



Full Paper

DOI: 10.1002/prop.201700268

Effect of Alcohol Carbon Chain on Enthalpy of Combustion and Ignition Delay Time for Gelled Hypergolic Propellant System

Muhammad N. Shoaib⁺,^[a] Botchu V. S. Jyoti⁺,^{*,[a]} Seung Wook Baek,^{*,[a]} and Jeongmoo Huh^[a]

Abstract: Study conducted for this paper was to understand the effect on a) enthalpy of combustion and b) ignition delay for gelled hypergolic propellants for the alcohol family, when carbon chain length is varied from ethanol to heptanol. Gel propellant formulated from the alcohol family, ethanol to heptanol, using organic gel with least weight percent added was 2 wt% by weight of the gelling agent. It was observed that the enthalpy of combustion of only pure ethanol gel fuel shows a marked increase in energy with respect to pure liquid and metalized gelled ethanol. Whereas, in the case of other alcohol fuel from propanol to heptanol, the enthalpy of combustion of both gel and metalized gel case is lower with respect to their respective liquid state. Hypergolicity of the formulated gel propellant were achieved

using two catalyst CCAT (Copper (II) chloride) and MCAT (Manganese (II) acetylacetonate) with Hydrogen Peroxide (Purity > 90%). The ignition delay time of the formulated gel system with hydrogen peroxide in the presence of catalyst was also investigated and it was observed that the ignition delay time of the all the investigated gels (both pure and metalized) were lower with MCAT with respect to CCAT. The delay time increases for both the catalysts with formulated gel alcohol fuel with increasing carbon chain. At the same time with increase in carbon chain and decrease in vapor density of the fuel, the respective investigated fuel in liquid phase were not hypergolic in the presence of MCAT and CCAT catalyst except for propanol and butanol, which showed hypergolicity only with CCAT.

Keywords: Alcohol · Hydrogen peroxide · Enthalpy · Hypergolicity · Ignition delay

1 Introduction

Development of monopropellant and bipropellant propulsion systems raises some environmental issues, most commonly, regarding the toxicity of the combustion by-product gases. The nature of exhaust gases (toxic or non-toxic) directly dependent on the type of propellant utilized. Over the past few decades of research and development and awareness regarding environmental issues, alternate green propellant is an emerging field of interest for propulsion scientist. Despite the fact most effective propellants are hazardous in nature, they are also unstable difficult to store and are very expensive to synthesis. Storbility, economy and good performance, when choosing a propellant for propulsion application, are also important among other issues. This switched the interest of the researchers in the field of non-toxic propellants [1–3].

ADN, HAN and HNF are most promising as high energy green propellants, these propellants have complex and consists of large complex organic molecular structures, which are very expensive and difficult to synthesize. For propulsion application these propellants are formulated in an ionic liquid state. These ionic propellants require elevated pressure and temperature to initiate decomposition. On the other hand, the propellant grade hydrogen peroxide is simple and economical to synthesize and requires lower pres-

sure and temperature to initiate the decomposition. In terms of performance, relatively the ionic liquid propellants require expensive metal catalyst such as Pt, R, Ir, Ag, etc. to generate decomposition which in turn provides the specific impulse, I_{sp} , ranging from 225 s to 280 s. Rocket grade Hydrogen peroxide (HP, purity > 90%) can generate a similar I_{sp} and higher (280 to 300 s) with economical catalyst such as MnO, MnO₂, CuCl₂ and acetates [1–3].

The physical property of HP is close to water with three noticeable differences: (1) higher density (1.45 g/cm³), (2) lower vapor pressure (666 Pa), (3) freezing point based on HP concentration (for 100% purity freezing point is -0.43°C , for 60% purity freezing point is at -55°C). All these values are at standard temperature and pressure (at 1 atm and 20°C). It remains in the liquid state at ambient pressure in a wide range of temperature and is relatively easy to handle with respect to other liquid rocket propellants like dinitrogen tetroxide, HNO₃ (density = 1.51 g/cm³, vapor pressure = 6399.5 Pa and freezing

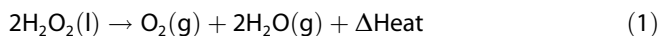
[a] M. N. Shoaib,⁺ B. V. S. Jyoti,⁺ S. W. Baek, J. Huh
Department of Aerospace Engineering
Korea Advanced Institute of Science and Technology
291 Daehak-ro, Yuseong-Gu, Daejeon 34141, South Korea
*e-mail: jyotiv@kaist.ac.kr
swbaek@kaist.ac.kr

[⁺] Equal Authorship

point = -42°C), LOx (density = 1.141 g/cm^3 , and freezing point = -218.79°C) [4–11].

Hypergolicity is one of the important parameter to make the bipropellant propulsion system simpler, due to reliability of self-ignition system that does not use a separate igniter hardware and associated triggering system for ignition. Most of the existing traditional hypergolic liquid bipropellant system such as UDMH-RFNA, MMH-RFNA, MMH-NTO are very toxic, corrosive and carcinogenic, hence not environmental friendly. One alternative to these propellants is to use alcohol-hydrogen peroxide for bi-propellant system. Alcohol and hydrogen peroxide based propulsion system is non-toxic and economical, which is a demand for present and advance propulsion application. This type of propulsion has already been proposed during world war II, in systems such as V2 rockets. The problem is the instability which is inherited from ethanol, due to its high vaporization rate. To overcome this problem an additional compound is introduced in the alcohol which act as a gelling agent and form a stable gel propellant.

The gelation of such bipropellant system will add additional advantages to the fuel. Firstly, the gellant used being organic in nature actively participate in combustion. Secondly, The gel system have the benefits of both liquid and solid propellant [4–11]. Hypergolicity of such bipropellant system with hydrogen peroxide can be achieved through suitable catalyst as a catalytically driven hypergolic bipropellant system [12–21]. The range of heat generated (ΔHeat) is from 54 kJ/mole to 400 kJ/mole based on the decomposition technique [1]. The decomposition of HP in presence of catalyst as follows;



Catalytically promoted alcohol-hydrogen peroxide based bipropellant system (Eq. 1) is very eco-friendly and proven to be effective not only for conventional propulsion system, as used in the past (V-2), but also for future propulsion system which can be further improved by gelation technology. The most frequently used catalyst materials for HP are metallic silver, permanganates of alkali metals, manganese oxides like manganese dioxide (MnO_2) and di-manganese trioxide (Mn_2O_3). For propulsion application as a hypergolic gel bipropellant system, the HP decomposes into steam and oxygen generating high temperatures in the presence of suitable catalyst. The high temperature of the decomposed products enables auto-ignition capabilities with additionally injected fuels such as alcohol etc. Experimental investigations showed the auto-ignition threshold at a chamber pressure of 1.6–2.2 MPa for ethanol with auto-ignition temperature between $580\text{--}615^{\circ}\text{C}$ which is generated at the inlet of the combustion chamber (where hydrocarbon fuels are introduced) for the given combustion chamber design [22–25].

In presented work the choice of fuel (alcohol) and oxidizer (hydrogen peroxide) for bipropellant system are con-

sidered based on toxicity, storability and simplicity of the overall propulsion system. In present study, efforts were made to understand the effect of “enthalpy of combustion”, hypergolicity and ignition delays (ID) for the formulated gel propellant. Propellant is formulated from alcohol family by varying carbon chain length from ethanol to heptanol, stabilized with cellulose based gelling agent. In past [18,19], weight percent of the gelling agent was reduced up to 6 wt.%, in present studies this weight percent was further reduced. The weight percent (wt.%) of gelling agent for gelation with respect to the formulated gel propellant are discussed in the previous publications [6–8,17–19], this is done to dominate the parent propellant properties and to reduce the effect of gelling agent as much as possible, for better performance. Propellants are generally characterized based on its thermal energy generated during their combustion for propulsion application. For a safe and better analysis of these formulated propellants, the gross calorific value (GCV) was conducted using “Parr Oxygen Bomb Calorimeter” [26–28]. The choice of propellants used was, firstly, liquid alcohol with carbon chain varying from C2 to C7, as a base line value for gel alcohol family. Secondly, for the formulated gel alcohol (C2–C7), the fuel is further split into two categories, a pure gel and an energized gel. The energized gel consists of the suspension of the metal nanoparticles (Al) [29].

2 Experimental Section

Parent propellant utilized for the experiments consists of ethanol to heptanol with 99.8% purity, these propellant were purchased from Sigma Aldrich Corp., South Korea. The gelling agent used for gelation is a cellulose derivative (propyl cellulose). The gelling agent (GA) with molecular weight 1000000, and powder with 20 mesh particle size was used which will be presented as SP_2 .

The oxidizer used is a propellant grade liquid hydrogen peroxide (purity $>90\%$). In order to reduce the decomposition rate of the hydrogen peroxide and to maintain the concentration of purity higher than 90%, the oxidizer was kept in a refrigerator at a temperature of about 0 to 2 degree Celsius. To avoid contamination the oxidizer was kept in clean and light free place.

To achieve hypergolicity with the base fuel, catalyst has to be introduced to the fuel, the catalyst used for the experimentation are, first, copper chloride hydrous ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 99.999% pure, CAS No. 7447–39–4, Sigma Aldrich Corp., South Korea), and the second catalyst used was Manganese (II) acetylacetonate ($\text{C}_{10}\text{H}_{14}\text{MnO}_4$, CAS No.14024–58–9, Sigma Aldrich). These catalysts will be represented as CCAT and MCAT respectively.

Initially the propellants used for experimentation are in pure liquid state to establish base line values for each liquid propellant ((Ethanol (E_{Liq}), Propanol (Pro_{Liq}), Butanol (B_{Liq}), Pentanol (Pen_{Liq}), Hexanol (Hex_{Liq}), Heptanol (Hep_{Liq})). Secondly the gel propellant were formulated with organic (cel-

lulose derivative) gelling agents along with parent fuel for each liquid propellant. The gelled propellants are categorized as follows, first, in pure state, and second, with addition of aluminium nanoparticles. These alcohol fuel gel samples comprise of 2 percent by weight (wt.%) of the gelling agent (GA, SP2), which is considered as a pure case ((Ethanol (E._p), Propanol (Pro._p), Butanol (B._p), Pentanol (Pen._p), Hexanol (Hex._p), Heptanol (Hep._p)), while for energized case, 2 percent by weight of nano-sized Al (100 nm) energetic particle was suspended, and all the samples were referred in the nomenclature and hereafter will be represented as ((Ethanol (E._{Al}), Propanol (Pro._{Al}), Butanol (B._{Al}), Pentanol (Pen._{Al}), Hexanol (Hex._{Al}), Heptanol (Hep._{Al})) respectively.

The gel formulation of a parent fuel requires the following key components; firstly, parent fuel and secondly, the type of gelling agent and its weight percent. The weight percent of gelling agent affects the viscoelastic properties of any formulated gel fuel, which is one of the key requirements for system to be considered as a gel. In this article, the choice of mass fraction of components in a gel fuel was based on these parameters (type of gelling agent and its weight percent). The criterion for choosing the mass fraction of components for gelation of parent fuel is based on the viscoelastic property which in turn depends on type and weight percent of gelling agent [6–11]. The references [6–11] discuss the detailed understanding of gel fuel formulation and its rheological characterization.

The hypergolicity of the formulated bipropellant was achieved using transition metal salts along with 90% pure hydrogen peroxide. The metal salts used are Manganese (II) acetylacetonate (C₁₀H₁₄MnO₄, Sigma Aldrich) and Copper (II) chloride (CuCl₂, Sigma Aldrich) which will be represented as MCAT and CCAT, respectively. The experimental setup (Figure 1) and methodology to calculate the ignition delays are similar to those discussed in reference [17–19]. Measured volume of oxidizer is introduced using Eppendorf dropper onto the propellant, catalyst mixture, with the high speed camera the events are recorded and the time is calculated

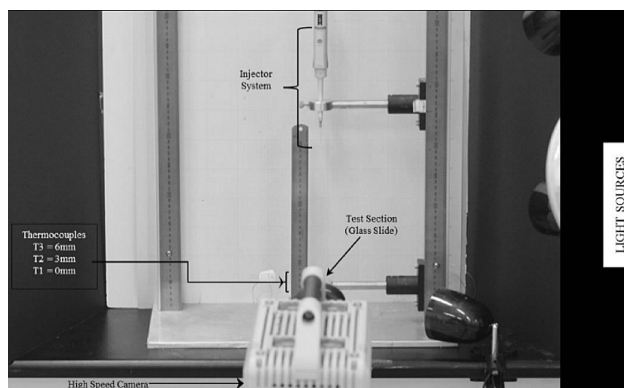


Figure 1. Hypergolicity and Ignition delay measurement setup, with this setup flame temperature can be calculated with three thermocouples positioned as shown.

from, when the propellant and oxidizer comes in contact to, first visible spark or flame, this provides us with the ignition delays. The camera used to study the ignition delays was “Photron SA-X2” with the following settings;

Pixel density: 1024 × 1024

Frames per second: 5000 fps

Total frames captured: 21839

Total run time: 4.3678 s

Time per frame (This is the least count for the measures ignition delay time): 2×10^{-4} sec

The Gross Calorific Value (GCV) of the formulated gel propellant was determined using the “1314 Oxygen Bomb Calorimeter with 6772 Calorimetric Thermometer from Parr Instrument Company” and compared with those for the liquid parent fuel, and gelling agent calorific value. The oxygen bomb calorimeter consists of two basic parts: (i) a constant temperature jacket and (ii) the calorimeter bomb. The latter contains one gram of weight sample in the sample combustor. Heat liberated during the combustion reaction in oxygen environment at constant pressure of 15 atm is transferred to the stirred water in the temperature jacket (2 liter of water) from the calorimeter bomb. A rise in the temperature of the calorimeter water, after correction for heat exchange with the jacket, is proportional to the enthalpy of combustion of the test sample. The bomb calorimeter was calibrated for enthalpy of combustion using known mass of benzoic acid as a reference material.

3 Results and Discussion

3.1 Enthalpy of Combustion

Energy of the propellant that it submits to the system is vital for propulsion system. In order to determine the amount of energy delivered by the fuel, its enthalpy of combustion has to be measured [26–28]. For fuel that are formulated with the gelling agent consists of two basic compounds, firstly the parent fuel and secondly the gelling agent. The choice of parent fuel generally gives off high heat energy or have high calorific values, but, the selection of gelling agent has an important contributing factor, the selected gelling agent, changes the physio-chemical properties of the parent fuel which is causing the parent fuel to have thixotropic properties. Gelling agent that cause an overall increase in the propellant density, density impulse and actively participate in combustion is considered to be a suitable gelling agent for propulsion application.

The gross calorific values of the parent fuel (liquid) with respect to the formulated gel and metalized gel propellant along with thickening agent are considered using Oxygen

Bomb Calorimeter [26–28] and are given in Figures 2 and 3. The results obtained are the average of at least four sets of experiments. The errors introduced during the experiment are from temperature measurements and length of nichrome wire. The Parr Oxygen Bomb Calorimeter (Model: 1341), gives a temperature error of 0.002 °C/min, whereas for nichrome wire, the minimum error is 1 mm (least count of the instrument). The weight of the fuel is approximately 1 gram with an error of 0.001 g. The pressure maintained in the bomb calorimeter is about 15 atm with an error of ±0.5 atm [26–28].

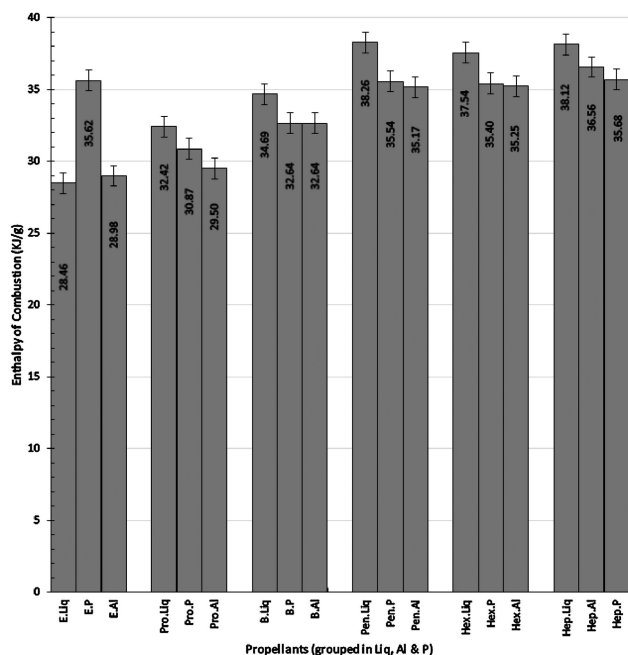


Figure 2. Calorific value study for alcohol from C2 to C7, categorized as Liq. (liquid state), P (pure gel), Al (aluminum nanoparticles).

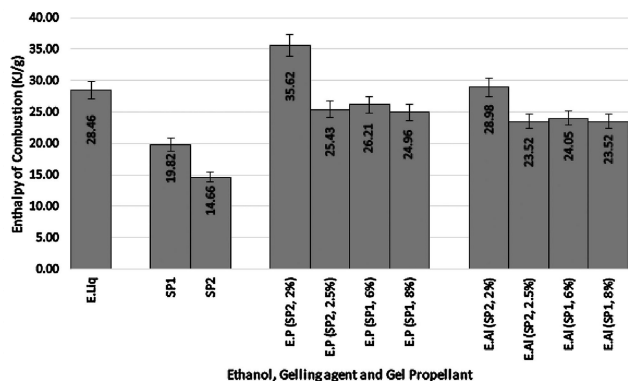


Figure 3. Calorific value study for ethanol in liquid and gel state with different wt.% and two different gelling agent (SP1 & SP2).

This study will help to understand the enthalpy of combustion of the investigated system. The whole process of thermal utilization of fuels is influenced by the kind of fuel used and its physio-chemical properties (e.g. carbon chain, bulk density, vapor density, calorific value etc.) and also its chemical composition. These parameters are the fundamental data for the measurement and the evaluations of its efficiency and performance parameters which in turn define the commercial value of such fuel for end application. The basic characteristic, that is necessary for the definition of the energetic content of the materials, is the “Gross Calorific Value” (GCV) or high heating value. This value represents the absolute specific energy of combustion of the fuel for unit mass of a fuel burned in oxygen medium in a bomb calorimeter [26–28].

During the enthalpy of combustion experimentation it was observed that all the organic fuels (both liquid and gel) undergo a complete combustion without any residual, which shows that the organic gelling agent participate in the combustion process of gel fuel (Figure 2). Residual was observed, only in the case of energetic gel fuels suspended with metal nanoparticles (Al) [29]. Lower calorific value was observed in the case of pure gel and metalized gel system with respect to parent liquid fuel for all the investigated alcohol family except for ethanol case (Figure 2). For metalized case such observation, could be possible due to the absorption of thermal energy by the suspended metal nanoparticles in the gel system, during their oxidation process occurring at the recommended operating pressure for the bomb calorimeter (15 bars). The confidence interval for the number of experiments conducted is about 95%.

Ethanol gelled propellant with 2 wt.% of thickening agent shows a higher enthalpy of combustion than the parent liquid fuel. Similarly, metalized gel shows higher enthalpy of combustion than parent liquid fuel but lower than ethanol pure gel (Figure 2).

For better understanding a detailed study of ethanol gelled propellant was carried out to evaluate the GCV for 8 different formulations. These formulations of gel ethanol consist of two different kind of gelling agent. With these ethanol gel formulations, it was observed that the gel system with low wt.% (SP2) of GA along with higher molecular weight gives a higher enthalpy of combustion than the gel system with high wt.% (SP1) of GA, of low molecular weight as seen in Figure 3. From Figure 3 it can be deduced that the wt.% of gelling agent contributes to the GCV, which in turn can help to modify the enthalpy of combustion of the formulated gel propellant and overall performance of the gel propulsion system. Based on this observation the critical wt.% of the selected GA was used for the formulation of high carbon alcohol family, gel systems. Hence, it can be suggested that the gelation or solidification through gelation technology with high wt.% of GA results in significant decrease in the GCV value of the formulated gel system, which in turn will decrease the enthalpy of combustion and

Table 1. Ignition delay time of liquid and gel fuel.

FUEL TYPE	Fuel Weight (g)	Catalyst	Catalyst wt. %	Oxidizer (μ l)	Ignition Delay (ms)
Ethanol Liquid	0.2	CCAT	4	30	Rapid decomposition
Propanol Liquid	0.2	CCAT	4	30	119.6
Butanol Liquid	0.2	CCAT	4	30	194.5
Pentanol Liquid	0.2	CCAT	4	30	Rapid decomposition
Hexanol Liquid	0.2	CCAT	4	30	Rapid decomposition
Heptanol Liquid	0.2	CCAT	4	30	Rapid decomposition
Ethanol Gel	0.09	MCAT	4	10	7.3
Ethanol Gel	0.09	CCAT	4	30	Rapid decomposition
Ethanol Al Gel	0.09	MCAT	4	10	12.8
Ethanol Al Gel	0.09	CCAT	4	30	38.3
Propanol Gel	0.09	MCAT	4	30	10.6
Propanol Gel	0.09	CCAT	4	30	Rapid decomposition
Propanol Al Gel	0.09	MCAT	4	30	14.6
Propanol Al Gel	0.09	CCAT	4	30	41.0
Butanol Gel	0.09	MCAT	4	10	15.5
Butanol Gel	0.09	CCAT	4	10	264.6
Butanol Al Gel	0.09	MCAT	4	10	18.0
Butanol Al Gel	0.09	CCAT	4	10	73.6
Pentanol Gel	0.09	MCAT	4	10	40.5
Pentanol Gel	0.09	CCAT	4	30	303.0
Pentanol Al Gel	0.09	MCAT	4	30	37.0
Pentanol Al Gel	0.09	CCAT	4	30	198.9
Hexanol Gel	0.09	MCAT	4	10	121.8
Hexanol Gel	0.09	CCAT	4	30	354.9
Hexanol Al Gel	0.09	MCAT	4	20	38.5
Hexanol Al Gel	0.09	CCAT	4	30	Rapid decomposition
Heptanol Gel	0.09	MCAT	4	50	139.4
Heptanol Gel	0.09	CCAT	4	50	Rapid decomposition
Heptanol Al Gel	0.09	MCAT	4	50	98.8
Heptanol Al Gel	0.09	CCAT	4	50	Rapid decomposition

the overall performance of the gel propellant for the propulsion application.

The choice of selecting ethanol based gel propellant, formulated using SP2 gelling agent is considered to provide a significant advantage over its counterpart. Pure ethanol gel shows a significant increase in the enthalpy of combustion, which is above 35 kJ/g, jumping to levels of high carbon chain alcohols, such as pentanol, hexanol and heptanol (Figure 2). It is also evident that higher molecular weight, organic gelling agent, when introduced into ethanol at critical wt.% provides significant energy with respect to lower molecular weight, organic gelling agent (Figure 3). For propulsion lower molecular weight, of byproduct, is better in order to achieve higher Isp, ethanol, as a parent fuel, fulfil this requirement, as it has 98 wt.% in the gel formulation, this shows a significant chemical properties of parent fuel resulting in improved performance with respect to parent liquid fuel.

3.2. Comparative Ignition Delay Time

Space propulsion application, the choice of parent fuel and its performance is vital, similarly, from alcohol family the selection criteria are based on the molecular weight of its by-

product gases which determines the exhaust velocity giving off high Isp. The hypergolicity of parent fuel is an important property for propulsion system as well. In alcohol family the hypergolic ignition is mainly dependent on the choice of catalyst, the length of carbon chain and state of the propellant, liquid or gel (Table 1).

In previous section it was determined that alcohol gel along with gelling agent participate in GCV. Further studies were conducted where gelled alcohol family was compared to the parent fuel respectively. The study performed for the alcohol parent liquid fuel from ethanol to heptanol (Table 1) indicates for the choice of two catalysts (MCAT and CCAT) only CCAT shows the hypergolicity for propanol and butanol with long delay times. With addition of a selected gelling agent, SP2, the formulated gel propellant of investigated alcohol family shows a promising trend in hypergolicity and ignition delay (Table 1).

The volume of oxidizer was varied from 10 to 50 μ l to achieve hypergolicity for the formulated gel fuels. The increment in the oxidizer volume is by 10 μ l. All the fuels were initially experimented, firstly with 10 μ l of oxidizer and the data was recorded for fuels that ignited at this volume. The volume of oxidizer was then increased to 20 μ l and the gel fuels were re-experimented, while data was recorded for

fuels that ignited at this volume. Similarly, the volume of oxidizer was incremented up to 50 μl which is a significant volume for a very small quantity of gel fuel. Based on these experiments the least volume of oxidizer was observed for different gel fuels to successfully achieve hypergolicity. Therefore, based on these observations, Table 1 indicates the minimum volume of oxidizer required for each formulated fuel from ethanol to heptanol, to achieve hypergolicity with ignition delays. The experimental conditions for the hypergolicity and ignition delay are fuel rich conditions. While keeping fuel rich conditions oxidizer volume was varied from 10 μl up to 50 μl to achieve hypergolicity in all the cases and to measure ignition delays. This is to generate more bi-product gases when propellant and oxidizer comes in contact and rapidly decomposes. For propulsion system fuel rich system is preferred as more bi-product gases are generated which in turn provide proportional amount of thrust to the vehicle. In case of stoichiometric conditions the bi-product gases are reduced and in turn generate more heat which is undesirable for the propulsion system.

Hypergolicity and ignition delay study were performed for the alcohol family, from ethanol to heptanol using transition metal salt catalyst, CCAT and MCAT, while oxidizer (H_2O_2) was dropped from the Eppendorf injector. using the experimental setup and procedure as mentioned in reference [16], it was observed that all the gel systems, both pure and metalized gel show hypergolicity with both CCAT and MCAT. Comparatively lower ignition delay time of gel system was obtained with MCAT (Table 1). The ignition criterion for ignition delay study is based on visual analysis of the captured images through high speed camera. The ignition delay calculations were performed as follows:

The frame number was recorded when the volume of oxidizer was introduced on the surface of gel fuel bed to the frame number when first visible flame or spark was observed. The difference between two frame numbers, when multiplied by the fps (captured frames per second) gives the time between the introduction of oxidizer to the visible flame or spark. All of these calculations are made possible by using the application software (Photron FASTCAM Viewer) provided along with the camera.

Base line study was performed with respective liquid fuel for hypergolicity and ignition delay time using both CCAT and MCAT, for better understanding of the investigated fuel behavior in liquid and gel phase and was observed that all the investigated liquid fuel were not shown any hypergolicity with hydrogen peroxide in the presence of CCAT and MCAT except for liquid ethanol and propanol, which showed hypergolicity with CCAT only. The only explanation for such behavior of liquid fuel could be the difference in the vapor pressure density with increase in the carbon chain of the investigated fuel. With increase in carbon chain vapor density decreases and hence the volatility which demand higher energy for ignition than the fuel with lower carbon chain. Therefore, propanol and butanol shows

hypergolicity with CCAT in liquid phase (Table 1) and others show rapid decomposition but no ignition.

With long carbon chain alcohol family and its respective formulated gel fuels, it is observed that for larger carbon chain demands high wt.% of catalyst to achieve hypergolicity even with longer ignition delay time. A similar trend was observed for the oxidizer volume except for butanol.

From Figure 2, 3, and Table 1, it can be deduced that the enthalpy of combustion is increasing with an increase in carbon chain of the investigated alcohol family for liquid system, whereas with gelation it decreases moderately except for ethanol gel. At the same time when it comes to ignition delay study, the delay time is increasing with increase in carbon chain for all the formulated alcohol gel fuel in presence of catalyst. With this, choice of catalyst is also important indicating that MCAT, which do not participate in any hypergolic ignition with parent liquid fuel, actively participate with gelled alcohol giving least ignition delay for ethanol and gradually increases with the gelled propellant formulated with higher carbon chain. CCAT on the other hand shows hypergolic ignition with energized ethanol gel up to hexanol gel, but for higher carbon chain do not participate, similar ignition delay trend are observed for MCAT. The ignition delays for CCAT are higher than that of MCAT and the ignition delay of lower carbon chain are lower with MCAT. For the case of energized gel propellant [29], the ignition delay increases for ethanol up to butanol, from pentanol the ignition delay reduces for energized system and significant reduction is observed for the hexanol. In alcohol family from ethanol to butanol (5.95 kPa to 0.93 kPa), these fuels have high vapor pressure. Even in the gel state, a slight temperature variation in the presence of hydrogen peroxide, can initiate a rapid decomposition which is more rapid in pure gel state than metalized gel state. With the help of catalyst a suitable ignition process can be achieved. For higher alcohol family (pentanol to heptanol) (0.29 kPa to 0.02884 kPa) the vapor pressure is very low. Therefore the time of heat energy generation due to the presence of hydrogen peroxide is prolonged, during which the thermal energy is absorbed by the metal nanoparticles, resulting in the increase of the temperature in its vicinity. This is one of the possible explanations for the metalized gel fuel (pentanol to heptanol) to reach its auto-ignition temperature faster in comparison to the parent fuel.

4 Conclusions

Hypergolic gelled bi-propellant system was formulated based on a choice of fuel from alcohol family and hydrogen peroxide respectively using organic gelling agents. For the energetic gel bipropellant system Al nanoparticles were introduced in the formulation for hypergolicity and ignition delay studies. Hypergolicity was achieved using MCAT and CCAT and was observed that MCAT shows a better perform-

ance than CCAT. It was determined that the hypergolicity and ignition delay time were varied depending upon the type of fuel, carbon chain and catalyst. For liquid case only propanol and butanol were hypergolic with CCAT due to its vapor pressure density comparable to hexane and octane than other investigated alcohol fuel with higher carbon chain. In order to examine more detailed discussions, the calorific value study was performed for a better understanding of the heat release generated by the formulated system and its participation in combustion.

Ethanol shows a significant increase in its GCV when Gellized with SP2 at critical concentrations, where its GCV values are comparable to pentanol in liquid state. Ethanol gel shows marked increase in its GCV values even when energetic nanoparticles are present in the system, compared to liquid ethanol. Hypergolicity and ignition delay studies for the ethanol gel with MCAT, having 4 wt.%, in the presence of 90% pure hydrogen peroxide gives a reasonable ignition delay times. Similar behavior is observed for propanol and butanol, but for higher carbon chain the formulated system shows hypergolicity but their ignition delays were relatively longer. These properties indicate that ethanol when gelled with a least wt.% of gelling agent of higher molecular weight, in the presence of MCAT, gives significant advantage over the investigated fuels.

Acknowledgements

Dr. Jyoti is supported by the Korean Research Fellowship Program funded by the Ministry of Science, ICT and Future Planning through the National Research Foundation of Korea (No. 2015H1D3A1061637)

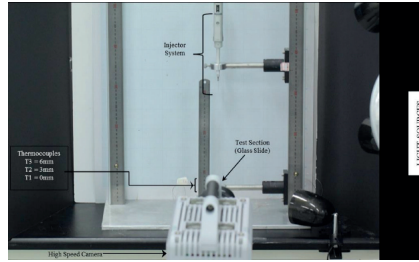
References

- [1] J. J. Rusek, B. Lormand, Non-toxic hypergolic miscible fuels for In-suit decomposition of rocket-grade hydrogen peroxide, *1st Annual International Symp. of High Test Peroxide*, **1998**, August, Surrey, UK.
- [2] B. M. Melof, M. C. Grubelich, Investigation of hypergolic fuels with hydrogen peroxide, *37th Joint Propulsion Conference*, AIAA J. **2001**, 2001–3837, 8–11 July, Salt Lake City, UT, U. S.A.
- [3] S. A. Frolik, B. L. Austin, Development of hypergolic liquid fuels for use with hydrogen peroxide, *AIAA J.* **2001**, 2001–0013.
- [4] S. Rahimi, D. Hasan, A. Pertz, Development of laboratory scale gel propulsion technology, *J. Propul. Power* **2004**, *20*, 93–100.
- [5] B. Natan, S. Rahimi, The status of gel propellants in year 2000, *Int. J. Eng.* **2002**, *5*, 172–194.
- [6] B. V. S. Jyoti, S. W. Baek, Formulation and comparative study of rheological properties of loaded and unloaded ethanol-based gel propellants, *J. Eng. Mater. Technol.* **2015**, *33*, 125–139.
- [7] B. V. S. Jyoti, S. W. Baek, Rheological characterization of ethanolamine gel propellants, *J. Eng. Mater. Technol.* **2016**, *34*, 260–278.
- [8] B. V. S. Jyoti, S. W. Baek, Rheological characterization of metalized and non-metalized ethanol gel propellants, *Propellants Explos. Pyrotech.* **2014**, *39*, 866–873.
- [9] B. V. S. Jyoti, S. W. Baek, Rheological characterization of hydrogen peroxide gel propellant, *Int. J. Aeron. Space Sci.* **2014a**, *15*, 199–204.
- [10] B. V. S. Jyoti, S. W. Baek, Flow and dynamic rheological characterization of ethanolamine gel propellant with hybrid gelling agent, *Sci. Technol. Energ. Mater.* **2015**, *76*, pp.62–67.
- [11] N. L. Munjal, B. L. Gupta, M. Varma, Preparative and mechanistic studies on unsymmetrical dimethyl hydrazine-red fuming nitric acid liquid propellant gels, *Propellants Explos. Pyrotech.* **1985**, *10*, 11–117.
- [12] M. Varma, B. V. S. Jyoti, Ignition and combustion studies of heterogeneous UDMH-RFNA gel propellants, *Int. J. Eng.* **2011**, *10*, 259–275.
- [13] E. M. Dambach, K. Y. Cho, T. L. Pourpoint, S. D. Heister, Ignition of advanced hypergolic propellants, *AIAA J.* **2010**, 2010–6984.
- [14] R. Arnold, P. H. S. Santos, M. DeRidder, O. H. Campanella, W. E. Anderson, Comparison of mono methyl hydrazine/hydroxy propyl cellulose and hydrocarbon/silica gels, *AIAA J.* **2010**, 2010–422.
- [15] J. D. Dennis, T. L. Pourpoint, S. F. Son, Ignition of gelled mono methyl hydrazine and red fuming nitric acid in an impinging jet apparatus, *AIAA J.* **2011**, 2011–5706.
- [16] Y. Solomon, S. J. DeFini, T. L. Pourpoint, W. E. Anderson, Gelled MMH hypergolic droplet investigation, *AIAA J.* **2011**, 2011–5705.
- [17] B. V. S. Jyoti, M. S. Naseem, S. W. Baek, Hypergolicity and ignition delay study of pure and energized ethanol gel fuel with hydrogen peroxide, *Combust. Flame* **2017**, *176*, 318–325.
- [18] M. S. Naseem, B. V. S. Jyoti, S. W. Baek, H. J. Lee, S. J. Cho. Hypergolic studies of ethanol based gelled bi-propellant system for propulsion application, *Propellants Explos. Pyrotech.* **2017**, *42*, 149–156.
- [19] B. V. S. Jyoti, M. S. Naseem, S. W. Baek, H. J. Lee, S. J. Cho, Hypergolicity and ignition delay study of gelled ethanolamine fuel, *Combust. Flame* **2017**, *183*, 102–112.
- [20] B. Palaszewski, Metalized propellants for the human exploration of Mars, *J. Propul. Power* **1992**, *8*, 1192–1999.
- [21] H. W. Coleman, G. Steele, Experimental and uncertainty analysis for engineers, *2nd Edition*, John Wiley and Sons **1999**, Inc., Hoboken, New Jersey.
- [22] L. Micoli, M. Turco, Decomposition of H₂O₂ on monolithic MnO_x/ZrO₂ catalysts for aerospace application, *Chem. Eng.* **2015**, *43*, 1819–1824, doi: 10.3303/CET154330
- [23] F. F. Maia, L. H. Gouvea, L. G. F. Pereira, R. Vieira, F. de Souza Costa, Development and optimization of a catalytic thruster for hydrogen peroxide decomposition, *J. Aerosp. Technol. Manag.* **2014**, *6*, 61–67, doi: 10.5028/jatm.v6i1.286
- [24] C. Bramanti, A. Cervone, L. Romeo, L. Torre, L. d'Agostino, A. J. Musker, G. Saccoccia, Experimental characterization of advanced materials for the catalytic decomposition of hydrogen peroxide, *42nd ALAA/ASME/SAE/ASEE Joint Propul. Conference and Exhibit* **2006**, 9–12 July, Sacramento, California, <https://doi.org/10.2514/6.2006-5238>
- [25] D. Krejci, A. Woschnak, C. Scharlemann, K. Ponweiser, Hydrogen peroxide decomposition for micro propulsion: simulation and experimental verification, *47th AIAA/ASME/SAE/ASEE Joint Propul. Conference and Exhibit* **2011**, 31 July-03 August, San Diego, California, <https://doi.org/10.2514/6.2011-5855>
- [26] G. Toscano, E. F. Pedretti, Calorific value determination of solid biomass fuel by simplified method, *J. Agric. Eng. Res.* **2009**, *3*, 1–6.
- [27] M. S. Kharasch, Heats of combustion of organic compounds, *Natl. Bur. Stand. [Tech. Rep.] NBSIRd* **2012**, *2*, 359–426.

- [28] K. L. Churney, A. E. Ledford, M. L. Reilly, E. S. Domalski, A multi-kilogram capacity calorimeter for heterogeneous materials, *J. Res. Natl. Bur. Stand.* **1986**, *91*, 2772–298.
- [29] C. Rossi, Al-based energetic nanomaterials: design, manufacturing, properties and applications, *1st Edition, ISTE Ltd and*

John Wiley and Sons, Inc. **2015**, 5 June, Great Britain and United State, DOI:10.1002/97811190074

Received: November 2, 2017
Published online: ■ ■ ■



M. N. Shoaib, B. V. S. Jyoti, S. W. Baek*, J. Huh*

1 – 9

Effect of Alcohol Carbon Chain on Enthalpy of Combustion and Ignition Delay Time for Gelled Hypergolic Propellant System
