Hypergolic Systems based on Hydrogen Peroxide Oxidizer

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Abstract

Hydrogen peroxide, H_2O_2, is a promising and nontoxic oxidant. In recent years considerable attention has been paid to the development of hypergolic system compositions, because the use of them not only markedly simplifies the engine design and rocket system operation but also provides the possibility of their repeated use. Moreover, their high performance, high environmental compatibility and low toxicity make them highly preferable. The present review considers recent works on hypergolic systems involving hydrogen peroxide as the oxidizer and various green propellants of organic and inorganic nature with or without certain additives.

Some Abbreviations

AB	:	Ammonia borane
ABH	:	Aluminum borohydride
AND	:	Ammonium dinitramide
AN	:	Ammonium nitrate
CBH	:	Cyanoborohydride
CCB	:	Consumable catalytic bed
MMH	:	Monomethylhydrazine
NTO	:	Nitrogen tetroxide
DETA	:	Diethylenetriamine
DCPD	:	Dicyclopentadiene

DMAZ   :   2-Dimethylaminoethylazide

EILs   :   Energetic ionic liquids

HNIW   :   Hexanitrohexaazaisowurtzitane

HDPE   :   High-density polyethylene

HTP   :   High-test peroxide

HAN   :   Hydroxyl ammonium nitrate

HNF   :   Hydrazinium nitroformate

HTPB   :   Hydroxyl terminated polybutadiene

HSF   :   Hypergolic solid fuel

ID   :   Ignition delay

IDT   :   Ignition delay time

ILs   :   Ionic liquids

IRFNA :   Inhibited red fuming nitric acid

IGHP   :   Industrial-grade hydrogen peroxide

L02   :   Liquid oxygen

MIMB   :   Methyl imidazolium borane

MON   :   Mixed oxides of nitrogen

RCS   :   Reaction control system

RGHP   :   Rocket grade hydrogen peroxide

RTILs   :   Room temperature ILs

1.   Introduction

Hypergolic systems

The term 'hypergolic' includes igniting spontaneously upon contact with the complementary explosive or energetic substance. Hypergolic ignition means, i.e., ignition of a fuel upon contact with an oxidizer. An ignition delay time exists between initial propellant contact and the ignition event. The ignition delay (ID) is composed of a physical delay (controlled by heating, diffusion, mixing, atomization, and evaporation), as well as a chemical delay controlled by the chemical kinetics of the propellant

combination. The chemical delay is mainly dictated by the activation energy characteristic of a given propellant combination. In the case of gaseous propellants, the physical delay stands for the time necessary for heating, diffusion, and mixing. Whereas, for liquid propellants, the physical delay depends and is lengthened by atomization and evaporation processes. It is greatly influenced by the injection technique and the physical properties of the propellants that control mixing, viscosity, surface tension, and miscibility. Since there is no oxygen to support combustion beyond the Earth's atmosphere, satellites and space stations that remain in orbit for a considerable period of time rely on hypergols. Extensive research was performed in 1960s and 1970s to understand the mixing, spray, and ignition processes of hydrazine-based and NTO-based hypergolic propellants injected with an unlike-doublet injector. Propellants which are considered as hypergolic as well as storable high-performance propellants necessarily fulfill a wide variety of properties and mission roles in launch vehicle and spacecraft propulsion. Among them liquid oxygen/liquid hydrogen and monomethylhydrazine/nitrogen tetroxide are to be mentioned as the best performing propellant combinations in the cryogenic and hypergolic liquid propellant categories, respectively. Among the hypergolic propellants, monomethylhydrazine (MMH) represents the state-of-the-art fuel [1, 2].

Hypergolic reactions may be useful both in civil and military applications. In the area of rocket propulsion, they constitute a potential field due to the reduced weight and complexity of fuel injection systems, allowing controllable use of the propulsors. This mini review aimed at presenting different hypergolic systems and their particularities, comparing them with chemical propulsion systems, which are most commonly employed in rocket motors.

Hypergols are useful for space propulsion since propulsive reaction can be initiated or terminated just by opening or closing some appropriate valves. Hypergolic liquid propellants are strongly preferred over solid fuels or oxidizers since they exhibit excellent hypergolic ignition in addition to low ignition delay time, high specific impulse, and better thrust control. For many years, hydrazine, and its methyl substituted derivatives, have been mostly fuels of choice based on favorable combustion characteristics, and high specific impulse. However, these positive properties are accompanied by many drawbacks including, not only the volatility of these fuels but their carcinogenic and toxic nature, which require costly handling procedures to fulfill environmental requirements during manufacture, storage, shipping, and application.

On the other hand, the most prevalent oxidizers include nitrogen tetroxide (NTO), mixed oxides of nitrogen (MON) and inhibited red fuming nitric acid (IRFNA). They have excellent performance characteristics in terms of specific impulse, density impulse, ignition delays and reliability. However, most of the oxidizers over mentioned are highly corrosive in nature. Note that for long duration space missions storing highly toxic propellants onboard poses a major safety hazard [3,4]. On the other hand, catalytically promoted fuels have been designed in order to reduce toxicity greatly compared to the hydrazine-based fuels and have a potential for high thermodynamic and kinetic performance [4].

In contrast to those drawbacks of the oxidizers mentioned, hydrogen peroxide appears to be very effective greene oxidizer.

2. Hypergolic Systems with Hydrogen Peroxide Oxidizer

For many years, all the dangerous incidents and catastrophic accidents occurred with hypergolic propellants have been related mainly to the toxic compounds based on hydrazine derivatives and dinitrogen tetroxide. However, there are many ways to prevent unwanted events with the implementation of some being necessary to avoid or mitigate possible technical problems, incidents or even accidents. Usage of hydrogen peroxide is one of the remedies to the problem. The historical role of hydrogen peroxide has been as a mono-propellant and a liquid oxidizer. Guseinov et al., have reviewed hypergolic propellants based on hydrogen peroxide and organic compounds in terms of historical aspect and current state in 2018 [5].

Rocket Grade Hydrogen Peroxide (RGHP) plays a major role in the processes leading to the ignition of a catalytically promoted fuel. The ignition process relies on the energetic decomposition of RGHP to heat up, vaporize, and ignite the fuel. The ignition delay times show that the decomposition of RGHP starts very early in the ignition process. Such a rapid event can be attributed to the highly reactive nature of RGHP, as well as to the high degree of miscibility between RGHP and the fuel used [4]. The energetic decomposition of RGHP enhances the atomization and vaporization of the fuel, thus ignition occurs once the auto-ignition temperature of the fuel vapor is reached.

Hydrogen peroxide has been used in many applications for propulsion and power in the past years. Ventura and Mullens in their paper discussed the fundamental characteristics of the propellant, and provided an overview of the history of hydrogen peroxide applications, as well as discussed the current usage and its relation to the past

[6]. It is to be noted that research on non-hydrazine systems may also provide some new applications in nonperformance driven systems, such as aircraft emergency power units, ground based hot gas vacuum aspiration systems (wind tunnels, rocket engine vacuum facilities), reaction control systems (RCS) and other applications.

In most of the cases, the hazards and risks associated with the handling, transportation and storage of hypergolic propellants are based on highly concentrated hydrogen peroxide as an oxidizer. In recent years, the main focus has been placed on the assessment of possible hazards and preventative methods for the protection of technical staff and hardware associated with 98% hydrogen peroxide and the fast developing new "green" hypergolic propellants as well. Concentrated hydrogen peroxide, H_2O_2, is a high-density liquid oxidizer with the unusual characteristic of being able to decompose exothermically into steam and oxygen. When H_2O_2 was first developed, it was one of the most powerful chemicals that could be used safely as a mono propellant. It is important to note that when H_2O_2 was initially used as a monopropellant, it was not possible to use hydrazine effectively. In the category of propellant application, H_2O_2 has been used as a hot gas generator for various applications, such as a monopropellant for reaction control system (RCS) thrusters, as a liquid oxidizer for a bipropellant rocket engines, and for other more exotic applications [6-8].

Generally accepted that H_2O_2 has potentially bright future due to the need for alternate chemicals to hazardous nitrogen tetroxide, hydrazine and hydrazine derivatives. In certain applications, such as close association with humans (re-usable space planes, weapon systems, etc...), H_2O_2 competes directly with liquid oxygen (L02). Whenever, applications that do not want the time constraints or handling complexities of cryogenics are considered then one may select H_2O_2 over L02 [6,7].

Note that bipropellant rocket propulsion systems mainly consist of oxidizer and fuel propellant tanks, pressurizing system, plumbing, valves, and an engine. A pressurant gas tank or gases from a gas generator pressurize the oxidizer and fuel propellant tanks. When the oxidizer and fuel valves open, the pressurized oxidizer and fuel force the propellants through the plumbing into the engine where the propellants are mixed and ignited. The propellant may be ignited either by ignition aids or by hypergolic chemical reaction. Since, ignition aids take up valuable space and weight in the propulsion system, a hypergolic chemical reaction is the preferred ignition method. Certain combinations of fuel and oxidizer are so reactive with one another that they lead to ignition upon contact with one another. The chemical reaction between the fuel and the oxidizer occurs so

rapidly that enough heat is generated to continue the combustion reaction in the engine, producing thrust.

Maschio et al., presented the design and firing test of a 50 N bipropellant thruster based on the H_2O_2 90 wt% − monoethanolamine-ethanol hypergolic pair catalyzed by cupric ions [9]. They performed 5 s firing test, conducted under a swirl injection scheme, yielded average values of 50.38 N, 147 s, and 1210 m/s for thrust, I_{sp}, and c^*, respectively, with the target value of 5 bar for the chamber pressure being reached after 2 s of operation. Alongside with a c^* efficiency of 84%, these results suggest that the assessed green hypergolic bipropellant pair may be a promising alternative for applications in the low-thrust range.

The hypergolic ignition of a solid hydrocarbon fuel with hydrogen peroxide has been achieved by Castaneda and Natan by embedding catalyst particles into the fuel [10]. Additive sodium borohydride can enhance ignition of the solid fuel upon contact with 90% hydrogen peroxide. In the work, ignition delay times were measured in drop-on-solid tests at atmospheric as well as at elevated pressure conditions. Qualitative descriptions of the hypergolic behavior were given. The results have demonstrated that the ignition of the hydrocarbon (polyethylene) matrix used is feasible, especially at high pressures. Ignition delay times of less than 10 ms were observed at atmospheric conditions whereas less than 5 ms at pressures above 0.5 MPa. Also some additional tests were performed employing radial oxidizer injection over a hollow cylindrical surface, proving the viability of the concept [10].

On the other hand, in the further experiments it was observed that the hypergolic ignition of the tested fuels with hydrogen peroxide was highly improved with increasing pressure. Meantime, the ignition delay times decreased by almost half when the pressure increased from 0.1 MPa to approximately 1 MPa. In average, at high pressure, the ignition delay times of less than 4 ms were obtained for samples containing high content of additive and slightly above 4 ms for samples containing 25% wt. of $NaBH_4$. The explosive effect of the hypergolic reaction obtained at the ambient conditions tests was diminished in the test cases above atmospheric pressure, thus allowing ignition of the samples instead of exploding. It was found that improvement of parameters such as the additive particle size, the oxidizer droplet size, as well as initial temperature of the fuel and surface properties have resulted in shorter ignition delay times and in better burning of the hydrocarbon matrix [10].

Recently the concept of novel hypergolic pairs for the enhanced ignition performance

of hypergolic propellants has been proposed by Park et al. [11]. The proposed hypergolic combinations comprised of ionic liquid fuels, namely some salts, such as 1-ethyl-3-methyl-imidazolium-thiocyanate (EMIM SCN) and 1-butyl-3-methyl-imidazolium-thiocyanate (BMIM SCN), and oxidizer hydrogen peroxide (H_2O_2) with some oxidizing additives. The nitrates, $LiNO_3$ and NH_4NO_3 were used as the oxidizing additives, which were dissolved in 60–95 wt% H_2O_2 in order to enhance the physical properties and ignition performance. Addition of the oxidizing additives decreased the theoretical performance of the hypergolic pairs, however, the presence of oxidizing additives drastically reduced the freezing point of the mixture with 95 wt% H_2O_2. Particularly, with the $LiNO_3$ additive, an abrupt change was observed in the freezing point of the mixture. For instance, addition of only 5 wt% $LiNO_3$, decreased the freezing point down to −30 °C. The ignition performance of the novel hypergolic pairs was significantly enhanced by the introduction of oxidizing additives. In the drop test, the $LiNO_3$ additive exerted a substantially greater effect on the enhancement of ignition performance than that exerted by NH_4NO_3. Furthermore, this positive contribution was maximized with the decrease in the hydrogen peroxide concentration. Although the addition of NH_4NO_3 to 90 and 95 wt% H_2O_2 adversely has affected the ignition performance, the combination of BMIM SCN and 60 wt% H_2O_2–containing $LiNO_3$ extended the hypergolicity limit. This study was claimed to be the first attempt to introduce nitrate salts as oxidizing additives in hydrogen peroxide with ionic fuels, including SCN anions. Note that the nitrate salts exhibited some potential to serve as additives that can be used with hydrogen peroxide to enhance the properties of oxidizers. The usage of nitrate salt helps not only lowering the freezing point of oxidizers, but furthermore, it shortens the ignition delay time of the hypergolic pairs [11].

Conventional hypergolic propellants such as MMH/NTO are highly toxic. Therefore, research was conducted by Lauck and coworkers to find suitable, less toxic propellant candidates as replacement [12]. In Germany (at DLR) a hypergolic propellant combination which is comprised of highly concentrated hydrogen peroxide and an ionic liquid, so-called HIP-11, has been identified and the hypergolic ignition of it has been verified with drop tests. In the investigation, first results of the hypergolic ignition of HIP-11 under flowing conditions has been presented. An impinging jet injector was designed, manufactured and tested in a dedicated hypergolic ignition test setup. The ignition was studied under different injection conditions. It was observed that the average ignition delay time ranged between 7.8 ms and 4.9 ms depending on the operating point. Also, a continuous combustion over a wide range of operating conditions was observed.

As a result, HIP-11 was found to be able to produce fast and reliable hypergolic ignitions and to sustain the combustion. Therefore, it is claimed that the composition employed is a very promising candidate for the substitution of conventional hypergolic propellants [12].

Based on some experimental data, Kang and Kwon have recently suggested two speculations on the nontoxic hypergolic propulsion using hydrogen peroxide as an oxidizer [13]. Drop tests were repeatedly performed with the nontoxic hypergolic combination, called stock 3 fuel, and hydrogen peroxide, to measure the ignition delay. Their stock fuels were Stock 0: Tetraethylene glycol dimethyl ether (Tetraglyme)/Sodium borohydride, Stock1: Tetraethylene glycol dimethyl ether (Tetraglyme)/ Tetrahydrofuran/Sodium borohydride and Stock 2: Tetraethylene glycol dimethylether (Tetraglyme)/Tetrahydrofuran/Toluene/Sodium borohydride [14]. Whereas Stock 3 was essentially tetrahydrofuran (THF) and some amount of THF was mixed with diethylenetriamine (DETA) so that the mixture became more volatile and flammable. Note that THF was also compatible with sodium borohydride[15].

Especially for high concentrations of hydrogen peroxide, it has been actively studied for space propulsion systems because it can be easily decomposed by a catalyst without the preheating process of the catalyst bed in the thruster. Stabilizers in the form of cations and anions play an important role in keeping the status of the H_2O_2 stable for a long period of time. Note that the content of the stabilizers in rocket-grade hydrogen peroxide was strictly regulated to prevent the performance degradation of the thruster due to the poisoning effect of the catalyst bed [13]. The first speculation was to review the content of the stabilizers in hydrogen peroxide. The speculation implies technical benefits when the restriction on the content of the stabilizers was relaxed with the nontoxic hypergolic technique. The second speculation was to determine the minimum content of the ignition source for the nontoxic hypergolic fuel. The results showed that the ignition delay was dramatically changed depending on the content of the ignition source. When the content of the ignition source was relatively low, it was observed that the success rate of the hypergolic initiation could be strongly associated with the encounter probability between the oxidizer and the substances of the ignition source dissolved in the fuel. Whereas in the opposite situation, the physical properties of the propellants became the key factors to determine the ignition delay. It was confirmed that the mixture of Stock 3 fuel remained stable for four months in the lab scale storability test. The theoretical performance of the green hypergolic combination (Stock 3/HTP) would be achieved about 96.7% of the equilibrium specific impulse and about 105.7% of the density specific impulse. In the

study, through a simple drop test, the hypergolicity of the green hypergolic combination was verified [15].

Kang and coworkers interested in bipropellant thruster using non-toxic hypergolic fuel and hydrogen peroxide [15]. The propellant was the combination of energetic reactive fuel (Stock 2) and 90 wt.% H_2O_2 and the static firing test was employed. This work successfully demonstrated the steady-state operation of the thruster for 3.5 s, which implies that the concept of the green hypergolic bipropellant thruster is feasible [15].

Florczuk and Rarata in their work have introduced some benefits through the evaluation of ignition delay time, performance and handling requirements for new green hypergolic propellant systems based on highly concentrated hydrogen peroxide, at 98% of concentration, used as oxidizer [16]. The novel green propellants combinations for the spacecraft mainly based on such substances as ammonium dinitramide (ADN) and hydroxyl ammonium nitrate (HAN), and are LMP-103S and AF-M315E, respectively. Nonetheless, highly concentrated hydrogen peroxide, H_2O_2, can also be used widely, not only in monopropellant, but also in bipropellant thrusters, especially in hypergolic systems. Highly concentrated hydrogen peroxide in contact with some organic fuel mixtures can lead to their self-initiated combustion, with reliable ignition that results in ignition delay time (IDT) on the level of several milliseconds. However, their finding is that this is very dependent on the activity and amount of additives mixed with selected fuels. On the other hand, performance of such propellant compositions (liquid organic substance plus additive) can be similar to the toxic ones or even higher, in sense of density impulse. Thus, the propulsion units based on 98% hydrogen peroxide can be successfully used for many various missions of the near-future spacecraft. Moreover, some of these fuels are characterized by relatively low toxicity and they can be stored under normal conditions for very long periods of time without any aging or performance loses. The theoretical Isp provided by the tested propellant compositions have been in the range of 305-330 s, that is very comparable to Isp = 321 s of MMH/NTO composition. Their remark after all is that the utilization of highly concentrated hydrogen peroxide in the space sector can significantly decrease the total cost of satellite missions, due to its low toxicity, high power density, high stability, long duration storability and relatively cheaper safety and handling procedures [16]. For this reason the next step in the development of stable and nontoxic hypergolic fuels with 98% hydrogen peroxide (that can be used in real rocket or space propulsion systems) would be designing of a thruster platform to investigate injection and impinging behavior of selected fuels. Their work

presented in this study is an introduction for understating hypergolicity of novel fuel compounds with HTP prior to design of sophisticated laboratory scale thruster [16].

Quintens et al., in one of their recent articles presented an experimental comparison of the catalytic activity of different alumina-based catalysts for highly concentrated hydrogen peroxide (85% w.) decomposition [17]. Three pellet-shaped catalysts with manganese oxide or platinum active phases were considered. The performances of catalysts were investigated by measuring the temperature increase in the catalytic bed after several injections of 100 μL of hydrogen peroxide in a constant-volume chamber. This setup underwent a loss of reactivity after several injections of the oxidizer which was due to water poisoning. The pellets were, then, tested in a small-scale catalytic chamber plugged into a combustor. Hydrogen peroxide was injected at various mass flow rates (from 4.5 to 9.0 g·s−19.0 g·s−1) through the catalytic chamber. The temperature evolution at the exhaust products was recorded via a thin thermocouple (1 mm) and the data were used to compare the activity of the different catalysts. After the tests, the specific surface area, the active phase amount, and the platinum dispersion were measured. It was observed that the catalysts experienced a decrease of those values, which was the evidence of ageing of the catalytic material. Preliminary combustion tests were performed for all catalysts in a hydrogen peroxide/n-decaneperoxide/n-decane bipropellant combustor. Results were compared to evaluate the influence of the efficiency of the catalytic system on combustion performance [17].

Liquid monopropellant thruster systems are suitable for spacecraft control because of their simplicity, versatility, and long lifetime. Due to these advantageous properties, intense research on green monopropellants to replace carcinogenic hydrazine and hydrazine derivatives in these thrusters has been performed. Hydroxylammonium nitrate (HAN) and ammonium dinitramide (ADN)-based ionic liquid propellants and rocket-grade hydrogen peroxide are considered as the ideal candidates. HAN and ADN-based liquid propellants are mixtures of aqueous solutions of HAN or ADN, an oxidizer, and alcohol-based fuel. They are classified as premixed propellants. These premixed propellants have a higher vacuum specific impulse than hydrazine because the catalytic combustion of the fuel and oxidizer occurs within the propellant. Nevertheless, high-thermal-resistance catalysts are required because of their high adiabatic decomposition temperature. The usage of rocket-grade hydrogen peroxide, (it has a higher vacuum density specific impulse than hydrazine) which is a completely green propellant because its catalytic decomposition produces only water vapor which appears as another alternative to oxygen gas.

Baek and coworkers interested in hydrogen peroxide and ethanol system [18]. They used green liquid monopropellant thrusters which provide an alternative to toxic hydrazine. In this research a premixed liquid monopropellant based on hydrogen peroxide with ethanol blending was employed to replace hydrazine. The maximum theoretical vacuum specific impulse was 282 s for a certain mixture ratio. Two propellants (A and B) were fabricated using 70 wt % hydrogen peroxide and ethanol according to the blasting-cap test results. A 10-N-scale monopropellant thruster was used for performance evaluation. Platinum with porous gamma-phase alumina support was employed as a catalyst. A preliminary firing test was performed for 5 s with propellant A, which had 181 s of vacuum specific impulse. Catalytic combustion occurred without an additional igniter with 87.7% efficiency in a preliminary firing test. Propellant B, which possessed 214 s of vacuum specific impulse and 276 $(g \cdot s)/cm^3$ of vacuum density specific impulse, was selected as an alternative to hydrazine. A thruster firing test was performed for 5 s, the efficiency was measured as 95.3%, and the chamber-pressure oscillation was approximately $\pm 13\% \pm 13\%$. To reduce the combustion instability, lanthanum hexaaluminate (a high-thermal-resistant catalyst support) was applied in an additional firing test. The pressure oscillations were measured as $\pm 3.8\% \pm 3.8\%$, with 92.8% of efficiency in an additional firing test. These results have demonstrated the feasibility of an ethanol-blended hydrogen peroxide thruster as a high-performance and green-propellant thruster for space missions [18].

The authors have conjectured that further improvements could increase the performance of hydrogen peroxide-based premixed monopropellant thrusters with different propellant mixture ratios and could increase the performance of high thermal-resistance catalyst supports for higher propellant performance and a higher decomposition temperature. They have also pointed out that high-performance green monopropellant thrusters would have various future research directions for green space technology and may solve the problems caused by the handling of toxic hydrazine.

Conventional hypergolic propellant combinations, relied on using hydrazine and its derivatives as fuels and dinitrogen tetroxide based oxidizers, have been applied in spacecraft for attitude and roll control systems for more than couple of decades. However, due to their highly toxic nature and potential carcinogenic character, investigations in recent decades have turned their direction to alternative green propellants which have been an active field in current research efforts. Promising alternative propellant candidates are combinations of hydrogen peroxide and suitable

hypergolic room-temperature ionic liquids. Lauck et al., in their work, tested imidazole thiocyanate ionic liquids with hydrogen peroxide [19]. For this purpose, a newly developed automated drop test setup was designed and implemented. As a result, 1-ethyl-3-methylimidazolium thiocyanate (EMIM SCN) and 1-butyl-3-methylimidazolium thiocyanate (BMIM SCN) occurred to be hypergolic with highly concentrated hydrogen peroxide (96.1%). The ignition delay time on the average was found to be 31.7 ms for EMIM SCN and 45 ms for BMIM SCN. Also the theoretical performance of the two ionic liquids was calculated with NASA CEA and compared to a conventional hypergolic propellant combination (monomethyl hydrazine/dinitrogen tetroxide). The specific impulse of the green propellants is nearly 5% lower, but the density specific impulse is increased by 10%. Furthermore, the ignition delay time was reduced by dissolving a catalytic additive, copper thiocyanate, in the EMIM SCN. The lowest average ignition delay time of 13.9 ms was achieved for EMIM SCN having 5 wt% of copper thiocyanate. For higher copper concentration the ignition delay time was not further reduced. The fuel with EMIM SCN and 5 wt% of copper thiocyanate and the pure EMIM SCN were further characterized by thermal and spectroscopic methods. Fluid properties like density, viscosity and surface tension were also determined in laboratory investigations. Also thermo gravimetric analysis and Fourier-transformed infrared spectroscopy (FTIR) were performed as well as density, viscosity, and surface tension measurements [19]. In conclusion, they have stated that thiocyanate ionic liquids are hypergolic with highly concentrated hydrogen peroxide with a short ignition delay times (on the order of tens of milliseconds). This finding is significant because only very few pure substances are hypergolic with hydrogen peroxide. Furthermore, the calculated performance of the ionic liquids in terms of I_{sp} and $\rho\,I_{sp}$ is close or better than the conventional toxic propellants. Therefore, thiocyanate ionic liquids and hydrogen peroxide are very promising pair for potential candidates in order to replace the current hypergolic propellants in orbital propulsion systems.

Kang and Kwon in their research dealt with the concept of green hypergolic combination to replace the toxic hypergolic combinations [15]. Hydrogen peroxide was selected as a green oxidizer. A novel recipe for the non-toxic hypergolic fuel (Stock 3) was suggested. The main ingredient of Stock 3 was diethylenetriamine. Sodium borohydride was blended into the mixture of energetic hydrocarbon solvents as an ignition source for hypergolic ignition. By mixing some amount of tetrahydrofuran with diethylenetriamine, the mixture was observed to become more flammable and volatile. The mixture of Stock 3 fuel remained stable for four months in the lab scale

storability test. Through a simple drop test, the hypergolicity of the green hypergolic combination was verified. Comparing to the toxic hypergolic combination MMH/NTO as the reference, the theoretical performance of the green hypergolic combination would be achieved about 96.7% of the equilibrium specific impulse and about 105.7% of the density specific impulse. The applicability of the green hypergolic combination was successfully confirmed through the static hot-fire tests using 500 N scale hypergolic thruster.

The development of hypergolic materials has aroused great interest due to their important applications in aerospace technology. Zhao et al., prepared six new energetic complexes and comprehensively characterized them [20]. All the energetic complexes they studied had isostructural characteristics, which made them ideal candidates for studying their structure–performance relationships. These energetic complexes had good thermal stabilities and excellent specific impulses. The vacuum-specific impulses were found to be in the range 264.0–271.9 s, which were greater than most of the reported solid hypergolic materials. Moreover, the hypergolic performance of these compounds was examined by using 100% HNO_3 as the oxidizer. Their catalytic performance was comprehensively studied and it was in the range of the hypergolic reaction of typical energetic ionic liquids and 90% H_2O_2. All compounds displayed excellent hypergolic performance with the shortest ignition delay time of 4 ms. The examined copper-containing energetic complexes displayed excellent catalytic activities for the hypergolic reaction between energetic ionic liquids and 90% H_2O_2. The shortest ignition delay time of the examined hypergolic reactions was 31 ms. The suitable physicochemical properties, excellent energetic properties, and high catalytic activity of all the hypergolic reactions have demonstrated the great potential of these energetic complexes as promoters for the development of green hypergolic bipropellants.

Kopacz et al., in their paper discussed the potential use of hydrogen peroxide as oxidizer for solid rocket propulsion [21]. Hydrogen peroxide is a liquid in normal conditions, but it may be used in solid rocket motor grains. The authors have proposed usage of hydrogen peroxide of HTP class (High Test Peroxide). Although it has been known for many decades, its utilization has been historically limited to liquid propellants. Until recently its application even in liquid state in rocket propulsion for space and defense uses has been limited due to storability and safety issues. However, with the availability of new grades of HTP having higher purity and concentrations, enhanced performance, safety and storability, many applications have been possible. These results

allow usage of HTP in a wide range of rocket propulsion systems such as oxidizer in bipropellant and hybrid propulsion systems, as well as a monopropellant. To ensure proper analysis of the potential uses of HTP in next-generation solid rocket propellants, the authors in this paper have reviewed the existing rocket propulsion applications of HTP. It is noteworthy that modern use requires high performance and common current composite propellant compositions utilize ammonium perchlorate (AP) as oxidizer, what has several disadvantages, which have been discussed in the article. Alternative oxidizing compounds include ammonium dinitramide (ADN), ammonium nitrate (AN), hydrazinium nitroformate (HNF), hexanitrohexaazaisowurtzitane (HNIW) and several other secondary explosives. In the article key properties of solid propellant oxidizers are listed and discussed. The need for further alternatives (despite numerous recent advances) in solid rocket oxidizer technology have been justified. Theoretical performance of solid rocket motors using solid grains containing a high mass fraction of HTP is presented. This includes performance considering several fuels and additives and different oxidizer loadings. Up to date concepts of using hydrogen peroxide in solid propellants have been reviewed. Solid cryogenic propellants using hydrogen peroxide are mentioned, but focus is given to solid propellants which could ensure flexible operations, thus use in state-of-the-art solid rocket motors. Also challenges of HTP application as an oxidizer for solid propulsion are listed which includes a discussion concerning its reactivity, thus limited compatibility with organic materials. Additionally, some recommendations for further experimental work have been proposed. Potential technological applications are listed with explanations why these particular benefits from utilization of the new solid propellant technology. Note that the global push forward high performance green propulsion is one of the main motivations behind considering HTP for solid rocket propulsion.

The hypergolic reaction between the recently developed green propellant combination consisting of an ionic liquid and highly concentrated hydrogen peroxide has been investigated by Stützer et al., for various fuel to oxidizer ratios [22]. The influence of the catalytic amount of copper additive on the ignition delay time (IDT) was analyzed. Flame emission/absorption spectroscopy revealed the chemical constituents. It has been observed that all the emission spectra were dominated by the sodium D-lines at a wavelength of $\lambda = 589$ nm. Further lines of alkali metals such as lithium and potassium were found. The copper additive showed its characteristic lines according to its amount in the fuel. The emission spectra of the ultraviolet regime showed the characteristic OH*

molecular lines around a wavelength of $\lambda = 306$ nm with its temperature dependent intensity ratios. It was noticed that the catalytic addition of copper (I) thiocyanate (CuSCN) increases the temperature of the OH* molecule in the flame while it decreases the IDT from 31 ms for pure ionic liquid to 15 ms (5% mass percentage).

Jeong et al., in their very recent article have emphasized that in recent years, hydrogen peroxide (H_2O_2) has been attracting attention as an alternative oxidizer to replace the traditional toxic hypergolic oxidizers [23]. However, hypergolic solid fuel (HSF) candidates for H_2O_2 are few in number and offer limited applications for space propulsions. In this work, the authors have studied various activated carbon (AC)-supported catalysts for a H_2O_2 hybrid rocket to improve the hypergolicity of hypergolic solid fuel (HSF), thereby widening the selection range for hypergolic fuels. For this purpose, Jeong et al., in the work managed to deposit eleven H_2O_2 catalyst candidates (Cr, Mn, Fe, Co, Ni, Cu, Ru, Pd, Pt, Pt–Ru, and Pb) onto AC supports at contents of 20 wt% [23]. The nanostructure and metal particle size distribution of these prepared catalysts were investigated via transmission electron microscope imagery. The oxidation states of the supported catalysts were determined by X-ray diffraction, while the ignition characteristics of the pure catalysts and HSFs with catalyst additives were examined by conducting hypergolic drop tests using a 95 wt% H_2O_2. Also the hypergolicity of the prepared catalysts was evaluated by measuring their reaction delay and ignition delay times. Among the studied catalysts the combinations of Pt/AC, Ru/AC, and Pt–Ru/AC exhibited the shortest reaction delay time of 0.3 ms. Moreover, in the work the dependences of the reaction delay time on the presence of Na^+ ions in Mn/AC and Mn concentration were established. Finally, the ignition delay time of an HSF containing 25 wt% ammonia borane and 75 wt% polyethylene decreased from 20.3 to 9.8 ms after the addition of 1 wt% Pd/AC. All these results obviously provide a variety of additive options for improving hypergolicity of solid fuels with H_2O_2.

During the past decades, green hypergolic propellants have been extensively studied. Various green hypergolic propellants have been reported. However, the definition of "greenness" remains ambiguous. In modern times, the concept of greenness should be carefully reevaluated to ascertain whether a green hypergolic propellant will be able to reduce costs by simplifying propellant handling operations. With regard to safety, the concept of greenness may be controversial, because the propellant handling procedures for toxic propellants have been very well-established on the basis of well-developed protective gears since the early 1960s. Through the decades, some investigators

developed new compositions while some others improved the techniques. Kang et al., attempted to improve the measurement technique for the ignition delay in hypergolic reactions by using a drop-test apparatus [24]. The evaluation method for the hypergolicity is important because an increase in the diversification of green hypergolic combinations is inevitable. In the study of Kang et al., concentrated hydrogen peroxide (90 wt%) was used as an oxidizer, and six different reactive fuels were prepared. Sodium borohydride was employed as an ignition source for the fuels. Optical and acoustic sensors were employed to reliably measure the ignition delay. The proposed measurement technique used in this study accurately reflected the physical phenomena of the hypergolic interactions. A high-speed camera were experimentally investigated in order to established the technical limitations in the conventional measurement technique. They observed that liquid-phase reactions were dominant in the hypergolic reactions of the glyme-based reactive fuels. Gas-phase reactions significantly influenced the hypergolic reactions of most of the amine-based reactive fuels. Whereas, the pyridine-based reactive fuel had a longer delay time for the gas-phase reaction process than the liquid-phase reaction process. It is worth mentioning that recognizing the rate-determining step of the hypergolic ignition is necessary not only for designing a rocket injector, but also reducing combustion instability, e.g., reactive stream separation [24].

Energetic ionic liquids (EILs) have been widely investigated as hypergolic non-toxic bipropellant fuel along with green and non-toxic concentrated hydrogen peroxide oxidizer. These combinations of propellants are being pursued to replace conventional bipropellant fuels involving hydrazine class of fuels and nitric acid based oxidizers. In the pursuit of less hazardous bipropellant fuels, caged ionic liquids like azoles, boranes, *etc.,* are being used. They play a pivotal role in enhancing the performance of the propellant systems. In the oxidizer front, hydrogen peroxide is the promising candidate which is capable of replacing the toxic and hazardous storable propellant oxidizers currently in use.

Sam et al., explored the possibilities of energetic ionic liquids as non-toxic hypergolic bipropellants in liquid rocket engines [25]. The combination of energetic ionic liquids and hydrogen peroxide can be potentially used in the emerging multimode propulsion concept for small satellite applications. The review by Sam et al., describes the efforts pursued on less hazardous energetic ionic liquid (EIL) based bipropellant fuels that are spontaneously ignitable or hypergolic with green oxidizer hydrogen peroxide. Focus is given to EILs characterized with low vapor pressure, reduced toxicity, superior performance and excellent combustion characteristics [25].

The research of Mezyk et al., is focused on investigating the possibility of harnessing the thermal decomposition of highly concentrated hydrogen peroxide (98%) utilizing a decomposition process initiated and maintained solely by a temperature source for low thrust propulsion system applications [26]. This early study of the authors investigates the influence of the initial temperature of the heater, power input condition and chamber pressure on the behavior and stability of the prototype thruster. However, based on the present results reported, it is still too early to conclude on the practicality of the research. However, it demonstrates that a stable configuration with good transient start-ups times is indeed achievable [26].

Various researchers have investigated dissolution and/or addition of materials to liquid fuel (solvent), which are reactive with or cause catalytic decomposition of H_2O_2. Increasing the viscosity of the fuel by addition of a gelling agent was necessary reactive particles in a suitable form. It was observed that increasing the viscosity of the fuel by addition of a gelling agent was necessary to maintain the reactive particles in a dispersed state whereas the rheological properties of the gel permitted the fuel to flow under shear.

In the study of Connell et al., experimental counter flow and impinging jet studies and modeling analysis of hypergolic hydrogen peroxide (H_2O_2) have been considered. Moreover, tests including gel hydrocarbon fuel/particle mixtures have been conducted to characterize the condensed phase reaction rates and ignition delay times [27]. The mixtures consisted of n-dodecane, n-heptane, and kerosene containing fumed silica and sodium borohydride ($NaBH_4$) particles. Scanning electron microscopy, x-ray photoelectron spectroscopy, and simultaneous thermo gravimetric and differential scanning calorimetry analysis were performed on $NaBH_4$ particles to characterize the particle size, size distribution, geometry, surface composition, and thermal decomposition. Also, liquid-phase counter flow experiments were performed to derive a global rate constant for the condensed phase reaction between hydrogen peroxide and $NaBH_4$. Chemical kinetics calculations were carried out using data from the condensed phase global reaction coupled with a detailed gas phase mechanism for hydrocarbon oxidation to study the ignition process. It was observed that shorter ignition delays were achieved when fuel flow was established before the oxidizer injection. Ignition delay decreased with $NaBH_4$ addition until a limiting loading was achieved, so that after which the ignition delay remained nearly constant. Consistent with fuel volatility trends, elevating the reactant temperature reduced the ignition delay. Modeling results have indicated that the ignition process relies upon the reaction between $NaBH_4$ and H_2O_2 in

order to gasify and heat an ignition kernel to the H_2O_2/fuel mixture auto ignition temperature [27].

Through the decades, hypergolic bipropellants based on high-test peroxide (HTP, > 85% H_2O_2) have been developed and traditionally emerged as low-toxicity propellants for space applications. However, the late-ignition performance of HTP-based fuels restrict their potential use in particular applications, such as high-precision auxiliary response thrusters. In the work of Kim and coworker, the synergistic effects of new hybrid additives (reactive additive: catalytic additive), such as $NaBH_4$:NaI, and $NaBH_4$:NH_4I were, demonstrated to improve the ignition performance of low-toxicity fuels with 95 wt.% H_2O_2 [28].

Low-toxicity polar organic fuels were examined in order to determine their ability to solubilize polar additives. The alcohol family of solvents is advantageous because of the low toxicity, low cost, and moderate specific impulse [28]. However, alcohols were excluded because of the slow reaction of primary alcohols with sodium borohydride. Instead, solvents with alkylene amine and amide groups have relatively low toxicity and can easily dissolve the catalytic and reactive additives. Among the alkali borohydrides, sodium borohydride ($NaBH_4$) has been widely used as a reactive additive for hypergolic fuel applications because it is hypergolic with H_2O_2.

The effect of changes in the weight percentage ratios of the reactive and catalytic additives on the ignition performance have been investigated by Kim et al., [28]. It was observed that the fuels without additives were non-hypergolic with 95 wt.% H_2O_2. However, at specific concentrations, the hybrid additives in fuels markedly lowered the ignition delay time (IDT) to less than 3 ms. Notably, ethylenediamine, containing 10 wt.% hybrid additives of $NaBH_4$:NaI and $NaBH_4$:NH_4I at a specific additive weight ratio (6.5:3.5) yielded an average ignition delay time of 2.75 and 2.69 ms, respectively. Thermal analysis revealed that the hybrid additive improved the thermal stability of the fuels. The theoretical vacuum-specific impulse of these fuels was calculated using the NASA-CEA code. The results of this study confirm validity of the approach for developing relatively low-toxicity hypergolic fuels for space propulsion.

To replace the conventional nitrogen tetroxide (NTO) and hydrazine propulsion systems, with a hypergolic, bipropellant system having low toxicity, but high performance is desired for long period of time. Hydrogen peroxide exothermically decomposes to water, and oxygen, which makes it an ideal oxidizer for more environmentally friendly propulsion systems. Unfortunately, the choice of fuel for such

systems is not as clear. Many factors such as the ignition delay, performance, toxicity, storability, and cost are to be considered. Melof and Grubelich have screened numerous candidate fuels and fuel/catalyst mixtures by using a simple laboratory setup and visual observation [29]. A mixture of ethanolamine and 1% copper (II) chloride was found to ignite rapidly with 90% hydrogen peroxide. It is known that hydrogen peroxide and ethanolamine are much less toxic than NTO and hydrazine. Hydrogen peroxide and ethanolamine have a calculated specific impulse of 245 seconds compared to 284 seconds for NTO and monomethyl hydrazine. A low-freezing blend of furfuryl alcohol (47.5%), ethanolamine (47.5%), and copper (II) chloride (5%) was successfully test fired in a small rocket engine with both 90% and 99% hydrogen peroxide. Hypergolic ignition of this mixture was achieved with 70% hydrogen peroxide.

All catalysts except copper (II) acetylacetonate reacted quickly and violently with 90% hydrogen peroxide. Manganese, copper, and iron compounds gave the most vigorous reactions followed by silver, cobalt, ruthenium, and vanadium compounds. Whereas, DMAZ, diethylenetriamine, ethylenediamine, pyrrole, ethanolamine, and triethyl aluminum/hexane just reacted with the peroxide. The only fuels that ignited were pyrrole, ethanolamine, red phosphorous, and triethylaluminum/hexane. A small addition of (1%) of copper (II) chloride to pyrrole and ethanolamine gave rapidly hypergolic mixtures with 90% peroxide. However, upon storage, the pyrrole and copper (II) chloride mixture polymerized, thus leaving catalyzed ethanolamine as the only practical hypergolic fuel among the all.

In the work of Wang et al., a series of unprecedented one-dimensional (1D) copper bromide-based inorganic–organic hybrids were synthesized which exhibited hypergolic fuel character [30]. They observed that in the absence of promoters, all one-dimensional hybrids showed good hypergolic activity toward oxidant HTP (H_2O_2 with concentration of >95 %). Among the hybrids, the 1-propargyl-3-methylimidazolium bromide-based complex achieved the shortest ignition delay (ID) of 12 ms. The structure-performance relationships have revealed that the abundant copper alkynyl bonds distributed in the one-dimensional infinite Cu-Br chain functioned as interconnecting hotspots, which greatly promote the hypergolic efficiency [30]. This work have demonstrated that the hybrids combined with HTP are some candidates having potential applicability as green hypergolic bipropellants for rockets.

The development of new hypergolic propellants implies testing in terms of ignition delay, which is defined as the time from the physical contact of the fuel and the oxidizer

to the onset of ignition. Note that its low value has crucial importance for a smooth engine restart. There are two main approaches for the determination of hypergolic ignition delay, specifically a drop test and an impingement test. The first one is usually preferred, even though the ignition delay obtained by the drop tests can be significantly different from the ignition delay times obtained in the rocket engine.

The effect of fuel temperature and environmental pressure on hypergolic ignition delay of triglyme (triethylene glycol dimethyl ether) with the addition of sodium borohydride and hydrogen peroxide has been investigated by Kapusta and coworkers [31]. The research was conducted in a constant volume chamber, using a drop-test method where the oxidizer drop was released into the fuel pool. The environmental pressure (absolute) was 0.1, 0.5, 1, 1.5 and 2 MPa, while the fuel temperature was adjusted to 22, 40 and 60 °C. The main advantage of this study is that the effects of pressure and temperature were not investigated separately but the tests have been done for full matrix conditions. This approach allowed the evaluation of the effect of fuel temperature at ambient as well as elevated pressures. To determine the effect of environmental pressure for ambient and elevated fuel temperatures (based on direct ignition delay measurements) has been a unique feature of this research. Additionally, the dispersion of the results was analyzed in terms of repeatability of droplet parameters (i.e. Weber number) as well as the diameter and velocity separately, along with eccentricity. The results have shown a huge influence on the ignition delay of both the fuel temperature and the environmental pressure. It was noticed that the average values of the Weber number and the droplet eccentricity remained at a similar level for all the measurement points. The observations together with the trends of ignition-delay-dependence on pressure and temperature suggest that the main difference in the evident ignition delay resulted from a chemical delay which is assumed to be mainly dependent on a direct reaction between the metal hydride and hydrogen peroxide, as well as on hydrogen peroxide decomposition.

The combination of ionic liquids (ILs) and hydrogen peroxide seems one of the most promising approaches for the replacement of conventionally used hypergolic bipropellants consisting of nitrogen tetroxide and hydrazines. Some protic ionic liquids with thiocyanate anions were synthesized by Ricker and coworkers [32]. Protic ionic liquids with imidazolium-based cationic structures and thiocyanate anions have been presented as new fuels for green hypergolic bipropellants (then for the first time). All the seven presented substances are hypergolic with hydrogen peroxide and surpass the

density specific impulse of the previously mentioned conventional bipropellants. One of them stands out in particular, because so far no other transition metal-, hydride- and boron-free ionic liquid with an ignition delay time as short as 7.3 ms was found with hydrogen peroxide. This extremely good ignition behavior of the (at room temperature solid) IL offers great potential not only for hybrid propellants, but also for the liquid hypergolic bipropellant combinations. Out of a mixture of 35 wt% [HIM][SCN] and 65 wt% [EMIM][SCN], a remarkable new liquid bipropellant combination (named HIM-35) has been formed with a very low ignition delay time of 16.7 ms and a particularly high maximum density specific impulse $\rho \, I_{sp}$ of 429 s·g·cm^{-3} [32].

For a long time, hypergolic solid fuels and hydrogen peroxide oxidizers have been attracting considerable attention for the development of safe hybrid rocket propulsion systems. Rang et al., have explored a new approach in order to develop a safe hypergolic hybrid propulsion system using industrial-grade hydrogen peroxide (IGHP) (~70 wt%) [33]. Initially, the propulsion performance of different hypergolic solid fuels with an industrial-grade hydrogen peroxide was calculated using the NASA CEA code to find an appropriate propellant combination. The theoretical specific impulse of the hypergolic solid fuel was 27.8 % over hydrazine and 13.4 % over LMP-103S. Based on theoretical investigations, hypergolic solid fuels, named such as HSF-1 to HSF-10, were fabricated using various molding and pressing methods. The ignition delay times were measured using the drop-test method. Interestingly, samples called, HSF-3 and HSF-4 exhibited very short ignition delay times of 4.92 and 8.75 ms, respectively, with industrial-grade hydrogen peroxide. In addition, the drop test results of hypergolic solid fuel with varying compression pressure in the pressing method confirmed that a pressure above the compressive strength of the binder shortens the ignition delay times deviation. Further, hypergolic solid fuel (HSF) was also ignited even at low concentration of industrial-grade hydrogen peroxide (>40 wt%) which opens the new area of research in combustion science. Overall, low-toxicity hypergolic solid fuels and industrial-grade hydrogen peroxide appear to be promising alternatives to conventional toxic hypergolic propellants [33].

A significant step to a lower-toxicity bipropulsion system would be the demonstration of hypergolicity (spontaneous ignition) between an ionic liquid (IL), which is a paragon of low vapor toxicity, and a safer oxidizer. Apart from cryogens, hydrogen peroxide seems to be especially promising because of its high performance, less-toxic vapor and corrosivity, and its environmentally benign decomposition products.

Due to all these beneficial properties, Schneider et al., tested various ionic liquids (ILs) with 90% and 98% H_2O_2 [34].

They used simple drop tests which place only upper limits on the ignition delays because ignition may be initiated by hydrogen, which burns with an almost invisible flame. However, these tests have demonstrated that an RTIL with a complex aluminum borohydride (ABH) anion is universally reactive with traditional rocket oxidizers including lower-hazard H_2O_2. Note that in view of the advantages of high hydrogen content, RTILs containing $Al(BH_4)_4$ ions may be viewed as a densified form of hydrogen, stabilized by metal atoms.

The development of hypergolic materials has aroused great interest since their significant application in bipropellant systems [35]. The hybrid propulsion systems that use a hypergolic fuel and green H_2O_2 oxidizer, capable of deep throttling and restarting from "cold", is a very challenging task. Das et al., described a new synthetic approach for the synthesis and characterization of conceptually new hydride- and boron-free, and air/moisture stable solid H_2O_2-hypergols, based on Cu and Co complexes of bis(5-tetrazolyl) amine (H2BTA) ligand [35].

Wang et al., in their work, considered five energetic complexes to demonstrate hypergolic performance with the green oxidizer hydrogen peroxide [36]. The compounds used were comprehensively characterized. Organic ligand of these complexes acted as fuel. The decomposition temperatures of these compounds were in the range from 228.8 to 295.5 °C. One of the compounds exhibited quite thermal stability. The density of these compounds ranged from 1.389 to 1.502 g·cm^{-3} which was higher than most of the known hypergolic materials. Furthermore, the hypergolic performance of these materials were evaluated with 90% H_2O_2 by an "oxidizer-to-fuel" standard droplet test. For the examined hypergolic combinations, the shortest ignition delay time was only 3 ms. This ultra-short ignition delay time was shorter than that of most hypergolic combinations and attributed to synergy between different components in the energetic complexes. The copper-ion metal center was the key promoting factor, affecting hypergolic performance of the target compounds. Supposedly, the organic ligand acted as an energetic fuel while the NO_3^- counter ions further improved the hypergolic performance. Integrating these components into one complex and demonstrating their hypergolic performance with hydrogen peroxide as the oxidizer was successfully achieved [36]. The hypergolic phenomenon observed in this work between energetic complexes and hydrogen peroxide may lead to a new approach for the development of green hybrid propulsion systems.

The H_2O_2/kerosene bipropellants also tend to be formulated as hypergolic. Additives containing salts of transition metals and combustible organic compounds (the former the catalyst and the latter the promoter) are added to kerosene. The catalyst, the promoter, and the complex formed by them are all soluble in kerosene to make the fuel homogeneous. The fuel is hypergolic with high-concentration hydrogen peroxide, the same as the well-known hypergolic bipropellant of nitrogen tetroxide and monomethyl hydrazine.

Hydrogen peroxide (H_2O_2)/kerosene has emerged as a promising bipropellant due to its high-energy content. Additionally, it has high storage density, and environmentally benign properties. The possibility of making a hypergolic system by using it rendered this option even more attracting. The U.S. Air Force and U.S. Navy, a long time ago, had begun to consider the use of H_2O_2/kerosene as a bipropellant in rocket propulsion systems [37]. Since then, studies on the bipropellant technology using high-concentration rocket-grade hydrogen peroxide have been extensively conducted. The operation of such an engine is based on a two-stage process. That is, first H_2O_2 is decomposed into a high-temperature and oxygen-rich steam as it comes in contact with a catalyst medium, then kerosene is injected, which can then be auto ignited to release sufficient heat without any requirement of an ignition system. In this mode, some heterogeneous catalysts (in particular silver screen type catalyst systems) is to be employed.

In the work of Cong et al., self-ignitable H_2O_2/kerosene bipropellants were prepared by combining different candidate catalysts and promoters [38]. The authors conducted a dropping-test method and obtained preliminary screening evaluations. Propulsive performances of the combinations which passed the satisfying dropping-test requirements then were investigated on a specially designed thrust engine. The results revealed that short ignition delay and reliable propulsion performances could be acquired in both steady-state and pulse-mode operations. Also it was observed that the combination of kerosene with additives and H_2O_2 of 90% concentration could still have good performances after three months of storage time. It has been expected that the combination of H_2O_2 and kerosene can be an efficacious alternative for storable toxic propellants used currently.

Based on results of open-cup tests and firing tests, it can be concluded that, by utilizing high-concentration (90%) hydrogen peroxide and additive-added kerosene, it is feasible to prepare self ignitable propellant combinations. Green and nontoxic hypergolic H_2O_2/kerosene bipropellants are promising candidates as effective alternatives for toxic propellants currently in use.

Methanol-based fuels that are hypergolic in the presence of highly concentrated hydrogen peroxide (greater than 95%) had been considered by the US Navy. However, a shortcoming of using methanol (or other low molecular weight alcohols) exists that is its low flash point.

Hypergolic bi-propellant propulsion systems are provided that contain a fuel composition and an oxidizer composition. The fuel composition usually contains an azide compound that has at least one tertiary nitrogen and at least one azide functional group, as well as a catalyst that contains at least one transition metal compound [2]. The oxidizer composition contains hydrogen peroxide in water. Preferably, the transition metal catalyst is selected from the group consisting of compounds of cobalt and manganese. The oxidizer composition preferably contains hydrogen peroxide at a concentration of 85% (or greater).

Hypergolic fuel propulsion systems of the invention contain two components—a fuel composition and an oxidizer composition [2]. In an engine, the two components are contacted with one another to produce a fuel mixture that spontaneously ignites. Preferably, ignition should occur within 10 milliseconds of contact. The two components of the bi-propellant fuel systems are generally stored separately until they are contacted with one another in the engine to provide thrust. The oxidizer or oxidizer composition is generally held separately in one tank while the fuel composition containing the fuel compound or compounds and any other additives is held in another tank.

As for the fuel composition, it contains an azide compound that has at least one tertiary nitrogen atom and at least one azide functional group (N_3) on the molecule. Upon oxidation after contact with the oxidizer composition, the azide compound loses nitrogen and reacts to produce the energy needed to provide thrust. A preferred azide compound is one represented by the structure $R_1R_2N\text{-}L\text{-}N_3$ where L is a linking group and R_1 and R_2 are independently alkyl or substituted alkyl groups. Alternatively, R_1 and R_2 together may form a cyclic group. In general, L can be any divalent linking group that connects the azide functional group with the tertiary nitrogen. The cyclic group contains the nitrogen to which R_1 and R_2 are attached. It may further comprise other atoms eg., carbon, nitrogen, sulfur, and/or oxygen. As an example, the ring formed by groups R_1 and R_2 may be a pyrollidine or morpholine ring [2].

It has been found that addition of the transition metal catalyst to the fuel composition made the fuel propulsion system hypergolic when the fuel composition is contacted with the oxidizer composition.

The fact that HP hybrid systems tend to optimize at high mixture ratios which is a benefit in reducing the size of the expensive, high-pressure combustion chamber that contains the fuel grain. In order to quantify the combustion behavior of the HP/PE hybrid propellant combination, Wernimont and Heister focused on the system. They selected polyethylene as the fuel because it is readily accessible and is easily machined. Also, it was found to be much simpler than HTPB to manufacture [39].

In the article by presented by Wernimont and Heister, results from 100 tests of lab-scale hybrid rocket motors using hydrogen peroxide and polyethylene are considered [39]. The tests utilized 85% hydrogen peroxide with low-density polyethylene. Also, a new consumable catalytic-ignition device has been developed to provide rapid, reliable ignition by using stabilized hydrogen peroxide. Regression measurements have indicated that at low chamber pressures (100 psi) a classic diffusion-dominated behavior is noted (with mass flux exponents very near the theoretical value of 0.8). However, at higher chamber pressures tested (200 and 400 psi), radiative-dominated behavior is noted for average mass fluxes varying between 0.1 and 0.3 lbm/(in.2 s). Through the optimization, combustion efficiencies in excess of 95% were obtained in these tests. They reported that no significant nonacoustic or acoustic instabilities were observed in these tests. The chamber pressure fluctuations were less than 3.5% zero-to-peak of the mean.

Although this paper summarizes combustion measurements from testing of the HP/PE hybrid rocket propellant combination and the bulk of the tests used 85% HP with LDPE, some data have been also reported for other types of PE. A new consumable catalytic bed (CCB) design has been used to provide rapid, reproducible ignition using stabilized HP. Once the CCB is consumed, the HP undergoes thermal decomposition as a result of exposure to combustion gases emanating from the ignited fuel grains. The device provides a simple, low cost (and weight) alternative for ignition of hydrogen peroxide hybrid rockets. The measured regression rates indicate a classic turbulent diffusion dominated behavior at chamber pressures of 100 psia, with flux exponents very near the theoretical value of 0.8. However, at higher pressures, the situation is different. This time radiation-dominated behavior in which regression appears to be insensitive to changes in flux, happens for mass flux levels ranging between 0.1 and 0.3 lbm /(in.2 s). This behavior can lead to pressure-related amplications of regression rate as high as 75% when compared to the low pressure (100 psia) data. These conclusions should carry to larger scales because radiation effects are presumed to be scale-independent. The results have shown to be comparable to those obtained from other

researchers using HP as oxidizer with various other fuels. High combustion efficiencies (>95%) were obtained at the higher chamber pressure (200 and 400 psia) conditions by using different mixing procedures. Smooth combustion was observed in all the testings, with typical chamber pressure fluctuations in the range of 1–2% (zero-to-peak) of the mean. The authors have hypothesized that the high mixture ratio (5–8) operation of this propellant combination plays a role in reducing the amount of energy available to drive nonacoustic instabilities that the fuel (solid) contributes. They noticed some minor activity in the range of 20–80 Hz for some of the 100 motors that were tested in these efforts.

As the key features of the work, a new CCB was designed and used to provide rapid, reproducible ignition using stabilized HP. Once the CCB is consumed, the HP undergoes thermal decomposition as a result of exposure to combustion gases emanating from the ignited fuel grain. The device provides a simple, low cost (and weight) alternative for ignition of hydrogen peroxide hybrid rockets [39].

Traditionally, carbon synthesis is an energy-consuming process that requires heating of an organic precursor in an oven at elevated temperature for certain periods of time. Therefore, along with this respect, Chalmpes et al., thought that the development of fast, spontaneous and energy-liberating (e.g., exothermic) preparative methods at ambient conditions would be of great value in synthesis of carbon materials. Hence, hypergolic reactions could offer a useful tool in the rapid and spontaneous synthesis of a wide range of carbon nanomaterials at ambient conditions [40-43].

In their work, Chalmpes et al., presented a rather odd synthesis of carbon nanosheets and fullerols (or hydroxylated fullerenes) through spontaneous ignition of coffee-Na_2O_2 and C_{60}-Na_2O_2 hypergolic mixtures, respectively. They used sodium peroxide (Na_2O_2) acting as strong oxidizer (*e.g.*, source of highly concentrated H_2O_2) [44,45]. In the first case, a mixture of coffee grains and sodium peroxide Na_2O_2 was ignited with a small amount of water to result in a crude carbon residue that after it had been thoroughly washed it afforded a fine black powder. The new systems composed of coffee or fullerene as the combustible fuel and sodium peroxide as the strong oxidizer. In all instances, the syntheses were fast, spontaneous and exothermic at ambient conditions. Thus, the syntheses enable not only facile carbon formation but also the generation of useful work (e.g. photovoltaic or chemical). The coffee-derived carbon nanosheets, due to their flat surface and blackness, seemed to serve as an effective solar energy absorbent, whereas fullerols themselves exhibit important properties and uses. Overall, the present

work altogether with the previous works of the group, shows the wider applicability and generic character of hypergolic reactions in carbon materials synthesis [44,45].

For many years, chemists worldwide have searched ways to develop alternative environmentally friendly hypergolic ionic liquid propellants as fuels. Anions of these type of salts, which include dicyanamide, dicyanoborate, cyanoborate, azide, nitrate, aluminum borohydride, nitrocyanamide, etc., appear to play the major role in determining hypergolic properties. Although, it has been observed that cations generally play a lesser role, some of them are distinguished and are most frequently nitrogen-containing alkyl and aromatic species, e.g., substituted alkyl ammonium, imidazolium, imidazolium-substituted with alkyl, vinyl, propargyl groups, etc. New stable, dense, and storable oxidizers are needed in order to address the demands for energetic systems. Because, the typical oxidizers are likely to be cryogenic or corrosive substances, and /or unstable liquids. Stable room temperature oxidizers that possess positive chlorine or bromine atoms, e.g., azo bis (bromochloro FOX), exhibit appropriate properties when reacted with fuels.

Alternative hypergolic combinations can be used instead of hydrazine-based propellants such as monomethyl hydrazine (MMH) to obtain fast ignition and efficiency [10]. Natan et al., achieved hypergolic ignition of gelled kerosene with hydrogen peroxide by embedding metal hydride particles into the gelled kerosene, enabling hypergolic ignition with the oxidizer [46]. They have showed that the hypergolic reaction produces enough heat to initiate combustion between the fuel and the oxidizer. Sodium borohydride can enhance ignition of the solid fuel upon contact with 90% hydrogen peroxide. They measured the ignition delay times by means of drop-on-solid tests at atmospheric and elevated pressure conditions. Also, qualitative descriptions of the hypergolic behavior are presented. The results have demonstrated that the ignition of the hydrocarbon matrix used (polyethylene) is feasible, especially at high pressures. Ignition delay times of less than 10 ms were observed at atmospheric conditions and less than 5 ms at pressures above 0.5 MPa [10].

To obtain hypergolic ignition of a solid hydrocarbon fuel with hydrogen peroxide, catalyst particles were embedded into a hydrocarbon matrix. It was found that for all of the catalyst additives chosen for this study, it was not possible to cast samples using HTPB. This could be because of either the fuel itself or the cross linking agent react with the additive, thus deactivating its potential for hypergolic ignition or making impossible the casting process of the samples. As a result, low density PE was chosen as the

hydrocarbon matrix fuel, which showed non-reactive behavior with the embedded additives. Theoretical performance analysis shows that embedding these catalyst particles into polyethylene barely varies the specific impulse and the adiabatic flame temperature. Although, hypergolic reactions occurred in all the samples tested, only with sodium borohydride, the combustion of the hydrocarbon fuel was achieved. Metal hydrides such as lithium aluminum hydride ($LiAlH_4$), lithium borohydride ($LiBH_4$) and others, might also provide the required heat to ignite the polyethylene matrix. However, they were not used due to their hygroscopic nature. In the study, samples containing various contents of sodium borohydride were burned using the drop-on-solid tests at atmospheric conditions. Ignition delay times varied according to the additive load embedded in the hydrocarbon matrix. For high additive content, there was 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 $NaBH_4$.

At atmospheric conditions, the flames obtained from the ignition of the samples were not as strong as they were under pressure and lasted very little, because of the explosive behavior of the reaction of $NaBH_4$ with H_2O_2. Hollow cylindrical samples were casted and burned by means of axial injection using a syringe. The results showed that hypergolic ignition of the hydrocarbon fuel with hydrogen peroxide occurred after a very short time, as well as flame buildup and expansion happened as the oxidizer is injected. Shutdown and re-ignition tests were performed showing that these are feasible for PE fuel. At inappropriate oxidizer-to-fuel ratios, the surface of the solid fuel may become "wet" , thus deactivates further hypergolic ignition or delays the flame build-up and expansion. The test showed that hypergolic ignition of the tested fuels with hydrogen peroxide was highly improved with increasing pressure. Ignition delay times decreased by almost half when the pressure increased from 0.1 MPa to approximately 1 MPa. As the average, at high pressure, the ignition delay times of less than 4 ms were obtained for samples containing high content of additive and slightly above 4 ms for samples containing 25% wt. of $NaBH_4$. The explosive effect of the hypergolic reaction obtained at the ambient condition tests diminished in the cases above atmospheric pressure, allowing ignition of the samples. Improvement of the parameters such as, the additive particle size, the oxidizer droplet size, as well as the fuel initial temperature and surface properties can result in shorter ignition delay times and better burning of the hydrocarbon matrix. Hydrogen peroxide was used as oxidizer because of its non-hazardous properties, as it only decomposes into oxygen and water, and its high energetic potential [6].

Zhao and coworkers prepared, six energetic complexes and used them as promoters for the hypergolic reaction of 1-ethyl-3-methylimidazolium cyanoborohydride (abbreviated as [EMIM][BH$_3$CN]) and 90% H$_2$O$_2$ [47]. The structures of these compounds were studied by FT-IR spectroscopy, powder XRD, and single crystal X-ray diffraction. The results revealed that all the compounds were isostructural and each metal center was coordinated with four organic ligands and two counter ions. The decomposition temperatures of these compounds ranged from 169.6–255.9 °C. After adding 10 wt.% of prepared complexes to an ionic liquid, [EMIM][BH$_3$CN], the shortest ignition delay time achieved was 94 ms. Moreover, the formed homogenous catalytic fuels had similar densities, thermal stabilities, as well as specific impulses similar to that of pure [EMIM][BH$_3$CN]. Because of the simple preparation method, excellent yield, as well as high performance of these compounds make them promising promoters for use in green hypergolic bipropellants.

Environmentally friendly hypergolic combinations of ionic liquid fuels and hydrogen peroxide as an oxidizer obviously offer opportunities to replace the commonly used conventional toxic, corrosive and carcinogenic hydrazine-based liquid hypergolic combinations. Researchers have been investigating several non-toxic hypergolic fuel combinations, but a limited number of fuels have been discovered that achieve desirable rocket performance. Various research opportunities await regarding the detailed investigations of green hypergolic ionic liquids (HILs) with rocket grade hydrogen peroxide (RGHP, > 85% H$_2$O$_2$). In the work of Bhosale et al., the combustion of HILs, 1-ethyl-3-methyl imidazolium cyanoborohydride ([EMIM][BH$_3$CN]), 1-allyl-3-ethyl imidazolium cyanoborohydride ([AEIM][BH$_3$CN]), and various HIL-additive mixtures with 95% H$_2$O$_2$ were investigated [48]. As a new additive, 1,3-dimethyl imidazolium copper iodide ([diMIM]$_n$ [Cu$_2$I$_3$]$_n$) was synthesized successfully and its structural investigation was achieved using single-crystal x-ray diffraction analysis through which a crystal density of 3.22 g/cm 3 was obtained. The physicochemical properties (density, viscosity, and decomposition temperature) as well as performance parameters (e.g., ignition delay and specific impulse) of 2 to 15 wt% of [diMIM] n [Cu$_2$I$_3$]$_n$ in [EMIM][BH$_3$ CN] were determined. A sample of 15 wt% of [diMIM]$_n$ [Cu$_2$I$_3$]$_n$ exhibited ignition delay time (IDT) values of 13 and 29 ms under fuel-rich and oxidizer-rich conditions, respectively. These IDT values are 100 times lower than those for [EMIM][BH$_3$CN]. Interestingly, [diMIM]$_n$ [Cu$_2$I$_3$]$_n$ - [EMIM][BH$_3$CN] combinations possessed high density (> 0.98 g/cm 3), good thermal (> 200 °C) and chemical stability, and 5.6–6.0% higher density specific impulse than those found for unsymmetrical

dimethyl hydrazine. The additive-promoted hypergolic combustion of HIL with RGHP opens a new path to the replacement of conventional toxic hypergolic combinations [48].

Solid hypergolic fuels are typically used as a fuel grain in hybrid propellants. Solid hypergolic fuel grain includes hydrazones, thiocarbohydrazones, monocyclohexanoethiocarbohydrazone (CHTCH), tagaform (polybutadiene with an aromatic amine), metal hydrides, etc. which are commonly used in hybrid rocket propulsion. Liquid hypergolic fuels, hydrazine-based derivatives, such as monomethyl hydrazine (MMH) and unsymmetrical dimethyl hydrazine (UDMH) have considerable importance in bipropellant applications, because, these fuels have high performance in combination with oxidants such as HNO_3 and N_2O_4. However, these liquid propellant combinations, as mentioned many times, are highly toxic to humans and the surrounding environment.

Research on green hypergolic fuels ignited with hydrogen peroxide (H_2O_2) offers a number of opportunities in space propulsion with regard to replacing conventional toxic propellant combinations. Bhosale et al., synthesized some green hypergolic fuels, having B-H bond-rich zwitterions and ionic liquids (ILs) and investigated their hypergolic reactivity with 95% H_2O_2 [49]. Remarkably, ammonia borane (AB) and 1-ethyl-3-methyl imidazolium borohydride ([EMIM][BH$_4$]) exhibited the lowest ignition delay times of 8.1 and 18.5 ms, respectively. For a comprehensive application, the authors studied the reactivity of liquid and hybrid fuel blends. A liquid fuel blend, abbreviated as [EMIM][BH$_4$] and methyl imidazolium borane (MIMB) (1:1, w/w) exhibited the ignition delay time of about 35 ms. Further, they prepared a solid hybrid fuel blend consisting of 40% AB-paraffin which revealed a hypergolic ignition delay time of 9.2 ms. Additionally, the gas phase heat of formation and specific impulse values were calculated using G09 and NASA-CEC-71 programs, respectively. The specific impulse of AB was 273 s, which is higher than the stated hypergolic zwitterions. Hence, the BeH bond-rich zwitterions and ILs seem to be promising choices for new generation green hypergolic liquid and hybrid rocket propulsion.

Provided that the involved reagents are slowly mixed (unlike an explosion event where energy is released in a violent manner) in hypergolic ignition the energy is released in a smooth and continuous manner. Carbon is an energetic material and plentiful, cheap, non-toxic and also non-corrosive that is however scarcely used as solid fuel in hypergolic propellants for rocket engines, probably due to the lack of hypergolicity and ignition difficulties. Bourlinos taking into consideration that carbon hypergolicity is a rare

phenomenon mentioned in the literature, presented a new type of carbon-containing hypergolic compositions based on water-ignitable C-NaH mixtures [50]. In these formulations, fullerenes, C_{60}, multiwall carbon nanotubes (MWNTs), charcoal or active carbon might be the carbon source, whereas sodium hydride NaH and water react exothermically upon contact to trigger the carbon combustion and ignition of the mixtures at ambient conditions. Hence, carbon allotropes appear as potentially new solid fuels in hypergolic propellant compositions, so that meriting further attention in this direction. Such a hypergolic pair uniquely combines with high energy value, low-toxicity, low corrosiveness and low-cost carbon allotropes with sodium hydride, giving fast and spontaneous ignitions at ambient conditions by the drop wise addition of water catalyst, and producing fewer CO_2 emissions due to conversion of the greenhouse gas into Na_2CO_3. As a future outlook, the author conjectured that coal, hydroxylated fullerenes, graphite oxide, fluorinated graphite, single-walled carbon nanotubes, carbon nanofibers and carbon dots could be some additional examples of carbon materials that could be successfully tested.

The article by Nath et al., describes a comprehensive characterization of ignition properties of a metal-hydride based non-toxic hypergolic hybrid rocket propellant [51]. The propellant consists of rocket grade hydrogen peroxide (RGHP) as oxidizer, high-density polyethylene (HDPE) as fuel and sodium borohydride ($NaBH_4$) as the additive. The additive was embedded in the HDPE matrix. Ignition quality of the test sample was characterized in terms of ignition delay, ignition probability and flame spread. In a drop-test setup, ignition characteristics were determined as a function of seven parameters which were RGHP concentration, additive loading, oxidizer droplet volume, oxidizer droplet impact velocity, diluent gas, pressure and environmental exposure. The parameters encompass thermo-chemical, as well as the fluid/droplet dynamics and environmental factors affecting ignition. Ignition delays as low as 3 ms were observed. An overwhelming majority of conditions tested yielded ignition delays of less than 10 ms and 100% ignition success. All conditions tested affected ignition to varying degrees depending on RGHP concentration, $NaBH_4$ loading and drop impact velocity (significantly affecting ignition). Further, contrary to expectations, exposing sanded fuel samples to humidity for a few hours enhanced the ignition instead of hampering it and exposure for 24 hours did not lead to any ignition degradation. Tests with diluent gases other than air (at atmospheric and elevated pressures) revealed that atmospheric oxygen played a negligible role in the reaction process. This have proved that oxygen for the initial ignition event was obtained from RGHP decomposition, but not from the

atmospheric oxygen which is playing no role in ignition performance. Aside from demonstrating excellent ignition characteristics, their results further have shown a need to go beyond thermo-chemical properties. To consider the aspects of ignition other than ignition delay in hypergolic propellant research, enables one with a complete understanding of the chosen propellant's role in the ignition processes. The comprehensive ignition characterization demonstrates the ability in order to overcome the ignition challenges in hybrid rockets and serves for its further development [51].

Wang et al., studied tetrahydroborate (BH_4^-)/cyanoborohydride (BH_3CN^-) anion-based ionic liquid fuel systems in combination with high test peroxide (>90% H_2O_2, HTP) oxidizer [52]. However, most of the BH_4^- and BH_3CN^- anion-based ionic liquids are sensitive to water, making it difficult to store them. In the work, novel difunctional promoters were designed for hypergolic ignition of BH_4^-/BH_3CN^- anion-free ionic liquids with 90% H_2O_2. The transition metal in anions of promoters is expected to catalyze the exothermic decomposition of H_2O_2. The substituted borohydride in the cations of promoters acts as the ignition source. These novel difunctional promoters show good solubility in commercially available 1-allyl-3-methylimidazolium dicyanamide and 1-butyl-3-methylimidazolium dicyanamide ionic liquid fuels. The composite fuels considered in the work exhibited high density, acceptable viscosity, and high thermo stability. The addition of difunctional promoters ensures that the smooth hypergolic ignition of BH_4^-/BH_3CN^- anion-free ionic liquid fuels arise with a minimum ignition delay time of 34.0 ms. No apparent micro explosion and secondary combustion were observed during the ignition process. Moreover, by increasing the amount of the promoter, it was observed that density specific impulses of the composite fuels improved gradually. The work presented in the article provides a strategy for designing promoters by synergy of cations and anions to seek green bipropellants.

An experimental investigation was conducted by Castaneda and Natan to determine the hypergolic ignition delay time and behavior of various solid fuels containing sodium borohydride together with high-grade hydrogen peroxide [53]. It has been observed that the hypergolic reaction between sodium borohydride and hydrogen peroxide provides the heat necessary to cause the ignition and combustion of the fuels tested. Ignition delay times ranging from 5.5 ms to 10 ms were measured for the tests performed at ambient conditions. The hypergolic ignition has also been studied at elevated pressures, resulting in decreased ignition delay times for most of the cases. As the pressure increases (eg.10 bar), ignition delay times as short as 2.93 ms were measured for the tests. The

theoretical specific impulse values of the tested fuels were found to be comparable to other liquid hypergolic propellants as well as the common hybrid rocket combinations. Also some additional tests were conducted using radial oxidizer injection over a hollow cylindrical surface to prove that the hypergolic ignition of the selected fuels is certain. Approximated ignition and combustion delay times averaged 23.1 ms. The results imply that in a hypergolic-hybrid rocket configuration, it is possible to achieve short ignition delay times, thus eliminating the need for a separate ignition system [53]. Since, solutions of lithium aluminum hydrides and $LiBH_4$ in ethers have demonstrated H_2O_2 hypergolicity, then Rusek, has conjectured that the same behavior from ILs with metal hydride anions might be expected [54].

However, the development of energetic room temperature ILs (RTILs) with metal hydride anions involves a number of technical challenges. Simple metal hydride anions are poor liquefying agents. Furthermore, heterocyclic, unsaturated salts, including imidazolium, triazolium, pyridinium, and other common IL cations are reduced by BH_4^- ions, thus negatively affecting their thermal stability. Therefore, saturated ammonium/heterocyclic cations might be better candidates for RTIL metal hydrides. Indeed, there are at least two patents that feature quaternary ammonium aluminum hydrides. Examples are trioctyl-n-propylammonium aluminum hydride (m.p. 65–668C) and trioctylmethylammonium aluminum hydride (viscous liquid). While these data are interesting, a cation that results in a stable, free flowing RTIL with a simple metal hydride might not be easily found.

Another approach to liquefying metal hydrides is to replace hydrogen atoms of the hydride with other groups. Of those, 1-Butyl-2,3-dimethylimidazolium cyanoborohydride (CBH) was reported to be a low-viscosity IL. In 2008, a few dicyanamide-containing ionic liquids were first reported to be hypergolic [40]. In the intervening time, ionic liquids comprised of a variety of cations and anions have been synthesized and tested for hypergolic properties [55,56]. Currently the majority of ionic liquids that have been demonstrated to be hypergolic contain either the dicyanamide or nitrocyanamide anion.

A variety of new CBH ILs were prepared, [55] and Zhang and Shreeve prepared novel dicyanoborohydrides (DCBH) ILs [56]. While all of these compounds are fast-igniting with nitric acid, their tests with CBH ILs and H_2O_2 revealed excessive ignition delays of several seconds. It appears that the role of the cation is to tune the properties of the resulting ionic liquids, which is consistent with the point that the anions play the determinative role in the hypergolic ignition process [56]. Zhang and Shreeve also

obtained negative results with 1-butyl-3-methylimidazolium tetracyanoborate, then it is probable that DCBH ILs are another approach that would allow to combine an IL with aluminum borohydride (ABH) in order to form complex anions such as $Al(BH_4)_4^-$. Tetrabutylammonium (TBA)Al-$(BH_4)_4^-$ has a melting point of 508 C, which is lower than the uncomplexed borohydride [57]. Noeth and Ehemann reported a "triple hydride" (which describe complexes or co-ordination compounds consisting of three different hydrides) trioctyl-n-propylammonium $Al(BH_4)_4^-$ as a "viscous oil crystallizing very slowly" [58].

Titov et al., reported on their efforts to prepare RTIL borohydrides with subsequent conversion to $Al(BH_4)_4^-$-RTILs and the reactivity of both toward oxidizers including hydrogen peroxide [57]. They repeated a previously reported preparation of TEA $Al(BH_4)_4^-$, a solid with a decomposition point of 1508 C, and obtained its X-ray crystal structure. The new material, called (THTDP)BH_4 is a viscous RTIL and was characterized by NMR and Raman spectroscopy. Subsequent reaction with a slight excess of ABH produced quantitatively the first RTIL that incorporates a $Al(BH_4)_4^-$ ion. The compound was colorless and free-flowing. It was characterized by NMR and Raman spectroscopy, differential scanning calorimetry (DSC), and mass-balance and hydrogen analyses. A simple vacuum thermal stability test and isothermal thermo gravimetric analysis (TGA) at 758C (48 h) revealed that no mass loss occurred. The vibrational spectroscopy proved the structure, which was especially useful as the cation and anion stretch vibrations. The simple drop tests place only upper limits on the ignition delays because ignition may be initiated by hydrogen, which burns with an almost invisible flame. However, these tests demonstrate that an RTIL with a complex ABH anion is universally reactive with traditional rocket oxidizers including lower hazard H_2O_2. Furthermore, this new class of ILs possess the potential for enabling high-performing, noncryogenic, green bipropulsion for the first time [34].

Hypergolic, heterogeneous combustion systems have been attractive for propulsion applications, as they simplify ignition process and engine restart. However, most conventional hypergolic propellants as mentioned previously are toxic or environmentally hazardous. The work of Sippel et al., is one of the pioneering studies for the development of less toxic, hypergolic metal hydride-based propellants for application to liquid and hybrid propulsion systems [59]. In their work, results on the measurement of the hypergolic ignition delay of lithium aluminum hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$) in the form of dicyclopentadiene (DCPD) hybrid fuels and rocket

fuel, RP-1 slurry fuels with hydrogen peroxide have been presented. Ignition delay for $LiAlH_4$ and $NaBH_4$ slurries and neat metal hydride powders with 90% hydrogen peroxide are all less than 20 ms, and 10 ms, respectively. The observable preignition process of $LiAlH_4$ slurries is different from that of $NaBH_4$ slurries. At the time scales investigated, while the $LiAlH_4$ slurry preignition process produces gas-phase products, the $NaBH_4$ slurry preignition occurs almost completely in the condensed phase. Droplet tests on DCPD-metal hydride fuel pellets indicate a ignition processes similar to those of the slurries. That hypergolic ignition of a fuel grain cannot be relied upon as the sole source of ignition. However, DCPD's ability to protect the metal hydride seems to be promising.

The authors also interested in the preignition dynamics of $LiAlH_4$ and $NaBH_4$ slurries and DCPD pellets and they appear to be very different from each other. Lithium aluminum hydride fuels produce preignition gas, which is ignited by burning metal or metal hydride. Whereas, the ignition process of fuels containing $NaBH_4$ occur on a time scale faster than that of the current study. It is expected by the authors that RP-1 by itself does not sufficiently protect the metal hydride from aging. Results of the DCPD ignition delay tests show, however, that the exterior cast surfaces of fuel pellets, especially with $LiAlH_4$, are capable of protecting the metal hydride from reaction with RGHP. Also the long ignition delays and sensitivity to surface condition suggest that hypergolicity cannot be exclusively relied upon to DCPD-metal hydride ignition, but that DCPD may prevent aging of metal hydrides. Therefore, their future slurry work might be developing of an effective surfactant coating procedure and quantify the ability of slurry and DCPD to prevent metal hydride aging.

Also, based upon tests using $NaBH_4$, the authors plan to modify the casting formulation in order to prevent settling during the curing process. A detailed study to quantify DCPD's protective properties will be conducted. They contemplate that future DCPD efforts will focus on further characterization of the ignition process and decreasing ignition delay through introduction of other hypergolic fuel additives or reduction of metal hydride particles in size. Adjustment of $NaBH_4$ particle size and addition of nanoscale fuels will also be investigated as a means of preventing settling in $NaBH_4$ fuels [59].

The authors also remarked that the chemical processes that occur in the gas phase during preignition would be studied in order to determine composition of the gases released during the preignition process. The physical processes occurring in the condensed phase during preignition should also be examined. Droplet experiments using

both solid pellets and slurry fuel should also be conducted using higher magnification and time resolution in order to better understanding of the processes that occur immediately prior to ignition.

Some new HILs with metal- containing cationic structure and borohydride cluster anionic structure are impressive. Some new iodocuprate-containing salts showed promising hypergolic properties with green oxidizer of hydrogen peroxide [60]. In their review, Jin et al., have outlined the major advances of the recently developed HILs with new structures and their applications as new-generation green propellant fuels in the field of chemical propulsion. As their conjecture, the research of new HILs mainly will focus on the structural innovation and performance improvement for meeting the demand of practical propulsion applications [60].

3. Conclusion

In recent years interest in the hypergolic propellant systems has noticeably increased among the countries searching for new classes of low-toxic propellants having much higher energy potential compared to known propellants. A hypergolic propellant system also seems to be the most secure and controllable system to be developed. While searching for new propellant formulations or developing the already existing ones, the required properties are possession of high specific impulse, minimized ignition delay, and stable and complete combustion. In these studies, the most appealing and the most challenging task is to develop a hypergolic propellant based on common fuels and highly concentrated hydrogen peroxide. Note that a particular hypergolic combination of components which are favorable for one property may give rise to unfavorable one for some other propellant system. Therefore, the search has been still in progress for new high-energy components and ignition initiators compatible with the fuels used most often with hydrogen peroxide as well as ensuring environmental safety. However, none of the known hypergolic mixtures yet seem to reach the characteristics that are attained with pure hydrazine hydrate.

In recent years, attention of researchers has been shifted to ionic liquids, which possess potential for the production of new high-performance green propellant formulations suitable for hypergolic reactions with hydrogen peroxide. Another branch of research has been expanding on additives which improve certain hypergolic properties of the combinations.

On the other hand, considering the interaction between liquid compounds for

hypergolic reaction one should keep in mind that it is important to give special attention to contact area between the hypergolic system components.

Overall, the present mini review aimed to show the wider applicability and generic character of hypergolic systems with hydrogen peroxide.

References

[1] Kubal, T., Dambach, E.M., Son, S., Anderson, W., & Pourpoint, T. (2010). Aspects of monomethylhydrazine and red fuming nitric acid ignition. AIAA 2010-6902. 46th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit. 25-28 July 2010, Nashville, TN. https://doi.org/10.2514/6.2010-6902

[2] Hallit, R.E.A., & Bauerle, G. (2005). Hypergolic azide fuels with hydrogen peroxide. US 6,949,152 B2.

[3] Mahakali, R., Kuipers, F.M., Yan, A.H., Anderson, W.E., & Pourpoint, T.L. (2011). Development of reduced toxicity hypergolic propellants. *47th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit*. 31 July - 03 August 2011, San Diego, California. https://doi.org/10.2514/6.2011-5631

[4] Pourpoint, T.L., & Anderson, W.E. (2007). Hypergolic reaction mechanisms of catalytically promoted fuels with rocket grade hydrogen peroxide. *Combustion Science and Technology*, *179*(10), 2107-2133. https://doi.org/10.1080/00102200701386149

[5] Guseinov, S.L., Fedorov, S.G., Kosykh, V.A., & Storozhenko, P.A. (2018). Hypergolic propellants based on hydrogen peroxide and organic compounds: historical aspect and current state. *Russian Chemical Bulletin, International Edition*, *67*(11), 1943-1954. https://doi.org/10.1007/s11172-018-2314-1

[6] Ventura, M., & Mullens, P. (1999). The use of hydrogen peroxide for propulsion and power. AIAA 1999-2880. *35th Joint Propulsion Conference and Exhibit*. 20-24 June 1999, Los Angeles, CA, USA. https://doi.org/10.2514/6.1999-2880

[7] Andrews, D. (1990). Advantages of hydrogen peroxide as a rocket oxidant. *Journal of the British Interplanetary Society*, *43*(7), 319-328.

[8] Harlow, J., Hydrogen peroxide - A U.K. Perspective. Lecture at University of Surrey Symposium on Hydrogen Peroxide, July 20-24, 1998.

[9] Maschio, L.J., de Araújo, E.P., Pereira, L.G.F., Gouvêa, L.H., Vieira, R. (2021). Assessing the performance of a green liquid fuel hypergolic with hydrogen peroxide in a 50 N bipropellant thruster. *International Journal of Energetic Materials and Chemical Propulsion*, *20*(1), 21-30. https://doi.org/10.1615/IntJEnergeticMaterialsChemProp.2020032684

[10] Castaneda, D.A., & Natan, B. (2019). Experimental investigation of the hydrogen peroxide – solid hydrocarbon hypergolic ignition. *Acta Astronautica*, *158*, 286-295. https://doi.org/10.1016/j.actaastro.2018.05.058

[11] Park, S., Lee, K., Kang, H., Park, Y., & Lee, J. (2022). Effects of oxidizing additives on the physical properties and ignition performance of hydrogen peroxide-based hypergolic propellants. *Acta Astronautica*, *200*, 48-55. https://doi.org/10.1016/j.actaastro.2022.07.051

[12] Lauck, F., Witte, J., Negri, M., Werling, L., & Schlechtriem, S. (2022). Hypergolic ignition investigations with an impinging injector of an ionic liquid fuel with hydrogen peroxide. *Space Propulsion*, 2022, 09-13. https://elib.dlr.de/187226/

[13] Kang, H., & Kwon, S. (2018). Experiment and speculations on nontoxic hypergolic propulsion with hydrogen peroxide. *Journal of Spacecraft and Rockets*, *55*(5), 1230-1234. https://doi.org/10.2514/1.A34177

[14] Kang, H.J., Jang, D.W., & Kwon, S.J. (2016). Demonstration of 500 N scale bipropellant thruster using non-toxic hypergolic fuel and hydrogen peroxide. *Aerospace Science and Technology*, *49*, 209-214. https://doi.org/10.1016/j.ast.2015.11.038

[15] Kang, H.J., & Kwon, S.J. (2017). Green hypergolic combination: diethylenetriamine-based fuel and hydrogen peroxide. *Acta Astronautica*, *137*, 25-30. https://doi.org/10.1016/j.actaastro.2017.04.009

[16] Florczuk, W., & Rarata, G. (2017). Performance evaluation of the hypergolic green propellants based on the HTP for a future next generation spacecrafts. AIAA 2017-4849. *53rd AIAA/SAE/ASEE Joint Propulsion Conference*. Atlanta, GA. https://doi.org/10.2514/6.2017-4849

[17] Quintens, H., Boust, B., Bellenoue, M., Beauchet, R., & Batonneau, Y. (2022). Experimental comparison of hydrogen peroxide catalysts for a hydrogen peroxide/n-decane bipropellant combustor. *Journal of Propulsion and Power*, *58*(5), 2022-09. https://doi.org/10.2514/1.B38593

[18] Baek, S., Jung, W., Kang, H., & Kwon, S. (2018). Development of high-performance green-monopropellant thruster with hydrogen peroxide and ethanol. *Journal of Propulsion and Power*, *34*(5), 1-6. https://doi.org/10.2514/1.B37081

[19] Lauck, F., Balkenhohl, J., Negri, M., Freudenmann, D., & Schlechtriem, S. (2021). Green bipropellant development – A study on the hypergolicity of imidazole thiocyanate ionic liquids with hydrogen peroxide in an automated drop test setup. *Combustion and Flame*, 226, 87-97. https://doi.org/10.1016/j.combustflame.2020.11.033

[20]   Zhao, X., Wang, Z., Qi, X., Song, S., Huang, S., Wang, K., & Zhang, Q. (2021). Hunting for energetic complexes as hypergolic promoters for green propellants using hydrogen peroxide as oxidizer. *Inorg. Chem.*, *60*(22), 17033-17039. https://doi.org/10.1021/acs.inorgchem.1c02149

[21]   Kopacz, W., Okninski, A., Kasztankiewicza, A., Nowakowskia, P., Rarata, G., & Maksimowski, P. (2022). Hydrogen peroxide – A promising oxidizer for rocket propulsion and its application in solid rocket propellants. *FirePhysChem*., *2*(1), 56-66. https://doi.org/10.1016/j.fpc.2022.03.009

[22]   Stützer, R.G., Balkenhohl, J., Lauck, F., Oschwald, M., & Schlechtriem, S. (2022). Hypergolic reaction between green ionic liquid EMIM SCN and hydrogen peroxide in lab-scale drop test chamber. *International Journal of Energetic Materials and Chemical Propulsion*, *21*(1), 87-100. https://doi.org/10.1615/IntJEnergeticMaterialsChemProp.2021038219

[23]   Jeong, J., Rang, S., Ugolini, V.M.P., & Kwon, S. (2022). Hypergolicity improvement by activated carbon-supported catalysts for hydrogen peroxide oxidizer. *Acta Astronautica*, *198*, 720-727. https://doi.org/10.1016/j.actaastro.2022.06.011

[24]   Kang, H., Park, S. Park, Y., & Lee , J. (2020). Ignition-delay measurement for drop test with hypergolic propellants: Reactive fuels and hydrogen peroxide. *Combustion and Flame*, *217*, 306-313. https://doi.org/10.1016/j.combustflame.2020.04.017

[25]   Sam, I.I., Gayathri, S., Santhosh, G., Cyriac, J., & Reshmi, S. (2022). Exploring the possibilities of energetic ionic liquids as non-toxic hypergolic bipropellants in liquid rocket engines. *Journal of Molecular Liquids*, *350*, 118217. https://doi.org/10.1016/j.molliq.2021.118217

[26]   Mezyk, L., Gut, Z., Mohan, K., Kindracki, J., & Rarata, G. (2022). Initial research on thermal decomposition of 98% concentrated hydrogen peroxide in thruster-like conditions. *Engineering Science and Technology, an International Journal*, *31*, 101054. https://doi.org/10.1016/j.jestch.2021.08.011

[27]   Connell, T.L. Jr., Risha, G.A., & Yetter, R.A. (2018). Ignition of hydrogen peroxide with gel hydrocarbon fuels. *Journal of Propulsion and Power*, *34*(1), 170-181. https://doi.org/10.2514/1.B36458

[28]   Kim, K-S., Bhosale, V.K., & Kwon, S. (2021). Synergistic effect of a hybrid additive for hydrogen peroxide-based low toxicity hypergolic propellants. *Combustion and Flame*, *231*, 111450. https://doi.org/10.1016/j.combustflame.2021.111450

[29]   Melof, B.M., & Grubelich, M.C. (2001). Investigation of hypergolic fuels with hydrogen

peroxide. AIAA 2001-3837. *37th Joint Propulsion Conference and Exhibit*. 8-11 July 2001, Salt Lake City, UT, USA. https://doi.org/10.2514/6.2001-3837

[30] Wang, Y-J., Wang, X-Y., Xu, H., Ren, W-W., Pang, R., Yang, L., Tong, W-C., Wang, Q-Y., & Zang, S-Q. (2023). One-dimensional copper bromide based inorganic-organic hybrids as fuels for hypergolic bipropellants with hydrogen peroxide as oxidizer. *Chemical Engineering Journal*, *455*, 140587. https://doi.org/10.1016/j.cej.2022.140587

[31] Kapusta, Ł.J., Boruc, Ł., & Kindracki, J. (2021). Pressure and temperature effect on hypergolic ignition delay of triglyme-based fuel with hydrogen peroxide. *Fuel*, *287*, 119370. https://doi.org/10.1016/j.fuel.2020.119370

[32] Ricker, S.C., Brüggemann, D., Freudenmann, D., Ricker, R., & Schlechtriem, S. (2022). Protic thiocyanate ionic liquids as fuels for hypergolic bipropellants with hydrogen peroxide. *Fuel*, *328*, 125290. https://doi.org/10.1016/j.fuel.2022.125290

[33] Rang, S., Jeong, J., Bhosale, V.K., & Kwon, S. (2022). Reactivity of hypergolic hybrid solid fuel with industrial grade hydrogen peroxide. *Fuel*, *330*, 125543. https://doi.org/10.1016/j.fuel.2022.125543

[34] Schneider, S., Hawkins, T., Ahmed, Y., Rosander, M., Hudgens, L., & Mills, J. (2011). Green bipropellants: hydrogen-rich ionic liquids that are hypergolic with hydrogen peroxide. *Angew. Chem. Int. Ed*., *50*, 5886-5888. https://doi.org/10.1002/anie.201101752

[35] Das, J., Shem-Tov, D., Wang, S., Zhang, L., Flaxer, E., Zhang, S., Stierstorfer , J., Wang, K., Yan, Q-L., Dobrovetsky, R., & Gozin, M. (2021). Hydride- and boron-free solid hypergolic H2O2-ignitophores. *Chemical Engineering Journal*, *426*, 131806. https://doi.org/10.1016/j.cej.2021.131806

[36] Wang, K., Wang, Z., Zhao, X., Qi, X., Song, S., Jin, Y., & Zhang, Q. (2022). Unearthing hidden hypergolic potential of energetic complexes with hydrogen peroxide. *Combustion and Flame*, *244*, 112235. https://doi.org/10.1016/j.combustflame.2022.112235

[37] McNeal, C.I., Jr., & Anderson, W.E. (1999). The peroxide pathway. *Proceeding of the 2nd International Hydrogen Peroxide Propulsion Conference*, Purdue Univ., West Lafayette, IN, pp. 211-219.

[38] Cong, Y., Zhang, T., Li, T., Sun, J., Wang, X., Ma, L., Liang, D., & Lin, L. (2004). Propulsive performance of a hypergolic H_2O_2/kerosene bipropellant. *Journal of Propulsion and Power*, *20*(1), 83-86. https://doi.org/10.2514/1.9189

[39] Wernimont, E.J., & Heister, S.D. (2000). Combustion experiments in hydrogen peroxide/polyethylene hybrid rocket with catalytic ignition. *J. Propul. Power*, *16*(2), 318-326. https://doi.org/10.2514/2.5571

[40] Schneider, S., Hawkins, T., Rosander, M., Vaghjiani, G., Chambreau, S., & Drake, G. (2008). Ionic liquids as hypergolic fuels. *Energy Fuels*, *22*, 2871-2872. https://doi.org/10.1021/ef800286b

[41] Baikousi, M., Chalmpes, N., Spyrou, K., Bourlinos, A.B., Avgeropoulos, A., Gournis, D., & Karakassides, M.A. (2019). Direct production of carbon nanosheets by self-ignition of pyrophoric lithium dialkylamides in air. *Mater. Lett.*, *254*, 58-61. https://doi.org/10.1016/j.matlet.2019.07.019

[42] Chalmpes, N., Spyrou, K., Bourlinos, A.B., Moschovas, D., Avgeropoulos, A., Karakassides, M.A., & Gournis, D. (2020). Synthesis of highly crystalline graphite from spontaneous ignition of in situ derived acetylene and chlorine at ambient conditions. *Molecules*, *25*, 297, 1-6. https://doi.org/10.3390/molecules25020297

[43] Chalmpes, N., Asimakopoulos, G., Spyrou, K., Vasilopoulos, K.C., Bourlinos, A.B., Moschovas, D., Avgeropoulos, A., Karakassides, M.A., & Gournis, D. (2020). Functional carbon materials derived through hypergolic reactions at ambient conditions. *Nanomaterials, 10*, 566, 1-13. https://doi.org/10.3390/nano10030566

[44] Chalmpes, N., Spyrou, K., Vasilopoulos, K.C., Bourlinos, A.B., Moschovas, D., Avgeropoulos, A., Gioti, C., Karakassides, M.A., & Gournis, D. (2020). Hypergolics in carbon nanomaterials synthesis: New paradigms and perspectives. *Molecules*, *25*, 2207. https://doi.org/10.3390/molecules25092207

[45] Bourlinos, A.B., Chalmpes, N., Gournis, D., & Karakassides, M.A. (2022). Hypergolic materials synthesis: A review. *J. Nanotechnol. Res.*, *4*(2)*, 059-096. https://doi.org/10.26502/jnr.2688-85210031

[46] Natan, B., Perteghella, V., & Solomon, Y. (2011). Hypergolic ignition by fuel gelation and suspension of reactive or catalyst particles. *J. Propul. Power*, *27*(5), 1145-1149. https://doi.org/10.2514/1.B34130

[47] Zhao, X., Wang, J., Jin, Y., Wang, K., & Zhang, Q. (2022). Energetic complexes as promoters for the green hypergolic bipropellant of EIL-H2O2 combinations. *FirePhysChem*, *2*(29),185-190. https://doi.org/10.1016/j.fpc.2021.11.006

[48] Bhosale, V.K., Jeong, J., Choi, J., Churchill, D.G., Lee, Y., & Kwon, S. (2020). Additive-promoted hypergolic ignition of ionic liquid with hydrogen peroxide. *Combustion and Flame*, *214*, 426-436. https://doi.org/10.1016/j.combustflame.2020.01.013

[49] Bhosale, V.K., Jeong, J., & Kwon, S. (2019). Ignition of boron-based green hypergolic fuels with hydrogen peroxide. *Fuel*, *255*, 115729. https://doi.org/10.1016/j.fuel.2019.115729

[50] Bourlinos, A.B. (2022). A new generation of carbon-containing hypergolic fuels based on

water-ignitable C-NaH mixtures. *Journal of Nanotechnology Research*, *4*(1), 001-009. https://doi.org/10.26502/jnr.2688-85210026

[51] Nath, S., Laso, I., Mallick, L., Sobe, Z., Koffler, S., Blumer-Ganon, B., Borzin, E., Libis, N., & Lefkowitz, J.K. (2022). Comprehensive ignition characterization of a non toxic hypergolic hybrid rocket propellant. *Proceedings of the Combustion Institute*, in press. https://doi.org/10.1016/j.proci.2022.07.118

[52] Wang, B., Wang, Z., Jin, Y., & Wang, K. (2022). Designing difunctional promoters for hypergolic ignitions of green bipropellants combining ionic liquids with H_2O_2. *Ind. Eng. Chem. Res.*, *61*(48), 17433-17439. https://orcid.org/0000-0002-4965-6719

[53] Castaneda, D.A., & Natan, B. (2022). Hypergolic ignition of hydrogen peroxide with various solid fuels. *Fuel, 316*, 123432. https://doi.org/10.1016/j.fuel.2022.123432

[54] Rusek, J.J. (2004). Hydrogen peroxide for propulsion and power applications: A swift perspective. *Proceedings of the 2nd International Conference on Green Propellants for Space Propulsion* (ESA SP-557), 7-8 June 2004, Sardinia, Italy.

[55] Schneider, S., Hawkins, T., Rosander, M., Ahmed, Y., Mills, J., & Hudgens, L. (2011). Green hypergolic bipropellants: H_2O_2/Hydrogen-rich ionic liquids. *Prepr. Am. Chem. Soc. Div. Pet. Chem.*, *55*, 158.

[56] Zhang, Y., & Shreeve, J.M., (2011). Dicyanoborate-based ionic liquids as hypergolic fluids. *Angew. Chem. Int. Ed.*, *50*, 935-937. https://doi.org/10.1002/anie.201005748

[57] Titov, L.V., Gavrilova, L.A., Eremin, E.R., Mishchenchuk, S.S., & Rosolovskii, V.Y. (1971). Tetrabutylammonium borohydride and its complex with aluminum borohydride. *Izv. Akad. Nauk SSSR Ser. Khim.*, *6*, 1354-1356. https://doi.org/10.1007/BF00855404

[58] Noeth, H., & Ehemann, M. (1967). Triple hydrides of aluminum and beryllium. *J. Chem. Soc. Chem. Commun.*, *14*, 685-686. https://doi.org/10.1039/C19670000685

[59] Sippel, T.R., Shark, S.C., Hinkelman, M.C., Pourpoint, T.L., Son, S.F., & Heister, S.D. (2011). Hypergolic ignition of metal hydride-based fuels with hydrogen peroxide. *Organized by the Eastern States Section of the Combustion Institute and Hosted by the Georgia Institute of Technology*, Atlanta, GA, March 20-23, 2011.

[60] Jin, Y., Zhang, W., Zhou, Z., Liu, T., Xia, H., Huang, S., & Zhang, Q. (2022). Recent advances in hypergolic ionic liquids with broad potential for propellant applications. *FirePhysChem.*, *2*, 236-252. https://doi.org/10.1016/j.fpc.2022.04.001