



Enhancement in hypergolic properties of paraffin wax hybrid rocket fuel

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Abstract

Hybrid rocket fuel systems continue to be considered promising compared to other options (solid and liquid) due to reliability and safety in handling operations. Herein, paraffin fuel combustions with chemical additives such as elemental boron has been examined showing enhancement in the ignitions and combustions for paraffin (PW) fuels using sodium borohydride (NaBH_4) and total energy. Measurements of ignition delays by applying hydrogen peroxide (H_2O_2) as liquid oxidizer using high-speed imaging on the most recommended compositions PSB2 were tested. Hypergolicity was improved by increasing the percentage of (NaBH_4) (6%, exothermic reaction) between NaBH_4 and H_2O_2 which convert B(s) to B(g) thus enhancing the spontaneous reaction. High heat of formation (ΔH_c) of boron combustion products increases more than 2 times when pure paraffin wax was tested, as the mass percentage of B increases. Different propellant compositions with different percentage of boron ranging from (30:38) and (NaBH_4) ranging from (4:12) % were also calculated theoretically using CEA NASA code. An experimental testing for heat of combustion for the more candidate compositions PSB2 have been tested using a bomb calorimeter model Parr1621. The experimental result 12.7 J kg^{-1} is higher than theoretical values 8.92 J kg^{-1} according to the high pressurize oxygen environment on bomb calorimeter. H NMR test have been performed to determine the change occurred in PW during mixing and casting and the result showed that there is no change occurred and this is a good feature for additives compatibility with PW matrix. The recommended composition PSB2 for experimental testing or bulk production is selected on safety and processing grounds. Decreasing the ignition time (IDT) reveals the utility of the application of this propellant fuel mixture for “green” and high energetic propulsion systems.

Keywords: Sodium borohydride; boron; Hydrogen peroxide; Heat of combustion; ignition time delay; propellant; energetic propulsion systems; Paraffin fuel

1. Introduction

The contemporary need for rocket fuels is clearly evident considering the contemporary frequency of launches of space vehicles calling for sustainable media (harmless fuels/reusable vehicles) [1]. More and more countries have established new space programs; in the news headlines also are efforts of private companies as (SpaceX, Rocket Lab, space solutions, etc.) to make unprecedented progress in space travel and casual space travel (space tourism). The issues of reusability and environmental sustainability (green chemistry) are very important issues for this sector, especially with respect to fuels (handling, storage, usage, reliability). Space vehicles require fuel and also oxidant combinations; the chemistry toxicity of some current chemical systems

(and safety as always) are important issues driving further research and development [REFS]. Hybrid propulsion which is friendly environment and design simplicity system as it comprises of solid fuel and gaseous oxidizer, as shown in figure (1)

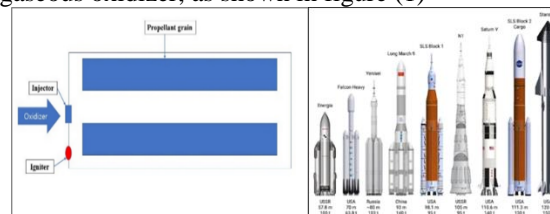


Figure 1(a) (left) hybrid rocket system. (1b) (right) Comparison Super heavy-lift launch vehicle [2].

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The launching vehicles have been varied according to pay load and their desirable missions and certain criteria have been a focal point of gauging future fuels. Figure (1b) shows the variations of different NASA space vehicles according to size and payload [IS-2005-05-015-KSC (Rev.2007)]. The thermal energy transferred to the fuels (Heat flux) which mainly originate from the exothermic reaction between H_2O_2 and NaBH_4 is a main parameter for hypergolicity and spontaneous ignition for the fuels. Another important for. the heat flux available to the fuel surface, it can be determined the regression rate of the fuels. The chemical reaction between the solid fuel (PW matrix) and oxidizer occurred in the boundary layer and the limitation of thermal and mass conductivity delivered to the fuel surface lead to low regression rate [3]. Different methods have been investigated for enhancement the regression rate including nonconventional design for fuel (propellant) grain and application of new oxidizer injection to improve the mixing mechanism inside combustion chamber [4–5]. Inserting the energetic material in the solid fuel matrix is the most preferred approach chemical solution for increasing the overall regression rate [6]. Different research groups/fields have studied the using of metal salts, ionic liquids, and metal hydrides for enhancement the hypergolicity [7–9]. For example, the research of Galette et al. in 2013 showed the application of metal hydrides such as lithium aluminum hydride (LiAlH_4) and (magnesium hydride (MgH_2)) to help increase the regression rate of paraffin wax [10]. Lithium (Li(s)) (group 1) is a very reactive metal and it helps increase the regression rate for paraffin wax; however, the heat of oxidation is lower in comparison with different metals as aluminum or boron [11]. The effect of the addition of lithium in compound form such as lithium hydride (LiH) to an HTPB fuel on the primary combustion mechanism and the pressure dependence of the combustion have been demonstrated in reference [12]. Smoot et al. in 1966 studied the effect of increasing the oxidizer mass and the change of the combustion mechanism from the pressure independent diffusion-controlled combustion to the pressure dependent combustion. Increasing the amount of lithium–aluminum hydride 50 % in the environment of nitrogen gaseous nitrogen in the range of 20–350°C produce high increase in exothermic reaction which make lithium–aluminum hydride is more candidate in airbreathing propulsion applications [12]. Hybrid combustion-based gas generator for an airbreathing rocket is shown in figure (2).

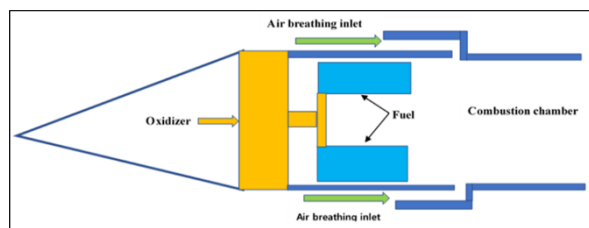


Figure (2) Air breathing based gas generator

Another Group 1 metal compound of wide use is sodium borohydride (NaBH_4). The usage of 25% NaBH_4 in dicyclopentadiene solid fuel was been studied by Shark et al. in 2013. The authors found that the ignition delay reduced to ~1.4 s and reached 1.1 s when using % 50 sodium borohydride [13].

Metals other than Group 1 have been studied in this context. The application of ammonia borane with epoxy fuel have been tested through the use of white fuming nitric acid (WFNA) as oxidizer; short delay times of 3.5 ms were found by drop testing in this study. It is depicted in figure (3) that different metals have higher values than elemental aluminum (Group 2) based on gravimetric and volumetric heat of combustion data [14].

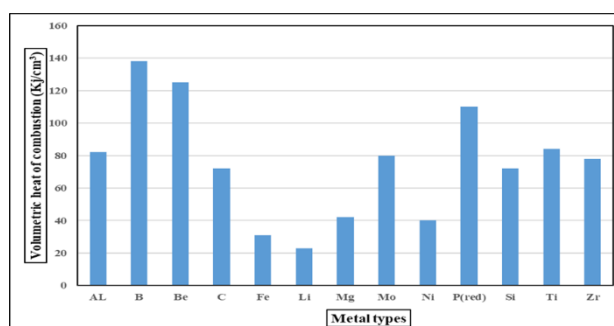


Figure (3). Volumetric heat of combustion for some metals.

However, Al is more preferred as a metal additive for energetic materials due to their safety record and high reliability [14-15]. Boron (Group 2) is the most intriguing candidate fuel for the use of future energetic materials; the disadvantages however of using B its high ignition temperature is something that needs to be tackled [16]. With respect to B research, Sidi et al. have recently investigated (2019) five different (elemental) metals to help the enhancement of the combustion of boron metal fuels [17]. In addition to boron, beryllium (Group 3) also has very high heat of combustion but it is not recommended to be used due to its high toxicity [18]. Other metals such as tungsten and titanium (Group 4) have high values of heat of combustions; however, they have limited application due to element expense [19].

Our present research is concerned with the application of additives such as boron as an energetic fuel component and sodium borohydride for increasing the ignitability and decreasing the ignition delay of the propellant based on paraffin matrix [20–22]. Many advantage for hydrogen peroxide as safety and reliability and its decomposition product to water and oxygen making it the ideal oxidizer for more environmentally green propulsion systems also, the high oxygen content and the heat liberation during decompositions make Hydrogen peroxide is a good recommendation for our research[23-24]. Regarding this research trajectory, the influence of pressure with addition of hypergolic additives on the ignition delays have been investigated by Carayon et al. They showed that the ignition delay decreases with increasing applied pressure [25]. Theoretical calculations using NASA (CEA) code have been applied for 5 compositions to choose the more promising compositions for preparations and experimental testing. The characterization and testing measurements for the more recommended compositions PSB2 due to safety and reliability during processing and testing has been done using bomb calorimeter and also using H NMR test. Introducing a hybrid green propellant based on paraffin wax containing (boron –sodium borohydride) and using hydrogen peroxide is the first approach for novel green propellant can be used for ducted ram jet and different applications for hybrid rocket propellant.

2- CEA Theoretical Combustion performance for different hypergolic compositions with different percentage of additives.

Many thermodynamic computer codes are commercially or publicly available and can be used for modelling the combustion parameter for explosives (detonation and shock wave) and pyrotechnics. The CEA NASA code was used for this study because of its significantly greater data base and its proven good ability with propellant compositions. Ignoring the influence of the air on the combustion of the hypergolic compositions and using the thermodynamic values resulted from (CEA) NASA Code which calculate the combustion characteristics based on the chemical formula of the elements, density, and heat of formation. Thermo chemical calculations were carried out for 5 different percentage of additives on hypergolic compositions boron based (PSB) (Table1).

Table 1. Different percentage of hypergolic compositions boron based

Compositions	PSB1	PSB2	PSB3	PS4	PS5
Paraffin wax	74	74	60	60	60
Boron	22	20	18	16	14
NaBH ₄	4	6	8	10	12

The heats of formation of NaBH₄ and Paraffin used in this study were 227 kJ/mole and 2460.5 kJ/mole respectively. The majority of the computer calculations were conducted assuming adiabatic combustion. NaBH₄ percentages are changed from 4 to 12% and B from 14 to 22% respectively. The percentage of PW remain constant at 74 % for easily processing and more safety during manufacturing. As shown in figure (4) The heat of combustion decreases with increasing the NaBH₄ ratio this due to the more percentage of NaBH₄ at the expense of Boron which have higher heat of formation

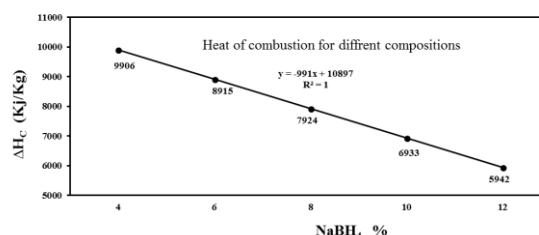


Figure (4). Effect of different percentage of NaBH₄ on the theoretical heat of combustions.

3- Experimental methods (Methodology)

3.1. Materials and [PSB] fuel Fabrication.

The paraffin wax used in fuel fabrication is provided by (Samchun) with melting point (56–58 °C) and boiling point > 350 °C. Boron with high purity > 95 % provided by (Sigma Aldrich) and sodium borohydride (Sigma Aldrich) with high purity > 98 % and melting point (400°C). The oxidizer used is 90% H₂O₂ which is very candidate for different advantages as safety and reliability including easily, testing and low cost it was supplied by Shanghai Habo Chemical Technology. The paraffin which is the main fuel matrix components are first melted using a heater at approximately 100°C. NaBH₄ added with small quantity till finishing addition the determined mass. The compositions were stirred for 5 minutes then starting the addition of required amount of Boron. All the three ingredients have been mixed to obtaining homogenous mixture with decreasing temperature. The mixture is the n casted into sample container figure (5). Increasing the percentage of NaBH₄ more than 6% reduce the safety during processing and testing and produce vigorous burning and the lower percentage more than 6% no ignition occurred, so the more candidate compositions PSB2 was tested and characterized.



Figure (5). Sample of PSB after casting.

3.2 Drop-on-solid at atmospheric conditions setup

Solid hypergolic fuel samples with a cross-section of 7×6 mm and length of approximately 8 mm were placed over glass plate. The test was done after cutting the surface with in period don't exceed 3 minutes for decreasing the exposure to environmental air conditions. Hydrogen peroxide drops have been applied over the sample using a syringe.

3.3 high speed camera recording

Hypergolicity and ignition delay were examined using a UX100 high speed camera by Photron Ltd. The data have been processed and the ignition delay (T_d) was measured by image processing as the time elapsed between fuel-oxidizer contact and starting the reaction. The reaction chamber has one window: one to allow light and another thin shield through which the camera can record frames of the ignition and burning of the chosen chemical sample. The position of the camera was settled with an angle relative to the shield to allow view of the ignition surface for precise measurement of the ignition delay. A pressure syringe was used to contain hydrogen peroxide and produce the drops for the ignition tests. After the syringe was filled with the oxidizer, the pressure was increased manually 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 (6).

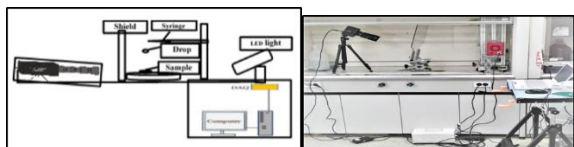


Figure (6). (left) Cartoon of preferred standard experimental setup for drop test and ignition delay measurements. (right) Photograph of our laboratory experimental setup used for drop test and ignition delay measurements.

4– Results and discussion

4.1 Heat of combustion of the paraffin based solid fuel .

The Heat of reaction in our experiments were measured using a bomb calorimeter model Parr 1621 using Isoperibol methods as shown in figure [7]. Isoperibol methods can measure the calorific values of the sample by burning ~ 1.0 g of the sample in a closed high-pressure oxygen container. The surrounding water jacket around the burning sample is controlled and maintain at constant temperature. When the tested sample is ignited, the heat liberated from the sample is transferred from the vessel to the water in the bucket and the temperature rise have been recorded to determine the calorific value of the tested sample. The heat of combustion of samples composed of PSB2 was measured using pure oxygen as oxidizer; the measured value of the heat of combustion was determined to be 12.7 kJ g^{-1} .



Figure (7). Bomb calorimeter model Parr 1621.

4.2– Drop test on PSB2 solid fuels on atmospheric conditions

The first step of this research was to identify the role of additives that can produce sufficient heat to secure rapid decomposition of hydrogen peroxide and fast ignition of the solid hydrocarbon fuels. The main component for PSB propellant formulation was designed to help the ignition delay decrease, NaBH_4 provide fast ignition as it contacts with H_2O_2 oxidizer, also the high heat of combustion of boron enhance the spontaneous ignition for the propellant compositions. The more candidate compositions PSB2 which contains 6% wt. NaBH_4 and 20 %wt. B was selected as it has the optimum percentage between additives and paraffin polymer matrix. PSP2 is easily and safely during processing as the high percentage of paraffin wax maintain the required coating efficiency against environmental conditions for both NaBH_4 and boron. Also, the high percentage of NaBH_4 is not recommended despite it has an advantage in decreasing the ignition delay, it has also disadvantage for lower the heat of combustion and therefor lower the efficiency of the PSB propellant. Physical and chemical change have been observed above the sample, where ignition occurs upon contact between H_2O_2 droplet and the PSP2 fuel. The sequence of ignition events has been presented in figure (8).

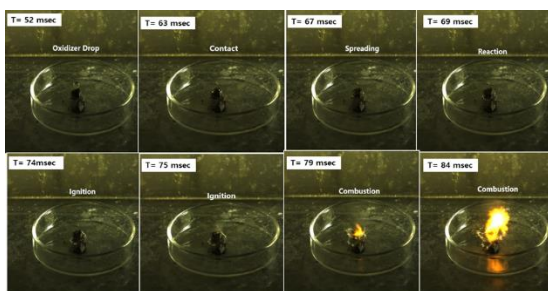


Figure (8). Ignition and combustion of PSB2 fuel – H_2O_2 drop.

After the H_2O_2 droplet has completely wetted the surface of the sample, gases and heat liberated from attached area on the surface. $NaBH_4$ particles reacting with the droplet of H_2O_2 oxidizer. The reaction between $NaBH_4$ and H_2O_2 oxidizer is highly exothermic producing hydrogen rich decomposition phenomena. As the heat released, the paraffin wax begins to melt creating liquid layer on the surface accompanying by gases liberation and increasing the temperature in the gas phase and the deflagration wave can be seen above the sample. The ignition propagates rapidly from point in the fifth frame figure (6) creating more heat and the combustion become spontaneously firstly by the aid of the oxidizer and secondly by atmospheric oxygen as shown in the combustion frame figure (6). The ignition delay between the first contact between the H_2O_2 oxidizer droplet and the sample surface is averaging 3 msec.

4.3 Morphology of the PSB2 solid fuel

Scanning Electron Microscope manufacturing by JEOL Ltd., model: JSM-it 800, Tokyo, Japan. figure (9) used to describe the SEM image of BSB2 fuel.



Figure (9). JSM-IT800 Field Emission Scanning Electron Microscope.

The SEM images of the PSB2 solid fuel–paraffin based after dispersion and agitation under normal conditions has been shown in figure (10) which describe the PSB2 micromorphology. The paraffin

wax forms protective layer against environmental conditions when crystallizing.

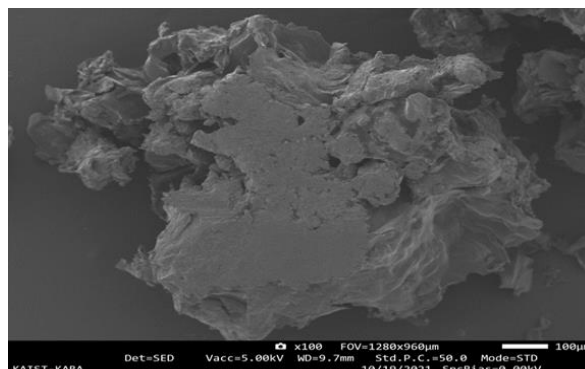


Figure (10). SEM image for the PSB2 composition.

A good dispersion of the solid additives in the paraffin matrix can be observed, with no evidence of aggregation or entanglement figure (11). Figure (11) confirms that the additives including boron and sodium borohydride elements were distributed in the PW matrix in various paths and spots.

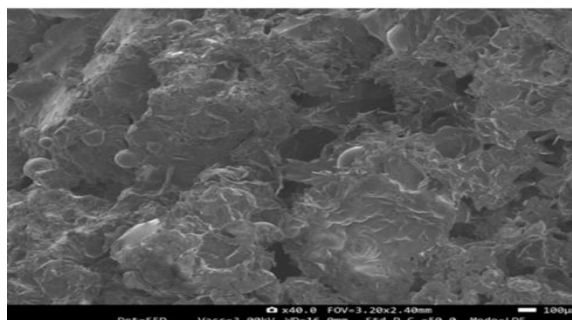


Figure (11). Additive dispersion of PSB2 composition.

The additives created multiple spots that supports hypergolic efficiency of the solid fuels when contacting with H_2O_2 as the oxidizer. Moreover, the solid additives of boron and sodium borohydride were totally and regularly covered by paraffin, without any microcracks or loose interfaces. The additives seem to be physically bonded at the surface of the paraffin's micro-platelets.

4.4 $-H$ NMR spectra comparison for original paraffin wax and paraffin wax in solid fuel matrix

All measurements were performed using a Bruker Avance III500 MHz UltraShield spectrometer. The measurements were conducted at 293 K for the two solid paraffin samples and. The temperature was adjusted to be constant over the measurements. All NMR spectra were recorded in the base opt mode using the Bruker standard zg pulse sequence with a pulse angle of 90° , 32 scans (NS), and 2 prior dummy scans (DS). The measurements were performed without rotation. The chemical shifts were referred to

the TMS signal. It is an essential issue to choose an appropriate solvent that features good dissolving characteristics. An obvious problem is the residual solvent signal of CHCl_3 which needs to be excluded from integration. Other solvents tested either showed residual solvent signals inside the interesting areas as well (hexane- d_6 , benzene- d_6 , impurities of CCl_4), or their dissolving capability is too low (D_2O). The advantage of using CDCl_3 is its acceptable solving feature on the one hand. On the other hand, the residual solvent signal can very easily be excluded in contrast to CCl_4 where multiple signals of impurities have to be considered. This is the reason why the measurement of the hard paraffin sample was performed in CDCl_3 instead. Spectra A representative ^1H NMR spectrum of the paraffin wax is showing Figure (12) and the paraffin solid fuel is represented in figure (13). Basically, the two figures composed of two signals on the aliphatic regions, and the protons typically resonate at 1.29 ppm and 0.93 ppm with no shift between the two samples. This result confirms that there is no change in the physical and chemical properties of the paraffin wax during manufacturing of PSB solid fuel for hybrid rocket propellant and this will be a good advantage and compatibility for the additives with PW in PSB fuel matrix

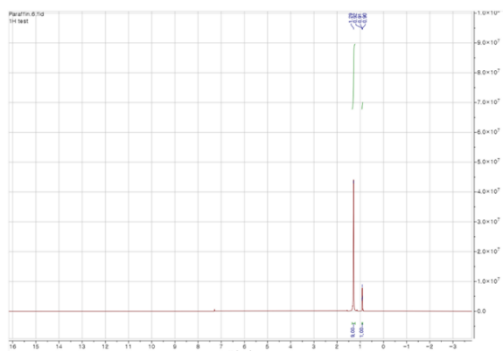


Figure (12). Processed ^1H NMR spectrum of the original paraffin wax

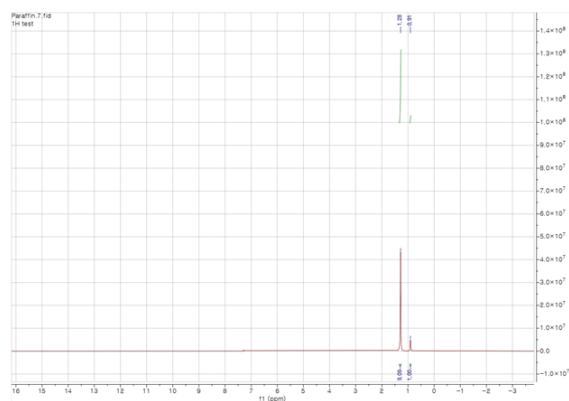


Figure (13). Processed ^1H NMR spectrum of the paraffin wax solid fuel matrix.

6. Conclusions

The prediction method which depends on the heat of combustions resulted from NASA (CEA) code can be used for reducing the cost and the laboratory work for fuel selection in the hybrid rocket systems. In this research we investigate the feasibility of using NaBH_4 and Boron in paraffin fuel matrix by using different compositions. The ignition delay time for the recommended composition containing 6 % NaBH_4 22% Boron and 74 % paraffin with H_2O_2 as an oxidizer is 3 ms and the ignitions is accompanying with spontaneous combustion for the PSP2 fuel. The percentage of this composition was selected according to the easily in the processing and safety. The H NMR analysis confirm that there is no change for chemical properties in PW according to manufacturing with solid additives and this will confirm the compatibility for the additives with PW. We proposed that PSB2 can be candidate for using in future research application for green, and energetic hybrid propulsion systems, such as the solid fuel ramjet system. Our future research will be enhancement the mechanical properties of (PSB2) and application of different energetic fuel to increase the combustion efficiency of Boron.

7. Declaration of competing interest

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

8. Refrances

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