ignition delay time. But the definition of "short" is variable. When the first hypergolic propellants were assessed in the 1940s, an ignition delay below 50 ms was accepted. In contrast, conventional hypergolic propellants have an ignition delay in the order of several ms [28]. A short ignition delay is required to avoid hard start events in combustion chambers and to enable short and precise impulse bits.

The aforementioned hypergolic ionic liquid fuels with hydrogen peroxide have been tested until now in drop tests.
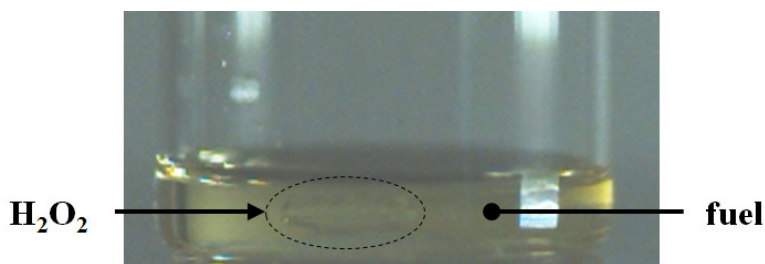
1.2 Previous work

Figure 1: Mixing of hydrogen peroxide and 1-buty-3methylimidazolium acetate

In previous research activities, a theoretical screening was conducted to evaluate fuel candidates [29]. The fuel was chosen from the group of commercial available ionic liquids. Requirements for ionic liquids fuels were identified and on the basis of these results, fuel candidates were screened. The requirements included density, viscosity, melting point and performance. For the performance calculation with NASA code Chemical Equilibrium and Applications (CEA) [30] of the considered ILs the enthalpy of formation had to be published. The screening focused on ionic liquids with an imidazolium cation and different anions. As promising candidate in terms of the selected requirements 1-buty-3-methylimidazolium acetate (BMIM Ac) was chosen. The IL was tested in the so called drop test with hydrogen peroxide but proved not to be hypergolic. Furthermore mixing of the two components was very poor. Figure 1 shows the result of the drop test. A drop of hydrogen peroxide is inside the yellow BMIM Ac fuel and no reaction can be observed. To introduce a hypergolic behavior two catalytic additives, namely copper (II) acetate and manganese acetate tetrahydrate (MAT) were dissolved in the IL. MAT was already used in the fuel Block 0 and has proven to react as a catalytic additive. The amounts of additives were varied and drop tests were conducted. The ignition delay time was determined by analyzing recordings with high speed camera. The ignition delay time in the case of the copper based additive was in the order of several 100 ms, which was concluded as not suitable. The MAT based additive behaved differently. Figure 2 shows snapshots of a typical drop test. In the case of 10% MAT additive the oxidizer drop impacts on the surface of the fuel. Within 10 ms vapor is generated and the HP drop rebounds from the surface again due to the decomposition products generated at the boundary layer between fuel and oxidizer. The reason is the poor miscibility between the IL fuel and hydrogen peroxide as well as the high viscosity of the fuel.
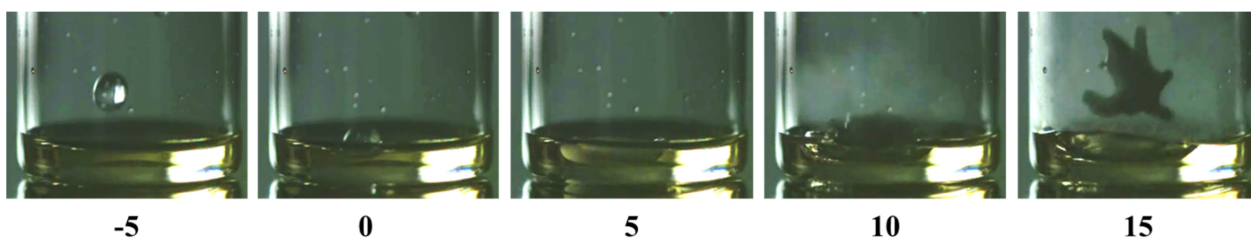

Figure 2: Drop test with BMIM Ac and 10 wt% MAT

This investigation aims to enhance mixing and to reduce viscosity of the highly active catalytically promoted fuel. Therefore a suitable solvent is chosen and this solvent is introduced to the fuel. Drop tests are conducted and analyzed with focus on mixing of fuel and oxidizer and ignition delay times.

2. Procedure

2.1 Screening for solvents

To introduce a better mixing between the IL fuel, namely BMIM Ac, with the catalytic additive and hydrogen peroxide a solvent is to be introduced. The resulting fuel consists of three components: the IL fuel, the catalytically additive and a solvent for a better mixing behavior. In a first step a suitable solvent had to be found, which is able to be solved with the IL fuel and also insure better miscibility with hydrogen peroxide. Highly concentrated hydrogen

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peroxide is miscible with many organic liquids that are also miscible with water such as isopropanol, acetone, pyridine and ethanol [31].

The IL fuel, BMIM Ac, is used as solvent for agricultural products. But for process design it may be required to reduce the viscosity by introducing a solvent. Fendt et al. investigated different solvents for BMIM Ac to reduce the viscosity. They used 3 common solvents: acetonitrile, ethylene glycol, dimethyl formamide [32]. For acetonitrile the addition of 8,9 wt % to BMIM Ac reduce the viscosity from 485 mPa s to 148 mPa s (at 25 °C). They concluded that even a small concentration of diluent is able to reduce the viscosity of the IL. After the observation of the pervious experiments [29] it is expected, that a reduced viscosity may result also in a better miscibility of the IL with hydrogen peroxide. For this investigation a theoretical screening was conducted with different common solvents. The performance of the ionic liquid solution was determined with NASA CEA code [30]. As reference case for the calculation an ArianeGroup 400 N MMH/NTO apogee thruster was chosen. The chamber pressure is 10 bar and nozzle expansion ratio is 330 [33]. The calculations assumed frozen expansion. Different common solvents were compared such as ethanol, acetonitrile, ethylene glycol, dimethyl formamide, methanol, isopropanol, ethyl acetate and propandiol. In Figure 3 the vacuum Isp values of the screening are shown. The gray bar corresponds to the pure IL fuel composed of 90 wt % BMIM Ac and 10 wt % MAT as reference. The black bars refer to fuels composed of 80 wt % BMIM Ac with 10 wt % MAT and 10 wt % of the given solvent in the figure. The results show that the vacuum Isp increases with adding a solvent and the increase is in the same order for all screened solvents. For this investigation ethanol was chosen, because of low toxicity and good expected miscibility with hydrogen peroxide. Two concentrations of solvent were investigated: 10 wt % and 20 wt % of solvent. With higher concentration of solvent the density of the fuel is decreasing, which also decreases the density specific impulse.
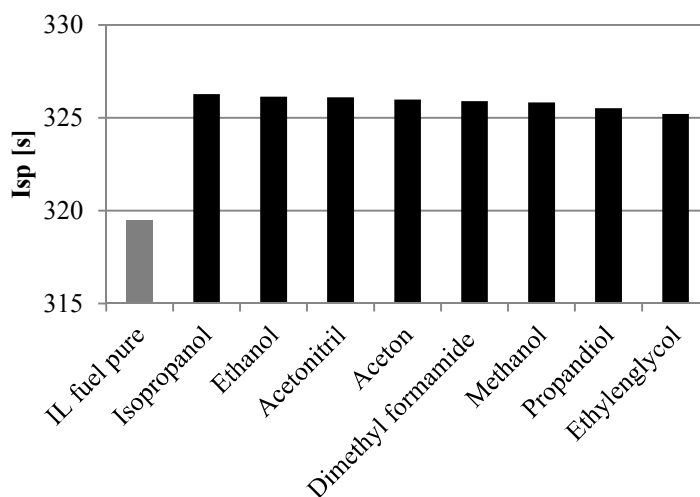

Figure 3: Results of screening with different solvents compared to the baseline IL fuel (gray)

2.2. Substances used and methods

The BMIM Ac was purchased by Iolitec, Germany with a purity of 98%. The IL was used without further purification. Hydrogen peroxide (PROPULSE® 980) was purchased from EVONIK, Germany. The concentration was determined by density measurements and specified to 97.1 %. The manganese (II) acetate tetrahydrate was purchased from Alfa. The ethanol absolute (>99.5%) was purchased from VWR.

Densities of hydrogen peroxide and the fuels were determined with a density meter Easy D40 by Mettler-Toledo at 25 °C. The reference density values of H_2O_2 were tanken from [34]. The viscosities were measured with an Ubbelohde viscometer class II. The measurements of viscosities and densities were performed three times and the average values are given.

2.3 Drop test: method

The drop test is a simple and fast approach to determine hypergolic behavior of two substances. In the presented investigation a drop of hydrogen peroxide is released from the tip of a pipette. A drop of the fuel is located in a disposable weighing boat 80 mm below the pipette tip. The scheme and a frame during a test are shown in Figure 4.

The volume of the hydrogen peroxide is approximately 0.05 ml. An amount of 0.1 ml of the fuel was placed with an Eppendorf pipette. During the experiment a high speed camera records the mixing of the two components. The mixing process and determination of the ignition delay time can be analyzed by means of the recordings. The ignition delay time is defined by the time period between the first contact of the two components until the first flame is visible. The drop tests were recorded by a Phantom SX2.1 high speed camera with a frame rate of 2000 fps. All drop tests were conducted inside a fume hood. After each tests water was sprayed on the mixture to suppress further reactions.
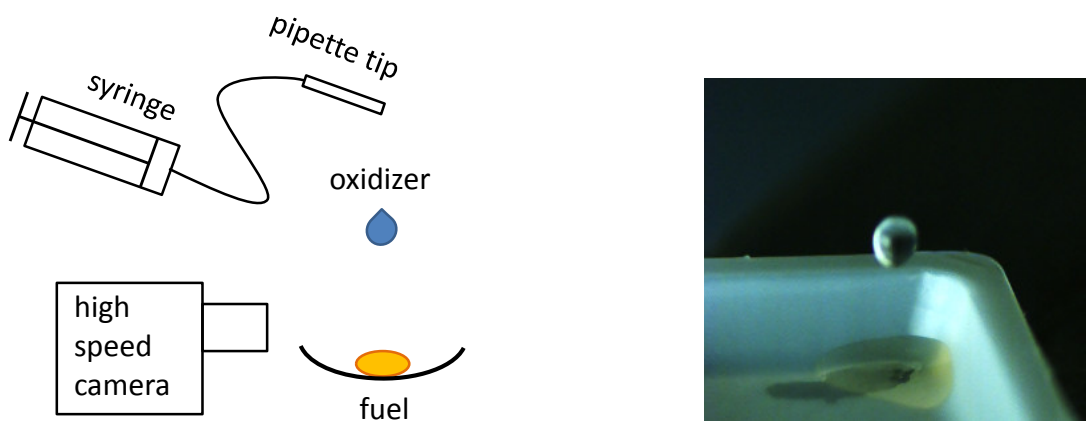

Figure 4: Drop test scheme (left) and frame before contact with high speed camera one drop of fuel in a disposable weighing boat (right)

3. Results and discussion

Fuel preparation was conducted as following: First, 10 wt % of the catalytic promoter, namely manganese acetate tetrahydrate was dissolved via stirring in the ionic liquid. In a second step, the promoted ionic liquid was diluted by the chosen solvent. The resulting concentrations were determined via scaling during preparation. Examples of the different stages of the fuel production are shown in Figure 5. In the following, the different fuels are referred as given in Table 1.
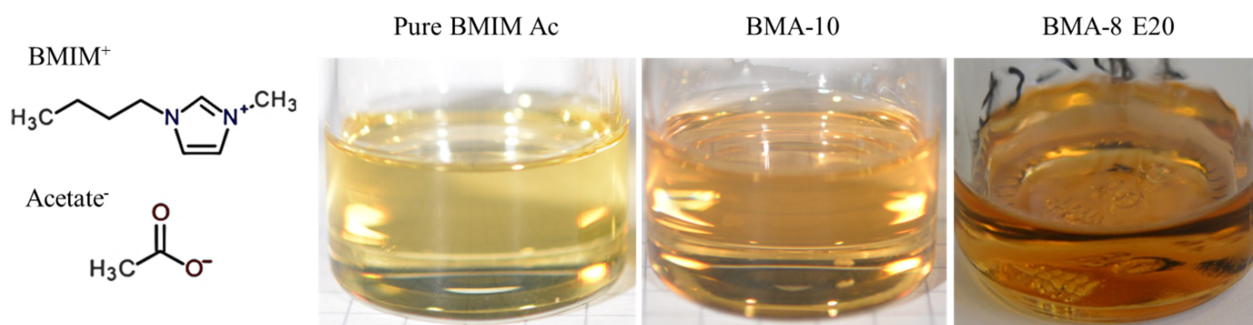

Figure 5: Structural formula of the IL (left), pure IL, fuel IL and diluted fuel IL (right)

Table 1 shows the composition of different fuels and their corresponding viscosities and densities. If not remarked, the values were determined as described in 2.2. Furthermore, the table lists the calculated vacuum Isp values determined with NASA CEA as described in 2.1. With the dilution of 10 wt % of ethanol in the IL fuel the viscosity is reduced by more than 100 mPa s. Further dilution decreases the viscosity down to 37.4 mPa s for BMA-8 E20. The density is also reduced by adding more diluent. Due to the fact that the maximum vacuum Isp is almost identical of the two diluted fuels, the corresponding density Isp is reduced.

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Table 1: Properties of investigated fuels

Name	BMIM Ac [wt %]	Ethanol [wt %]	MAT [wt %]	Dynamic viscosity [a] [mPa s]	Density [a] [g/cm³]	Isp [s]
BMIM Ac	100	0	0	208[b]	1,05	322,1
BMA-10	90	0	10	--	--	319,5
BMA-9 E10	81,3	10	8,7	97,3	1,05	326,1
BMA-8 E20	72,8	19,4	7,8	37,4	1,02	326,3

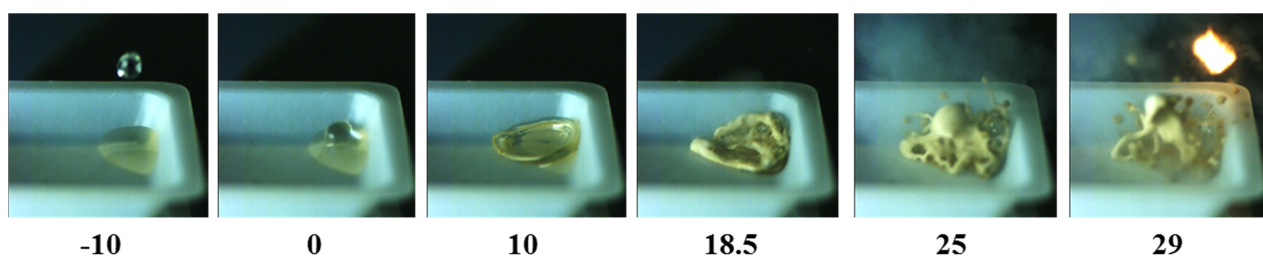[a] measured at 21 °C   [b] from [35] at 25 °C

Figure 6: Snapshots during drop test with BMA-9 E10, time is given in ms

Figure 6 shows a series of snapshots during a drop test with IL fuel and 10% ethanol. A fuel drop is inside the weighting boat and a drop of hydrogen peroxide falls into the fuel. The timescale below the snapshots is given in milliseconds. The first frame where hydrogen peroxide and fuel come into contact is defined as 0. The framerate of the high speed camera was 2000 fps. After contact of fuel and oxidizer the components mix. At 10 ms the mixture starts to turn from transparent to yellow foam. The yellow foam starts to bubbling and at 18.5 ms and the surface of the fuel oxidizer mixture breaks up. Vapor generation can be observed. The fuel bubbling becomes more violently more vapor is generated at 25 ms. The propellant mixture break up and some small drops are released and filaments are generated. At 29 ms the ignition take place at a small drop released from the rest. After ignition, the flame propagates fast in the vapor and ignites the rest of the fuel within a few milliseconds.
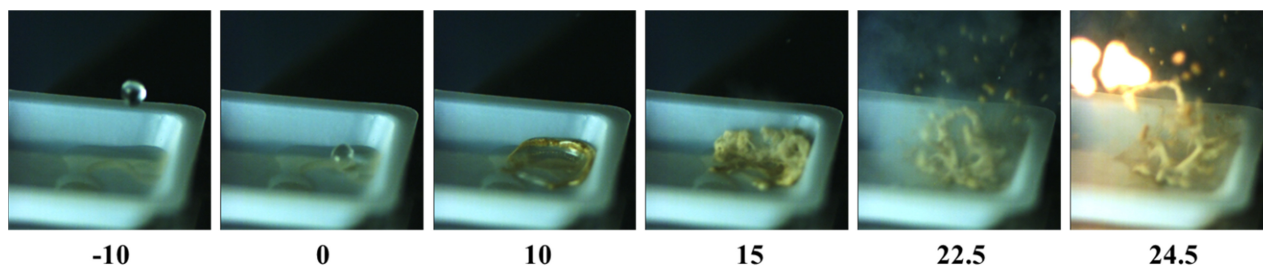

Figure 7: Snapshots during drop test with BMA-8 E20, time is given in ms

Figure 7 shows a series of snapshots during a drop test with IL fuel and 20% ethanol. The first contact of oxidizer and fuel is defined as starting point. The mixing process is similar as described above. The components mix after contact and the mixture turns into the foam. After 15 ms the surface breaks up and vapor is generated. The bubbling of the fuel becomes more violently and forms small drops, which are released. The ignition in this particular test takes place at 24.5 ms.

The change from the propellant from transparent into the bubbling foamy substance is caused by the decomposition reaction of the hydrogen peroxide. The decomposition heats the mixture, which increases the decomposition rate again. The faster becoming decomposition reaction generates more vapors which lets the propellant break up. At some point the ignition temperature is reached in one of the small drops and the flame starts to propagate. In contrast

to the previous investigations it is obvious that the hydrogen peroxide penetrates the fuels surface and both are able to mix. None of the oxidizer is rebound from the fuel compared to Figure 2. Ignition occurred in all drop tests.

Table 2: Results of the drop tests

fuel	time to vapor generation [ms]	Standard deviation [ms]	Ignition delay time [ms]	Standard deviation [ms]
BMA-10	9,7[a]	0,6[a]	--	
BMA-9 E10	15,6	1,03	28,4	3,03
BMA-8 E20	13,5	0,94	27,5	1,54

[a] from [29]

Table 2 shows the results of the conducted drop test. The drop tests of the fuels were repeated 5 times. The average values for the time to breaking up of the fuel and the first obvious vapor release is given as well as the ignition delay time and the corresponding standard deviations. Additionally, the time to vapor generation of the catalytically promoted ionic liquid fuel is given from the previous research [29]. The average ignition delay time of the two investigated fuels differ less than a millisecond and amounts to around 28 ms. The difference is in the order of the measuring uncertainty of the ignition delay time due to the frame rate of the camera. The standard deviation is higher in the BMA-9 E10 case. So it can be concluded that the average ignition delay time of both fuel mixtures is almost identical. But this ignition delay time is much higher than compared to conventional hypergolic propellants. The time to vapor generation is longer for the diluted IL fuels compared to the basic BMA-10. Furthermore the higher content of ethanol (20%) leads to an earlier break up and vapor generation than the 10% fuel. This may be related to the higher amount of ethanol which could lead to more volatile solution and which promotes an earlier vapor production. Additionally, the amount of catalyst is decreased by the procedure used of diluting with ethanol. Moreover the viscosity of the higher diluted fuel is lower which could also have a positive effect on mixing and the vapor generation. Overall both diluted fuels are obviously miscible with hydrogen peroxide, because after contact fuel and oxidizer merge and in every drop test ignition is achieved.

In contrast to the highlighted improvements compared to the previous research [29], the more volatile fuels vitiate the main advantage related to ionic liquids namely their very low vapor pressure. Besides, the density of the fuel is reduced due to the relatively low density of common solvents. For these reasons, a better approach would be to use the high versatility of ionic liquids. This means to directly change the composition of the basic ionic liquid to a less viscous, more reactive and better miscible substance with hydrogen peroxide.

4. Conclusions

In the previous research a highly active catalytically promoted ionic liquid fuel with hydrogen peroxide was found, but due to poor miscibility of fuel an oxidizer reliable ignition was not achieved. For introducing a better miscibility of fuel and hydrogen peroxide different suitable solvents for the IL fuel were screened with NASA CEA calculations. Ethanol was chosen as solvent due to low toxicity and high performance. Two different fuels were prepared based on the high catalytic active fuel from the previous research. In both cases viscosity was decreased, miscibility with hydrogen peroxide was achieved. Furthermore repeatable ignition was observed in drop tests. The ignition delay was in the order of around 28 ms. Introducing the solvent on the other side effects the advantage very low vapor pressures and high densities of ionic liquids. Therefore alternative ionic liquids, which have beneficial properties, should be investigated in future.

5. Acknowledgments

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7. Abbreviations

Ac^-	Acetate
AFRL	Air Force Research Laboratory, Edwards, USA
ATV	Automated Transfer Vehicle
BMA	1-Butyl-3-Methylimidazolium with solved catalytic manganese acetate tetrahydrate additive
$BMIM^+$	1-Butyl-3-Methylimidazolium
CEA	Chemical Equilibrium With Applications, thermodynamic code of NASA
HTP	High Test Peroxide
ICT	Fraunhofer Institute for Chemical Technology, Pfinztal, Germany
IL	Ionic Liquid
MAT	Manganese Acetate Tetrahydrate
MMH	Monomethyl Hydrazine
MON	Mixed Oxides of Nitrogen (NO in N2O4/NO2)
NTO	Dinitrogen Tetraoxide

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REACH   Registration, Evaluation, Authorization of Chemicals

SCAPE   Self-Contained Atmospheric Protective Ensemble

UDMH   Unsymmetrical Dimethyl Hydrazine