# Experimental Investigation of the Hydrogen Peroxide – Solid Hydrocarbon Hypergolic Ignition

David A. Castaneda\* and Benveniste Natan\* \*Faculty of Aerospace Engineering Technion – Israel Institute of Technology, Haifa 3200003, Israel

#### Abstract

Hypergolic ignition of a solid hydrocarbon fuel with hydrogen peroxide is achieved by embedding a catalyst into the fuel. Sodium Borohydride exhibits the required properties to enhance ignition of the solid fuel upon contact with 90%  $H_2O_2$ . Ignition delay times were measured by Drop-on-Solid tests at atmospheric and elevated pressure conditions. The results demonstrate that ignition of the hydrocarbon matrix used (polyethylene) is feasible, especially at higher pressures, resulting in shorter ignition delay times. Additional tests were performed with axial oxidizer injection over a hollow cylindrical surface, proving the viability of the proposed fuel.

#### **1. Introduction**

Hybrid rocket advantageous operational capabilities as throttling and shutdown, as well as its potential to high performance, encourage the work on more efficient hybrid systems that may provide the requirements for rocket mission success. Fast ignition and transient processes along with stable combustion and efficiency are necessary for such systems [1]. Hybrid rockets high performance is feasible due to the dual use of, mostly, a solid fuel and a liquid oxidizer, allowing also throttling capabilities and safety of both manufacturing and storage. But for effective combustion of a hybrid rocket, essential components such as a pre-combustion and aft-combustion chambers, necessary for proper heat up of the oxidizer and complete combustion of the fuel, are needed in hybrid rockets, making them long and heavy. Furthermore, in order to obtain grain ignition, external systems are added. In many cases, a catalytic bed, which heats up the oxidizer, is placed before the grain in order to achieve ignition. This catalytic bed has proven to be efficient during a first ignition, but decays with time, worsening ignition processes, efficiency and oxidizer heat up [2].

The fuels used for hybrid propulsion include hydrocarbon fuels such as *HTPB*, polyethylene, paraffin and ABS, which are commonly burned with liquid or gaseous oxygen, IRFNA, NTO, nitrous oxide or hydrogen peroxide as oxidizers. But for all of these configurations, either external ignition systems or consumable catalytic beds are used [2-4]. In the present work, a hypergolic fuel ignition, i.e., ignition of the fuel upon contact with the oxidizer, is proposed. This ignition is fast and does not deteriorate with time, preventing ignition processes and efficiency to decay throughout the operation of the motor. In addition, it allows throttling and shutdown of the motor, which is very important in mission abort or in reusable igniters that behave as small-scale rocket propulsion systems. Hydrazine-based propellants such as monomethyl hydrazine (MMH) together with nitrogen tetroxide (NTO) are known to be highly hypergolic resulting in proper ignition in rocket engines [5]. However, these propellants involve health hazards and are not environmentally friendly, or "green". Alternative hypergolic combinations can be used to obtain fast ignition and efficiency. Natan et al. [6] achieved hypergolic ignition of gelled kerosene with hydrogen peroxide, by embedding metal hydride particles into the gelled kerosene, enabling hypergolic ignition with the oxidizer. They showed that the hypergolic reaction produces enough heat to enhance combustion between the fuel and the oxidizer. Hydrogen peroxide was used as the oxidizer due to its non-hazardous properties, as it only decomposes into oxygen and water, and its high energetic potential [7].

Hypergolic ignition of hydrogen peroxide with metal hydrides embedded in Dicyclopentadiene (*DCPC*) was studied by Sippel et al. [8]. They used two metal hydrides: sodium borohydride and lithium aluminum hydride, in order to obtain hypergolic ignition of the fuel. Ignition was obtained only for some of the casted samples they tested, even though the load of metal hydride catalyst in the hydrocarbon matrix was very high. They tested the difference between the contact surfaces of the samples, showing that newly pure cut surfaces are optimal for ignition. Short ignition delay times were obtained for the samples where ignition was obtained. A study to analyze the effect of embedded particles in a hydrocarbon fuel was done by DeSain et al. [9] who investigated the effect of embedding lithium aluminum hydride in paraffin wax for hybrid rockets. Although they did not test the hypergolicity of the obtained fuel, they showed that the addition of such catalyst in the hydrocarbon matrix increases the regression rate of the fuel. This is advantageous, since hybrid rockets exhibit low regression rates, compared to regression rates in solid propellants, resulting in lower thrust and system potential. Experimental and theoretical investigations have been made to show that metal hydrides such as sodium borohydride and aluminum hydride [10-12] are additives that improve the regression rate of the fuel in hybrid rockets.

The present study analyses the hypergolic ignition and feasibility of a hydrocarbon based fuel containing hypergolic catalysts embedded in it, in order to be able to obtain hypergolic ignition of the hydrocarbon solid fuel with high concentration hydrogen peroxide. Both *HTPB* and Polyethylene were used as potential hydrocarbon matrices, and different catalysts were chosen. Ignition delay times and processes are evaluated both quantitatively and qualitatively to understand the hypergolic ignition of the fuel.

# 2. Hypergolicity and Theoretical Performance

A number of hypergolic solid catalyst with hydrogen peroxide that will enhance the ignition of the fuel, whether HTPB or Polyethylene, were selected according to their melting point, hypergolicity and availability. From various hypergolic catalyst candidates, Copper (II) Chloride ( $CuCl_2$ ), Sodium Borohydride ( $NaBH_4$ ), Iron (II) Chloride ( $FeCl_2$ ) and Iron (III) Chloride ( $FeCl_3$ ) were chosen to be embedded into the hydrocarbon to test ignition feasibility and theoretical performance. All of these have high melting point, and are highly hypergolic with hydrogen peroxide. Other catalysts like Lithium Aluminum Hydride ( $LiAlH_4$ ) and Lithium Borohydride ( $LiBH_4$ ) were also candidates, but were excluded because of their high instability and sensitivity to moisture, making handle conditions complicated. The chosen catalysts are also sensitive to moisture, but unlike  $LiAlH_4$  and  $LiBH_4$ , they can be openly handled for a short time without deactivating their hypergolic effect.

Reaction/Ignition delay times for the chosen catalysts were calculated and a qualitative description of their hypergolic reaction process is given in Table 1. Powder catalysts were placed over an aluminum plate and reaction delay times were measured with a high-speed camera. All of the catalyst tested except for  $CuCl_2$  showed an explosive reaction with 90% hydrogen peroxide, but only Sodium Borohydride presented flames in the hypergolicity tests.  $CuCl_2$  and  $FeCl_3$  hypergolic reactions released a lot of vapours without showing any signals of flame. However, both  $CuCl_2$  and  $FeCl_3$  reactions left a burned aluminum plate, suggesting that the heat released in the reaction may be enough to have an effect in the hydrocarbon matrix, and thus induce its ignition.

	Reaction Delay [ <i>ms</i> ]	Flame	Smoke	Explosive
CuCl <sub>2</sub>	$100 \pm 20$	No	Yes	No
NaBH <sub>4</sub>	4	Yes	No	Yes
FeCl <sub>2</sub>	0.5	No	No	Yes
FeCl <sub>3</sub>	4	No	Yes	Yes

#### Table 1: Pure Catalyst Hypergolic Test

Theoretical performance was calculated for the different catalysts chosen together with HTPB and PE, but only results with sodium borohydride and polyethylene are shown. Later on it will be shown that ignition was only feasible with the use of sodium borohydride embedded in polyethylene. Theoretical performance was calculated for different weight percentages of  $NaBH_4$  in PE, using pure and 90% hydrogen peroxide, which is the oxidizer used in this work. The results are shown in Table 2 and Table 3. Theoretical specific impulse decreases as the percentage in weight of sodium borohydride is increased, whereas the flame temperature increases with the addition of more  $NaBH_4$ . In addition, lower optimal oxidizer-to-fuel ratios are needed as the load of  $NaBH_4$  is increased. As expected, the theoretical specific impulse acceptably decreases due to the lower purity of  $H_2O_2$ , by no more than four seconds. For optimal oxidizer-to-fuel ratios, the density specific impulse barely varies as  $NaBH_4$ 's concentration in the hydrocarbon increases.

	100% wt. PE H <sub>2</sub> O <sub>2</sub>	20% wt. NaBH <sub>4</sub> 80% wt. PE H <sub>2</sub> O <sub>2</sub>	25% wt.NaBH <sub>4</sub> 75% wt.PE H <sub>2</sub> O <sub>2</sub>	33% wt.NaBH <sub>4</sub> 67% wt.PE H <sub>2</sub> O <sub>2</sub>	40% wt.NaBH <sub>4</sub> 60% wt.PE H <sub>2</sub> O <sub>2</sub>	50% wt. NaBH <sub>4</sub> 50% wt. PE H <sub>2</sub> O <sub>2</sub>
I <sub>sp</sub> [s] Adapted at S.L.	277.9	277	276.8	276.5	276.2	275.7
$\rho I_{sp} \left[ s \left[ s \right] g /_{cm^3} \right]$	365	364	364	363	363	362
Flame Temp.[K]	2995	2999	3001	3006	3010	3018
<b>0</b> / <b>F</b> <sub>0pt.</sub>	6.9	6.2	6.05	5.75	5.5	5.15

Table 2 : Theoretical Performance of  $PE - NaBH_4$  wt. % hybrid fuel, with pure  $H_2O_2$ 

Table 3: Theoretical Performance of  $PE - NaBH_4$  wt. % hybrid fuel, with 90%  $H_2O_2$ 

	100% wt. PE 90% H <sub>2</sub> O <sub>2</sub>	20% wt. NaBH <sub>4</sub> 80% wt. PE 90% H <sub>2</sub> O <sub>2</sub>	25% wt. NaBH <sub>4</sub> 75% wt. PE 90% H <sub>2</sub> O <sub>2</sub>	33% wt. NaBH <sub>4</sub> 67% wt. PE 90% H <sub>2</sub> O <sub>2</sub>	40% wt. NaBH <sub>4</sub> 60% wt. PE 90% H <sub>2</sub> O <sub>2</sub>	50% wt. NaBH <sub>4</sub> 50% wt. PE 90% H <sub>2</sub> O <sub>2</sub>
I <sub>sp</sub> [s] Adapted at S.L.	274	273.3	273.2	272.9	272.6	272.3
$\rho I_{sp} \left[ s \left[ s \right] g /_{cm^3} \right]$	358	357	356	357	356	356
Flame Temp.[K]	2898	2900	2903	2909	2912	2919
$O/F_{Opt.}$	7.8	7.05	6.85	6.45	6.2	5.8

The minor decrease in the theoretical performance parameters as well as the relatively small changes in the theoretical flame temperature, suggest that even for a high concentration of metal hydride embedded in the polyethylene, the specific impulse of the engine is barely affected, whereas the advantages of hypergolic ignition are achieved. Furthermore, in comparison to a common hybrid rocket system such as  $HTPB/H_2O_2$  [8], the proposed hypergolic fuel in this work has slightly higher values of specific impulse and density specific impulse.

# 3. Fuel Preparation and Description

Hydroxyl Terminated Polybutadiene (*HTPB*) is a common fuel used in solid and hybrid rockets, and its properties are very well known. Because of this, as a first approach, it was chosen to be the matrix to contain the catalyst which will induce the fuel burning when getting in contact with the hydrogen peroxide. Compatibility tests were performed between *HTPB*, the cross-linker (DDI) and the catalysts chosen. The results showed that the samples cannot be manufactured because there is a reaction between either the catalyst, the cross-linker or the HTPB. For the metal hydride catalyst, hydrogen bubbles were observed when trying to cast the sample, whereas for the reminder catalysts chosen, either a reaction between components was observed or there was a very fast polymerization making impossible the casting of any sample. Polyethylene is known to be stable, non-reactive and easy to handle, as well as allowing high performance parameters as HTPB does [2]. In addition, reaction between polyethylene and the catalysts in unprovable thanks to the chemical structure of Polyethylene. The melting points of all the catalysts chosen are high enough to allow them to stay solid during the mixing process with the hydrocarbon matrix. PE was selected as the main fuel, and the catalysts were embedded in it in order to obtain hypergolic ignition of the fuel.

All of the catalysts used were powders with grain sizes of approximately  $50 - 100 \mu m$ . The Polyethylene type used was low density PE in order for it to be able to contain within itself as much solid catalyst particles as possible. In order to prepare the samples for the drop-on-solid tests, the polyethylene was initially heated above its melting point in a metallic beaker. When it was completely melted, the needed amount of catalyst was added inside the beaker and then well mixed with the polyethylene until a homogenous mixture was obtained. For samples with a high load of catalyst, agglomerations might appear, resulting in a longer mixing process. For these cases, care was taken with the heating source in order avoid burning of the polyethylene. The melted *PE* with the catalysts embedded was then casted into Teflon made moulds to give them the shape of a 5x5x30 mm rectangular rod. Teflon was used so that the samples

do not stick to the mold. The Teflon mold was preheated in order to maintain the polyethylene hot enough to be reshaped. It is important to mention that the viscosity of the melted PE is very high. Without a source of heat, at standard conditions, it rapidly solidifies into the given shape. The fact that the melted polyethylene is highly viscous and that it solidifies rapidly is advantageous since no catalyst solid particle sedimentation can occur. Melted *PE* needs seconds to solidify at standard conditions. As the polyethylene melts at higher temperatures than 100 °C, and the catalyst are only weighted and rapidly added into the hot melted *PE*, there is no need to make the mixing process in a neutral environment in order to avoid reaction of the catalysts with moisture. In addition, as polyethylene rapidly solidifies giving the desired shape, the already solidified samples can be rapidly stored into sealed bags, which keep the samples away from reacting with moisture.

All of the samples' appearances were similar, independent on the load of catalysts. Samples were homogeneous and resembled the mechanical properties of polyethylene. Identification between the samples was simple as they acquired the pigment of the catalyst used.

Images of the cross-section of a cut surface taken with a microscope of a sample containing  $40\% wt. NaBH_4$  and 60% wt. PE are shown in Figure 1. Figure 1(a) shows a newly cut surface with embedded solid particles of NaBH<sub>4</sub> contained within the polyethylene matrix. Figure 1(b) shows a different cut surface of the sample, containing solid particles of sodium borohydride reacting with ambient moisture after approximately five minutes from the time the cut surface was exposed to ambient moisture. Sodium borohydride hygroscopic sensibility is observed as bubbles that slowly increase their size with time. The reaction with moisture deactivates  $NaBH_4$ 's hypergolic effect with hydrogen peroxide by replacing the hydrogen atoms with oxygen ones. The polyethylene structure seems to be rigid and without any cracks or pores.



Figure 1: Microscope Images of 40% wt. NaBH<sub>4</sub> – 60% wt. PE cut surfaces

In addition to the samples manufactured for the drop-on-solid tests, hollow cylindrical samples were manufactured in order to prove ignition of the hypergolic fuel proposed. Explanations will be given later. To prepare these samples, the hot homogeneous mixture between polyethylene and the catalyst was placed into stainless steel preheated hollow cylindrical tubes where the fuel was then casted into the cylinder's shape. The cylinders had a diameter of 4 *cm* and approximately 3 *cm* length. Figure 2 shows a sample of the casted cylindrical fuel. Even though the stainless steel molds were heated up below the melting point temperature of polyethylene, they were hot enough to prevent fuel's solidification before the desired shape was achieved.



Figure 2: Hollow Cylindrical Sample containing 25% wt. NaBH<sub>4</sub> + 75% wt. PE

# 4. Experimental Setup

In the present work, three different experimental setups were built in order to test drop-on-solid at standard conditions, hollow cylindrical fuel ignition and drop-on-solid ignition under different pressures. For all of the setups a high-speed camera was used to measure the ignition delay times as well as to analyze the ignition process. For the tests performed, the high-speed camera was set to 1000 frames per second. It is expected that the ignition delay of the solid hypergolic mixture of polyethylene with catalyst increases compared to the pure catalysts. The speed of 1000 frames per second is enough to measure ignition delay times and analyze the process. For the ignition delay measurements, ignition delay was defined as the time between the instant the bottom of the drop of hydrogen peroxide touches the solid, until the moment a flame can be identified. In the cases where no flame was observed at all, the reaction time between the  $H_2O_2$  droplet and the solid fuel surface was calculated.

# 4.1 Drop-on-Solid Standard Conditions Setup

Solid hypergolic fuel samples with a cross-section of  $0.5x0.5 \ cm$  and length of less than half centimeter were placed over an aluminum plate located over a big absorbent lab paper. These samples were obtained from cutting the  $0.5x0.5x3 \ cm$  casted samples. Every test was done with a newly cut surface, which was less than a minute exposed to moisture. This ensures that there is no reaction of the catalyst with moisture before the  $H_2O_2$  drop touches the sample. The high speed camera was focused on the samples in such way that the moment of contact between the hydrogen peroxide drops where dropped using a pipette. Figure 3 shows a schematic image of the experimental setup used for these tests. As some of the hypergolic reactions are expected to be explosive, absorbent lab paper was used to determine how far the hydrogen peroxide would be thrown away due to the explosive reaction. As an example, for fuels containing  $NaBH_4$ , wet areas were seen at even more than 30 [cm] from the solid fuel sample, and for some of the tests, the "shrapnel" of the explosion was hot enough to easily ignite the lab paper.



Figure 3: Drop-on-Solid Standard Conditions Setup Scheme

# 4.2 Hollow Cylindrical Solid Fuel Setup

These tests were conducted in order to prove hypergolic ignition of the fuel under standard conditions. For these tests, hydrogen peroxide was injected radially outwards from the center of the hollow cylinder, towards the hypergolic fuel, using a 1 mL glass syringe. For all of the tests only 0.5 mL of hydrogen peroxide was injected manually "as fast as possible". This resulted in an injection that holds between 150 and 250 ms. A stainless steel needle with lateral openings was built in order to radially inject the  $H_2O_2$ . It is important to notice that as the hydrogen peroxide passes through the openings of the needle at high speeds, the size of the droplets are much lower than using the pipette, improving the results of hypergolic ignition. Scheme of the experimental setup for the ignition of the hollow cylindrical hypergolic solid fuel can be seen in Figure 4. For protection of the high speed camera and the operator of the syringe, Perspex windows were placed before and after the cylindrical hollow sample. The sample itself was held in front of the camera by using a metallic lab grip.



Figure 4 : Hollow Cylindrical Solid Fuel, Test Experimental Setup Scheme

#### 4.3 Drop-on-Solid at Elevated Pressures Setup

To test the ignition delay of the hypergolic solid fuel under pressure, an inert environment was obtained by filling in a pressure chamber with nitrogen. The pressure chamber has two windows: one to allow light, and another through which the camera can film the burning sample. The camera was placed with an angle relative to the chamber windows in order to be able to see the particle's surface so that the ignition delay can be well measured. A high pressure syringe was used in order to contain hydrogen peroxide and produce the drops for the tests. Only the needle of the syringe came inside the chamber. After the syringe was filled with the oxidizer and was attached to the chamber, a screw held the syringe's plunger so that the increased pressure inside the chamber does not pull it out. In addition, the plunger was pushed in by driving in the screw, allowing a drop to come out from the needle and fall over the fuel sample. A scheme of this experimental setup is seen in Figure 5.



Figure 5: Drop-on-Solid at Elevated Pressures Setup Scheme

# 5. Results

# 5.1 Drop-on-Solid Standard Conditions Tests

The first stage of the study was to identify the potential catalysts or catalysts' behavior that will produce enough heat to allow rapid decomposition of hydrogen peroxide and rapid enough pyrolysis of a solid hydrocarbon, in order to result in a feasible hypergolic ignition that can be used in rocket propulsion. Samples containing 25% wt. of catalyst and 75% of polyethylene were casted, burned, and compared, using the drop-on-solid setup at standard conditions. For all of the cases, 90% hydrogen peroxide was used as the oxidizer and only cut surfaces were burned. This is to allow the catalyst to be completely exposed to the  $H_2O_2$  drop. Table 4 summarizes the results obtained for this test. At least five tests were performed for each one of the catalyst selected. Average ignition/reaction delay times and standard deviations were calculated.

Table 4: Ignition/Reaction Delay Times for 25% wt. Catalyst and 75% wt. PE

	Ignition Delay Avg. [ms]	Reaction Delay Avg. [ms]	Std. Deviation
CuCl <sub>2</sub>	-	~220	~100
$NaBH_4$	9.5	-	1.04
FeCl <sub>2</sub>	-	9.6	0.75
FeCl <sub>3</sub>	-	5.4	1.02

For Copper (II) Chloride, there is a long reaction delay and a lot of smoke. Through a very long time, the  $H_2O_2$  droplet reacts over the solid fuel sample releasing a lot of gases but not a lot of heat. For all of the  $CuCl_2$  tests, no polyethylene melted and no changes were observed after the reaction between the catalyst and the oxidizer occurred. In addition, the measured times varied a lot resulting in a very high standard deviation. As regards the pure catalyst  $CuCl_2/H_2O_2$  reaction, it was expected that the reaction will actually heat up enough polyethylene to obtain combustion. Unfortunately, this did not happen.

Both  $FeCl_2$  and  $FeCl_3$  showed a similar reaction with the  $H_2O_2$  drop when embedded in polyethylene. Both reactions were fast and slightly explosive, with a small amount of gases released. Similarly to  $CuCl_2$ , for all samples tested, no flame was observed, and only for part of the samples, some of the polyethylene surface structure changed. The reaction time for the  $FeCl_2$  catalyst was highly increased when embedded into the polyethylene structure compared to the reaction delay for the pure catalyst. This happened for all of the cases, but it was particularly noticeable for the Iron (II) Chloride case.

Solid fuel samples containing Sodium Borohydride embedded into the polyethylene matrix were successfully ignited with the drop-on-solid standard conditions tests. Compared to the pure catalyst reaction delay, the solid fuel ignited after an average of 9.5 *ms* with a minor amount of smoke released and noticeable flames. The flames were classified to weak, regular and strong flames, as for each of the cases, the "strength" of the flame varied. Figure 6 shows the process of the ignition delay of a sample of  $25\% wt. NaBH_4 - 75\% wt. PE$  as a sequence of images. For the case shown here, a strong flame that lasts approximately 4 ms is observed leaving the surface of the solid fuel sample. During the explosion, unburned liquid polyethylene is thrown away from the surface of the solid sample.



Figure 6: Ignition image sequence of 25% wt.  $NaBH_4 - 75\%$  wt. PE with 90%  $H_2O_2$ 

Catalysts showing flameless hypergolic reactions with hydrogen peroxide do not enhance any reaction between polyethylene and  $H_2O_2$ , even though these reactions can be highly exothermic. Moreover, flameless explosive reactions obtained with  $FeCl_2$  and  $FeCl_3$  catalysts did not result in ignition of the solid fuel samples. Finally, from the tests using 25% wt. catalyst, ignition was observed only for sodium borohydride embedded in polyethylene.

The results of the first stage of this work showed that  $NaBH_4$  embedded in polyethylene could produce a hypergolic ignition of the solid fuel with hydrogen peroxide. To analyze the effects of the catalyst load in the hydrocarbon matrix, a parametric experimental investigation of the weight percentage of  $NaBH_4$  in the solid fuel is done. Samples loaded with 33% wt., 40% wt. and 50% wt. of  $NaBH_4$ , together with polyethylene were casted using the same technique and sizes as for the 25% wt. samples. The limit was set to 50% wt. of sodium borohydride, since for higher loadings, big agglomerates were observed in the manufacturing process and also, at least for the method used to make the samples, polyethylene can barely hold the solids into it. In addition, it is desirable to decrease as much as possible the amount of catalyst used, because this will result in higher performance parameters. At least 10 samples were burned for each one of the four different loadings chosen. All samples had equal surface area of 0.5x0.5 cm. All the samples ignited upon contact with 90%  $H_2O_2$ , except for one sample containing 40% wt.  $NaBH_4$ . Average ignition delay times for all the samples were calculated as well as standard deviations. Results are shown in Table 5.

Table 5:  $NaBH_4 + PE$  solid fuel ignition delay times with 90%  $H_2O_2$ 

	Ignition Success	Ignition Delay Avg. [ms]	Std. Deviation
25% wt.NaBH <sub>4</sub> 75% wt.PE	12/12	9.5	1.04
33% wt. NaBH <sub>4</sub> 67% wt. PE	11/11	7	0.85
40% wt. NaBH <sub>4</sub> 60% wt. PE	9/10	7	0.78
50% wt.NaBH <sub>4</sub> 50% wt.PE	12/12	7.2	1.1

For the samples with 25% wt.  $NaBH_4$  most of the flames were regular flames. Samples with 33% wt.  $NaBH_4$  presented both strong and regular flames, whereas samples with 40% wt. and 50% wt. of  $NaBH_4$  mostly resulted in strong ignition flames. The results show a difference in the ignition delay when the load of sodium borohydride is increased from 25 to 33 percent. If the weight load of catalyst is further increased there is almost no change between the average ignition delay times obtained suggesting that there is an upper limit of catalyst load, for which the ignition delay is no further improved. Still, even though the average ignition delay does not vary with high load of catalyst, the flame strength does, affecting the ignition of the hydrocarbon fuel. For all the samples burned, there was a change in the surface of the solid fuel that was ignited, as well as melted polyethylene flying from the surfaces of the sample. Figure 7 shows a sequence of images of the ignition process of a sample containing 33% wt.  $NaBH_4$ . For this case, the ignition was achieved in only 6 ms. From Figure 7, at -1 ms the explosive reaction of the fuel begins, but no flame is observed. Two ms after the ignition moment the flame remains but it is very weak. After three ms, a second explosion occurs below the sample, making it fly away from the forceps. The camera did not catch this secondary explosion.



Figure 7: Ignition image sequence of 33% wt.  $NaBH_4 - 67\%$  wt. PE with 90%  $H_2O_2$ 

# 5.2 Hollow Cylindrical Solid Fuel Tests

The drop on solid tests showed that hypergolic ignition of polyethylene-based fuel can be achieved by adding sodium borohydride into the hydrocarbon matrix. However, even though the flame was strong for high loading percentages of sodium borohydride, it lasted very little and was just big enough to burn a small part of the polyethylene. In addition, for all of the samples, the flame looked "colder" than the flame obtained for the tests with pure  $NaBH_4$ . This of course implies that part of the heat of reaction between the catalyst and  $H_2O_2$  is absorbed by the polyethylene matrix. Yet, even if the drop-on-solid tests at standard conditions show ignition, there is uncertainty that the appropriate hypergolic ignition of the polyethylene based fuel can actually happen in a combustion chamber in a rocket motor.

From the drop-on-solid tests, it was observed that the explosion obtained at the contact surface between the solid fuel and the  $H_2O_2$  drop was massive, causing a rapid separation between oxidizer and solid fuel, preventing long lasting reactions/combustion of the fuel. In the drop-on-solid tests, many test had a second explosion that occurred below the sample. For these tests, some hydrogen peroxide was able to reach the bottom part of the sample, and reacted with the solid fuel producing very big visible flames that were much bigger than that obtained at the top of the sample (where the drop fell). Figure 8 illustrates one of these cases. As the drop falls on top of the sample, an explosion is observed with a very weak flame. However, some of the hydrogen peroxide reaches the bottom of the sample, reacting with the fuel, resulting in a very big flame.



Figure 8: 33% wt.  $NaBH_4 - 67\%$  wt. PE with 90%  $H_2O_2$ , hypergolic ignition below the sample.

The combustion of the hydrocarbon fuel actually happens between the products of the decomposition of hydrogen peroxide and products of the pyrolysis of this fuel. On the top of the sample, due to the explosive reaction, both combustion components are separated preventing any further ignition. When hydrogen peroxide reaches the bottom of the sample, the reaction is enclosed between the bottom of the sample and the aluminum plate, and the products of both  $H_2O_2$  decomposition and solid fuel pyrolysis cannot be separated by the explosion. Thus, reaction occurs and big ignition flames are observed. This suggest that enclosing the reaction will be a better test for hypergolic ignition, and a better proof that the suggested in this work is feasible.

The solution proposed is to enclose the products from the explosion of the hypergolic reaction by casting hollow cylindrical solid fuels with radially outwards hydrogen peroxide injection. This way, the products of the explosive hypergolic reaction around the inner walls of the cylinder will move towards the center of the hollow cylinder, thus mixing and reacting. As mentioned before,  $0.5 \ mL$  of  $H_2O_2$  were injected using a glass syringe. For these test, an initial hollow cylinder was casted with a catalyst concentration of 25% weight, the minimal percentage used in the drop-on-solid tests. The hollow cylindrical sample was burned, resulting not only in a fast ignition, but also in a noticeable burning of the hydrocarbon fuel.

As a result of the experimental test using the proposed cylindrical idea, five tests containing  $25\% wt.NaBH_4$  and 75% wt.PE were casted and burned. All of the tests demonstrated fast hypergolic ignition and burning of the polyethylene fuel. For some of the tests, in order to cause an improved ignition process, the inner surface of the fuel was scratched, for more surface area to be exposed to the liquid oxidizer. Figure 9 shows the ignition process for a hollow cylindrical fuel test containing  $25\% wt.NaBH_4$ . First flame is observed after 5 ms of oxidizer impact into the surface. For the test shown in here, between +3 to +6 ms, the explosive reaction, which separates the liquid oxidizer from the exploding surface at every contact point, results in a turbulent regime which causes a flame expansion through the surface of the fuel. This ignition pattern was similar for all of the samples. After 8 ms from ignition, the polyethylene surface is clearly burning, and burning particles are observed flying out of the enclosed environment.



Figure 9: 25% wt.  $NaBH_4$  with 75% wt. PE, Hollow Cylindrical hypergolic fuel test with 90%  $H_2O_2$ 

The same hollow cylindrical sample used in Figure 9 was re-ignited after a few minutes to test the re-ignition delay and the burning process of the fuel. Figure 10 shows the re-ignition and shutdown of the fuel due to the injection of the oxidizer, which, for this case, lasted for approximately 200 miliseconds. For this re-ignition case, the first flame ignition took more than expected: 10 ms, and flame buildup wasn't "sharp", i.e. lots of burning flying particles during long time before there is flame expansion and buildup over the surface of the fuel. Note that these "flying particles" are polyethylene particles that are already burning, means, ignition of the hydrocarbon fuel has been achieved already. This happens only +3 ms after the first flame is observed. After flame build-up and expansion occur, with continuous oxidizer injection, a clear fuel combustion flame is achieved at +95 ms. Unfortunately, the injection cut was not immediate and small drops of oxidizer kept touching the walls of the burning fuel feeding its diffusion flame. The fuel flame slowly turns off as the available oxidizer for combustion is decreased. Re-ignition is possible by simply adding the oxidizer into the fuel's surface, but care is need to be taken. Adding a very high oxidizer quantity to the fuel's surface may result in a "wet surface" that deactivates the catalyst effect, and prevent proper hypergolic re-ignition. For the re-ignition of the fuel. This also happened in the drop-on-solid tests at standard condition, for which for a large amount of  $H_2O_2$  damaged the surface, turning it into a hypergolic deactivated "wet surface".



Figure 10: 25% wt. NaBH<sub>4</sub> with 75% wt. PE, re-ignition test for hollow cylindrical grain with 90% H<sub>2</sub>O<sub>2</sub>

Considering the fuel ignition results for the  $25\% wt. NaBH_4$  tests, hollow cylinders samples containing 20 and 15 percent weight of  $NaBH_4$  were casted and burned, in order to examine ignition feasibility for even lower catalyst weight load than the tested until now. The results are summarized in Table 6. For samples containing  $20\% wt. NaBH_4$ , ignition of the fuel was obtained for all of the samples, however, for the samples with  $15\% wt. NaBH_4$ , only four out of six ignitions were successful.

Table 6:  $NaBH_4 + PE$  solid fuel, hollow cylinder ignition tests success results with 90%  $H_2O_2$ 

	Ignition Success
25% wt. NaBH <sub>4</sub> + 75% wt. PE	5/5
$20\% wt. NaBH_4 + 80\% wt. PE$	6/6
15% wt. NaBH <sub>4</sub> + $85%$ wt. PE	4/6

Hollow cylinder tests were performed in order to show feasible ignition of the hypergolic solid fuel, under the injection of 90%  $H_2O_2$ . Figure 11 shows the shutdown process of an already burning sample containing 20% wt. NaBH<sub>4</sub> when

#### DOI: 10.13009/EUCASS2017-107

#### EXPERIMENTAL INVESTIGATION OF THE HYDROGEN PEROXIDE-SOLID HYDROCARBON HYPERGOLIC IGNITION

the liquid oxidizer injection is rapidly cut. Clearly, wherever the oxidizer injection streams were directed, a hydrocarbon fuel flame is observed. This does not only prove that hypergolic ignition and diffusion flames of the hydrocarbon fuel are achieved, but also the importance of a well distributed oxidizer injection over the surface of the fuel, in order to obtain a uniform flame all over the fuel's surface. These flames do not expand with the absence of hydrogen peroxide, and turn off, for the case shown in here, in less than 400 ms.



Figure 11: Shutdown delay for a 20% wt. NaBH<sub>4</sub> – 80% wt. PE Hollow Cylinder Sample

For rocket shutdown as in mission abort or reusable igniters, less than 400 *ms* is very fast shutdown delay, which can be neglected, and can be taken as an instantaneous shutdown. Note that the ignition was done in ambient conditions where there is oxygen present that feeds the flame causing a larger shutdown delay. Inside a rocket motor, it is expected that not only the absence of oxidizer but also the high pressure, will reduce significantly the shutdown delay.

#### 5.3 Drop-on-Solid at Elevated Pressures Tests

Ignition delay times as well as ignition process analysis were done under two different pressures to identify how this one affects the solid hypergolic hydrocarbon ignition. Ignition delay times were measured under 5 and 10 *bar* with an error of  $\pm 0.5$  *bar*. All the samples used were newly cut samples as done for the drop-on-solid tests at standard conditions. It was found that the separation of fuel and oxidizer due to the explosive hypergolic reaction is diminished or eliminated, enabling combustion of the hydrocarbon fuel and allowing all of the samples tested at both pressures to result in clear ignition. In addition, the ignition delay times were considerably decreased with pressure increase for all of the catalysts load samples tested. Results are summarized in Table 7. Ignition delay times are also improved with catalyst load, yet, for high catalyst loads, a slight difference is seen when the catalyst load is varied.

Table 7:  $NaBH_4 + PE$  solid fuel ignition delay under pressure. Results 90%  $H_2O_2$ 

	Pressure [bar]	Ignition Success	Ignition Delay Avg. [ms]	Std. Deviation
25% wt. NaBH <sub>4</sub> 75% wt. PE	5	5/5	4.8	0.75
	10	5/5	4.25	0.83
40% wt. NaBH <sub>4</sub> 60% wt. PE	5	4/4	3.8	0.89
	10	4/4	3.6	0.41
50% wt. NaBH <sub>4</sub> 50% wt. PE	5	5/5	4.5	0.86
	10	5/5	3.4	0.73

Figure 12 shows the sequence of images of a burning sample containing 25% wt.  $NaBH_4$  at 10 bar. For this case, the ignition delay was only 3 ms. As shown in Figure 12, due to the pressure, the hypergolic reaction is less explosive, and a big flame is then built over the surface of the fuel. Pressure not only decreases the explosive effect of the hypergolic reaction of the catalyst, but also enhances the ignition of the hydrocarbon fuel with the oxidizer. With just one drop, the flame last for a very long time relative to the ignition delay time. This happened to all of the samples burned under pressure.

A very important phenomenon that occurred in most of the samples tested is the release of droplets that burn. These droplet may well be either melted hydrocarbon fuel or liquid hydrogen peroxide. This means that on the drop-on-solid tests under pressure, the solid fuel does not only burn at its surface, but also as liquid hydrocarbon droplets, which are produced by the fuel combustion and the relatively explosive reaction of the catalyst. In Figure 12, droplets can be observed throughout the combustion of the sample, and, at +29 ms, it is seen how the droplets that came out from the solid surface, burn as they move away from the burning sample. It is expected that in a rocket motor combustion chamber, together with the oxidizer atomization, the size of these droplets created by the combustion will decrease.



Figure 12: Ignition image sequence of 25% wt.  $NaBH_4 - 75\%$  wt. PE with 90%  $H_2O_2$  under 10 bar

# **6.** Conclusions

To obtain hypergolic ignition of a solid hydrocarbon fuel, hypergolic catalysts with hydrogen peroxide were embedded into a hydrocarbon matrix. It was found that for all of the catalysts chosen for this study, it is not possible to cast samples using *HTPB* because either the fuel itself or the crosslinking agent react with the catalyst, deactivating the catalyst potential for hypergolic ignition or making impossible the casting process of the samples. As a result, polyethylene was chosen as the hydrocarbon matrix fuel, showing non-reactive behavior with embedded catalysts. Theoretical performance analysis show that embedding a catalyst into polyethylene barely varies the specific impulse and adiabatic flame temperature. Hypergolic reactions occurred in all the samples, but only with sodium borohydride, the combustion of the hydrocarbon fuel was achieved. It is important to mention that other metal hydrides such as lithium aluminum hydride ( $LiAlH_4$ ) and lithium borohydride ( $LiBH_4$ ), among others, may provide the required heat to ignite the polyethylene matrix. These catalysts were not used in this work due to their high sensitivity to moisture.

Samples containing various contents of sodium borohydride were burned using drop-on-solid at standard conditions tests. These tests show that hypergolic ignition of the hydrocarbon fuel can be achieved by embedding a hypergolic catalyst in the fuel. Ignition delay times varied according to the load of catalyst embedded in the hydrocarbon matrix. For high weight loads of catalyst, there is no change in the ignition delay times of the samples. Minimal ignition delay times of 7 *ms* were obtained from samples containing more than 33% *wt*. of  $NaBH_4$ .

# EXPERIMENTAL INVESTIGATION OF THE HYDROGEN PEROXIDE-SOLID HYDROCARBON HYPERGOLIC IGNITION

At ambient standard conditions, the flames obtained from the ignition of the samples were not as strong as for ignition under pressure, and lasted very little, because of the explosive behavior of the hypergolic reaction of  $NaBH_4$  and  $H_2O_2$ . Hollow cylindrical samples were casted and burned by means of axial injection using a syringe. The results showed hypergolic ignition of the hydrocarbon fuel after a very short time, as well as flame buildup and expansion, as the oxidizer is injected. Shutdown and re-ignition tests were performed showing that these are feasible using the proposed solid fuel. Optimal oxidizer-to-fuel ratios are needed, as for very high ratios, the surface of the solid fuel may become "wet" deactivating further hypergolic ignition or delaying flame build-up and expansion.

The hypergolic ignition of the tested fuels was highly improved with pressure. Ignition delay times decreased by almost half when the pressure increased from one to approximately 10 *bar*. In average, ignition delay times, under pressure, of less than four *ms* were obtained for samples containing high content of catalyst, and slightly above four *ms* for samples containing  $25\% wt. NaBH_4$ . The explosive effect of the hypergolic reaction obtained at the standard conditions tests was diminished in the cases above atmospheric pressure, allowing ignition of the samples. Improvement of parameters such as catalyst particle size, oxidizer droplet size, as well as fuel initial temperature and surface properties may result in shorter ignition delay times and also in better burning of the hydrocarbon matrix.

# 7. Acknowledgements

The authors would like to thank Dr. Vrushali S. Bagalkote for her significant assistance.

# 8. References

- Kuo, K.K. and Chiaverini, M.J. 2007. Review of solid-fuel regression rate behavior in classical and nonclassical hybrid rocket motors. In Fundamentals of hybrid rocket combustion and propulsion, Progress in Astronautics and Aeronautics, pp. 37-126.
- [2] Wernimont E. J. and Heister S. D. 2000. Combustion experiments in hydrogen peroxide polyethylene hybrid rocket with catalytic ignition. *J. Propuls. Power*, 16: 318-326
- [3] Karabeyoglu, A., Zilliac, G., Cantwell, B.J., DeZilwa, S. and Castellucci, P. 2004. Scale-up tests of high regression rate paraffin-based hybrid rocket fuels. *J. Propuls. Power*, 20: 1037-1045
- [4] Wernimont, E. J., Meyer, S. E., and Ventura, M. C. 1998. Hybrid motor system with a consumable catalytic bed, a composition of the catalytic bed, and a method of using" U.S. Patent No. 5,727,368.
- [5] Sutton, G. P., and Biblarz, O. 2001. Rocket propulsion elements. 7th ed., Wiley, New York.
- [6] Natan, B., Perteghella, V., and Solomon, Y., 2011. Hypergolic ignition by fuel gelation and suspension of reactive or catalyst particles. *J. Propuls. Power* 27:1145-1149.
- [7] Ventura M. and Mullens P., 1999. The use of hydrogen peroxide for propulsion and power. AIAA paper 99-2880.
- [8] Sippel, T.R., Shark, S.C., Hinkelman, M.C., Pourpoint, T.L, Son, S.F. and Heister, S.D. 2011. Hypergolic ignition of metal hydride-based fuels with hydrogen peroxide. 7th National Combustion Meeting, Atlanta. H24
- [9] DeSain, J.D., Curtiss, T.J., Cohen, R.B. and Brady, B.B. 2007. Testing of LiAlH<sub>4</sub> as a potential additive to paraffin wax hybrid rocket fuel. Report for the Defense Technical Information Center.
- [10] Shark, S. C., Pourpoint, T.L., Son, S.F. and Heister, S.D. 2013. Performance of Dicyclopentadiene/H2O2-based hybrid rocket motors with metal hydride additives. *J. Propuls. Power* 29:1122-1129
- [11] Maggi, F., Gariani, G., Galfetti, L., and DeLuca, L.T. 2012. Theoretical analysis of hydrides in solid and hybrid rocket propulsion. *Int. J. Hydrogen Energy* 37:1760–1769.
- [12] Bazyn, T., Eyer, R., Krier, H. and Glumac, N. 2004. Combustion characteristics of aluminum hydride at elevated pressure and temperature. *J. Propuls. Power* 20:427-431.