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IGNITION INVESTIGATIONS OF A NOVEL HYPERGOLIC IONIC LIQUID WITH HYDROGEN PEROXIDE IN DROP TESTS

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ABSTRACT:

Conventional hypergolic propellants are highly toxic. Therefore, research is conducted in order to find suitable candidates as a replacement for these kinds of propellants. At DLR a promising propellant combination comprised of highly concentrated hydrogen peroxide and an ionic liquid was identified.

The used propellant combination showed an ignition delay time in drop tests of around 30 ms. These drop tests were conducted in a drop test setup keeping the test parameters constant. In the present study different external factors, which could have an impact on the ignition delay time were investigated: drop height, propellant amount and fuel or oxidizer as pool component.

For fuel as pool component no impact on the ignition delay time was observed when varying the drop heights or propellant amounts. A significant difference was observed between fuel or oxidizer pools. Here, the ignition delay time for oxidizer pools is twice as long as tests with in the fuel pool.

1. INTRODUCTION

Commonly used hypergolic propellants are based on hydrazines as fuel and nitrogen oxides as oxidizer. Hydrazine (N_2H_4) and its derivatives, such as unsymmetrical dimethyl hydrazine (UDMH) or monomethyl hydrazine (MMH), are highly toxic and carcinogenic. Further, it is possible that the use of hydrazine is restricted in near future in the European union due to the REACH regulation because of its high carcinogenic potential [1]. Dinitrogen tetroxide (N_2O_4) which is the main component of common hypergolic oxidizers, the so-called mixed oxides of nitrogen (MON), is also toxic and highly corrosive. Due to these adverse health effects the safe handling of common propellants is complex, time consuming and expensive.

Green hypergolic propellants, which are currently under development, are eager for the application of less toxic propellant components. This may allow for much more simplified handling procedures and offers a cost reducing potential. A suitable green oxidizer is highly concentrated hydrogen peroxide (H_2O_2) also referred to as high-test peroxide or HTP. HTP reaches similar performances and is less toxic compared to MON and NTO. On the fuel side, room temperature ionic liquids are very promising novel fuels due to their functional versatility. Furthermore, ionic liquids have a very low vapor pressure at ambient conditions. Thus, these kinds of fuels allow simpler handling procedures compared to common propellants. A number of ionic liquids have been demonstrated to have hypergolic behaviour with different oxidizers [2,3]. It is also possible to induce hypergolic behaviour using a suitable additive [4,5]. Recently, novel hypergolic combinations of hydrogen peroxide and ionic liquids with a thiocyanate anion were identified [6]. The propellant is called *HIP-11* for **H**ypergolic **I**onic **P**ropellant developed at the M**11** test facility of DLR Lampoldshausen.

For hypergolic propellants, the ignition delay time (IDT) is an important criterion: Long ignition delays can lead to accumulation of unburned fuel and oxidizer in a combustion chamber and result in a hard start event, when ignition occurs. Such an event could damage the propulsion system and spacecraft, putting the mission in danger. Early studies report that an ignition delay below 30 ms should be sufficient [7]. Today's conventional hypergolic propellants have an IDT in the order of several milliseconds [8].

The novel combination of 1-ethyl-3-methylimidazole thiocyanate (EMIM SCN) and highly concentrated hydrogen peroxide was tested in drop tests and showed an ignition delay on the order of 30 ms [6]. These drop experiments were conducted in a drop tests setup keeping the test parameters constant for all the tests, i.e. amount of fuel and oxidizer, drop height, and HTP falling into a fuel pool. But some of these factors could have an influence on the ignition delay time. In the present work a systematic investigation of the influence of the different factors on the ignition delay in drop tests is conducted. For hypergolic experiments on a lab scale a hypergolic ignition drop test setup was developed and put into operation. The setup provides a controlled environment for drop tests. In this study we investigate the influence of drop height, different propellant amounts and pool components. The results may help to gain an understanding what factor can have which impact on the ignition delay time of drop tests.

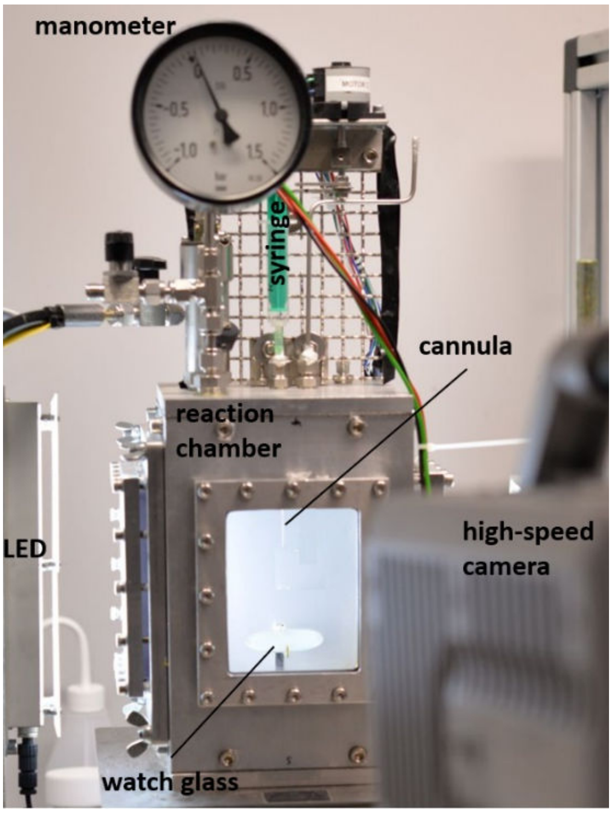

Figure 1 drop test chamber

2. METHOD

The drop test is a simple and fast method to investigate the hypergolic potential of fuel oxidizer combination in lab scale experiments. The hypergolic performance can be evaluated in terms of the ignition delay time. In a typical drop test experiment, a component of the propellant combination is dropped into a pool of the second component of the propellant. This is recorded with a high-speed camera. The ignition delay time is defined as the difference between the first contact of fuel and oxidizer and the first appearance of a flame (ignition).

The drop test setup is shown in Figure 1. The setup consists of a reaction chamber, a propellant supply, and measurement instrumentation. The chamber has a quadratic cross-section and consists of walls made of aluminium AW 6060. The inner volume is 140 x 140 x 216 mm³. In three of the four side walls cut-outs with windows offer optical access. One of the side walls (left in Figure 1) is removable to allow accessibility. A syringe pump assembly is placed on top of the reaction chamber. Thereby, the single components of the propellant can be supplied into the inside of the camber. The syringe pump assembly consists of two medical syringes, which are connected to cannulas and two linear motors. In Figure 1 only one of the syringes is mounted. The cannulas lead into the inside of the chamber and can release the “dropped” component of the propellant as well as the pool component. The plunger of the syringe is connected with a mount to the linear motors, so the plunger can be moved in or out. A scheme of the syringe assembly and the loading of propellant is shown in Figure 2.

The setup allows to test in an inert atmosphere or at reduced pressures. The pressure in the chamber is measured by a manometer connected to the chamber.

A watch glass is located below the two cannulas in the inside of the chamber. The watch glass provides the pool component for the drop test.

LEDs are used to illuminate the inside of the chamber. A *Photron fastcam SA-X2* high speed camera records the drop test with a frame rate of 3600 fps at 1000 x 600 pixel. The high-speed camera control software *PFV viewer* runs on a computer. A second computer controls the syringe pump using *LabVIEW* and a *NI Compact DAQ* with a *NI 9472* module. Some of the drop tests were also investigated with regard to flame emission spectroscopy. The dedicated paper on flame emission analysis can be found in the proceedings [9].

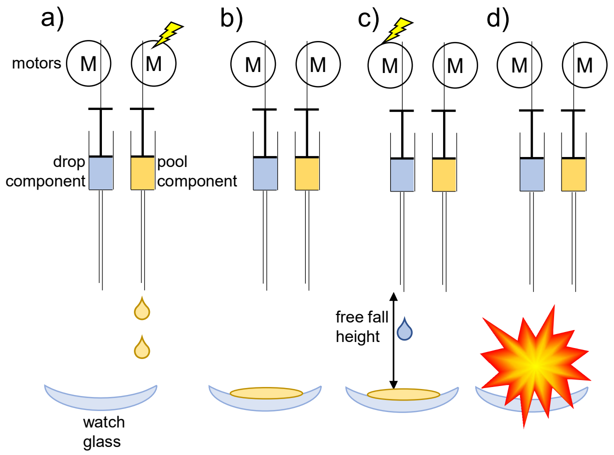

Figure 2 sequence of a drop test

The procedure of the drop tests is as follows: in a first step the pool component is supplied by releasing a certain number of drops of the 'pool component' from the syringe, see Figure 2 a). Because of the concave surface of the watch glass the drops gather in the middle and form the pool shown in Figure 2 b). In the second step the drop of the 'dropped component' is released from cannula which is located over the middle of the watch glass see Figure 2 c). The free fall height between the cannula tip and the watch glass determines the impact velocity of the falling drop. After the impact and mixing of the two components, an ignition can be observed shown in Figure 2 d).

Drop tests were conducted to investigate the influence of three factors on the ignition delay time:

- drop height
- propellant amount
- fuel or oxidizer as pool component

The mentioned factors were varied in five different drop test configurations. Table 1 lists the drop height, amount of the components and pooling component of the single configurations of the drop tests. *Configuration 0* is defined as the baseline measurement. It is conducted with a fuel pool and a single drop of the oxidizer. The diameter of the cannula was 1.1 mm and the length of the cannula was 120 mm. The outcome of this is a free fall height of 61 mm. In *configuration 1* the free fall height was increased. The cannula used had the same diameter but a length of 40 mm. Hence, the free fall height was increased to 141 mm. Because of the same cannula diameter, the cannula released a hydrogen peroxide drop of the same size. In *configuration 2* the size of the hydrogen peroxide drop is reduced by using a cannula with a diameter of 0.8 mm and 120 mm in length. The variation of the pooling amount of the fuel for *configuration 3* was implemented by reducing the numbers of drops of the pooling component, compare Figure 2 a). For this configuration only 4 drops of fuel were used instead of 8 for the other configurations. *Configuration 4* consisted of EMIM SCN as the dropping component from a cannula (diameter 1.1 mm, length 120 mm) on the hydrogen peroxide pool.

Table 1 test matrix

CONFIGURATION	**DESCRIPTION**	**AMOUNT OF OXIDIZER [µL]**	**AMOUNT OF FUEL [µL]**	**DROP HEIGHT**	**POOL COMPONEN**
0	baseline	14 ± 2.3	115 ± 2.0	61	EMIM SCN
1	higher drop	14 ± 2.3	115 ± 2.0	141	EMIM SCN
2	less oxidizer	11 ± 1.9	115 ± 2.0	61	EMIM SCN
3	less fuel	14 ± 2.3	58 ± 1.0	61	EMIM SCN
4	H_2O_2 pool	88 ± 1.9	14 ± 2.0	61	H_2O_2

98% hydrogen peroxide (*Propulse® 980)* was supplied by *EVONIK*. The peroxide was stored for two years in the aluminium bottles supplied by the manufacturer at 5°C. As the concentration decreases in time, the actual concentration of the H_2O_2 was determined by density measurements with a Mettler Toledo Density meter D40 and relating the measured density with the concentration value according to [10]. The concentration of the hydrogen peroxide thus determined was 96.1 wt%. The ionic liquid 1-ethyl-3-methyl-imidazole thiocyanate was supplied by *Iolitec GmbH*. The purity is specified with > 98% and was used without further purification.

The ignition delay time in drop tests is defined as the time period between the first contact of fuel and oxidizer and the first appearance of a flame. In this time period different phases can be distinguished. After initial contact of fuel and oxidizer physical mixing processes occur. During the mixing phase chemical reactions between fuel and oxidizer begin. These reactions raise the temperature and the

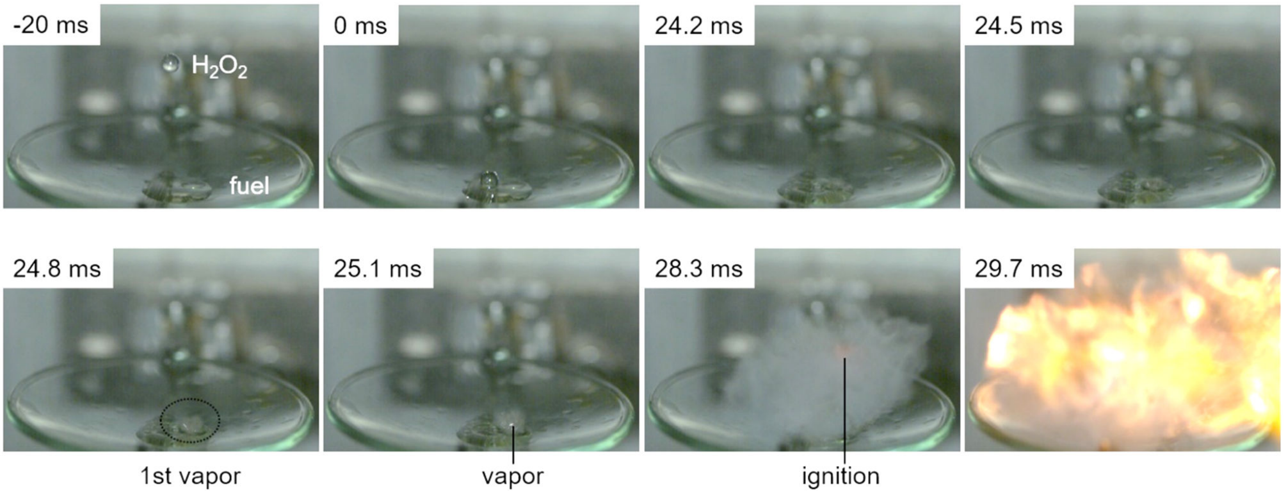

Figure 3 drop test of configuration 3

reaction rate is increased. Eventually the temperature is high enough, that vapor rises from the reacting mixture. In the vapor phase further reactions raise the temperature even more until the self-ignition temperature is reached. At this point the ignition occurs and a flame propagates in the gas phase. The duration between initial contact of the propellant components and the first obvious vapor generation is referred as the time to vapor generation (TVG).

High-speed imaging allows the determination of the first contact between fuel and oxidizer, begin of the vapor formation and ignition kernel. Therefore, the single video frames of the high-speed recording are analysed. Figure 3 shows an example ignition of a typical drop test of *configuration 3*. The first frame shows the drop of hydrogen peroxide 20 ms prior to impact. The first contact of fuel and oxidizer is defined as 0 ms. The following 4 frames show the mixture around the time of the first vapor generation. In this test, the first clear vapor is marked at 24.8 ms after initial contact. The first flame appears in the expanding vapor cloud at 28.3 ms after contact. After that the flame propagates rapidly in the vapor cloud. Following, in this test the TVG is 24.3 ms and the IDT is 28.3 ms.

The different amounts of the propellant components were estimated using the high-speed recordings. Single drops were assumed to be spherical and their diameter was determined in terms of pixels from the high-speed recording. A reference length was used to convert the pixel into a physical length. The uncertainty was assumed to be 3 pixels for the reference measurement and the diameter determination. The two uncertainties were summed according to Gaussian error propagation. The listed amounts in Table 1 are mean values of the tests of one configuration. The impact velocity was determined by analysing the frames before impact. The velocity was accounted by determining the time period the drop needed to fall one diameter shortly before impact. The uncertainty is assumed of the diameter uncertainty and the duration of one frame. The relative error of the impact velocity is in the

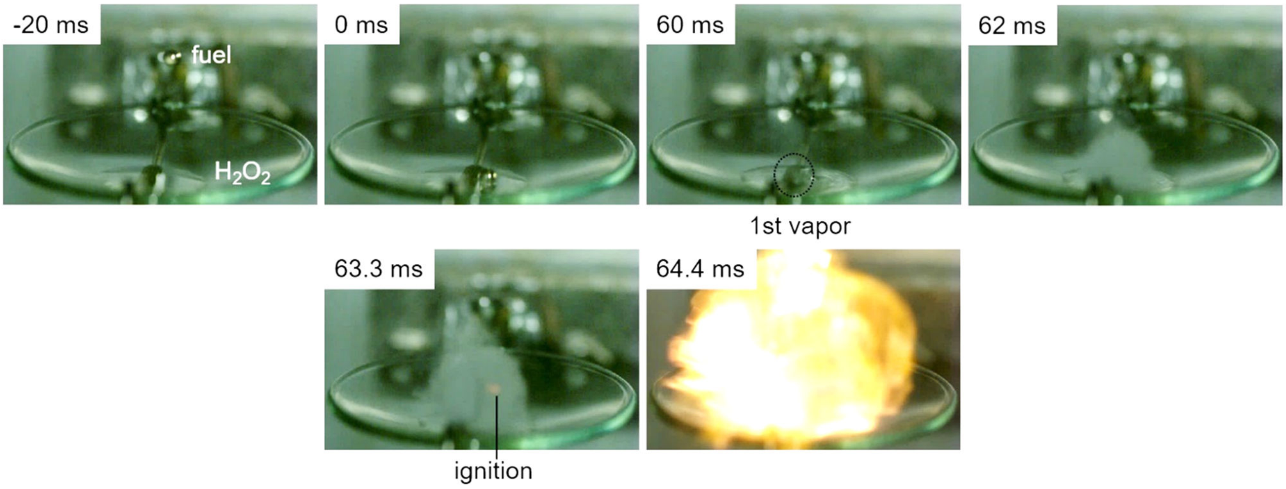

Figure 4 drop test of configuration 4

order of 25 %. Hence, the velocity before the impact is only roughly estimated with this determination. For higher accuracy, a higher frame rate and better resolution would be necessary.

3. RESULTS & DISCUSSION

The presented results summarize the TVG and IDT of 74 drop tests.

Configuration 0 is the baseline measurement. The drop tests in this configuration were repeated 20 times. The average ignition delay time is 31.3 ms and the TVG is 28.1 ms. The corresponding standard deviation are 3.7 and 3.6 ms. The velocity of the drop shortly before impact is in the order of 1 m/s.

Table 2 TVG and IDT

CONFIG	#	IDT	SD	TVG	SD	IDT-TVG
0	20	31.3	3.7	28.1	3.6	3.2
1	20	30.9	6.1	26.9	5.5	4.0
2	17	29.5	2.5	25.8	2.5	3.7
3	8	30.4	2.3	27.0	1.9	3.4
4	9	65.3	6.6	61.9	5.8	3.5

Configuration 1, where the hydrogen peroxide drops free fall is increased to 141 mm shows a similar IDT and also the TVG is in the same order. Thereby, the impact velocity is increased to 1.6 m/s. However, the standard deviations are higher as the reference. *Configuration 3* and *4* where different oxidizer are fuel amounts were used, lead to comparable IDT, TVG and standard deviations. The IDT and TVG are much higher in *configuration 4* compared to the reference. A typical example drop test with a oxidizer pool is shown in Figure 4. It is obvious that the time until obvious vapor is generated is longer compared to the tests with fuel as pool component. By comparison of the difference between TVG and IDT it is remarkable, that in the case of *configuration 4* the duration of the vapor phase is similar.

Table 3 lists literature values of heat capacities of pure H_2O_2 and EMIM SCN. The mass specific heat capacity of hydrogen peroxide is about 60 % higher than the IL. In *configuration 0* and *4,* the mass of the pool component was similar. Following, more energy is needed for heating the mixture with the hydrogen peroxide pool after contact until the vapor is released. The processes in the vapor phase may be comparable to the other configurations because of the similar duration. But the physical mixing and heating phase in the liquid mixture must be significant different between fuel and oxidizer pools. The difference of the ignition delay between fuel and oxidizer as pool component was also observed for other hypergolic combinations with H_2O_2 and so-called “Stock 2” fuel [12].

Table 3 heat capacities of IL and hydrogen peroxide

	EMIM SCN [11]	**H_2O_2 (100%)** [10]
c_p [J/mol K]	281.45	89.37
c_p [kJ/kg K]	1.663	2.627

For cases with H_2O_2 as dropped component, the oxidizer to fuel amount referred to the volumes are varied between 0.1 (Config. 2) and 0.24 (Config. 3). This variation did not show a significant influence on the IDT or the TVG.

In *configuration 1* the increased drop height seems to have no effect on the average IDT and TVG in our experimental conditions. At the higher impact velocities, one could expect that the physical mixing processes are more violent leading to faster ignition. Our velocity increase may not be high enough to affect the physical mixing processes. For a later application injection velocity are likely in the order of 10 – 20 m/s. Ignition delays in flowing conditions using impinging injectors can be shorter compared to drop tests [13].

For the configurations with fuel as pool component, there is no influence of different fuel or oxidizer amounts on the IDT of EMIM SCN and hydrogen peroxide. For further drop tests in our reaction chamber we can rely on the IDT determined with our baseline configuration. There is no significant change in IDT or TVG expected for higher impact velocities or different propellant amounts.

The pool component has a significant influence on the ignition delay time. Calculations predict a maximum I_{sp} at an oxidizer to fuel ratio of 4 [6], which is much different from the presented results. In further testing under flowing conditions it must be verified, if the ignition delay times are comparable to the low values of drop tests in with fuel pool or may be longer due to the higher oxidizer mass flow. Hence, it is obvious that ignition delay time of drop tests must be evaluated carefully in regard of a later application of the propellant under flowing condition i.e. in thrusters.

4. CONCLUSION

The ionic liquid EMIM SCN was tested with hydrogen peroxide in drop tests. Different factors of the drop tests which could have an influence on the ignition delay time were varied. Different drop height, propellant amounts and fuel or oxidizer as pool component were investigated and their results compared. For test with a fuel pool the ignition delay times were in the same order of close to 30 ms. No influence of different drop heights, and fuel or oxidizer amounts are observable. Also, the time to vapor generation remained similar for the different configurations. The comparison of fuel or oxidizer as pool shows a significant difference in the ignition delay time. The IDT for oxidizer pools is around twice as high as for fuel pools. The duration of the vapor phase until ignition is comparable. The drop test results need to be verified in further tests under conditions.

5. ACKNOWLEDGEMENT

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