HIM_30: HOT-FIRING TESTS AND CHARACTERISATION OF A GREEN HYPERGOLIC PROPELLANT BASED ON IONIC LIQUIDS AND HYDROGEN PEROXIDE

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Sophie C. Ricker [(1)], Felix Lauck[(1)], Philipp Teuffel[(1)], Florian Merz[(1)], Dominic Freudenmann[(1)] and Christoph Kirchberger[(1)]

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

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ABSTRACT:

In the New Space sector's search for alternative hypergolic propellants, the combination of hydrogen peroxide as oxidizer and ionic liquids as fuel is emerging as a promising avenue.

Ionic liquids possess properties such as negligible vapor pressure, high density and tailorable cation structures, which make them highly attractive for future space propulsion systems. The fuel HIM_30 is a blend of two ionic liquids that provides rapid hypergolic ignition with high test peroxide without the inclusion of transition metals or hydride-based additives. In this paper, not only a comprehensive characterization of this new green propellant combination is presented, but also the results of the first hot-firing tests are discussed, which represent the next step towards the application of this upcoming green space propellant.

1. INTRODUCTION

Since the toxic and carcinogenic fuels hydrazine, MMH (monomethyl hydrazine) and UDMH (unsymmetrical dimethylhydrazine) along with the oxidizer NTO (nitrogen tetroxide) are still the most commonly used hypergolic propellants, focus of our research is on alternatives to these substances. In the work presented here, ionic liquids (ILs) as fuels with hydrogen peroxide (H_2O_2) as oxidizer are investigated as advanced green space propellants.

Highly concentrated hydrogen peroxide, also often referred to as high test peroxide (HTP), offers several advantages as oxidizer for hypergolic propellants. Firstly, it is a storable liquid with a low vapor pressure, which facilitates handling compared to more volatile oxidizers such as nitrogen tetroxide [1]. In addition, hydrogen peroxide is less corrosive than other oxidizers such as concentrated nitric acid, which can simplify material selection and extend the life of propulsion system components [2]. Furthermore, its non-toxic decomposition produces water and oxygen further contribute to its potential as a greener alternative in space propulsion systems [3].

In recent years, ILs have become an increasingly attractive alternative to conventional fuels. The main reasons for this are the physical and chemical properties properties, which result from the ionic composition and differ from those of classic molecular liquids. An important aspect is the low vapor pressure of ILs, which generally minimizes the formation of volatile components and therefore simplifies handling compared to conventional hypergolic propellants [4]. The high density of ILs also makes them attractive for space applications, as they can be stored in smaller propellant tanks for a given propellant mass, which results in a lower structural weight and therefore lower overall costs [5].

Previously, our working group at DLR in Lampoldshausen has identified a number of thiocyanate-based ILs as suitable fuel candidates [6–8]. A variety of characterizations and tests have been carried out on laboratory scale in various projects, through which certain ILs have emerged as fuels with outstanding properties. Overall, the innovative green fuel combinations have shown to offer the potential to replace conventional hydrazine-based fuels in the future.

With HIP_11, a promising IL-based propellant combination was developed whose functionality has already been successfully demonstrated [9,10]. HIM_30 is a further evolution of this propellant, with the main distinction that it does not contain copper-containing components. HIM_30 is composed of 30 wt% [Him][SCN] (imidazolium thiocyanate) and 70 wt% [Emim][SCN] (1-ethyl-3-methylimidazolium thiocyanate). The physical and chemical properties of this fuel as well as an analysis of the propellant-relevant characteristics are presented herein. Moreover, a comparison with the properties of the conventionally utilized hypergolic combination MMH / NTO is drawn. Finally, this paper will present the results of hot-firing tests of the propellant in a 40 N battleship thruster at the test bench M11 in detail. Further, the analyzed data will be 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. 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.

3. PROPELLANT CHARACTERIZATION

3.1. Fuel Composition

The following section focuses on the characterization of the IL-based fuel component HIM_30.

HIM_30 consists of the two components 1-Ethyl-3-methylimidazolium thiocyanate [Emim][SCN] (70 wt%) and imidazolium thiocyanate [Him][SCN] (30 wt%). A detailed description of the properties of the single fuel components can be found in [8], this paper will focus on the most relevant properties of the fuel blend HIM_30. The IL [Emim][SCN] was purchased by Iolitec GmbH with a purity > 98 % and used without further purification. [Him][SCN] was synthesized in our physical-chemical laboratory at DLR. After synthesis and purification, the compound was analyzed via NMR- and IR-spectroscopy as well as ion chromatography and volumetric Karl-Fischer titration. Overall, the purity was also specified to be > 98 %. Table 1 shows values for the viscosity (μ) and the density (ρ) of the prepared fuel blend HIM_30.

Table 1. Density and Viscosity of HIM_30 at 25 °C.

	μ / (mPa·s)	**ρ / (g·cm^{-3})**
HIM_30	37	1.148

To characterize the thermal behavior of the IL combination HIM_30, simultaneous thermogravimetric (TG) and dynamic scanning calorimetry (DSC) measurements were conducted. The temperature has been increased from 30 °C to 600 °C at a heating rate of 10 K/min. The fuel samples were measured in closed aluminum crucibles under a stream of pure nitrogen gas with a flow rate of 50 ml·min^{-1}.

As Figure 4 shows, the decomposition onset of HIM_30 was specified to a temperature of 252 °C.

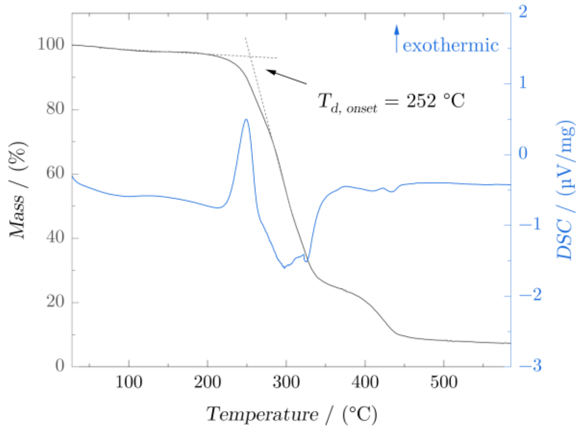

Figure 1. TG- (black) and DSC- (blue) diagram of HIM_30.

3.2 Theoretical Performance

For the analysis of the theoretical performance of the propellant, the standard enthalpies of formation of the ILs from Table 2 were used.

Table 2. Enthalpies of formation of the two ILs [Emim][SCN] and [Him][SCN].

	ΔH_f / (kJ·mol^{-1})
[Emim][SCN]	52.8 [11]
[Him][SCN]	-10.9 [12]

The theoretical performance calculations were carried out with NASA CEA (Chemical Equilibrium with Applications) code [13]. All calculations are based on an *Ariane Group* 400 N thruster with a chamber pressure of 10 bar and an expansion ratio of 330 [6,14]. Equation 1 was used to determine the ratio of oxidizer to fuel (ROF), with the oxidizer mass flow ($\dot{m}_{\text{oxidizer}}$) and fuel mass flow ($\dot{m}_{\text{fuel}}$).

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

The theoretical maximum specific impulse ($I_{sp,\ max}$) of HIM_30 and 98 wt% H_2O_2 of 314 s was found at a ROF of 3.6. The values of the theoretical performance parameters are compared with hypergolic propellant combination MMH / NTO. Table 3 gives an overview over the results.

Table 3. Maximum specific impulse and density specific impulse for HIM_30 / 98 wt% H_2O_2 and MMH / NTO.

	$I_{sp,\,max}$ / (s)	ROF @ $I_{sp,\,max}$	$\rho\ I_{sp,\,max}$ / ($s \cdot g \cdot cm^{-3}$)
HIM_30 / 98 wt% H_2O_2	314	3.6	429
MMH / NTO	337	1.7	398

A visualization of the calculated I_{sp} values over the ROF for both propellants is shown in Figure 1. The $I_{sp,max}$ of MMH / NTO exceeds that of HIM_30 / 98 wt% H_2O_2 by approximately 7 %.

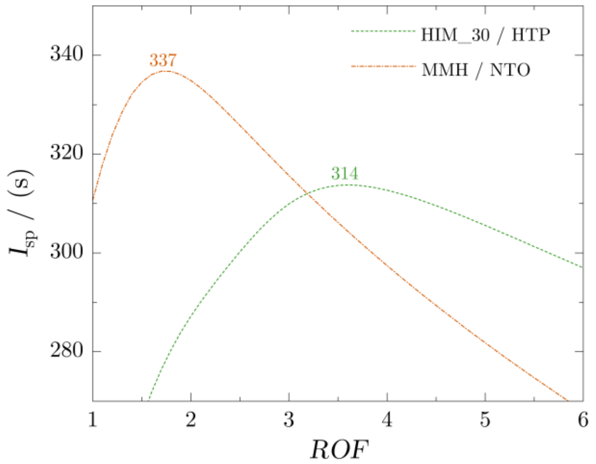

Figure 2. Comparison of I_{sp} over ROF of HIM_30 / 98 wt% H_2O_2 (green) and MMH /NTO (red).

To determine the volumetric specific impulse ($\rho\ I_{sp}$), the density of the overall propellant was calculated according to Equation (2).

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

Figure 3 compares the density specific impulses of the two hypergolic propellants. The maximum volumetric specific impulse of HIM_30 / 98 wt% H_2O_2 is significantly higher than that of MMH / NTO and therefore more beneficial in this respect.

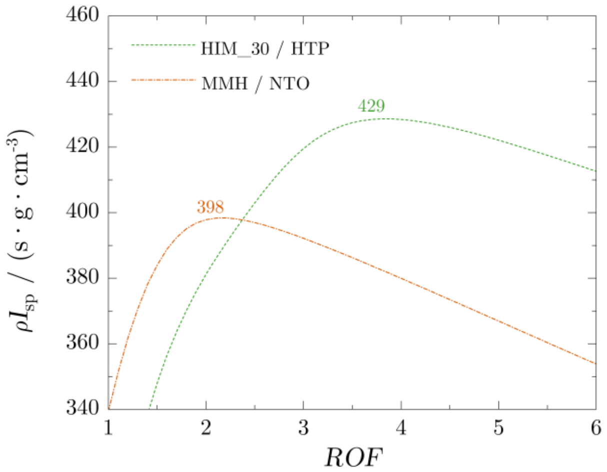

Figure 3. Comparison of $\rho\ I_{sp}$ over ROF of HIM_30 / 98 wt% H_2O_2 (green) and MMH /NTO (red).

To evaluate the hypergolicity of HIM_30 with hydrogen peroxide, drop tests were carried out. A set-up as shown in Figure 4 was utilized.

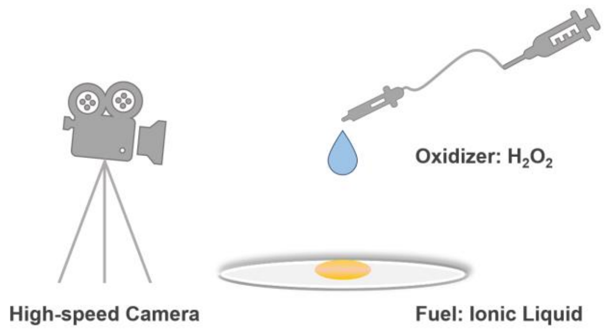

Figure 4. Drop test set-up.

The drop tests were filmed by a high-speed camera with a recording speed of 5000 frames per second. It was demonstrated that HIM_30 is able to ignite reliably with highly concentrated hydrogen peroxide (~97 wt%) with an ignition delay time of < 20 ms.

3.3 Upscaling of the fuel

For the hot-firing tests, [Him][SCN] was synthesized in a large-scale batch in the M3 laboratory. After synthesis, the composition and purity of the IL were confirmed. As described previously, [Emim][SCN] was purchased by Iolitec GmbH. Photographs of the solid [Him][SCN] and the prepared HIM_30 are shown in Figure 5.

Figure 5. Photographs of [Him][SCN] (left) and HIM_30 (right).

4. HOT-FIRING TESTS

The HIM_30 combination described above proved to be a suitable alternative fuel in lab scale characterizations and analyses. Therefore, a test campaign was performed to demonstrate the ability of using HIM_30 in a battleship thruster demonstrator.

4.1 Test bench setup

The test bench setup for hypergolic propellant combinations at DLR M11.5 had been used to demonstrate ignition and short fire duration tests. A schematic of the fluid plan is shown in Figure 6. Two tanks, one for fuel and one for oxidizer, can be pressurized by nitrogen independently. Each fluid line does contain pressure transducers (p) and thermo couples of type K (t). Additionally, Coriolis mass flow meters ($\dot{m}$) are used to measure the mass flow rates. The propellant supply to the injector and combustion chamber can be controlled by two flow control valves (FCV).

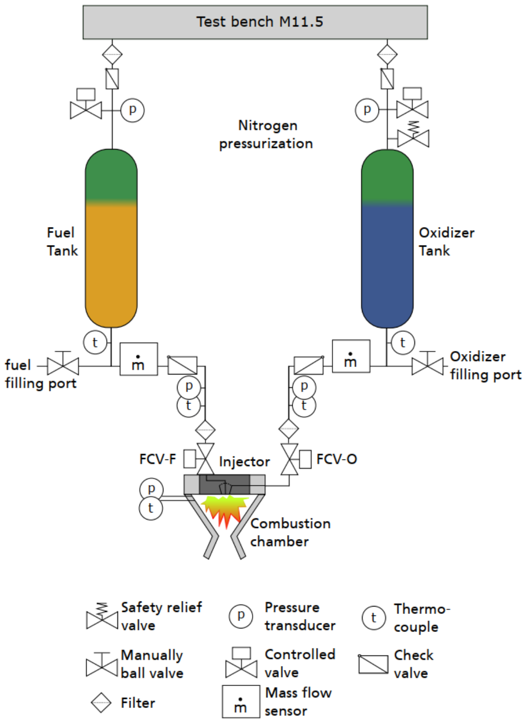

Figure 6: Schematic of the M11.5 test bench setup.

The combustion chamber pressure is measured with two pressure transducers. Additionally, the wall temperatures are measured with a set of thermo couples along the chamber wall.

4.2 Test hardware

For the initial test campaign using HIM_30 as propellant, a battleship thruster designed by M. Negri was used [9]. This design was further developed as described in [10].
The combustion chamber consists of stainless steel. Additionally, an extension was used to increase the combustion chamber length (L*= 1.2 m). This extension was made from Inconel 718 and was produced by additive layering manufacturing. The nozzle was designed with an expansion ratio of 100, but the nozzle was truncated at an expansion ratio of 2.5 to avoid flow separation at atmospheric conditions. A 4on1 unlike impinging injector was used. Here, the oxidizer is injected by four jets and the fuel is injected by a single jet.

Despite the battleship thruster was designed to operate with HIP_11, it was assumed as a sufficient starting point for initial hot firing tests with HIM_30. Additional design parameters of the battleship thruster are listed in Table 4.

Table 4. Design parameters of the used battleship thruster.

Chamber pressure / (bar)	10
ROF	4
Thrust (@ nominal conditions) / (N)	40
Oxidizer	H_2O_2 (97 wt%)
Fuel	HIM_30

4.3 Hot fire results

In Figure 7 and Figure 8, pressures and mass flow rates measured during an exemplary hot fire test of HIM_30 / HTP are shown. All single values, which are derived from the measurement transcriptions or then calculated are averaged between 1.47 s and 2.47 s. The operating conditions were set by the nitrogen pressurization to reach 10 bar of chamber pressure with a ROF of 3.7.

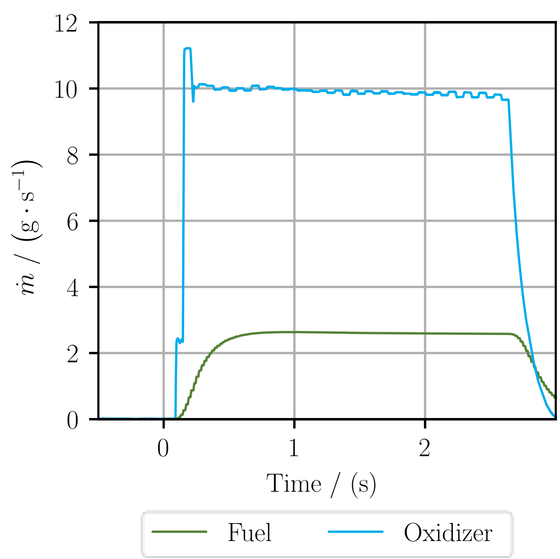

Figure 7. Mass flow of an exemplary test over time.

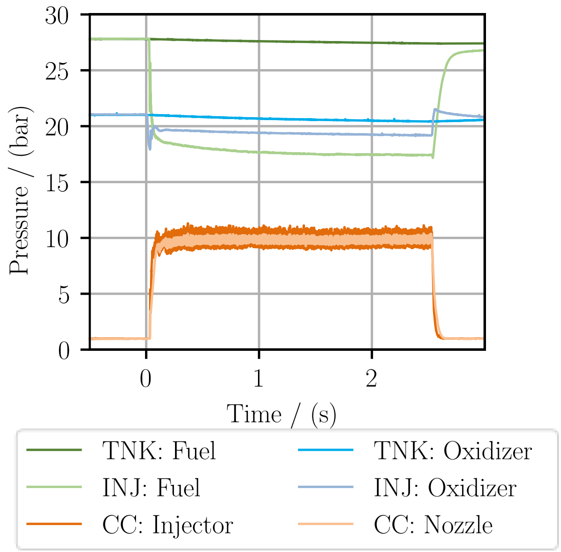

Figure 8. Various pressure measurements of an exemplary test over time.

At time 0 s the fuel and oxidizer flow control valves are triggered to open. The chamber pressure rises smoothly until 9.9 bar is reached. With an oxidizer mass flow rate of 9.8 g·s^{-1} and a fuel mass flow rate of 2.6 g·s^{-1} a steady combustion chamber pressure was achieved at ROF of 3.8. Pressure drops of 7.6 bar and 9.4 bar for oxidizer and fuel respectively, were measured. After 2.5 s, the flow control valves are triggered to close. The characteristic velocity efficiency η_{c^*} at this operating condition, calculated by

$$\eta_{c^*} = \frac{c^*_{\mathrm{exp}}}{c^*_{\mathrm{theo}}} \cdot 100\ \% \qquad (1)$$

is about 92.9 %. Here, the experimental characteristic velocity c^*_{exp} is divided by the theoretical characteristic velocity c^*_{theo} of this operating point. The theoretical characteristic velocity is computed via NASA CEA [13]. The experimental characteristic velocity is calculated from the averaged values derived from the test measurement data by

$$c^*_{\mathrm{exp}} = \frac{p_{\mathrm{cc}} \cdot A_{\mathrm{t}}}{\dot{m}}, \qquad (2)$$

where p_{cc} is the combustion chamber pressure, A_t the nozzle throat cross section area and $\dot{m}$ the sum of the oxidizer and fuel mass flow rate. In Figure 10 a snapshot of the hot fire test is shown.

Figure 10: Exemplary hot fire test of HIM_30 at the end of firing.

In Figure 9 a summary of different hot firing tests is given. Here, the measurement data was averaged as mentioned in the example test before. To get an initial idea about the performance of HIM_30 in a thruster, different operating points were tested. The ROF was varied from 3.5 to 4.8. Within these operating points the chamber pressure varied from 8 bar to 10.3 bar. Overall, it can be seen, that even with a not optimized battleship thruster, a range of operation points with high characteristic velocity efficiencies could be demonstrated.

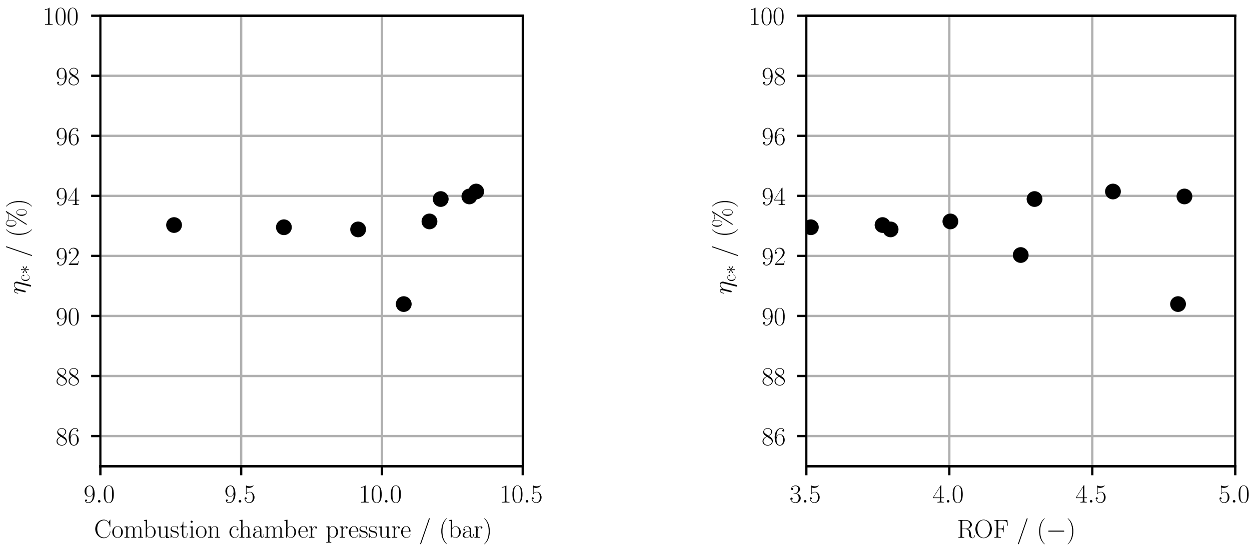

Figure 9: Characteristic velocity efficiency over (left) combustion chamber pressure and (right) ROF.

5. CONCLUSION AND OUTLOOK

Within this work, the development of a hypergolic bipropellant based on an ionic liquid fuel (HIM_30) and high test peroxide (HTP) is presented. The chemical composition of the fuel is described and physical properties like the viscosity, density and thermal behavior are discussed. Additionally, the calculation of the theoretical performance was carried out and the hypergolic ignition behavior in laboratory-scale drop tests is outlined.

Further, the hypergolic propellant combination HIM_30 / HTP was tested in a 40 N battleship thruster at test bench M11. The aim of these tests was to validate the hypergolic ignition and operation of the thruster. The thruster was equipped with an impinging type injector.

During the performed hot firing tests with firing durations up to 3 s, fast and reliable ignitions were demonstrated. Further, it was shown that stable and efficient combustion can be achieved with combustion efficiencies between 90 % and 94 %.

6. ACKNOWLEDGEMENT

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