Hypergolic Ignition of Triglyme and Hydrogen Peroxide Impinging Jets for Bipropellant Thrusters

C. Soudarin, ^{1†} E. Brodu, ¹ R. Beauchet, ² Y. Batonneau, ² P. Leroux, ³ B. Boust, ¹ M. Bellenoue ¹ ¹PPrime Institute, CNRS, ISAE-ENSMA, Université de Poitiers, Chasseneuil-du-Poitou, France ²IC2MP, Université de Poitiers, CNRS, 4 rue Michel Brunet B27, TSA 51106, 86073, Poitiers Cedex 9, France ³CNES, Space Transportation Directorate, 52 rue Jacques Hillairet, 75612 Paris Cedex, France

celia.soudarin@ensma.fr
† Corresponding Author

Abstract

Because of current environmental issues, space industry is looking for green and non-carcinogenic propellants to replace hydrazine. In these circumstances, many research studies investigate highly concentrated hydrogen peroxide (HTP: High Test Peroxide) and its use in hypergolic systems, which avoids adding an external ignition system and allows easy restarts. As the main application of this work is liquid propellants in space thrusters, in parallel to drop tests experiments, a dedicated set-up was designed to characterize the hypergolic ignition in impinging jets conditions. The ignition delays were determined considering the injection velocity of the propellants.

1. Introduction

Current environmental issues require to minimize the impact of the space industry over the environment. To allow easy re-ignition and re-usable engine, hypergolic systems are considered for storable space thruster nowadays. However, although hydrazine shows both great propulsive performances and hypergolic behavior in a bi-propellant thruster [1], the European Commission REACH – Registration, Evaluation, Authorization and Restriction of Chemicals – is placing hydrazine and its derivates as carcinogenic and harmful to the environment [2]. Hence, high concentrated hydrogen peroxide (HTP: High Test Peroxide) is presented as a greener candidate in order to replace these toxic propellants [3].

Since the beginning of the millennium, many research teams have studied hypergolic systems with hydrogen peroxide as oxidizer: Keese *et al.* [4], Melof *et al.* [5] and Dobbins *et al.* [6] studied many fuels doped with copper, sodium, aluminum, cobalt, manganese or iron-based additives. Only a few of these fuels ignited by contact with hydrogen peroxide. To select the most promising candidates, the ignition delay time – IDT – was defined as the time difference between the first contact and the ignition, which can be determined by conducting drop tests – a droplet of HTP is dropped on a pool of fuel and either a camera or a laser ensure the determination of the IDT [7]. A lower IDT would minimize the risks of hard starts in the engine [8]. On one hand, Anderson *et al.* [9] highlighted a very promising additive with low toxicity and IDT: sodium borohydride. On the other hand, Florczuk and Rarata [10] suggested copper-based additives such as copper chloride which was widely studied ten years later by the DLR [11] with another unknown additive: copper thiocyanate [12]. Although these three additives seem to be the most promising in terms of ignition performances, all being solid, a liquid fuel must be found to solubilize the additive.

In this study, the additive chosen is sodium borohydride and considering its solvent properties, the additive is solubilized in triethylene glycol dimethyl ether – known as triglyme. Some research, focused on the triglyme and sodium borohydride mixture, showed IDT lower than 20 ms with hydrogen peroxide concentrated around 90 wt. % [13,14] and lower than 10 ms with hydrogen peroxide concentrated at 98 wt. % [15,16]. A previous study shows that the IDT was optimum for a concentration of sodium borohydride in triglyme between 4 wt. % and 8 wt. % through drop tests [13] and is resumed on Figure 1. Hence, the concentration of NaBH₄ in triglyme is fixed to 6 wt. % in this paper.

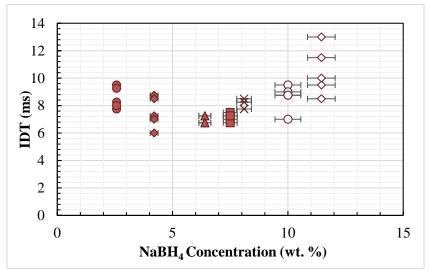


Figure 1 IDT for different concentration of NaBH₄ in triglyme with HTP 90 wt. % [13]

As drop tests do not reflect the real conditions of application - i.e. in a space thruster - this study target is to confirm the hypergolic behaviour of our propellants in impinging jets configuration and to compare their IDT with similar results obtained in drop tests configuration. A first part of this paper addresses the evolution of the ignition delays by varying the velocity of impact in drop test - hence the height of fall of the droplet is varied. Then, the second part is dedicated to results obtained in a new test bench fully designed to test hypergolic propellants in impinging jets, like in a real thruster. Injection velocity is also changed with the same order of magnitude as in drop tests.

2. Experimental set-up and propellants characterization

2.1 Drop test set-up

The experimental set-up to conduct drop tests under ambient air consists in a Pasteur pipette containing the oxidizer placed above a beaker containing the fuel pool, as shown on Figure 2. A fast camera is used to record the hypergolic reaction allowing the determination of the IDT. The set-up is fully presented in a previous study [13]. The height of the Pasteur pipette is changed to vary the velocity of impact of the HTP droplet on the fuel pool.

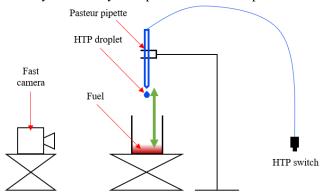


Figure 2 Experimental set-up for drop tests

2.2 Hypergolic impinging jets set-up

A dedicated facility was designed at PPrime Institute to study the hypergolicity between a fuel and high concentrated hydrogen peroxide. A picture of the experimental set-up is shown on Figure 3. Combustion is confined in a tank of almost 70 L to control the surrounding atmosphere. In the experiments performed for this study, ambient air atmosphere is changed for nitrogen atmosphere. Both the line of fuel and the oxidizer line ensure airtightness and are designed the same way: the tank is linked to a first security valve with a temperature sensor on its way. Afterwards the fluid goes through a flowmeter and a second security valve before reaching the fast valve protected by a filter and preceded by a pressure sensor. Then, a check valve prevents backflow in the pipes. After all, the fluid reaches the

injector which is constituted of two external oxidizer pipes and one central fuel pipe. The diameters of the injection pipes are 0.2 mm for both oxidizers and 0.6 mm for the fuel. The propellants impinge few millimetres after their exit

of the injector.

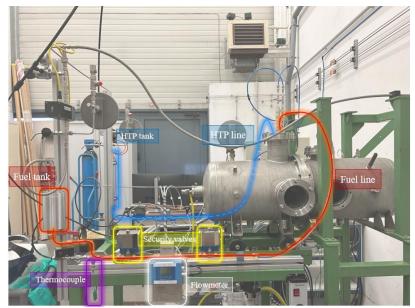


Figure 3 Picture of the experimental set-up for hypergolic impinging jets

To supplement the different sensors, a fast camera is added to capture the phenomenon inside the tank by shadow method. The camera is a FASTCAM SA-Z type 2100K-M-128GB-FD at a frequency of 20 kHz and a shutter speed of 1/400,000 s. The camera is placed 75° from the injection plane in such a way that the jets impingement is visible. In the present study the relative jets velocity (V_{ox}/V_{fuel}) is limited to low value in order to be comparable to the drop test configuration. However, the fuel jet velocity has been fixed to 4.7 m/s in steady state condition.

2.3 Propellants properties

The oxidizer considered in this work is hydrogen peroxide at a concentration of 98 wt. % (Evonik, Germany). Its density, dynamic viscosity and surface tension are detailed in Table 1 – data provided by Evonik. Considering the fuel mixture, triglyme (Thermo scientific, purity: 99 %) and sodium borohydride (Sigma Aldrich ®, purity: 99.2 %) are mixed together at a steady temperature in a set-up detailed in our previous study [13]. For this study, the concentration of sodium borohydride in triglyme is fixed to 6 wt. % which corresponds to the optimum in terms of ignition delays (cf. Figure 1). Physical properties were measured experimentally and are resumed in Table 1.

Table 1: Physical properties of HTP 98 wt. % and triglyme with 6 wt. % sodium borohydride at 20 °C

	Density (kg/m³)	Viscosity (mPa.s)	Surface tension (mN/m)
HTP 98 wt. %	1429	1.289	80
Triglyme + 6 wt. % NaBH ₄	1010	13	22

3. Results and discussions

3.1 Drop tests results

Our previous study evidenced the hypergolic ignition between a mixture of triglyme and sodium borohydride with HTP [13]. A parametric study highlighted the dependence of the IDT to NaBH₄ concentration, HTP concentration, and fuel temperature. Considering the velocity of impact, a small range of variation – between 1.6 m/s and 2.3 m/s –

allowed to show a small impact over the IDT. To establish a more precise influence of the velocity of impingement over the IDT, a larger range of values – between 0.8 m/s and 3.6 m/s – were tested in this paper and highlighted a huge influence over the IDT as can be seen on Figure 4. In this part, hypergolicity is tested in open air, as our previous work [13] showed that the results are the same in terms of IDT for drop tests performed under neutral atmosphere – being argon or helium.

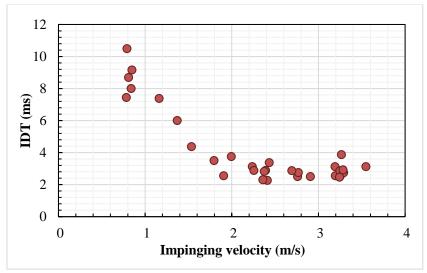


Figure 4 IDT in drop tests for different impinging velocity for a mixture of triglyme and 6 wt. % NaBH₄ and 98 wt. % HTP

When the velocity of impact is low – around 0.8 m/s, the IDT is the highest. After the first contact of both propellants, the droplet of HTP spreads over the pool of fuel. An ignition kernel then appears on the surface of the fuel as can be seen on the series A of Figure 5. By increasing the velocity, the droplet of HTP slowly starts to seep into the fuel leading to the decrease of the IDT. Over 2 m/s, the IDT seems unchanged and stabilized around 3 ms for this couple triglyme/6 wt. % NaBH₄ and 98 wt. % HTP. After this velocity of 2 m/s, the droplet of HTP splashes on the fuel pool and the ignition appears in the cloud of small droplets formed by the two propellants, as shown on the series B of Figure 5. One can notice that in any configuration, no gas phase generation can be observed at ignition time. As explained in our previous study [17], on the contrary of catalytic agents as additive, reactive agents do not produce HTP decomposition before ignition resulting to no gas phase. In practical application in a thruster, the impinging velocity would be higher than 3 m/s and an IDT of 3 ms has to be retained. However, the IDT evolution has to be verified in impinging jets configuration and compared to drop tests results for the same velocities.

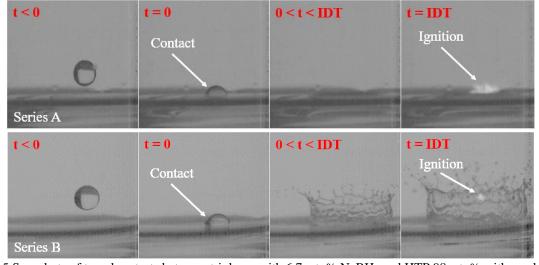


Figure 5 Snapshots of two drop tests between triglyme with 6.7 wt. % NaBH₄ and HTP 98 wt. % with a velocity of impact of 0.8 m/s for series A and 3.2 m/s for series B

3.2 Impinging jets results

In order to replicates the thruster conditions, our propellants were tested in impinging jets under controlled atmosphere. For this series of tests, the surrounding atmosphere was replaced by nitrogen. During a test, the injection fuel is supplied first, generating a steady state jet of fuel. The fuel tank pressure is fixed to 21 bar which corresponds to a mass flow rate of 1.3 g/s, inducing a constant jet velocity of 4.7 m/s. Secondly, the HTP valves are opened generating a jet, whose head impacts the steady fuel jet. Varying the HTP tank pressure allow to vary the relative impact velocity.

Figure 6 shows pictures of an impinging jets test between HTP 98 wt. % and triglyme with 6 wt. % NaBH₄. These pictures correspond to the beginning of a test, where one HTP jet impinges the fuel jet. In this configuration, the ignition happens between one HTP jet impinging one fuel jet. Ignition Delay Time is defined as the delay between impact of the head of the HTP jet with the steady fuel jet and ignition appearance (cf. Figure 6). This configuration will be called "two jets" hereafter.

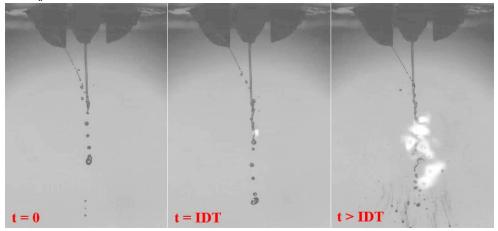


Figure 6 Snapshots of an impinging jets test between one HTP jet and the fuel mixture jet

When HTP jets are established before fuel injection, we obtained a three jets impingement. Hence, ignition delay is defined as the delay between impact of the head of the fuel jet with the steady double of HTP jets and ignition appearance. Figure 7 presents pictures of an impinging triglyme with 6 wt. % NaBH₄ jet with steady HTP 98 wt. % jets. This configuration will be called "three jets" hereafter. As underlinged in drop tests section, no gaseous phase is observed before the ignition.

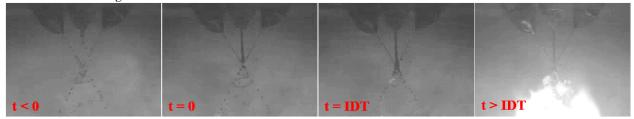


Figure 7 Snapshots of an impinging jets test between two HTP jets and the fuel mixture jet

From visualizations, in jets impingement, the propellants mix properly whatever the impingement velocity, as opposed to drop tests where, at low impingement velocities, the droplet of HTP only spreads over the fuel pool avoiding the propellants to mix properly. Considering the range of fuel and HTP mass flow rates in impinging jets, the overall mixture ratio is between 1.3 and 2.4 – stochiometric mixture ratio is equal to 3.5. In drop tests conditions, the mixture ratio is around 0.1, which causes the excess of fuel to absorb the heat and extend the IDT [13,18].

Figure 8 reports the IDT measurements versus the impinging velocity obtained for both series of tests detailed before. This figure highlights the same impinging velocity influence in impinging jets configuration as the behaviour observed during drop tests. IDT obviously decreases with impinging velocity. On the same scale of impinging velocities, the IDT measurements are just slightly lower than those obtained in drop tests. Moreover, IDT are almost the same whatever the configuration in two jets or three jets.

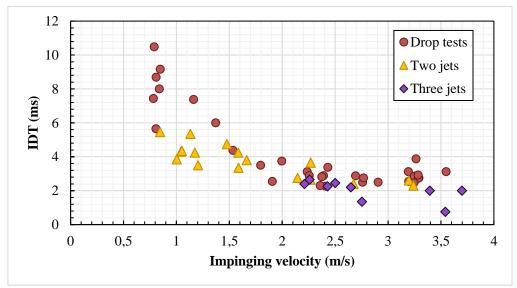


Figure 8 IDT in impinging jets for different impinging velocity for a mixture of triglyme and 6 wt. % NaBH₄ and 98 wt. % HTP

After ignition, a quasi-steady combustion takes place. Figure 9 presents an example of such a steady flame in the three jets situation. The anchoring position is more or less constant in all our tests: around 6-7 mm downstream the impingement position. This constant value of the anchoring position of the flame is certainly linked to the constant velocity imposed by the fuel jet, which is fixed to 4.7 m/s. The ratio between the distance and the fuel jet velocity corresponds to an advection delay of 1.4 ms which is the same order as the ignition delays observed for the impingement velocities greater than 2 m/s.

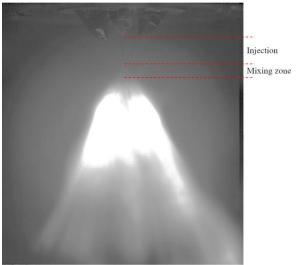


Figure 9 Steady flame observed in three jets impinging configuration

4. Conclusion

Drop tests and impinging-jets ignition tests have been performed for the same range of impact velocities. It has been observed the contact configuration – drop test, two jets or three jets impingement – does not influence the ignition delay. Impingement or impact velocity is the parameter that controls the Ignition Delay Time. Once ignition is reached, the steady flame is stabilized 6-7 mm downstream the impingement points with the fuel velocity value kept constant in this study.

Acknowledgments

CNES and "Région Nouvelle-Aquitaine" are gratefully acknowledged for co-funding this study. The authors acknowledge financial support for some apparatus from the European Union and "Région Nouvelle-Aquitaine".

References

- [1] G. P. Sutton, "Rocket Propulsion Elements: An Introduction to the Engineering of Rockets," New York, 1956.
- [2] REACH Institution, "Agreement of the Member State Committee on the Identification of Hydrazine as a Substance of Very High Concern," 2011.
- [3] Grafwallner, F., "Hydrogen Peroxide (HP) Potential for Space Applications," 2004.
- [4] Keese, D. L., Melof, B. M., Ingram, B. V., Escapule, W. R., Grubelich, M. C., and Ruffner, J. A., "Hydrogen Peroxide Based Propulsion and Power Systems," 2004. https://doi.org/10.2172/903157
- [5] Melof, B. M., and Grubelich, M. C., "Investigation of Hypergolic Fuels with Hydrogen Peroxide," 2001.
- [6] Dobbins, T. A., "A Novel Catalyst System for Rendering Organic Propellants Hypergolic with Hydrogen Peroxide," Vol. 302, 2001. https://doi.org/10.2514/6.2002-4340
- [7] L. O. Mays, "Analysis of Chemical Delay Time in Hypergolic Fuel and Fuel Mixtures [M.S. Thesis]," University of Alabama, Huntsville, Alabama, 1998.
- [8] Y. Miron, and H. E. Perlee, "The Hard Start Phenomena in Hypergolic Engines. Volume 2: Combustion Characteristics of Propellants and Propellant Combinations," Pittsburgh, Pennsylvania, March 1974.
- [9] Anderson, W., Lafayette, W., Dambach, E. M., Solomon, Y., Mahakali, R., and Yan, A., "Reduced Toxicity Hypergolic Propellants," US 2012/0273099 A1, Nov 01 2012.
- [10] Florczuk, W., and Rarata, G., "Assessment of Various Fuel Additives for Reliable Hypergolic Ignition with 98%+ HTP," 2015.
- [11] Carlotti, S., Caffiero, L., Orlandi, D., and Maggi, F., "Hypergolic Ignition of Amine-Based Fuels with Hydrogen Peroxide," 2023. https://doi.org/10.13009/EUCASS2023-471
- [12] Lauck, F., Balkenhohl, J., Negri, M., Freudenmann, D., and Schlechtriem, S., "Green Bipropellant Development A Study on the Hypergolicity of Imidazole Thiocyanate Ionic Liquids with Hydrogen Peroxide in an Automated Drop Test Setup," *Combustion and Flame*, Vol. 226, 2021, pp. 87–97. https://doi.org/10.1016/j.combustflame.2020.11.033
- [13] Soudarin, C., Chen, S., Beauchet, R., Batonneau, Y., Boust, B., Bellenoue, M., and Prévost, L., "Hypergolic Ignition between Triglyme and Hydrogen Peroxide," 2024. https://doi.org/10.2514/6.2024-1787
- [14] Mahakali, R., Kuipers, F. M., Yan, A. H., Anderson, W. E., and Pourpoint, T. L., "Development of Reduced Toxicity Hypergolic Propellants," 2011. https://doi.org/10.2514/6.2011-5631
- [15] Krzesicki, M., Boruc, Ł., and Kapusta, Ł., "Evaluation of the Possibilities of Adapting a Constant Volume Combustion Chamber for Research on Ignition of Hypergolic Propellants under Low and High-Pressure Conditions," *Combustion Engines*, Vol. 173, No. 2, 2018, pp. 9–13. https://doi.org/10.19206/ce-2018-202
- [16] Kapusta, Ł. J., Boruc, Ł., and Kindracki, J., "Pressure and Temperature Effect on Hypergolic Ignition Delay of Triglyme-Based Fuel with Hydrogen Peroxide," *Fuel*, Vol. 287, No. 119370, 2021. https://doi.org/10.1016/j.fuel.2020.119370
- [17] Chabaud, C., Soudarin, C., Boust, B., and Bellenoue, M., "Ionic Liquid versus Solvent-and-Reactive Agent Liquid Mixutre for Hypergolic Fuel Ignition with HTP," 2025.
- [18] Rarata, G., and Florczuk, W., "NOVEL LIQUID COMPOUNDS AS HYPERGOLIC PROPELLANTS WITH HTP," *Journal of KONES. Powertrain and Transport*, Vol. 23, No. 1, 2016, pp. 271–278. https://doi.org/10.5604/12314005.1213587