INVESTIGATION ON IONIC LIQUID COMBINATIONS AS FUELS FOR HYPERGOLIC PROPELLANTS WITH HYDROGEN PEROXIDE

SPACE PROPULSION 2022 **|** ESTORIL, PORTUGAL **|** 09 – 13 MAY 2022

Sophie C. Ricker(1), Dominic Freudenmann(2), Stefan Schlechtriem(3)

(1)(2)(3)Institute of Space Propulsion, German Aerospace Center (DLR), 74239 Hardthausen, Germany, Email: sophie.ricker@dlr.de

KEYWORDS: green propellants, hypergolic propellants, space propulsion, hydrogen peroxide, ionic liquids

ABSTRACT:

One of the most promising approaches for alternative hypergolic propellants for the New Space sector is the combination of hydrogen peroxide as oxidizer and ionic liquids as fuels. Ionic liquids are particularly characterized by their negligible vapor pressure, high density and flexible cation design. Upon these characteristics, they can offer advantageous properties for future space propellants. This work focuses on the combination of two ionic liquids whose properties complement each other advantageously. The fuel named **HIM_35** ignites with a delay of 16.7 ms with H_2O_2. The fast ignition of this hypergolic bipropellant is particularly remarkable, considering the fact that it does not comprise any transition metal or hydride-based additives. As the calculated volumetric specific impulse $\rho\ I_{sp,\ max}$ of 429 s·g·cm^{-3} of **HIM_35** with H_2O_2 exceeds the value of the conventional hypergolic propellant combination MMH/NTO under the same circumstances, it is an auspicious alternative “green” hypergolic bipropellant combination.

1. INTRODUCTION

Hydrazine or its derivatives MMH (monomethyl hydrazine) and UDMH (unsymmetrical dimethyl-hydrazine) as fuels in combination with NTO (nitrogen tetroxide) as oxidizer are still the most commonly used hypergolic propellant combinations. [1] However, hydrazines are classified as toxic, carcinogenic as well as environmentally hazardous and are on the list of substances of very high concern in Europe. [2] For this reason, research in suitable hypergolic propellant alternatives is of great importance. [3]

Ionic liquids (ILs) have raised great attention as new fuel alternatives in recent years. Just like regular salts, this substance class is entirely built out of ions. As their melting pint is below or around 100 °C, they are also termed “molten salts”. [4] The interest in ionic liquids has increased rapidly in the last decades which can be ascribed to their wide liquidus range, low vapor pressure, high thermal stability and ionic conductivity. [5]

However, while there is already a large body of work using ionic liquid fuels with WFNA (white fuming nitric acid) as an oxidizer, the choice of substances that react hypergolically with hydrogen peroxide is still relatively limited. [6–8] In our working group at the DLR Institute of Space Propulsion in Lampoldshausen, a new type of ionic liquids with thiocyanate anions was discovered to ignite hypergolically with hydrogen peroxide. [9] In further activities, the role of the cation structure towards ignition delay time (IDT) was investigated. [10] Recently, protic imidazolium ionic liquids have proven to be very promising candidates for hypergolic fuels, as some of them show remarkable low IDTs. The most outstanding candidate shows even an average ignition delay time as low as 7.3 ms. [11] Lately, a successful demonstration of a thiocyanate ionic liquid with a copper additive was conducted that showed the usability of this propellant class for spacecrafts. [12]

Herein we present the study of protic and aprotic ionic liquid combinations as hypergolic fuels with hydrogen peroxide. For this purpose, the chemical and physical properties of these fuels were investigated. Particularly, focus was on the thermal behavior of the ionic liquids, which was investigated by TG/DSC (thermogravimetric and differential scanning calorimetry) analysis. Furthermore, FTIR spectra were recorded to investigate the chemical interactions of the fuel combinations. Calculations regarding the theoretical performance were performed with NASA CEA (Chemical Equilibrium with Applications) based on an *Ariane Group* 400 N thruster. In this assumed case the expansion ratio is 330 and the chamber pressure is 10 bar. [13] The calculated combustion data of the new IL/H_2O_2 combinations was compared to conventional hypergolic propellants. In a final step, the ignition behavior with hydrogen peroxide as "green" oxidizer was evaluated at different temperatures and the suitability of the candidates as new hypergolic was discussed.

2. EXPERIMENTAL METHODS

Viscosity measurements were conducted using a *LOVIS 2000 M* micro viscosimeter (*Anton Paar*) at 25 °C. Density measurements of the RTILs were conducted with a density meter *Easy D40* (*Mettler-Toledo*) at 25 °C. The measurement uncertainty is specified as ±0.0005 g/cm³. Density of the solid IL was measured with an *Ultrapyc 5000 Micro* gaspycnometer (*Anton Paar*) at 25 °C. TG (thermogravimetric) and DSC (dynamic scanning calorimetry) measurements were carried out with a *STA 449 F3 Jupiter*® thermal analyzer (*Netzsch*). Measurements were conducted in aluminium crucibles under pure N_2-gas with heating rates of 10 K/min. FTIR spectra were measured on an *IRAFFINITY-1S* spectrometer (*Shimadzu*). The neat samples were directly placed on a diamond crystal and measured by ATR (attenuated total reflection) technique.

Focus of this work is the comprehensive characterization of the ionic liquid combination **HIM_35**, which is composed out of the solid ionic liquid [Him][SCN] and the commercially available RTIL (room temperature ionic liquid) [Emim][SCN]. [Emim][SCN] was purchased from IoLiTec GmbH with a purity > 98 %. [Him][SCN] was synthesized according to [11]. The compound was characterized via NMR- and FTIR-spectroscopy. Purity was checked by anion and cation ion chromatography and water content was measured by volumetric Karl Fischer titration. Fig. 1 shows a photography of the solid ionic liquid [Him][SCN] (left), the RTIL [Emim][SCN] (right) and a mixture of both (middle).

*Figure 1. Photography of the ionic liquid fuel candidates. Left: [Him][SCN] (solid); middle: **HIM_35** (liquid); right: [Emim][SCN] (liquid).*

3. DROP TEST SET-UP

The schematic experimental set-up for the hypergolic drop tests is shown in Fig. 2. The ionic liquid-based fuel (150 µl) was placed on a watch glass and a glass pipette containing the oxidizer hydrogen peroxide (97 wt%) was mounted above it in a distance of 8.7 cm. The pipette was attached to a syringe, for controlled dropping of the oxidizer (drop size: 45.5 mg ± 1.29 mg). The experiments were filmed by a *Photron fastcam SA-X2* color high-speed camera, with a recording speed amounted to 3000 fps. For safety, a quenching mechanism was installed in form of a separate syringe filled with water. Additionally, portable glass windows were placed in front of the set-up.

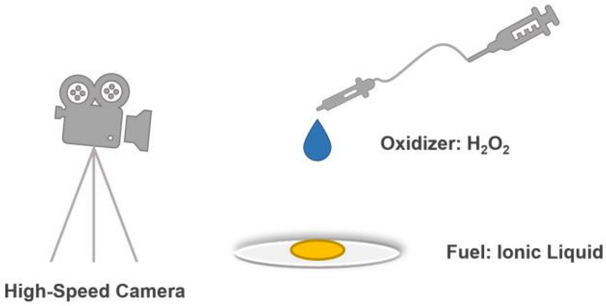

Figure 2. Drop test setup for determination of ignition delay times.

4. RESULTS AND DISCUSSION

In the following, first some preliminary ingestions on the ionic liquid combinations are presented. Subsequently, detailed knowledge about the thermal stability of the ionic liquids will be provided. Then, an analysis of the intermolecular interaction of the ionic liquid mixtures is conducted via FTIR-spectroscopy. Furthermore, combustion data of the bipropellant combinations are calculated with NASA CEA and the results for the specific impulses are compared with conventionally used hypergolic propellant combinations. In a final step, the hypergolic ignition behavior of the ionic liquid fuels with highly concentrated hydrogen peroxide as oxidizer will be highlighted.

4.1 Preliminary Investigations

For preliminary investigation, different mixing ratios of [Him][SCN] in [Emim][SCN] were prepared. The maximum solubility limit under ambient conditions was 35 wt% [Him][SCN] in [Emim][SCN]. This combination was named **HIM_35**. Fig. 3 shows the relationship of viscosity and density for different mixing ratios. It is clear that both quantities increase approximately linearly with increasing ratio [Him][SCN]. More details on the characterization of the other mixing ratios as well as the ignition delay time and the calculated combustion data can be found in [11].

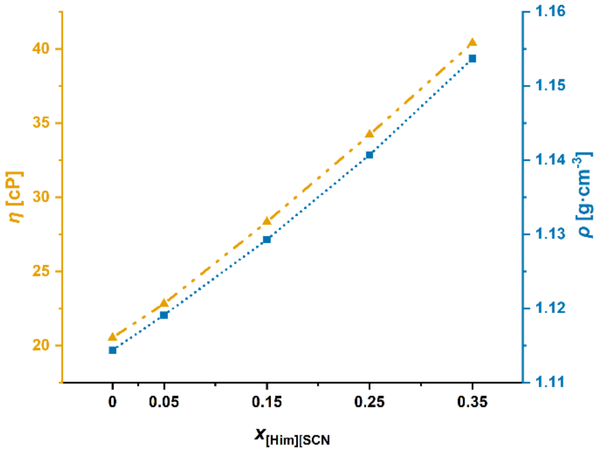

Figure 3. Dependency of viscosity (yellow) and density (blue) of various mixing ratios of [Him][SCN] in [Emim][SCN].

4.2 Thermal Analysis and Long-Term Stability

In order to characterize the thermal behavior of the IL combination **HIM_35**, simultaneous TG (thermogravimetric) and DSC (dynamic scanning calorimetry) measurements were carried out. Measurements were conducted with fuel samples in closed aluminum crucibles under a stream of pure nitrogen gas with a flow rate of 50 ml/min. For the short-term measurements, the initial temperature of 30 °C was increased by a heating rate of 10 K/min to a final temperature of 600 °C.

In Fig. 4, the TG-analysis with the associated DSC-curve of **HIM_35** in the temperature range between 30 °C and 600 °C is shown. As the onset of the decomposition was found at a temperature of 256 °C, **HIM_35** can be designated as a substance of high thermal stability.

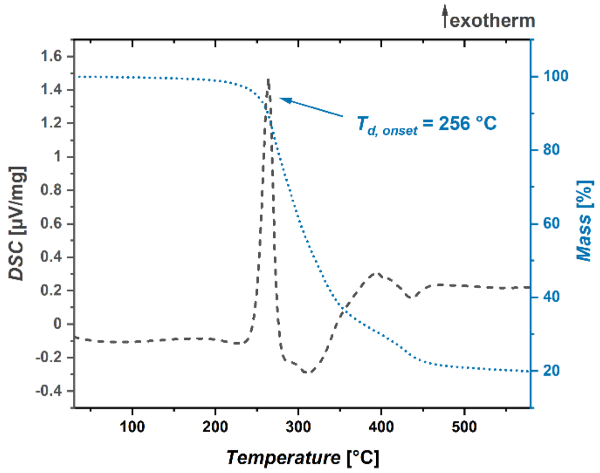

*Figure 4. DSC- (grey) and TG- (blue) diagram of **HIM_35**.*

In case of the long-term measurement of **HIM_35**, the starting temperature of 30 °C was increased by 10 K/min until a value of approx. 100 °C was reached. This temperature was then kept constant for a time span of 12 h. Results of the long-term stability measurements are presented in Fig. 5. Analysis of the TG-curve reveals, that a weight loss of < 1 % is detected over the whole measurement period. This proves that long-term stability is given for the fuel candidate, so it is expected to be unaffected under standard storage conditions in the tank of a space vehicle. ·

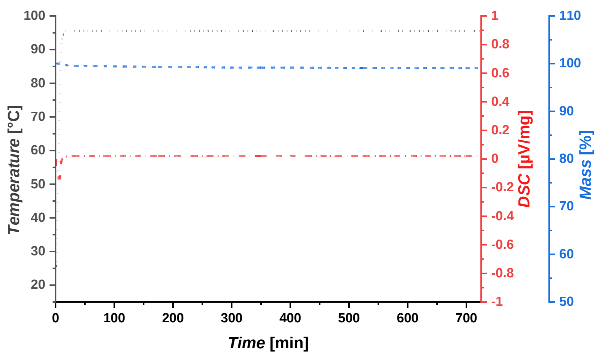

*Figure 5. Temperature (grey), DSC- (red) and TG- (blue) diagram of **HIM_35**.*

4.3 FTIR-Spectroscopic Analysis of IL-Interactions

For further analysis of the ionic liquid combination **HIM_35**, an FTIR-spectrum was recorded and compared to the initial compounds, as shown in Fig. 6. The three spectra share the very strong *v*(SCN)-signal at approx. 2050 cm^{-1}. In case [Him][SCN], the protic character of the ionic liquid is clearly visible in the form of symmetric an asymmetric stretching vibration of the N-H-moiety around 3000 cm^{-1}. This functionality is also visible in the FTIR-spectrum of **HIM_35** in an attenuated form.

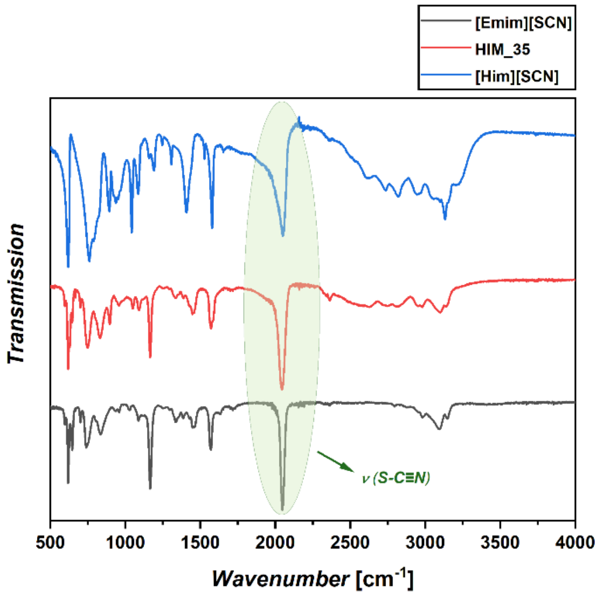

*Figure 6. Overlay of FTIR-spectra of [Him][SCN] (blue), **HIM_35** (red) and [Emim][SCN] (grey).*

4.4 Calculated Combustion Data

In this section, the theoretical performance of the ionic liquid bipropellant will be compared to the benchmark hypergolic bipropellant MMH in combination with NTO. For this purpose, the standard enthalpies of formation of the individual IL components were determined by bomb calorimetry measurements. The detailed procedure can be found in [11,14]. Based on these experimentally determined values for the standard enthalpies of formation, the specific impulse (I_{sp}) of **HIM_35** was calculated with NASA CEA (Chemical Equilibrium with Applications) code. [15] The combustion data was calculated based on an *Ariane Group* 400 N thruster with an expansion ratio of 330 and a chamber pressure of 10 bar. [9,13] The ratio of oxidizer to fuel (ROF) was calculated using the following equation, with oxidizer mass flow ($\dot{m}_{oxidizer}$) and fuel mass flow ($\dot{m}_{fuel}$) as in Eq. 1:

$$ROF = \frac{\dot{m}_{oxidizer}}{\dot{m}_{fuel}} \qquad (1)$$

In Fig. 7, the development of the I_{sp} at ROFs between 1 and 6 of **HIM_35** and 98 wt% H_2O_2 is compared with the hypergolic propellant combination MMH / NTO. As listed in Tab. 1, the maximum specific impulse ($I_{sp,\ max}$) of 337 s of this conventional propellant combination exceeds the $I_{sp,\ max}$ of **HIM_35** / 98 wt% H_2O_2 of 314 s.

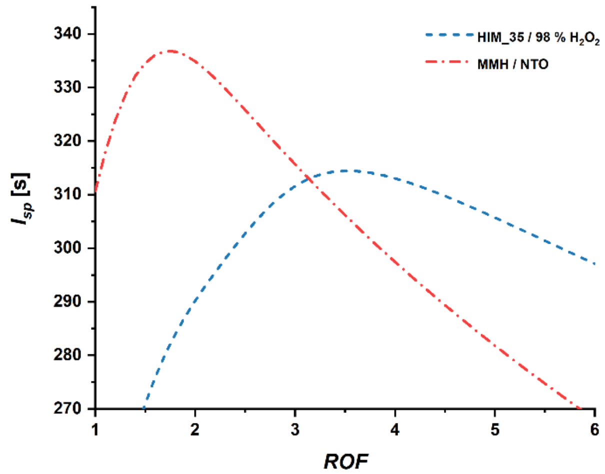

*Figure 7. Comparison of I_{sp} over ROF of **HIM_35** / 98 wt% H_2O_2 (blue) and MMH /NTO (red).*

Thereupon, the overall propellant density at the respective ROF was determined as:

$$\rho_{propellant} = \frac{\rho_{oxidizer} \times \rho_{fuel} \times (ROF+1)}{\rho_{oxidizer} + \rho_{fuel} \times (ROF)} \qquad (2)$$

Based on this, the volumetric specific impulse ($\rho\ I_{sp}$) was calculated. Fig. 8 shows the evolution of the density specific impulses of the two opposed hypergolic propellant combinations.

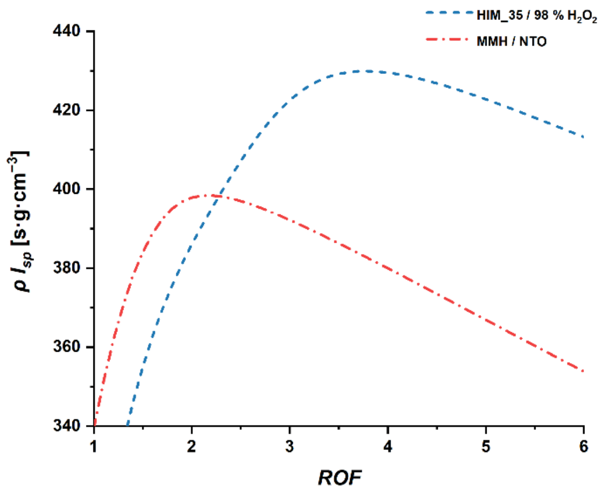

*Figure 8. Comparison of $\rho\ I_{sp}$ over ROF of **HIM_35** / 98 wt% H_2O_2 (blue) and MMH /NTO (red).*

However, as shown in Tab. 1, the maximum density I_{sp} ($\rho\ Isp,_{\ max}$) of **HIM_35** and 98 wt% H_2O_2 of 429 s·g·cm^{-3} surpasses the value of 392 s·g·cm^{-3} of MMH / NTO. Thus, the alternative propellant combination is significantly more advantageous from this point of view, since less propellant is required for the same transport mass of a space vehicle.

*Table 1. Maximum specific impulse and density specific impulse for **HIM_35** / 98 wt% H_2O_2 and MMH / NTO.*

	$I_{sp,\ max}$ [s]	$\rho\ I_{sp,\ max}$ [s·g·cm^{-3}]
HIM_35 / 98 wt% H_2O_2	314	429
MMH / NTO	337	392

4.5 Hypergolic Ignition with H_2O_2

In order to evaluate the hypergolic ignition behavior of the IL based fuels, drop tests with highly concentrated hydrogen peroxide (97 wt%) were carried out. Individual sequences of these tests are shown in Fig. 9. The first sequence (I) shows the hydrogen peroxide drop above the IL on the watch glass. In (II), the first contact of the oxidizer drop and the fuel can be noted. Afterwards in (III), the evolution of vapor is observed, which is followed by the first flame formation in (IV) and a rapid propagation of the flame in (V), respectively. A summary of the average ignition delay times along with the respective standard deviations (SD) can be found in Tab. 2. The IDT of [Emim][SCN] of 27.6 ms is reduced by the very short average IDT of the solid IL [Him][SCN], with a glance at the IL mixture of both **HIM_35**, which features an average IDT of 16.7 ms. With this substance, a liquid fuel is created, that is able to ignite with highly concentrated hydrogen peroxide in a very short time period of < 20 ms without the necessity of transition metal or hydride additives.

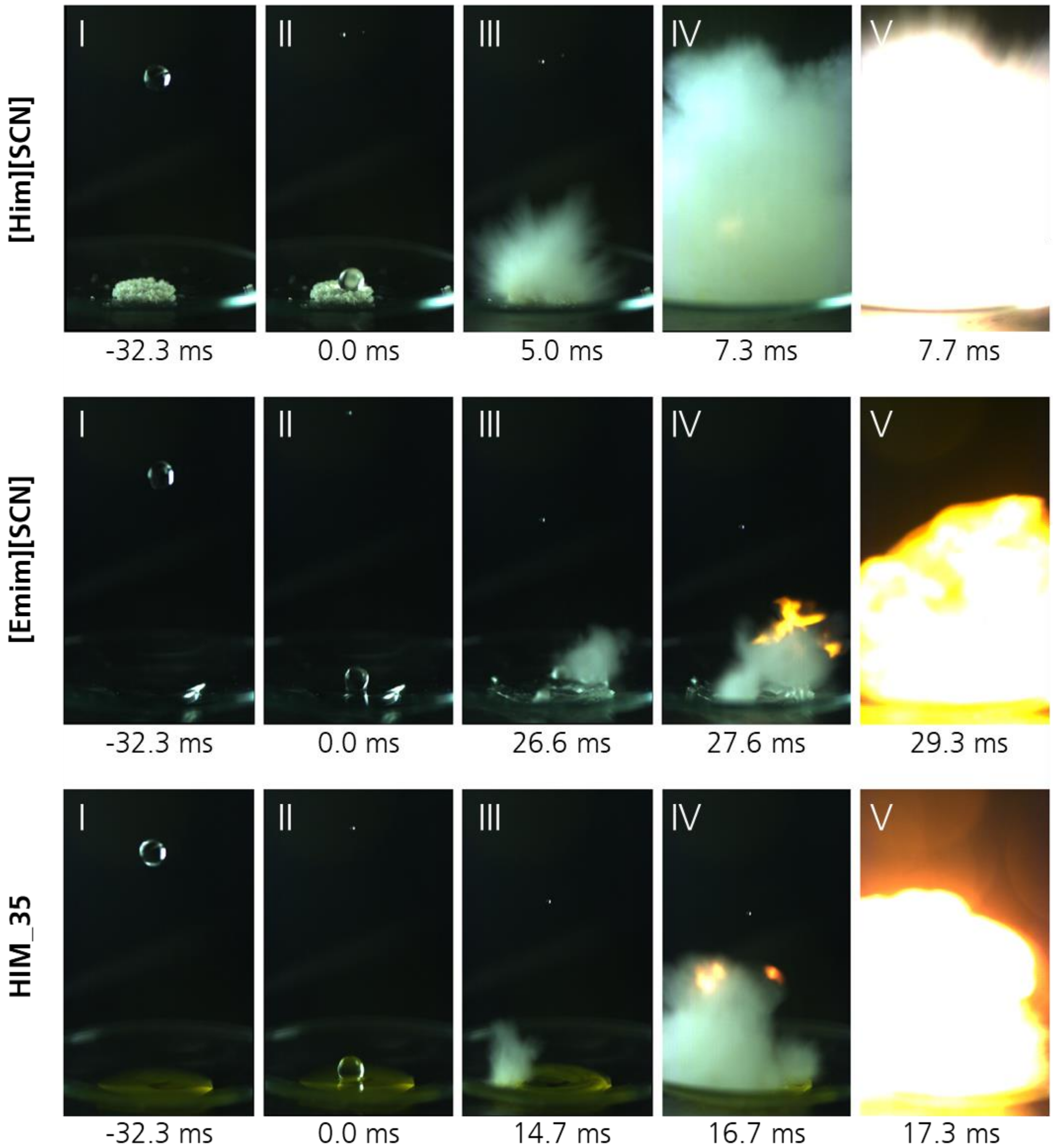

*Figure 9. Sequences of hypergolic drop tests with highly concentrated hydrogen peroxide (97 wt%) as oxidizer. Fuel: [Him][SCN] (top), [Emim][SCN] (middle) and **HIM_35** (bottom).*

*Table 2. Average IDTs (ignition delay times) and respective standard deviations of [Him][SCN], [Emim][SCN] and **HIM_35** with 97 wt% H_2O_2. For each fuel, at least three drop tests were carried out.*

	***IDT* [ms]**	***SD IDT* [ms]**
[Him][SCN]	7.3	0.7
[Emim][SCN]	27.6	4.1
HIM_35	16.7	0.7

5. CONCLUSION

In this paper, an alternative "green" hypergolic bipropellant is presented, which is intended to replace conventional toxic hypergolic fuels, such as the common combination of MMH and NTO, in the future.

For this purpose, highly concentrated hydrogen peroxide as an oxidizer is combined with the so-called fuel **HIM_35**, which is composed of two ionic liquids. The thermal behavior of this fuel was investigated by means of thermogravimetric analysis combined with dynamic scanning calorimetry. High temperature stability as well as long-term stability of the fuel was observed. Furthermore, **HIM_35** was investigated by FTIR spectroscopy and compared to the initial substances [Him][SCN] and [Emim][SCN] to further characterize the fuel.

The theoretically calculated volumetric specific impulse of **HIM_35** and H_2O_2 significantly exceeds that of MMH and NTO, so the alternative fuel combination offers great advantages in this regard. The higher volumetric specific impulse saves propellant mass that can be replaced by payload on the spacecraft. The ignition behavior of the hypergolic propellant was investigated by drop tests. An average ignition delay of < 20 ms was determined. To the best of our knowledge, we are not aware of any other transition metal- and hydride-free IL-based liquid fuel that has such a short ignition time with H_2O_2 as an oxidizer.

In the near future, hot fire tests on the M11 test bench with **HIM_35** and concentrated hydrogen peroxide are planned to further demonstrate the suitability of the hypergolic fuel combination.

6. ACKNOWLEDGEMENT

The authors would like to thank the team members of the *Chemical Propellant Technology* department and the M11 test bench team for their support.

7. REFERENCES

[1] E. W. Schmidt, *Hydrazine and its derivatives*: *Preparation, properties, applications*, Wiley-Interscience, New York, 2001.

[2] J. Malm, “Inclusion of Substances of Very High Concern in the Candidate List,” *European Chemicals Agency (EACH), Helsinki*, 2011.

[3] P. D. McCrary, G. Chatel, S. A. Alaniz et al., “Evaluating Ionic Liquids as Hypergolic Fuels: Exploring Reactivity from Molecular Structure,” *Energy & Fuels*, vol. 28, no. 5, pp. 3460–3473, 2014.

[4] R. D. Rogers and K. R. Seddon, “Chemistry. Ionic liquids--solvents of the future?,” *Science (New York, N.Y.)*, vol. 302, no. 5646, pp. 792–793, 2003.

[5] S. Zhang, N. Sun, X. He et al., “Physical Properties of Ionic Liquids: Database and Evaluation,” *Journal of Physical and Chemical Reference Data*, vol. 35, no. 4, p. 1475, 2006.

[6] S. Schneider, T. Hawkins, M. Rosander et al., “Ionic Liquids as Hypergolic Fuels,” *Energy & Fuels*, vol. 22, no. 4, pp. 2871–2872, 2008.

[7] S. Schneider, T. Hawkins, Y. Ahmed et al., “Green Bipropellants: Hydrogen-Rich Ionic Liquids that Are Hypergolic with Hydrogen Peroxide,” *Angewandte Chemie*, vol. 123, no. 26, pp. 6008–6010, 2011.

[8] C. Sun, S. Tang, and X. Zhang, “Role of Cation Structures for Energetic Performance of Hypergolic Ionic Liquids,” *Energy & Fuels*, vol. 31, no. 9, pp. 10055–10059, 2017.

[9] F. Lauck, J. Balkenhohl, M. Negri et al., “Green bipropellant development – A study on the hypergolicity of imidazole thiocyanate ionic liquids with hydrogen peroxide in an automated drop test setup,” *Comb. Flame*, vol. 226, pp. 87–97, 2021.

[10] S. C. Ricker, D. Freudenmann, and S. Schlechtriem, “The Impact of Cation Structures on Hypergolicity of Thiocyanate Ionic Liquids with Hydrogen Peroxide,” *Energy & Fuels*, vol. 35, no. 19, pp. 16128–16133, 2021.

[11] S. C. Ricker, D. Brüggemann, D. Freudenmann et al., “Protic Thiocyanate Ionic Liquids as Fuels for Hypergolic Bipropellants with Hydrogen Peroxide,” *Submitted to Fuel on February 11th 2022, publication in process*.

[12] M. Negri and F. Lauck, “Hot Firing Tests of a Novel Green Hypergolic Propellant in a Thruster,” *J. Propuls. Power*, pp. 1–11, 2022.

[13] ArianeGroupOrbital Propulsion, “Chemical Bi-Propellant Thruster Family, Taufkirchen,” *Chemical Bi-Propellant Thruster Family, Taufkirchen*, 2017.

[14] D. H. Zaitsau, V. N. Emel’yanenko, S. P. Verevkin et al., “Sulfur-Containing Ionic

Liquids. Rotating-Bomb Combustion Calorimetry and First-Principles Calculations for 1-Ethyl-3-methylimidazolium Thiocyanate," *Journal of Chemical & Engineering Data*, vol. 55, no. 12, pp. 5896–5899, 2010.
[15] B. J. McBride and S. Gordon, "Chemical Equilibrium and Applications, NASA," *Chemical Equilibrium and Applications, NASA*, 2004.