Titre: Title:	Reducing the Ignition Delay of Hypergolic Hybrid Rocket Fuels
Auteurs: Authors:	Bachar Elzein, Olivier Jobin, & Étienne Robert
Date:	2021
Type:	Article de revue / Article
Référence: Citation:	Elzein, B., Jobin, O., & Robert, É. (2021). Reducing the Ignition Delay of Hypergolic Hybrid Rocket Fuels. Journal of Propulsion and Power, 37(1), 77-85. https://doi.org/10.2514/1.b37918

URL de PolyPublie: PolyPublie URL:	https://publications.polymtl.ca/45943/
Version:	Version finale avant publication / Accepted version Révisé par les pairs / Refereed
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Titre de la revue: Journal Title:	Journal of Propulsion and Power (vol. 37, no. 1)
Maison d'édition: Publisher:	American Institute of Aeronautics and Astronautics
URL officiel: Official URL:	https://doi.org/10.2514/1.b37918
Mention légale: Legal notice:	

Reducing the Ignition Delay of Hypergolic Hybrid Rocket Fuels

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Paraffin-based fuels incorporating solid amine boranes are investigated to identify formulations suitable for use as hypergolic hybrid rocket propellants. Their ignition delays are measured following contact with 90% white fuming nitric acid droplets. The mechanical properties of the paraffin binder and of the melt layer it produces are modified using an alpha-olefin polymer. The tests are carried out at atmospheric pressure, with visible flame light emission as well as OH* chemiluminescence recorded. The ignition delays measured from both signals are nearly identical, confirming that OH* emission begins at the same time as the visible light emission from the boron-containing additive mixed with the fuel. Identification of the different steps of the combustion process is done with high-speed Schlieren imaging technique. Consistently shorter ignition delays are obtained by increasing the proportion of polymerized alpha-olefin. The effect of this addition on the viscosity of the melt layer produced in the fuel blend upon contact with the acid is inferred from rheological measurements realized on unburned samples.The effect of alpha-olefin addition on the theoretical thermochemical performance of the fuel is also computed. The results obtained confirm that polymer-based additives can be used to control mechanical and rheological properties in a way that lowers the ignition delays of hypergolic fuel systems based on paraffin, as required for use in space propulsion applications.

I. Introduction

Hybrid rocket engines, where liquid or gaseous oxidizer are stored separately from the solid fuel, can bring key advantages to a wide range of aerospace applications, mainly because of their relative simplicity, low development cost and the ability to control their thrust and re-ignite them following partial burns. A highly desirable characteristic in hybrid rocket engines is hypergolicity, avoiding the need for a separate ignition source. This allows for simple propulsion systems designs that can be precisely throttleable, making them ideal for spacecraft manoeuvring, attitude control and descent vehicles. Furthermore, rocket engines using such hypergolic propellants should have highly reliable restart capabilities, with near-instant contact ignition helping to reduce potential catastrophic hard starts. Common

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hypergolic fuels such as unsymmetrical dimethylhydrazine ($H_2N-N(CH_3)_2$), hydrazine (N_2H_4) or monomethylhydrazine ($H_2N-NHCH_3$) are also conveniently storable at room temperature. However, they require extensive safety precautions because these substances are typically corrosive, toxic and carcinogen, significantly increasing the total cost associated with their use.

The development of new high performance hypergolic fuel/oxidizer combinations for rocket propulsion applications must take into consideration several important parameters such as the propellants specific impulse, storability, ignition delay, stability and toxicity. Solid fuels that can form hypergolic propellants have the potential to address some of the drawbacks of the liquid alternatives listed above while maintaining their key advantages. Moreover, hybrid rocket engines are mechanically simpler compared to those using all-liquid propellants, potentially resulting in higher reliability and reduced costs. However, the operations and design of these engines depend heavily of the characteristics of the fuel, mainly its regression rate and, for hypergolic hybrids, its ignition delay. The latter needs to be known precisely and ideally be as short as possible to avoid excessive pressure spikes, which can lead to structural failure of the combustion chamber.

A particularly promising approach for hybrid rocket motors is to burn fuels based on solid hydrocarbons in which particles of energy-dense metal compounds are added to yield desirable combustion characteristics. In such propellant formulations, the hydrocarbon acts as both an energy source and a binder between the metal particles. A wide range of metallic additives can yield hypergolic hybrid propellants when mixed with paraffin if a suitable oxidizer is used. For example, aluminum particles have been demonstrated to improve the specific impulse of hybrid propellants relying on safe oxidizers with high energy density, such as hydrogen peroxide or nitrous oxide [1]. Additionally, amine boranes have been identified [2] as potentially good hypergolic hybrid rocket fuel additives, mainly because of their high theoretical specific impulse I_{sp} up to 300.3 s) and density specific impulse ρI_{sp} (up to 359.7 sg/cm^3) when used with inhibited red fuming nitric acid. These additives also have the benefit of air stability, storability and low-toxicity. Hypergolic ignition of amine boranes is also achieved with white fuming nitric acid (WFNA), which has inherent handling hazards because of its corrosive nature, albeit arguably less severe ones compared to propellants formulations involving hydrazine and nitrogen tetroxide, but can yield high density impulse because of its high density. Other oxidizers, such as hydrogen peroxide [3] can yield hypergolic propellants with attractive safety characteristics compared to hydrazine-based alternatives.

Paraffin waxes can appear as good candidates to serve as hydrocarbon binders due to their low cost, high regression rate and non-toxicity. However, in investigations of hydrocarbon binders for hypergolic hybrid rocket motors [2] it was noted that paraffin was among the least favorable, possibly due to its lack of rigidity and structural integrity. These characteristics result in slower ignition following contact between the fuel and the oxidizer, compared to other binders such as epoxy resin. Paraffin-based fuels, however, remain attractive from a safety and cost perspective, with research needed to identify energy dense formulations suitable for use in hybrid rockets. Moreover, because the surface melt layer has low surface tension and low viscosity [4–6], entrainment in a paraffin matrix hybrid rocket engine is higher compared to traditional solid fuels matrices such as hydroxyl-terminated polybutadiene (HTPB). The resulting increased fuel regression rate makes it possible for most applications to function with a single-port grain, further simplifying motor design [5]. But low viscosity and mechanical strength can also lead to excessive regression rates [7] that require prohibitively large oxidizer flows to maintain combustion performance.

This low rigidity of the fuel matrix is also believed to have adverse effects on the ignition delay in hypergolic propellants. This was demonstrated by the extensive experimentation of Pfeil [8], who showed that fuel matrices with higher compressive strengths and higher viscosities are typically associated with lower ignition delays. Efforts have been made in the past to modify the mechanical and rheological properties of paraffin-based fuels. For instance, Kim et al. [9] demonstrated that adding polymers such as low density poly-ethylene (LDPE) in proportions ranging from 5 wt.% to 10 wt.% increases the tensile and compressive strengths of fuels using paraffin as a binder. Stearic acid has also been reported to improve the mechanical properties of paraffin waxes, as characterized by Galfetti et al. [10], Toson et al. [11] and Kobald et al. [12]. Finally, Nakagawa et al. [13] demonstrated that the addition of Ethylene Vinyl-Acetate copolymer (EVA) in small proportions can also change the melted fuel viscosity in high regression rate paraffin-based fuels. However, since these investigations did not consider hypergolic fuels the ignition delay was not investigated.

Ignition delay is typically measured from the light emitted by the flame, providing a simple and non-intrusive means to characterize when and how combustion starts. Of particular interest is chemiluminescence, the narrowband radiation emitted by electronically excited species as they relax to lower energy levels. Chemiluminescence due to the transition of the electronically excited hydroxyl radical OH* is frequently used in combustion research. The emission line is in the near UV close to 307 nm and provides a very good, non-intrusive, measure of the location of reaction zones. Because OH* has a very short lifetime, it is only present when and where hydrocarbon oxidation reactions occur and its concentration is proportional to the intensity of these reactions. In the context of hybrid rocket fuel characterization, Jens et al. [14] used the OH* chemiluminescence intensity signal to correlate the fuel burn rate and the chamber pressures, using paraffin-based liquefying fuels. This high regression rate fuel was observed to produce less chemiluminescence compared to traditional non-liquefying hybrid rocket fuels for a fixed fuel consumption rate. This was explained by postulating that low-viscosity liquefying fuels can experience very vigorous entrainment, leading to droplets of fuel being advected outside of the combustion chamber before they can react completely. Although these results were again for a non-hypergolic propellant, they demonstrate that OH* chemiluminescence can be used to reliably extract information on the rate of a combustion reaction.

In the present study, ignition delays of hypergolic hybrid rocket fuels incorporating solid ammonia borane (AB) are measured. This is done through OH* radical chemiluminescence, visible light emissions and Schlieren imaging following contact with 90% WFNA droplets. The objective is to identify the proportion of polymer paraffin additives suitable to achieve mechanical and rheological properties that yield low ignition delays, by linking the viscosity of the paraffin-based matrices with the ignition delay of the fuel.

II. Methodology

A. Solid fuel composition and sample fabrication

For the work presented here, ammonia borane (BH_3NH_3, Boron Specialties, Ambridge PA, USA) is selected as the hypergolic fuel additive and is mixed with paraffin at a fixed concentration of 20% by mass. Ammonia borane has a very high hydrogen content (19.6 wt.%) and as a result it contributes to lowering the molecular weight of the combustion products, making it an ideal additive for rocket propulsion applications. The oxidizer used is 90% WFNA, a choice motivated by its advantageous cost, safety, energy density and ease of handling compared to other oxidizers such as nitrogen tetroxide (NTO), mixed oxides of nitrogen (MON) and red fuming nitric acid (RFNA). The combined use of strong nitric acid and AB provides two mechanisms of heat release following contact between the two substances, explaining the hypergolic nature of the mixture. Upon initial contact, the acid will essentially replace the borane in the AB and react with the amine. Simultaneously, the boron thus liberated forms a pyrophoric gas and also contributes to heat release. This increased heat generation results in a shorter ignition delay for AB compared to amines alone.

The paraffin used in the experiments is a microcrystalline wax (Micro Wax 195, Candle Making Supplies, USA), with a melting point of 87°C and a paraffin wax (FR5560, The Candlewic Company, USA), with a melting point of 70°C. The fuel matrices investigated are composed of paraffin, modified with the addition of polymerized alpha-olefin (Baker Hughes, Vybar 103, USA) in proportions ranging from 0% to 25% by mass. Ammonia borane particles are incorporated into the solid fuel matrices using the following procedure. The fuel matrix ingredients are first melted and mixed together using a water bath, with water being at approximately 95°C. The water is then cooled to let the fuel matrix solidify, resulting in a viscous paste. The ammonia borane particles are then added and the result is mixed once more. Ammonia borane cannot be added when the fuel matrix is in liquid phase because it will start to thermally decompose. The fuel blend is then cast and pressed in a mold until solidification, producing cylindrical fuel rods approximately 10 mm in diameter and 50 mm long. Smaller pellets with a thickness of approximately 3mm are then cut from the cylinder. Prior to testing, all fuel pellets are sanded using 80 grit paper to remove surface inconsistencies that could be created by the blade during the cutting process.

Four ranges of ammonia borane particle granulometry are used to assess the influence of this parameter on the ignition delay, when included in FR5560 paraffin wax. Using a metallic mortar, the ammonia borane particles were broken by hand and then separated with sieves with different mesh sizes varying from size 25 to size 60 (McMaster-Carr, USA), following the ASTM E11 standard. Following the milling and sieving procedures, the precise size distribution obtained was measured by photography and image analysis of a large number of individual particles, yielding the following 4 diameter ranges: $600\ \mu m < D < 710\ \mu m$, $500\ \mu m < D < 600\ \mu m$, $355\ \mu m < D < 500\ \mu m$ and $250\ \mu m < D <$

$355 \mu m$.

B. Viscosity measurements

To clearly establish the link between the increased viscosity of the melt layer of the formulated paraffin fuels and their ignition delays, rheological measurements were carried out using an Anton Paar MCR 302 rheometer. Featuring a sample size of 5 ml of melted paraffin with varying amounts of alpha-olefin additives, a single Couette flow configuration at a shear rate range of 10 to 1000 s^{-1} is used. Unfortunately, it was impossible to measure the viscosity of a melted fuel matrix containing the AB additives, as amine borane would begin to decompose and outgas before the paraffin would melt. However, as the AB concentration is low at 20%, the viscosity of the matrix should provide a representative value for the fuel blend. The measurements presented below were carried out at a temperature of 90°C for the Micro Wax 195 and 96°C for the FR5560. These are slightly higher than the melting temperatures of the two waxes, to ensure that they were entirely liquid. Only the viscosity values close to the melting temperatures are reported as for the ignition test conducted here, only a thin layer of paraffin melts before ignition takes place. As a result, as the upper layer of the fuel melts, phase change occurs at constant pressure and heat transfer to the solid fuel matrix below ensures that the temperature in the melt layer remains close to the melting temperature.

C. Compression strength measurements

Compression strength measurements were performed to evaluate the effect of the addition of alpha-olefin on the mechanical properties of the solid paraffin matrix. The preparation of the specimen and the test procedures are in accordance with ASTM D575-91 and ASTM E9-19 standards [15, 16]. A mixture of paraffin and alpha-olefin is melted and stirred by hand, then poured in a silicone mold and the samples are cured at room temperature. Two sizes of samples are used to determine the compression strength: 28.6mm in diameter by 12.5 mm thick and 13.0mm in diameter by 25.0 mm in thickness. The tests are carried out using a MTS Insight 50 Electromechanical Testing Systems (MTS Systems Corporation, MN). The compression strength is determined as the maximum load on the specimen before a fracture occurs. Tests were conducted with a 5mm/min displacement rate at room temperature.

D. Optical measurements

To measure the ignition delay, a droplet of WFNA is dropped on the fuel pellets, using a glass syringe held at a height of approximately 740 mm above the sample. This creates a thin liquid film of acid of constant thickness over the sample in approximately 1 ms. The flow rate is controlled by a syringe pump (NE-4000, New Era Pump Systems Inc.) to ensure that a single drop is used for every fuel pellet. The mass of WFNA dispensed in each drop is approximately 17 mg. The interaction of the oxidizer droplet with the fuel pellet is recorded simultaneously using two instruments to obtain independent measures of the ignition delay. The OH* chemiluminescence signal is acquired using a high-speed camera (Phantom V310, Vision Research), connected to an image intensifier (UVi-1850, High Speed Imaging Inc.). An optical filter (310FS10, Andover Corporation) is placed before the image intensifier to receive signals with a center wavelength of 310.0 nm and a FWHM of 10 nm, corresponding to the wavelength of photons emitted by OH* radicals. This ensures no interference from other excited radials. The ignition delay is also recorded in the visible spectrum as the time interval between the initial droplet impact on the sample surface and the first visible light emission from the combustion zone, as shown in the images presented in Fig.1. These images are extracted from a video acquired at 10 000 fps using a second high-speed camera (Photron Fastcam Mini AX200), available as supplemental video S1. For most of the results however, the two cameras are operated at 1000 frames per second.

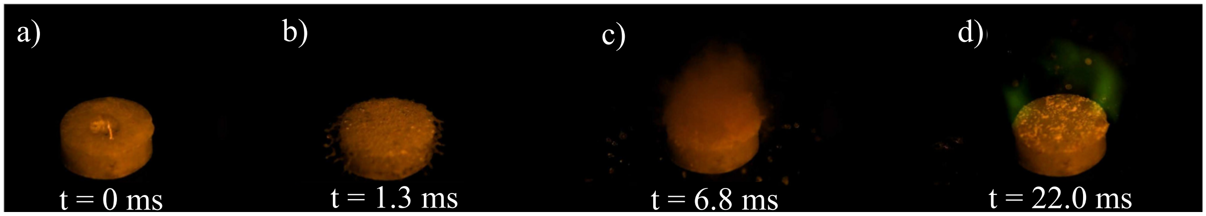

Fig. 1 Sequence of events following oxidizer droplet contact with the fuel pellet. a) Droplet prior to impact. b) Initial contact. c) First generation of smoke. d) First emission of visible light (green).

To obtain a temporal signal from the OH* chemiluminescence and visible light emission of the flame, the intensity of each pixel in each image of the sequences is summed. To avoid contamination of the signal by background noise, only pixels with a value above a certain threshold are summed up after a reference image has been subtracted from each frame. The result is two temporal signals, one from OH* chemiluminescence and one from the visible light emission. For the latter, only the green channel is used. With the camera used, the green channel sensitivity curve is maximum at 540 nm and is 100 nm wide (FWHM). The relative sentitivity of the green channel is approximately 0.7 compared to the red channel. Examples are shown in Fig. 2, revealing similar features for both signals. A sharp and short peak is visible at the beginning of each signal, corresponding to initial fuel ignition. The start of this first peak is selected as the ignition time and values thus obtained using both approaches are the same, within experimental uncertainties.

The very sharp initial light emission is followed by a broader and less intense peak. These two events are observed for all tests and together last up to 250 ms. They are followed by a period with very low light emission, both in the visible and for OH* chemiluminescence. When the reaction rate increases again, the dynamics have changed as the increase is very progressive and the intensity remains low. These observations lead us to believe that the initial sharp peaks visible in Fig. 2b) is the result of hypergolic combustion between the nitric acid and the AB, while the second broader peak is appearing when the paraffin begins to react. At this point the pellet is still covered with a liquid foaming film of WFNA, preventing atmospheric oxygen from contributing to the reaction. The change of dynamic observed after approximately 1.5 seconds as illustrated in Fig. 2a) is most likely the result of the exhaustion of liquid oxidizer on the

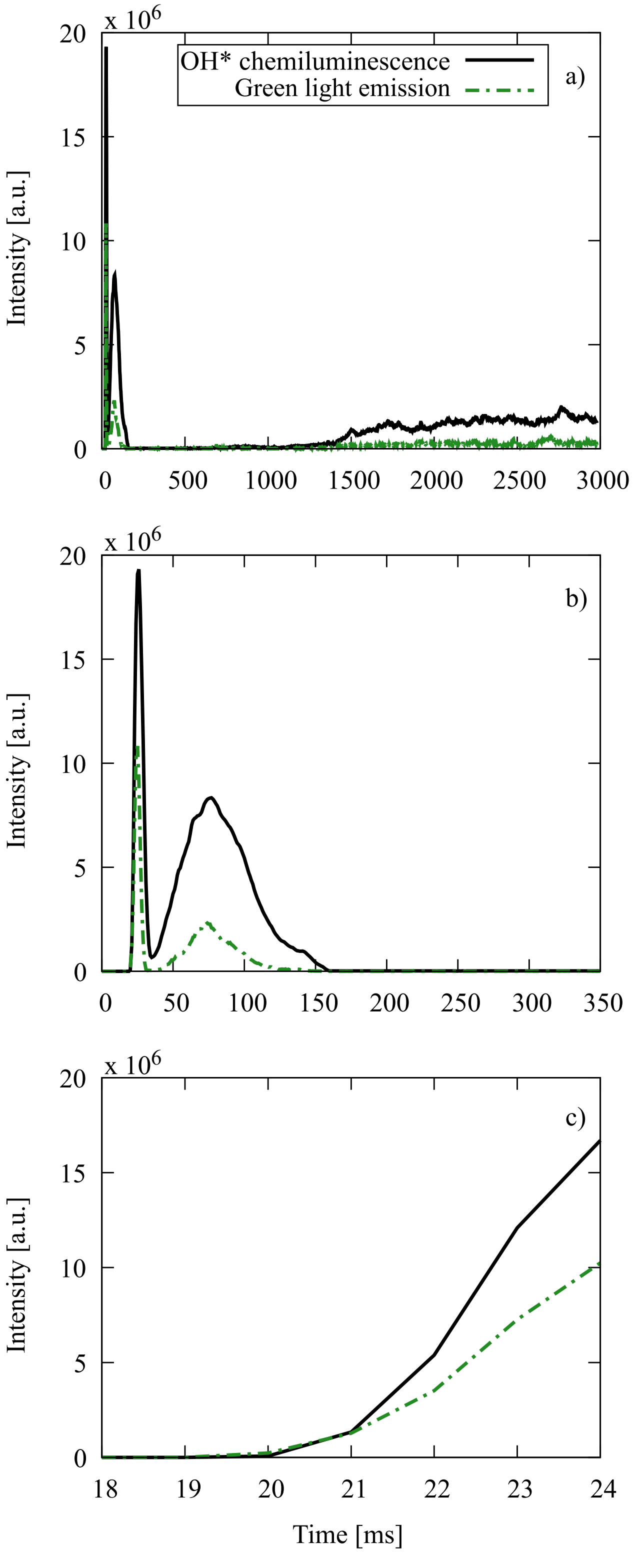

Fig. 2 Visible light emission and OH* chemiluminescence signals. a) Complete combustion events b) Close-up of the two distinct peaks in the first few 100 ms following droplet impact. c) Moment of ignition.

pellet and of the subsequent dominant role of atmospheric oxygen in the combustion reaction. For all results presented in the following section, all discussions will be limited to the initial ignition and hypergolic combustion of the fuel, with atmospheric oxygen assumed to play a negligible role.

In addition to the two imaging techniques selected, Schlieren imaging was also used to observe the changes of density in the gaseous atmosphere above the fuel samples during the reaction. A limited number of tests were carried out using this technique, since the experimental setup does not allow the use of three different cameras. A qualitative study of the results obtained by this technique is presented in Section III.G, with the Schlieren camera operated at 30 000fps.

E. Heat of combustion measurements

To assess the effect of polymerized alpha-olefin (Vybar 103) addition on the thermochemical performance of the fuel blends, its heat of formation was inferred through heat of combustion measurements. The heat of formation of AB particles and paraffin are already readily available in the literature. Bomb calorimetry experiments (6200 Isoperibol Calorimeter, Parr Instrument Company) were performed at constant volume, using a sample of 0.5g and repeating the test three times. The measured heat of combustion is 45.88±0.04 kJ/g and the tests are performed at 303K. The heat of combustion of polymerized alpha-olefin is higher than most polymers studied by Walters et al. [17], but is similar to polyethylene and polypropylene.

Alpha-olefins are by definition in the form of C_xH_{2x}. The polymerized alpha-olefin (C_xH_{2x})n used in this investigation has a molecular weight of 4400 g/mol and is composed of n monomers having between 14 and 44 carbon atoms, with the majority having between 20 and 24 [18]. From the molecular weight of the polymer, the number of monomer units n has been calculated for alpha-olefins having between 14 and 44 carbon atoms. The average value of 15 has been considered for the calculations presented below, corresponding to a polymer containing alpha-olefins monomers with 20 carbon atoms. Thus, the estimated chemical formula of the polymerized alpha-olefin additives is $(C_{20}H_{40})$n, with n equal to 15.

The heat of formation of polymerized alpha-olefins is then calculated assuming the following complete reaction of combustion with pure oxygen:

$$(C_{20}H_{40})_{15}(s) + 450O_2(g) \longrightarrow 300CO_2(g) + 300H_2O(l)$$

with:

$$\Delta H_{combustion} = \Delta H_{products} - \Delta H_{reactants} + \Delta n_{gas}RT$$

where $\Delta H_{combustion}$ is the heat of combustion, $\Delta H_{reactants}$ is the heat of formation of the reactants, $\Delta H_{products}$ is the heat of formation of the products, Δn_{gas} is the difference between gaseous moles of products and reactants, R is the gas constant and T the temperature in the bomb calorimeter. The heat of formation for Vybar 103 polymerized alpha-olefin was thus determined to be -1494.0 kJ/mol.

III. Results and discussion

A. Effect of alpha-olefin on viscosity

As expected, the addition of polymerized alpha-olefin to the paraffin matrix increases its viscosity in the fully melted state. This increase is monotonic for the entire range investigated, up to 25% alpha-olefin by weight, as shown in Fig. 3. This monotonic and regular trend hints that the polymer additive is homogeneously integrated in the paraffin matrix and that even at high mass loads the fuel blend keeps the same general behavior. At 25% polymer by mass, it remains a bright white solid that melts entirely at temperatures below 100 °C, but its viscosity is almost doubled compared to that of the pure paraffin. This effect is observable for both paraffin studied.

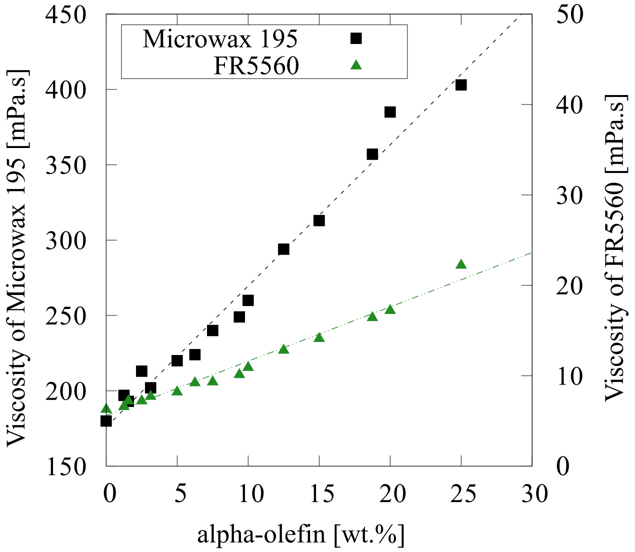

Fig. 3 Viscosity of the fuel matrices (R^2 is 0.991 and 0.989 respectively for the linear fits.)

B. Effect of alpha-olefin on mechanical properties

As more polymerized alpha-olefin is added to the fuel matrix, its compression strength increases. This increase is more important for the first 5 wt.% of the range covered. The Microwax 195 was found to be nearly 2 times more resistant under compression forces than the FR5560. The values reported here are in the same range as those reported in [7], although the compression strength of the Microwax 195 is the highest among those tested by Tang et al. Five test runs have been conducted for each data point. As seen on Fig. 4, the diameter of the sample does not appear to have a significant influence on the compression strength, with all four data sets revealing a similar trend for the effect of alpha-olefin addition.

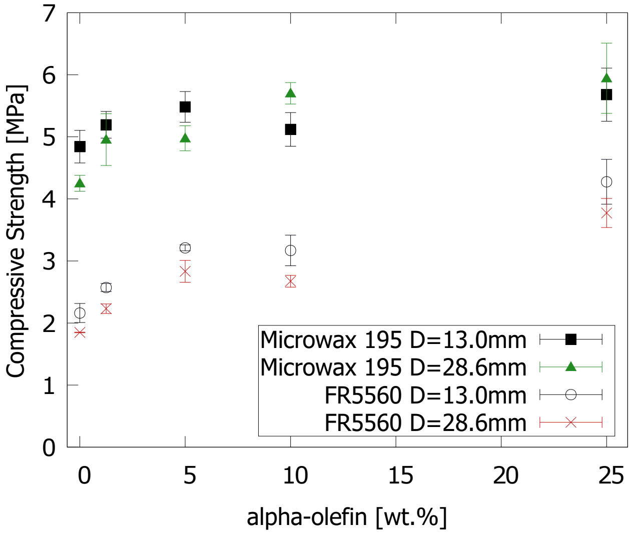

Fig. 4 Compressive strength of the fuel matrices.

C. Effect of alpha-olefin on ignition delay

The ignition delays measured following the procedure described in Section II.D are reported in Fig. 5. The error bars included in this figure are the standard deviation between measurements with identical nominal composition. With Microwax 195, between 5 and 8 test runs have been conducted for each data point on this figure. With the FR5506 paraffin, between 20 and 25 test runs are combined to yield a data points, because the effect of the diameter of AB particles was also investigated in this fuel matrix. In this figure, Microwax 195 is incorporating as-received AB whereas the ignition delay presented for the FR5560 is the average of all the different particle size ranges investigated.

This relatively large deviation can be attributed to the small number of test performed, implying that during the pellet fabrication and sanding process regions with local inhomogeneities in AB content can become preferentially exposed to the oxidizer. A statistical analysis was performed to validate the significance of the results, accounting for the sample size of the experiment. A one-way analysis of variance (ANOVA) using the *R* programming language was carried out on each of the two data sets corresponding to the two different paraffin matrices used. The *p-value* is computed with the one-way ANOVA as well as for adjusted *p-value* corresponding to post hoc analysis using Tukey's method with a 95% confidence interval. The latter method compares the difference between the average of pairs of values for each weight percentage of polymerized alpha-olefin. The *p-value* computed for the measured ignition delays of the sample using Microwax 195 is 0.9820 and is 2.2e-6 for the sample using the FR5560 paraffin. These results demonstrate that the ignition delay is not statistically affected by the addition of polymerized alpha-olefin to Microwax 195, but it is highly affected when FR5560 is used. Since the *p-value* of the first data set is well over the threshold value of 0.05, post hoc analysis was not conducted. Tukey's analysis of sample using FR5560 paraffin presents adjusted *p-values* lower than 0.05 for the following side-by-side comparisons: 25.0 wt.% vs. 0.0, 25.0 wt.% vs. 3.13, 25.0 wt.% vs. 6.25, 12.5 wt.% vs. 1.56, 12.5 wt.% vs. 1.56, 12.5 wt.% vs. 6.25. This shows that the difference of the average ignition delay is not statistically significant between 0 and 6.25 wt.%, but is significant over 6.25wt.%. The results from the statistical analysis are consistent with Fig. 5, as the reduction in delay is less obvious for Microwax 195 paraffin and seems less present for the first data points for FR5560 paraffin. Nevertheless, the reductions observed when 12.5 wt.% or 25.0 wt.% of polymerized alpha-olefin are added to the paraffin matrix are statistically significant.

As the alpha-olefin content of the matrix is increased, so does the viscosity of the melt layer and the compression strength of the solid fuel and this is associated with a reduction in the ignition delay. A trend is observable, especially for the FR5560 paraffin wax. When the Microwax 195 is used, the difference between the ignition delays measured with a pure paraffin binder (24 ms) and those of a fuel with 5% alpha-olefin in the matrix is on the order of 10%. However, as the alpha-olefin weight fraction increases beyond 5%, the viscosity and compression strength keep increasing but no further decrease in the ignition delay is observed.

The reduction of the ignition delay as more alpha-olefin is added to the fuel matrix is more important when FR5560 paraffin wax is used. Until the addition of 6.25 wt.% of alpha-olefin, no significant reduction of the ignition delay is observable. As the mass concentration of alpha-olefin is further increased, the delay of ignition is considerably reduced on the order of 50%. The compression strength is similar between the two fuel matrices but the viscosity of the pure microcrystalline wax (Microwax 195) is significantly higher than that of the FR5560 wax, as evaluated close to their melting temperatures. This hints that the ignition delay reduction is more affected by matrix viscosity rather than its rigidity. The ignition delay decreases more sharply for the least viscous matrix investigated as its viscosity is increased, but this effect saturates relatively quickly in the case of the Microwax 195, that is much more viscous to begin with. These observations were made with a AB weight fractions of 20% in the fuel and it should be kept in mind that the effect of viscosity on the ignition delay is most likely also highly dependent on this parameter.

The statistical analysis also gives insight on the effect of the viscosity on the reduction of the ignition delay since the reduction of the ignition delay is not statistically significant for the Microwax 195 paraffin, but is significant when more than 6.25 wt.% of alpha-olefin is added to the FR5560 paraffin. The viscosity of Microwax 195 being relatively high in its pure form, the addition of polymerized alpha-olefin to the fuel as a viscosity modifier is less relevant to the reduction of ignition delay. On the contrary, the FR5560 paraffin is more subject to this viscosity increases with the addition of Vybar 103, thus resulting in a reduced ignition delay.

As seen in Fig. 6, the reduction of the ignition delay seems to be more important for the higher particle sizes of AB. The first three frames of this figure show a reduction of delay as more alpha-olefin particle is added to the paraffin wax. However, this trend is getting more attenuated as the particle sizes of AB is reduced. Each data point in this figure corresponds to the mean of five test runs.

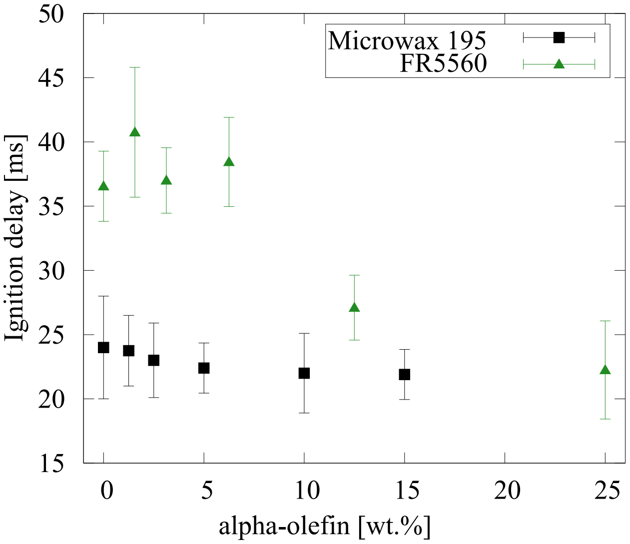

Fig. 5 Ignition delay as function of the mass concentration of alpha-olefin in the fuel matrix.

D. Effect of ammonia borane particle size on ignition delay

To characterize the impact of the particle size range of ammonia borane on the ignition delay, fuel pellets were prepared from four different ranges of AB particle sizes and tested using the same concentrations of AB and alpha-olefin as in the previous section. These tests were carried out only for the FR5560 wax, with the results shown in figures 6 and 7. Six test runs have been done for each data point of Fig. 7. Abnormal data points are found in the results of these two figures. An important potential cause for abnormally long ignition delays is off-center impact of the WFNA droplet on the sample. Clear miss-hits have been discarded, but since only one camera angle is available with visible light emission in this dataset, some tests with the droplet hitting the side of the sample most likely occurred and still resulted in ignition without a clear evidence that impact dynamics affected the results.

Baier et al. demonstrated that for pure AB powder reacting with WFNA, the ignition delay decreases as the particles are finer [19]. However, they reported that this trend was not observable when the AB is incorporated in a silicone elastomer binder. This is also observed in the first two frames of Fig. 7, when AB is included in pure paraffin and with paraffin mixed with a low concentration of alpha-olefin (1.56 wt.%) the ignition delay seems largely independent of the AB particle size. However, when more alpha-olefin additive is included in the paraffin matrix, a trend emerges, with larger AB particles associated with significantly shorter ignition delays. This can be seen in frames c) through e) of Fig. 7, corresponding respectively to 3.13 wt.%, 6.25 wt.% and 12.50 wt.% alpha-olefin addition. This trend is the opposite to what Baier et al. reported for pure AB particles. It is nevertheless consistent with an ignition delay mechanism controlled by viscosity in the melt layer, as discussed below, preferentially limiting contact between the acid and the small AB particles. The trend is however not observed for the highest alpha-olefin concentration investigated, highlighting the need for further research and experiments to clearly identify the physical mechanisms controlling the

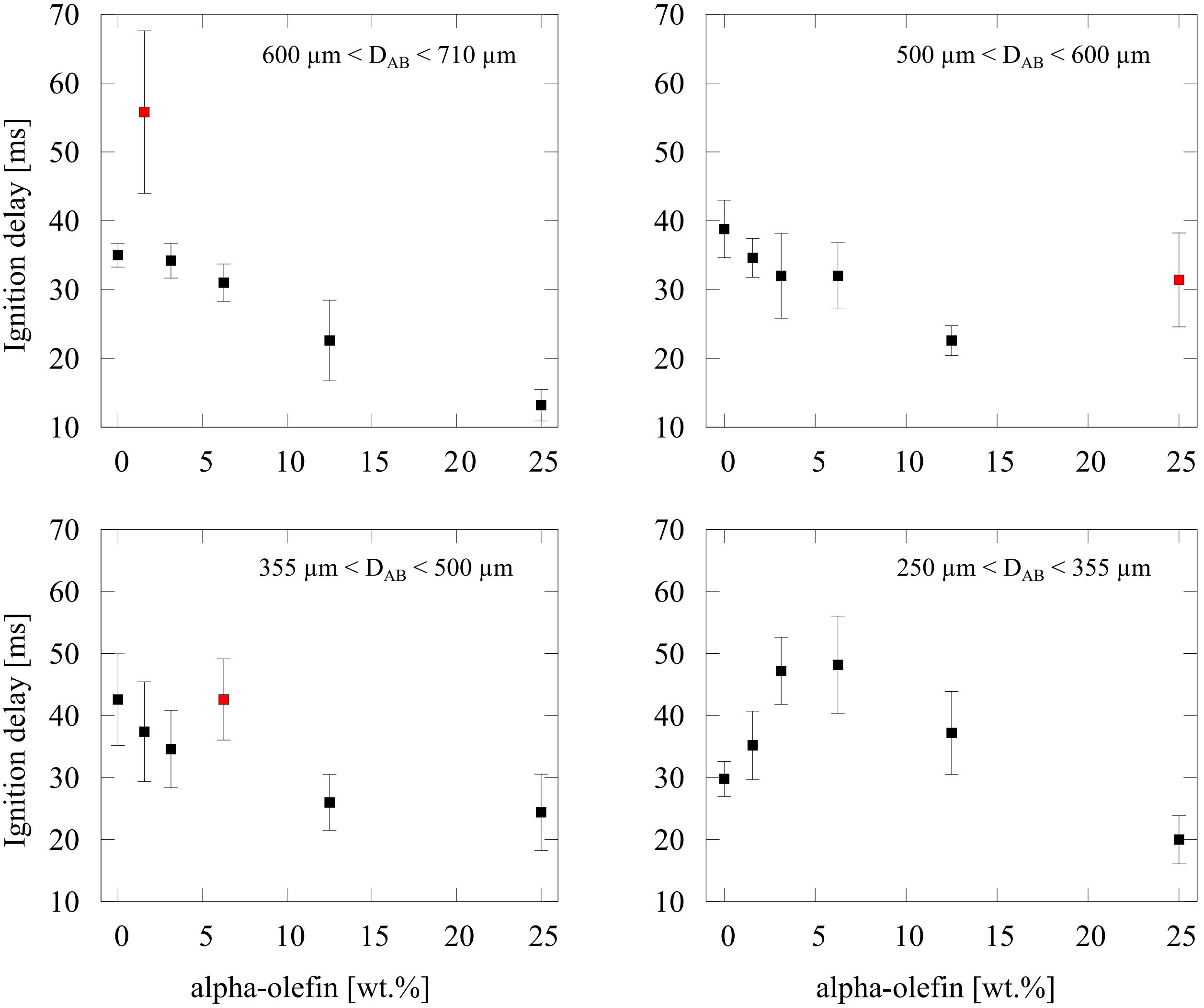

Fig. 6 Ignition delay as a function of the polymerized alpha-olefin content of the fuel matrix (FR5560 wax) melt layer, for different AB particle sizes. (Red squares represent data set where off-center droplet impacts or other isolated events of abnormally high ignition delays were observed.)

ignition delay in acid drop tests.

E. Observation of ignition using Schlieren imaging

Information on the physical and chemical processes occurring in the gas phase above the sample, where ignition occurs in the outgassing products escaping the region of contact between the acid droplet and the fuel, has also been obtained using the Schlieren imaging technique. The sequence of events immediately before and after ignition is presented in Fig. 8. Four tests implementing this technique were conducted using Microwax 195. The same distinct steps were observed before the ignition. A few milliseconds, averaging 3.95 ms with a standard deviation of 1.56 ms, after the WFNA droplet has completely wetted the surface of the pellet, heat and gas are produced from well-defined regions on the surface, often in unsteady bursts. Theses regions are assumed to be discrete AB particles reacting with the

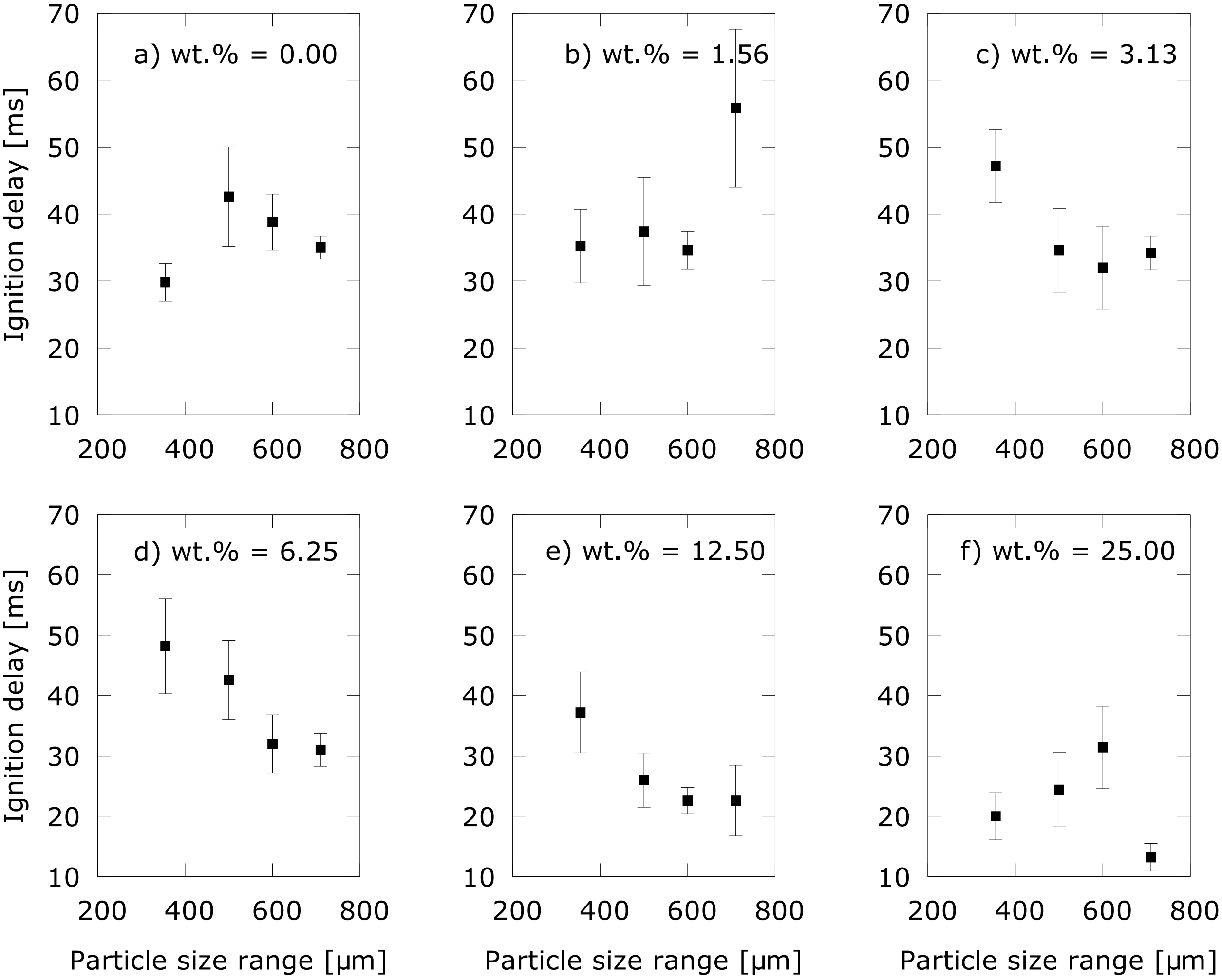

Fig. 7 Ignition delay as function of the granulometry of the ammonia borane additives in a FR5560 wax matrix, for different alpha-olefin content.

oxidizer. Since the Schlieren technique allows the visualization of refractive index gradients, the images of Fig. 8 reveal the combined effect of gaseous (species emissions) and heat emissions from the fuel sample following the impact of the acid droplet. The acid-mediated decomposition of AB is exothermic and therefore yields an hydrogen-rich outgassing, clearly visible from the third frame onwards in Fig. 8. During this initial heat release, the paraffin wax begins to melt and create a liquid layer on top of the samples. As further outgassing occurs and the temperature increases in the gas phase above the sample, ignition can clearly be seen as a deflagration wave that propagates radially from a discrete origin point, visible in the fifth frame of Fig. 8. This ignition creates more heat and the combustion becomes sustained, first burning with the acid droplet as the oxidizer, then relying on atmospheric oxygen. The delay between the first contact of the WFNA droplet with the sample and the ignition is averaging 18.83 ms with standard deviation of 8.78 ms for the four tests carried with the Schlieren technique.

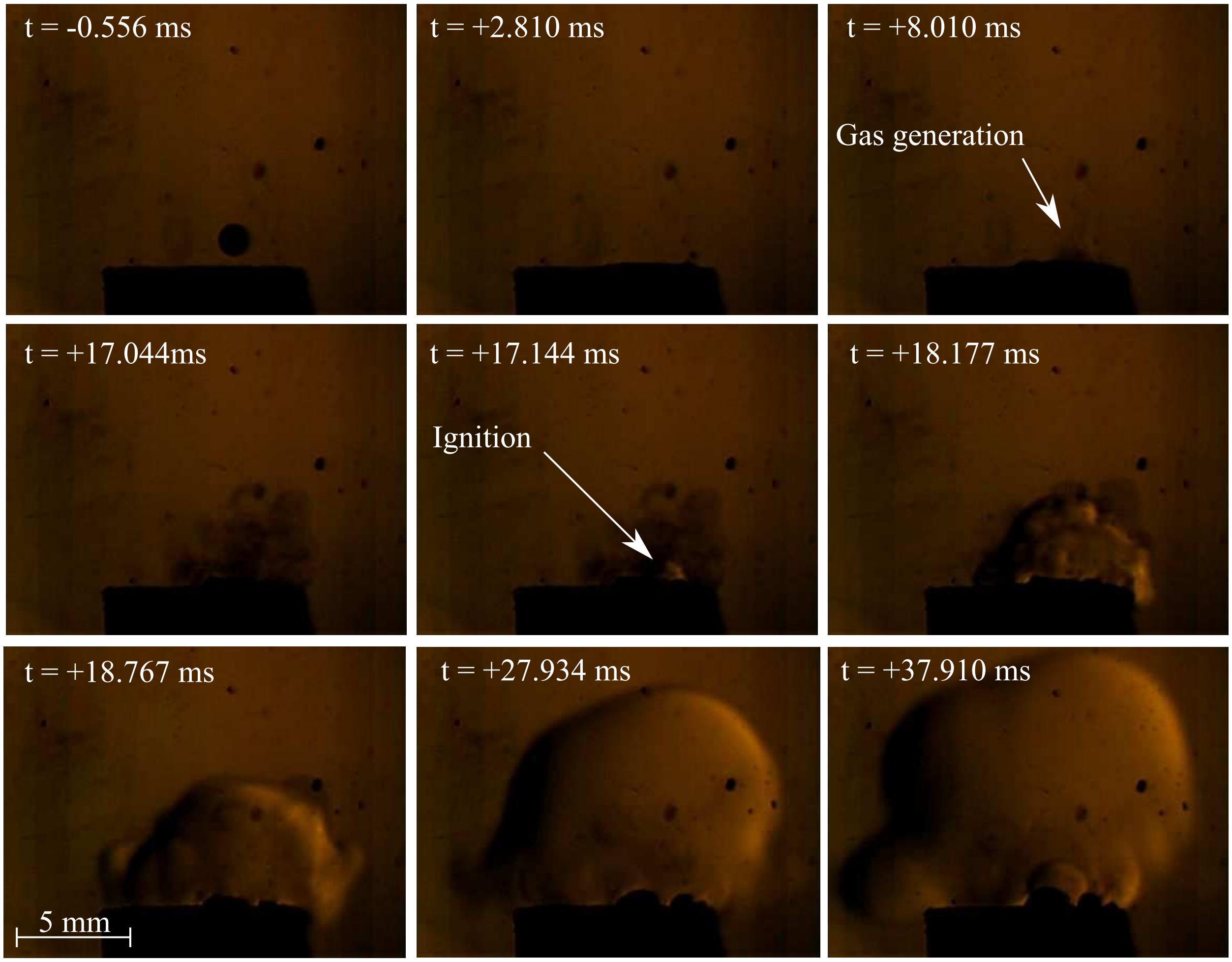

Fig. 8 Sequence of events immediately before and after ignition of fuel pellets following contact with a WFNA droplet, visualized using the Schlieren imaging technique and recorded at 30 000 fps.

F. Theoretical Performance

The theoretical propulsive performance of a fuel containing paraffin, polymerized alpha-olefin and AB is assessed using the CEA software from NASA [20]. Knowing the chemical formula and heat of formation of all of the fuel components, the theoretical specific impulse is computed. The oxidizer used is 90 wt.% WFNA. The exhaust gases are assumed perfectly expanded to atmospheric conditions and the combustion pressure is 6.89MPa (1000psi). The heat of formation of paraffin and ammonia borane, as well as the chemical formula of paraffin, were taken directly from CEA's database. The results are presented in Fig. 9. One can observe that the polymerized alpha-olefin has a slightly higher I_{sp} than paraffin, by approximately 2.5%, and that the oxidizer to fuel ratio (O/F) corresponding to the maximal I_{sp} is roughly the same. For comparison purposes, the performance of pure AB is also presented in this figure. The addition of ammonia borane in a paraffin and polymerized alpha-olefin binder increases the performances, but also expands the range of exploitable O/F ratio.

Computations were also carried out for mixture of paraffin, polymerized alpha-olefin and ammonia borane,

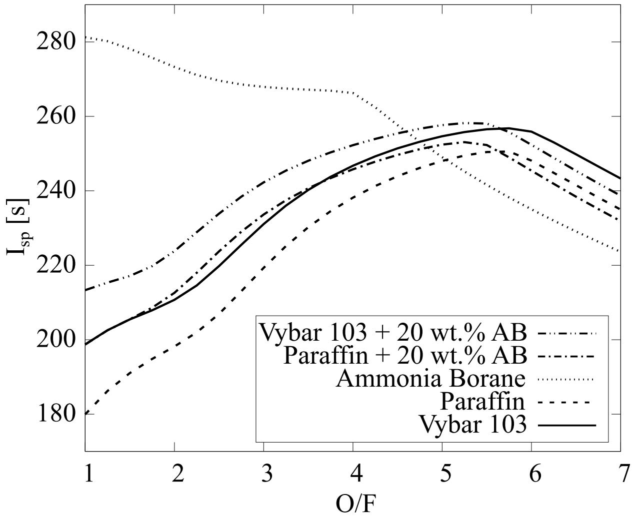

Fig. 9 Theoretical performance of paraffin, ammonia borane and polymerized alpha-olefin (Vybar 103), using WFNA as the oxidizer.

representative of the samples tested experimentally. Over the range of alpha-olefin addition to the paraffin matrix from 5 wt.% to 50 wt.% (with the AB fuel fraction fixed at 20%), the maximal I_{sp} is always at an OF ratio of 5.25. In these conditions, the I_{sp} increases weakly but linearly as more Vybar 103 is added to the fuel. Each weight percentage of alpha-olefin adds 0.06s of specific impulse. We can therefore state that alpha-olefin addition does not compromise the performance of the fuel blend, but rather slightly improves it in terms of I_{sp}.

G. Discussion of results

The mechanism responsible for the reduction of the ignition delay in fuel compositions having a more viscous melt layer is not known precisely. One can however postulate that if the melt layer is not viscous enough, the particles of additives responsible for the hypergolic character of the propellant might become less exposed to the oxidizer film present above the sample. The concentration of additive particles in the blend also strongly influences the ignition delay in hypergolic fuels, generally decreasing it as the concentration increases. The results presented above demonstrate that viscosity adjustments in the melt layer can be considered as an additional tool to tailor ignition delays for specific applications.

An upper limit for the ignition delay required for the safe operation of hypergolic hybrid motors cannot clearly be defined, contrary to the case for liquid or gaseous reactants [8]. In a liquid or gaseous fuelled rocket, when there is too much reactive mixture in the combustion chamber upon ignition, a hard start is initiated resulting in an undesirable pressure spike. In the case of hybrid rocket engines, overfilling the combustion chamber with excess oxidizer following a long ignition delay is possible but the amount of fuel actually reacting is limited by the surface area of the fuel grain. This makes it less likely that excessive amounts of mixed oxidizer and fuel can react simultaneously. Nevertheless, ignition delay plays a key role in the dynamic behavior of hypergolic rocket fuel propulsion systems upon start-up. A long ignition delay implies that oxidizer will be supplied to the combustion chamber for a long time before combustion starts, potentially leading to hazardous conditions downstream. An ignition delay below 10 ms is considered desirable for hypergolic propellants in aerospace propulsion applications [2]. The ignition delays of some hypergolic hybrid propulsion systems were investigated by Pfeil [8], he obtained values ranging from 3 to 7 ms when the binder matrix is sanded and 22 to 150 ms for cut fuel matrices. The hypergolic fuel additive used was ethylenediamine bisborane (EDBB) and it showed very short ignition delays with epoxy matrices. Using paraffin fuel matrices, the results were unsatisfactory, with very long ignition delays (50 to 100 ms). The author postulated that the rigidity of the fuel matrix could be the driving parameter for this strong difference.

The ignition delays reported here are longer than this target of 10 ms, but it is worth noting that our results were obtained at atmospheric pressure. Stober et al. [21, 22] demonstrated that increasing the pressure can dramatically decrease the ignition delay in hypergolic fuel, down to below 10 ms for paraffin wax mixed with lithium aluminum hydride (LAH) particles. However, they also observed that higher pressures can prevent ignition of hypergolic fuels. Thus, further works should be done at higher pressure using ammonia borane and polymerized alpha-olefin to determine if the reduction in ignition delay observed in this research is well suited for space applications.

The addition of polymerized alpha-olefin not only shorten the ignition delay, but also slightly increases the theoretical specific impulse as presented in Section III.F. As more polymerized alpha-olefin is added to the fuel, the compression strength and viscosity also increase. However, as Karabeyoglu et al. demonstrated [5], the entrainment regression rate, i.e. the regression rate of liquefying fuels, is inversely proportional to the viscosity if the fuel, meaning that as more Vybar 103 is present in the fuel matrix, the regression rate will decrease. Further studies should be conducted to measure the effect of the addition of polymerized alpha-olefin on the regression rate.

Although very simple, pellet ignition tests can provide valuable information on the combustion characteristics of hypergolic fuels, as demonstrated above. The work presented here treats of the ignition delay, but we also aim to extract information on the reaction rate of the different blends from the OH* chemiluminescence signals. By measuring the total amount of light emitted during the first few hundred milliseconds following droplet impact, when atmospheric oxygen is not expected to affect the reaction, one could measure qualitatively the amount of material that reacts. Efforts along these lines with the dataset described above have proved unsuccessful and no significant correlation could be found between matrix viscosity and total OH* chemiluminescence emission following droplet impact. This could be caused by small changes in the droplet impact point on the pellet that affect the total amount of oxidizer available on the surface. Inhomogeneities in the AB distribution on the pellet surface might also have an effect. However, if repeatability can be improved in future tests, comparison with a reference fuel composition could provide basic information on how the regression rates are affected by the modification of the fuel matrix. These results would have to be put in perspective with the geometry of the actual rocket motor, as they would not provide information on entrainment in the melt layer. Moreover, the surface finish of the samples most likely plays an important role in ignition delays [8], with more work required to assess combustion behavior of large fuel grains or re-ignition following partial burns, and the role played by melt layer viscosity in those conditions. Nevertheless, simple pellet tests are already attractive because of their low cost to screen a large amount of fuel compositions to optimize ignition delays and could potentially also provide useful information on the reaction rate.

IV. Conclusion

The work presented here demonstrates that short ignition delays for hypergolic hybrid rocket propellants using paraffin-based liquefying solid fuel matrices can be achieved by viscosity modification. Droplet tests were conducts with WFNA as the oxidizer and two different paraffin waxes (Microwax 195 and FR5560) incorporating ammonia borane and polymerized alpha-olefin. The first additives was chosen for its hypergolicity behavior when used with WFNA, whereas the latter was used to control the ignition delay. The mass percentage of ammonia borane in the samples was fixed at 20 wt.% and granulometry from 710μm to 255μm were used for this study. A range of 0.0 wt.% up to 25.0 wt.% of alpha-olefins were studied. Experimental results and statistical analysis reveal a clear correlation between shorter ignition delays and higher concentration of polymerized alpha-olefins, with the resulting higher viscosity believed to be the main explanation for this observation. OH* chemiluminescence, visible light emission and Schlieren imaging provided consistent values for the ignition delay. The ignition delay was reduced on the order of 50% when 25 wt.% polymerized alpha-olefins was mixed with the FR5560 paraffin wax. The theoretical performances of polymerized alpha-olefin were also computed with experimental heat of formation obtained by bomb calorimetry. Results indicate that Vybar 103 could achieve a slightly higher specific impulse when compared to paraffin with WFNA as the oxidizer. Further experiments are required to understand precisely through which physical mechanism the viscosity of the matrix melt layer affects the ignition delay of hypergolic fuels, although it is postulated that it alters the contact between the acid layer and discrete AB particles. Additionally, more works is needed to determine the behavior of the proposed additives under higher pressures.

Acknowledgments

Work supported by NSERC grant RGPIN-03622-2014 and Canadian Space Agency grant 18FAPOLB17. The authors would like to thank Dr. Sahar Nouri, at the Advanced Aerospace Composites Center at Polytechnique Montréal for help with the rheology experiments, as well as Prof. Charles Dubois.

References

[1] Karabeyoğlu, A., "Performance Additives for Hybrid Rockets," *Chemical Rocket Propulsion: A Comprehensive Survey of Energetic Materials*, edited by L. T. De Luca, T. Shimada, V. P. Sinditskii, and M. Calabro, Springer International Publishing, 2017, pp. 139–163. doi:10.1007/978-3-319-27748-6_5, URL `https://doi.org/10.1007/978-3-319-27748-6_5`.

[2] Pfeil, M. A., Kulkarni, A. S., Ramachandran, P. V., Son, S. F., and Heister, S. D., "Solid Amine–Boranes as High-Performance and Hypergolic Hybrid Rocket Fuels," *Journal of Propulsion and Power*, Vol. 32, No. 1, 2016, pp. 23–31. doi:10.2514/1.B35591, URL `http://arc.aiaa.org/doi/10.2514/1.B35591`.

[3] Bhosale, V. K., Jeong, J., and Kwon, S., "Ignition of boron-based green hypergolic fuels with hydrogen peroxide," *Fuel*, Vol. 255, 2019. doi:10.1016/j.fuel.2019.115729, URL `https://linkinghub.elsevier.com/retrieve/pii/S0016236119310816`.

[4] Karabeyoglu, M., Cantwell, B., and Altman, D., "Development and Testing of Paraffin-Based Hybrid Rocket Fuels," *37th Joint Propulsion Conference and Exhibit, Paper #2001-4503*, American Institute of Aeronautics and Astronautics, Salt Lake City, Utah, 2001. doi:10.2514/6.2001-4503, URL `http://arc.aiaa.org/doi/10.2514/6.2001-4503`.

[5] Karabeyoglu, M. A., Altman, D., and Cantwell, B. J., "Combustion of Liquefying Hybrid Propellants: Part 1, General Theory," *Journal of Propulsion and Power*, Vol. 18, No. 3, 2002, pp. 610–620. doi:10.2514/2.5975, URL `http://arc.aiaa.org/doi/10.2514/2.5975`.

[6] Karabeyoglu, A., Zilliac, G., Cantwell, B. J., Dezilwa, S., and Castellucci, P., "Scale-up Tests of High Regression Rate Paraffin-Based Hybrid Rocket Fuels," *Journal of Propulsion and Power*, Vol. 20, No. 6, 2004, pp. 1037–1045. URL `http://dx.doi.org/10.2514/1.3340`.

[7] Tang, Y., Suhang, C., Wei, Z., Ruiqi, S., T., D. L., and Yinghua, Y., "Mechanical Modifications of Paraffin-based Fuels and the Effects on Combustion Performance," *Propellants, Explosives, Pyrotechnics*, Vol. 42, No. 11, 2017, pp. 1268–1277. doi:10.1002/prep.201700136, URL `https://onlinelibrary.wiley.com/doi/abs/10.1002/prep.201700136`.

[8] Pfeil, M., "Solid Amine-Boranes as High Performance Hypergolic Hybrid Rocket Fuels," Ph.D. thesis, Purdue University, oct 2014. URL `http://docs.lib.purdue.edu/open_access_dissertations/347`.

[9] Kim, S., Lee, J., Moon, H., Sung, H., Kim, J., and Cho, J., "Effect of Paraffin-LDPE Blended Fuel on the Hybrid Rocket Motor," *46th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, Paper #2010-7031*, American Institute of Aeronautics and Astronautics, Reston, Virigina, 2010. doi:10.2514/6.2010-7031, URL `http://arc.aiaa.org/doi/abs/10.2514/6.2010-7031`.

[10] Galfetti, L., Merotto, L., Boiocchi, M., Maggi, F., and De Luca, L., "Ballistic and Rheological Characterization of Paraffin-Based Fuels for Hybrid Rocket Propulsion," *47th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, Paper #2011-5860*, American Institute of Aeronautics and Astronautics, Reston, Virigina, 2011. doi:10.2514/6.2011-5680, URL `http://arc.aiaa.org/doi/abs/10.2514/6.2011-5680`.

[11] Toson, E., Kobald, M., Cavanna, E., De Luca, L. T., Consolati, G., and Ciezki, H. K., "Feasibility Study of Paraffin-Based Fuels For Hybrid Rocket Engine Applications," *International Journal of Energetic Materials and Chemical Propulsion*, Vol. 13, No. 6, 2014, pp. 559–572. doi:10.1615/IntJEnergeticMaterialsChemProp.2014011243, URL `http://doi.org/10.1615/IntJEnergeticMaterialsChemProp.2014011243`.

[12] Kobald, M., Toson, E., Ciezki, H., Schlechtriem, S., di Betta, S., Coppola, M., and DeLuca, L., "Rheological, Optical, and Ballistic Investigations of Paraffin-Based Fuels for Hybrid Rocket Propulsion Using a Two-Dimensional Slab-Burner," *Progress in Propulsion Physics*, Vol. 8, EDP Sciences, Les Ulis, France, 2016, pp. 263–282. doi:10.1051/eucass/201608263, URL `http://doi.org/10.1051/eucass/201608263`.

[13] Nakagawa, I., and Hikone, S., "Study On The Regression Rate of Paraffin-Based Hybrid Rocket Fuels," *Journal of Propulsion and Power*, Vol. 27, No. 6, 2011, pp. 1276 – 1279. doi:10.2514/1.B34206, URL `http://doi.org/10.2514/1.B34206`.

[14] Jens, E. T., Miller, V. A., and Cantwell, B. J., "Schlieren and OH* Chemiluminescence Imaging of Combustion in a Turbulent Boundary Layer Over a Solid Fuel," *Experiments in Fluids*, Vol. 57, No. 3, 2016, p. 39. doi:10.1007/s00348-016-2124-x, URL `http://doi.org/10.1007/s00348-016-2124-x`.

[15] American Society for Testing and Materials, "D575-91 Standard Test Methods for Rubber Properties in Compression," West Conshohocken, PA, 2018. URL `http://astm.org`.

[16] American Society for Testing and Materials, "E9-19 Standard Test Methods of Compression Testing of Metallic Materials at Room Temperature," West Conshohocken, PA, 2019. URL `http://astm.org`.

[17] Walters, R. N., Hackett, S. M., and Lyon, R. E., "Heats of combustion of high temperature polymers," *Fire and Materials*, Vol. 24, No. 5, 2000, pp. 245–252. doi:10.1002/1099-1018(200009/10)24:5<245::AID-FAM744>3.0.CO;2-7, URL `https://doi.org/10.1002/1099-1018(200009/10)24:5<245::AID-FAM744>3.0.CO;2-7`.

[18] Foster, R., "Additive to Prevent Oil Separation in Paraffin Waxes," , U.S. Patent 20040040200A1, Mar. 4, 2004. Assignee: Baker Hughes Inc.

[19] Baier, M. J., Ramachandran, P. V., and Son, S. F., "Characterization of the Hypergolic Ignition Delay of Ammonia Borane," *Journal of Propulsion and Power*, Vol. 35, No. 1, 2019, pp. 182–189. doi:10.2514/1.B37075, URL `https://doi.org/10.2514/1.B37075`.

[20] Gordon, S., and Mcbride, B. J., "Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications - I Analysis," *NASA RP-1311*, October 1994.

[21] Stober, K. J., Thomas, A., Evans, B. J., and Cantwell, B. J., "Investigation of Green Hypergolic Propellants for Hybrid Rockets," *52nd AIAA/SAE/ASEE Joint Propulsion Conference, Paper #2016-4991*, American Institute of Aeronautics and Astronautics, Salt Lake City, Utah, 2016. doi:10.2514/6.2016-4991, URL `http://arc.aiaa.org/doi/10.2514/6.2016-4991`.

[22] Stober, K. J., Cantwell, B. J., and Otaibi, R. A. L., "Hypergolic Ignition of Lithium–Aluminum–Hydride-Doped Paraffin Wax and Nitric Acid," *Journal of Propulsion and Power*, Vol. 36, No. 3, 2020, p. 435–445. doi:10.2514/1.B37425, URL `https://arc.aiaa.org/doi/10.2514/1.B37425`.