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**IGNITION DELAY TIME OF HTP BURNING WITH A GELLED GREEN
FUEL WITH FUMED SILICA**

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Abstract. Recently, due global demands, the so called "green" propellants have gained attention. Concurrently, studies involving gelled propellants increased, since they combine some advances compared to liquid propellants. Highly concentrated hydrogen peroxide with a promoted fuel is a potential hypergolic alternative among researched propellants. Concentrations higher than 70% are required for its use as a propellant. In this sense, this ongoing experimental work aims to contribute with progress in gelled green hypergolic propellant. Using a high-speed camera, Hypergolic Ignition Delay Time (IDT) will be determined adopting High Test Peroxide (HTP) 85%vol as oxidizer and a blend of ethanolamine, hydrous ethanol, and hydrated copper nitrate as fuel. Gels are fluid substances with altered rheological properties, achieved through the addition of gelling agents. In this study, inorganic fumed silica was utilized as the gelling agent. The effect of changing gelling agent content on IDT is reported. Was found that the IDT increased exponentially with %wt of fumed silica, with no ignition guaranteed for more than 2.0%wt. A range between 1.60%wt and 1.90%wt of fumed silica was found to be appropriate for the present gel, aiming application in propulsion systems. However, IDT results obtained with drop test was significantly high comparing to green liquid fuels in literature. The next steps of this ongoing work will be the analysis of different temperatures during gelling agent addition and mixing, changing agitation levels and using different gelling agents on IDT by drop test and impinging jets test.

Keywords: green propellant, ignition delay time, gelled propellant, drop test, hypergolicity

1. INTRODUCTION

Hypergolic propellants have a rich history dating back to the early stages of rocket development, and they continue to be extensively employed in space propulsion systems. A hypergolic propellant is a combination of a liquid fuel and an oxidizer, which possess the unique ability to spontaneously ignite upon physical contact, eliminating the need for any auxiliary ignition source. This hypergolic nature not only simplifies the propulsion system but also enhances the reliability of (re)ignition. Conventional hypergolic fuels include hydrazine and its derivatives, such as monomethylhydrazine and unsymmetrical dimethylhydrazine (UDMH) (Kang et al., 2020).

Hydrazine and its derivatives have served as the conventional propellants for rockets and spacecraft for almost six decades. Despite their advantageous properties, their toxicity and the consequent high expenses in handling and storage have presented significant drawbacks (Mota et al, 2023).

The so called "green propellants" are propellants that can be applied in rocket, missiles, satellites, scramjets, or similar propulsion systems. Such new propellants must have low toxicity and high energy, presenting a high-performance and efficient alternative to conventional chemical propellants for future spacecraft.

Gelled fluids originate from liquids that have undergone a modification in their rheological characteristics through the introduction of gelling agents (Padwal et al., 2021). While in motion, certain gels demonstrate non-Newtonian fluid behavior, displaying pseudoplasticity, wherein their apparent viscosity diminishes with higher stress levels (Bertola, 2017). Additionally, these gels may exhibit thixotropic behavior, meaning their apparent viscosity decreases over time under the same shear stress conditions (Yang et al., 2022).

In space propulsion systems, gelled propellants have garnered significant interest in recent decades due to their superior safety features when compared to liquid and solid propellants. Additionally, gelled propellants can achieve

specific impulses as high as liquid propellants, making them a promising option. Nevertheless, gelled propellants do have higher viscosities, and their atomization poses greater challenges compared to liquid propellants (Dias et al. 2023).

Among the propellants currently under investigation, the combination of highly concentrated hydrogen peroxide with a promoted fuel stands out as a promising hypergolic alternative. While hydrogen peroxide is available in various concentrations with water, it is essential to use concentrations exceeding 70% for its effective utilization as a propellant (Mota et al., 2023).

The ignition delay time (IDT) acts as a key reference point for assessing the overall characteristics and behavior of a combustible fuel, it refers to the time interval between the initiation of a specific ignition source, such as a spark, a flame, or, in this case, the contact of an oxidizer drop with a bulk fuel, and the actual ignition or onset of combustion of a fuel-oxidizer mixture. It is a crucial parameter used to understand the ignition characteristics and reactivity of a fuel.

The drop test is a crucial procedure to verify the hypergolicity of newly developed green hypergolic propellants. Traditionally, in the drop test, a single drop of the oxidizer is mechanically released onto the surface of the fuel drop, or vice versa, to assess their hypergolic behavior (Kang, et al., 2021), mostly used for liquid fuels, but also used for solids and gel fuels.

This experimental work details the gelation process of a green liquid base fuel hypergolic with liquid hydrogen peroxide, the acquisition of HTP from Hydrogen Peroxide 200 vol (50%) and reports the IDT of the recently created gelled propellant as function of the amount of gelling agent added.

2. METHODOLOGY AND MATERIALS

The green liquid fuel base composition is 60 %wt of MEA, 30.1 %wt of ETOH and 8.9 %wt of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Figure 1a). Such formulation was used in this work once previous studies in the same laboratory have succeed at testing it (Feroni et al., 2020).

The addition of fumed silica (Figure 1b) was done under 2000 rpm mechanical agitation at ambient temperature of 20°C. The recently gelled propellant (Figure 1c) was so kept in ambient and used on drop test about 30 minutes from its preparation.

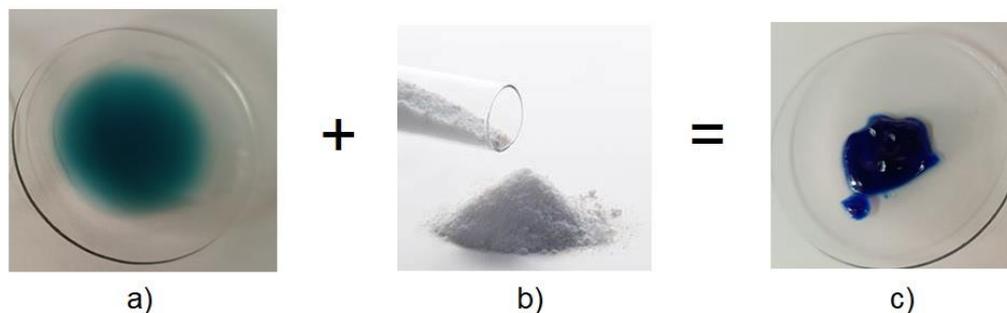


Figure 1. a) Liquid fuel base; b) Fumed Silica; c) Gelled propellant.

Hydrogen Peroxide at 50 wt.% was purchased and placed into a 250 mL beaker. It was then subjected to an evaporation process using a heating plate set to 90°C. When the initial Hydrogen Peroxide volume became around 1/5 of its initial volume, the heating plate was turned off. Once the Hydrogen Peroxide reached ambient temperature, its density was measured using a 1 mL pipette (previously calibrated with deionized water). The recently produced High Test Peroxide (HTP) was found to have a concentration of 85 wt.%, as determined by the online calculator provided on the website: http://mae-nas.eng.usu.edu/Peroxide_Web_Page/Calculations%20/calculator_H2O2.html

The present drop test experimental work consists of dropping a one micro liter HTP droplet using a micropipette located 20 cm above a watch glass containing the green Fuel (Figure 2).

A High-Speed Camera FASTEC TS3 acquiring 4000 frames per second and a background light source was used, according to Figure 2.

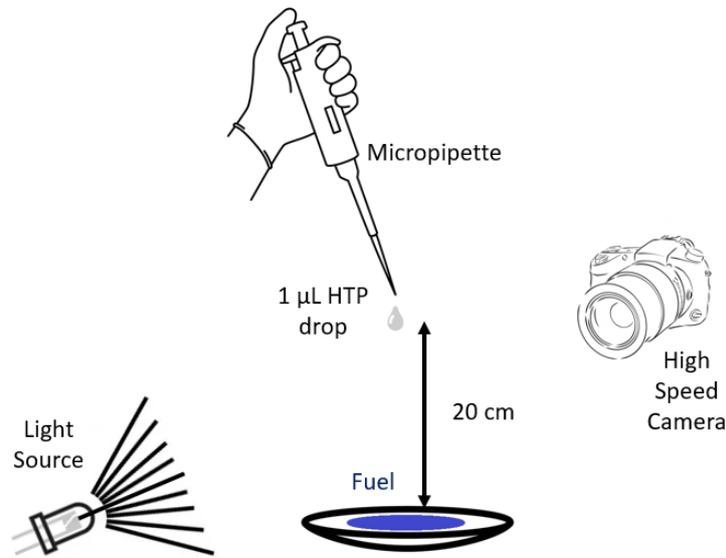


Figure 2. Schematic diagram of the experiment.

3. RESULTS

Some images from the High-Speed Camera can be seen in Figure 3. The images show key frames of the experiment for 2% wt of fumed silica.

After the HTP drop contact to Fuel, the first important event is the Vapor Delay Time (VDT).

In this context, the VDT is defined as the time interval between the moment of contact and the appearance of "vapor smoke." This parameter indicates the timescale for the initiation of the gel-phase reaction. Subsequently, the produced "vapor smoke" continues to ascend from the gel surface as the temperature increases, and the high-temperature region expands, as depicted in Figure 3 for time 10 milliseconds.

The second important event is the IDT. Seeking real propulsion applications, according to literature (Mota et al., 2023), IDT of about 10 ~ 30 milliseconds would be considered appropriate for green liquid propellants on drop tests.

The IDT appears very close to the gel surface for most cases, the same was not always found for the liquid base, as seen in Figure 4. This may be because by adding gellants, a polymeric chain is formed in the material, decreasing the vapor pressure.

It was also found that, when gelling the liquid green fuel, apparently its surface tension increases substantially and the HTP droplet seems to slide over the gel surface instead of instantly penetrate the fuel, as occurred for the liquid base without any gelling agent.

Another interesting finding was the flame region occupied by the pure liquid base and the gelled fuel. The former presented a larger flame comparing to its gelled formulation.

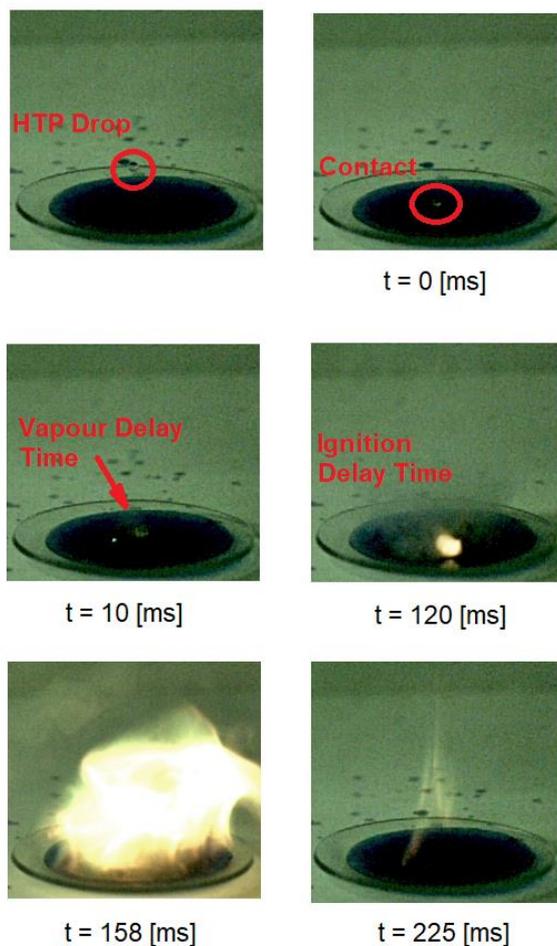


Figure 3. Drop test time steps for gelled propellant.

As seen in Figure 5, IDT starts from about 25 milliseconds and increases exponentially as %wt of fumed silica increased. At a certain point, between 2%wt and 4%wt, the gel was not hypergolic with HTP anymore, when stead of a flame, just clusters of bubbles were verified.

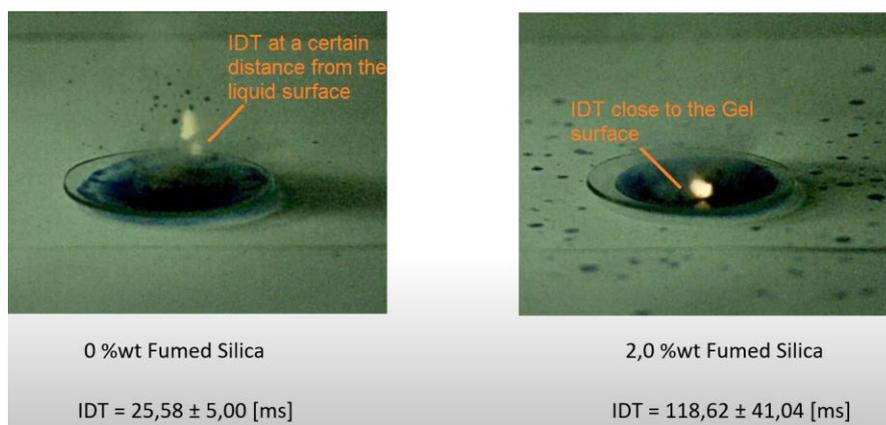


Figure 4. Drop test. Liquid base to its gelled formulation comparison. Please see the video on <https://youtu.be/6gFvkkhXVgM>.

To get advantage of gels, it must behave like a solid at rest, once one important advantage is the addition of solid energetic particles on it (Dias et al. 2023). The solid-like behavior was only qualitatively observed for Fumed Silica %wt > 1.5.

Considering the present experimental findings, the range between around 1.6%wt and 1.9%wt of fumed silica would be desirable for propulsion systems applications, once it clearly behaves like a gel and still ignites.

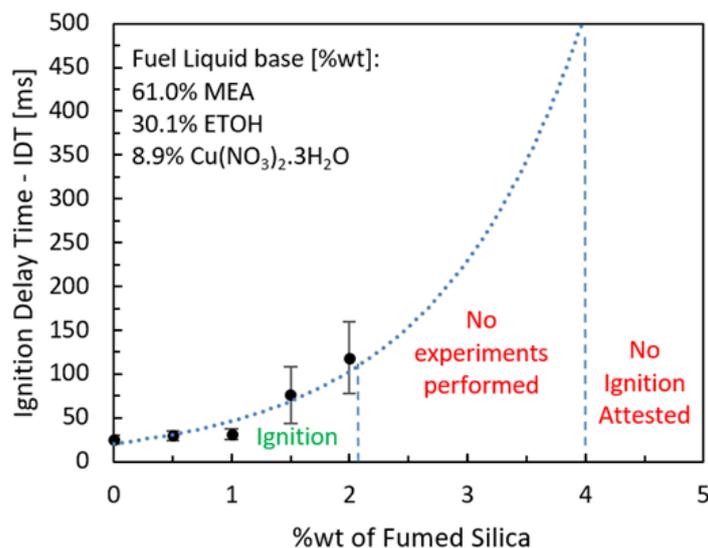


Figure 5. Ignition Delay Time for different %wt of Fumed Silica.

High surface tension and lower flame propagation are possibly connected with low evaporation rate and may be intended a drawback for the present gelled propellant in future propulsion system applications. However, the fuel must also be experimented under different conditions, for instance using an impinging jet injector, forcing one HTP jet to imping with other gelled fuel jet to promote faster mixing. The IDT results from drop test and impinging jets test may be significantly different. Impinging jets test will be performed in future works, using the present fuel formulation and others.

4. SUMMARY AND CONCLUSIONS

Gelled propellants present advantages when compared to its liquid bases, such as the addition of energetic material to increase propulsion efficiency. On the other hand, they also present some disadvantages, like the difficulty in atomizing due its high viscosity.

The usage of hypergolic propulsion systems eliminates the ignition spark system and may achieve high specific impulse.

This work presents the first attempt to produce a gelled green fuel by adding fumed silica into a liquid fuel, hypergolic with HTP.

The gelled propellant preparation was performed in ambient temperature by mechanically agitation at 2000 rpm for around 5 minutes and resting period of about 30 minutes before drop test.

During drop tests, a high-speed camera was used to measure the ignition delay time of the new gelled green propellant. The images revealed that IDT location was different for the gelled propellant compared to its liquid base. Also, the IDT was observed to increase exponentially as the %wt of fumed silica increases.

Apparently (not measured) the recently created gel presented higher surface tension compared to its liquid base, as a result, the HTP slid across the gel surface instead of penetrating instantly, apparently causing a delay in the mixing process, which could lead to an increase in IDT.

The appropriate amount of gelling agent for this gel to be used as a propellant was found to be between 1.60 and 1.90%, once less than 1.60%wt it apparently not behaves like a gel and more than 1.90%wt the ignition is not guaranteed.

Considering that IDT of about 10 ~ 20 milliseconds are expected for liquid green hypergolic propellant using HTP, the application of the present gel as a propellant must be analyzed with caution. In addition, further validation analysis such as thermal stability analysis also need to be performed prior to considering it for real propulsion applications.

When preparing the gelled propellant, influencing factors are the liquid base temperature (Padwal et al., 2021) and agitation level. The temperature can influence the ease of dispersion, the formation of agglomerates, and the final properties of the gel.

The next step of this effort is analyzing IDT results considering different temperatures and rpm during mixing, possibly with artificially decrease the temperature after mixing.

Another experimental test that will be carried out in the future is the impinging jets test. The IDT values on impinging jets may be significantly different from drop test, normally lower IDT values is found.

5. ACKNOWLEDGEMENTS

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6. DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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