



Review

# H<sub>2</sub>O<sub>2</sub> and HAN Green Monopropellants—A State-of-the-Art Review on Their Recent Development, Corresponding Synthesized Catalysts, and Their Possible Use as Thrusters

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**Abstract:** This review provides a state-of-the-art and up-to-date analysis of the design and development of green monopropellant thrusters based on hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and hydroxyl ammonium nitrate (HAN) as high-energy compounds for reaction control maneuvering of satellites. In summary, we introduce the new concept of Green Liquid Propellants (GLPs) that can serve as eco-friendly alternatives to conventional hydrazine thrusters. GLPs offer several advantages, including low toxicity, acceptable thermal decomposition and combustion behaviors, low onset temperatures of decomposition, stability, and long-term storability, compared to hydrazine. H<sub>2</sub>O<sub>2</sub> exhibits a low onset temperature; however, its storability does not match that of hydrazine. On the other hand, HAN boasts excellent storability; however, it comes with a higher onset temperature when compared to hydrazine. This review provides critical insights into the recent advancements in H<sub>2</sub>O<sub>2</sub> and HAN thrusters, along with an examination of the corresponding catalysts. The focus is on their application for the long-term maneuvering of satellites. We have chosen  $H_2O_2$  and HAN formulations to focus on these two GLPs due to their extensive use by various space agencies worldwide. Moreover, the future directives of both selected green propellants were discussed for potential applications. Finally, the choice between H<sub>2</sub>O<sub>2</sub> and HAN depends on the specific requirements of the propulsion system, taking into account factors such as performance, environmental impact, safety, and operational considerations. Each propellant has its advantages and challenges, and ongoing research aims to address some of the limitations associated with these green propellants.

**Keywords:** hydrazine; monopropellants;  $H_2O_2$ ; HAN; eco-friendly; conventional propellants; thruster; low toxicity; reaction control system



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## 1. Introduction

The need for satellite mobility has increased globally in recent years, which has increased rivalry in the commercial space sector. In order to succeed in this very competitive environment, cost-effectiveness, improved performance, and faster turnaround times are essential. More and more performance is required, especially in the area of propulsion systems that regulate the orbit and attitude of spacecraft, such as rockets, satellites, and space probes [1,2]. These systems must also be more affordable, easier to operate, and require less propellant. The next wave of propulsion systems will be shaped by the impending transition from hazardous alternatives to ecologically benign propellants, or "Green Liquid Propellants" (GLPs).

Common hydrazine ( $N_2H_4$ ) is currently the most extensively utilized monopropellant for in-space satellite propulsion systems. But the use of this material has brought up serious toxicity concerns. It was included as a hazardous compound of high concern in the European Union's Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) list in 2011. Although it is unlikely that hydrazine will ever be completely banned, its carcinogenic qualities and the strict safety precautions it requires continue to raise concerns. These issues have a disproportionately negative effect on smaller propulsion systems that use hydrazine in terms of cost and ease of usage. Consequently, a proactive search and development of substitute, low-toxicity GLPs is underway [3,4].

Actually, a number of researchers have been working on developing GLPs as an alternative to hydrazine for Reaction Control of Satellites (RCS). GLPs can be employed in pilot scale-up missions [5,6] because of their low toxicity, appropriate combustion/decomposition properties, stability, and storability for long-term usage [7,8]. The development of environmentally friendly and green propellants, such as hydroxyl ammonium nitrate (NH<sub>3</sub>OH<sup>+</sup>·NO<sub>3</sub><sup>-</sup>, known as HAN) [9–13] and ammonium dinitramide nitrate (NH<sub>4</sub><sup>+</sup>·N(NO<sub>2</sub>)<sub>2</sub><sup>-</sup>, known as ADN) [14–17], ionic liquid solutions, H<sub>2</sub>O<sub>2</sub> [18–20], LOx/LH<sub>2</sub> binary propellant [21], and electrolysis water propulsion systems [22,23], has initiated the replacement of hydrazine.

Recently, two books were published showing the recent progress in green energetic propellants for micropropulsion systems [24,25] such as HAN [26–28],  $H_2O_2$  [29,30], ADN [31], and honeycomb catalysts applied to their decomposition [32].

This review covers the evolution of  $H_2O_2$  and HAN as GLPs, including how they went from liquid states to being used in propulsion. Moreover, their application in different classes of thrusters was revised and shown.

## 2. Characteristics of H<sub>2</sub>O<sub>2</sub> and HAN Green Monopropellants

## 2.1. Characteristics of $H_2O_2$ Propellant

Since 1938,  $H_2O_2$  has been used as a monopropellant in a variety of aerospace applications [33]. The concentration of  $H_2O_2$  in an aqueous solution is used to classify it, while the concentration of stabilizers and contaminants is used to grade it [34]. Exceeding 85% weight concentration, High-Test Peroxide (HTP) is a very concentrated type of hydrogen peroxide. Rocket-grade HTP is used in space propulsion for low- and medium-thrust applications; it is usually concentrated to a 98% degree. The non-toxic nature of 98% HTP and its high density of approximately 1.43 g cm<sup>-3</sup> make it a desirable choice for propulsion system storage. It can be catalytically decomposed in monopropellant systems, at temperatures as high as 1222 K [35]. With 1 MPa and 50:1 expansion circumstances, HTP 98% performs 20% worse in monopropellant systems than hydrazine [36], resulting in a specific impulse (Isp) of about 186 s. But it can attain Isp exceeding 325 s (combustion temperature 2752 K) in bipropellant systems, especially with organic compounds such as ethanol [37], which makes it a very competitive propellant for this kind of propulsion system.

HTP 87.5% is a hydrogen peroxide concentration that is frequently employed. It has a density of about 1.38 g cm $^{-3}$  at 20 °C, an area ratio (Ae/At) of 7.841 at sea level, and a theoretical specific impulse of about 144 s when assessed at a chamber pressure of 1 MPa [38]. Using the shifting equilibrium model for the entire nozzle, hydrogen peroxide at concentrations of 90% and 85% was simulated on Rocket Propulsion Analysis (RPA). The results showed theoretical vacuum-specific impulses of 172.13 and 150.47 s, chamber temperatures of 1019.3 and 892.65 K at 1 MPa, and expansion ratios of 40:1 and 10:1, respectively [39].

Although the performance values of the Hydrogen Peroxide Aqueous Solutions (HPAS) class are not as high as those of other green monopropellants, it has an unusual feature that attracts the attention of rocket propulsion designers who want to maximize system performance while minimizing space. The hypergolic ignition of hydrogen peroxide with different propellants is a characteristic that sets it apart and makes it a promising option for in-space propulsion systems. The hypergolic ignition of hydrogen peroxide with organic compounds such as ethanol [40] and propyne [41] has been the subject of extensive investigation. Furthermore, ionic liquid fuels such as 1-ethyl-3-methyl imidazolium cyanoborohydride ([EMIM][BH<sub>3</sub>CN]) [42] and 1-allyl-3-ethyl imidazolium cyanoborohydride ([AEIM][BH<sub>3</sub>CN]) [43] were investigated for hypergolic ignition. Through these studies, new generations of green propellants known as green hypergolic ionic liquids, or HILs for efficient in-orbit bipropellant propulsion systems will be made possible [39,44].

#### 2.2. Characteristics of HAN Propellant

A lot of research was conducted on HAN-based formulations in the 1980s, when amines were important fuel ingredients. Diethylhydroxylamine (DEAN) was incorporated as an addition in the LGP 1898 mix, whereas triethylammonium nitrate (TEAN) was used in formulations including LGP 1845, LGP 1846, and XM46. Both additions functioned as energizers based on nitrate. As with ADN-based formulations, these propellants' adiabatic combustion temperatures depended on the amount of water and amine fuel they contained [45]. Investigations further revealed that ternary amines stabilized the HAN molecule's decomposition processes, preventing uncontrollably large gas phase events or micro-explosions [46]. Subsequent investigations revealed a pressure dependence in HAN degradation [47].

The original advanced HAN formulations with alternate fuel components that may ignite through catalytic decomposition included glycine or methanol as the main fuels in addition to thermal ignition. HANGLY26, a HAN formulation based on glycine, showed sensitivity to the commonly used Shell-405 (S-405) catalyst, hence guaranteeing sufficient compatibility and stability of the heat catalyst [48]. Conversely, formulations containing methanol burned at higher temperatures than those containing glycine, which limited the lifetime of solid catalysts. HAN-based monopropellants are generally highly sensitive to contaminants, temperature fluctuations, or pH changes in terms of storability and durability. For example, binary HAN–water solutions do not promote long-term stability because of autocatalytic processes that speed up in acidic environments. In addition to ammonium nitrate, byproducts including nitric acid and dihydroxylamine are produced. Since the dihydroxylamine that is created in the interim is naturally unstable in acidic settings, it decomposes down into water and nitrous oxide [49].

Apart from the aforementioned sensitivity to particular pH ranges, metallic contaminants resulting from HAN manufacturing or storage tank conditions have a substantial effect on HAN decomposition reactions. Iron and copper ions, among other metallic ions, can react with the  $[NH_3OH]^+$  cation. The resulting nitric acid can corrode tanks or feeding lines if it is untreated for a long time. This further restricts storability when combined with

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high temperatures [50]. The reductive character of iron and copper ions and their easy production of equivalent redox pairs is thought to be the cause of the HAN molecule's decomposition in their presence. Tests for material compatibility and chemical analysis of highly concentrated binary HAN–water combinations validated this claim. The propellant blend XM46 was used in experiments where steel and different metallic samples were stored for long periods of time at high temperatures (up to 65 °C). Consequently, samples that came into contact with nickel (such as Ni200) or copper alloys showed bluish staining of the aqueous fuels. Samples of propellant treated with pure tantalum and titanium metal showed no evidence of deterioration and were considered fit for storage. Moreover, it was discovered that a rise in temperature had a negative impact on the rate of HAN decomposition [51,52].

The aforementioned limitations concerning long-term stability, contamination, and the susceptibility of HAN molecule decomposition impede the ongoing utilization of these monopropellants in technical applications, even with the substantial experimental research conducted on the HAN-based formulation XM46. As a result, research into possible stabilizing agents has begun [53].

Chelation agents are compounds that are introduced in order to collect metallic impurities, as is standard procedure in chemical processing. Many possible candidates for HAN have been found and evaluated over time. This study placed special emphasis on polyphosphonates and ethylenediamine tetraacetic acid (EDTA) salts [54]. Still, the results turned out to be inadequate. The stabilizer's effectiveness was gradually reduced as a result of significant changes in the propellant's parameters brought about by internal chemical changes in the propellant composition brought about by chemical reactions [53].

A more modern monopropellant formulation, AF-M315E, was created by the Air Force Research Laboratory in the latter part of the 1990s. In the Green Propellant Infusion Mission (GPIM), it was used and tested in place of hydrazine [55]. Interestingly, AF-M315E has a density-specific impulse (Isp) that is around 50% greater than hydrazine [56]. Because its compounds have low volatility, AF-M315E has enhanced safety qualities when handling and storing. The ecologically benign ionic liquids (EILs) in this liquid blend are water, HAN, and hydroxyethyl hydrazinium nitrate (HEHN) [57].

Kakami et al. [58] revealed that HAN/hydrazinium nitrate (HN)-based monopropellants had a greater density, ranging from 1.4 to 1.5 g cm $^{-3}$ , compared to their hydrazine-based counterparts, which have a density of 1.0 g cm $^{-3}$ . The density-specific impulse is enhanced by this significant increase in density, which permits fuel tanks and other supporting structures to weigh less. Although they are slightly more viscous than alternatives based on hydrazine, their low solidifying point of  $-35\,^{\circ}$ C makes them more useful in low-temperature settings. The viscosity is controllable, depending on the composition; therefore, it is feasible to supply these monopropellants [58].

The development of liquid gun propellants (LGPs) in the U.S. Army is where HAN-based monopropellants first emerged [59]. Three LGP formulations were the focus of the development: LP1846, LP1845, and LP1898. These aqueous solutions are based on HAN/TEAN (tri-ethanol-ammonium nitrate) in the first two cases, and HAN/DEHAN (diethyl hydroxyl ammonium nitrate) in the third. However, because of their high combustion temperature (2500 K [8]) and relatively low combustion pressure [60], these propellants were determined to be inappropriate for use in rockets.

Following these constraints, the U.S. Air Force Research Laboratory (AFRL) developed the state-of-the-art Air Force Monopropellant 315E (AF-M315E), a HAN-based green monopropellant intended for space propulsion [38,61].

Another interesting HAN-based green propellant that has been developed since 2000 at the Institute of Space and Astronautical Science (ISAS)/Japan Aerospace Exploration

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Agency (JAXA) is Sei-Hori propellant (16.3% of methanol) (SHP163). This propellant, which contains 73.6 weight percent HAN, 3.9 weight percent ammonium nitrate (AN), 16.3 weight percent methanol (MEO), and 6.2 weight percent water, has a density of 1.4 g cm<sup>-3</sup> and a high volumetric specific impulse ( $\rho \times \text{Isp}$ ) of 396 g s cm<sup>-3</sup>, which is higher than AF-315E in certain circumstances (at 0.7 MPa chamber pressure and 50:1 nozzle expansion ratio at frozen conditions) [62]. It is noteworthy that the flame temperature rises to about 2400 K [38,62].

SHP163, one of the most energetic propellants for thruster use, is a good choice for a safe and environmentally friendly liquid propellant since it meets safety requirements and exhibits operating stability [63]. Remarkably, SHP163 can only be ignited at pressures of 1.0 MPa with the use of a heated catalyst bed [38,64,65]. Last but not least, the effectiveness of SHP163 was verified in orbit using the Green Propellant Reaction Control System (GPRCS) and a 1 N class thruster on the JAXA-launched Rapid Innovative Payload Demonstration Satellite 1 (RAPIS-1). The High-performance Non-detonating Propellant (HNPxxxx) family is a line of green propellants based on HAN/HN that was developed for more than ten years by IHI Aerospace Co., in Japan. HNP209, HNP221, and HNP225 are members of this green monopropellant family and are made of HAN, HN, methanol, and water [57]. Interestingly, compared to hydrazine, every member of this family has a volume-specific impulse ( $\rho \times Isp$ ) that is superior. Their comparatively low adiabatic flame temperature, when compared to other energetic ionic liquid monopropellants such as AF-M315E and SHP163, is what makes them unique. For example, HNP209 usually has a theoretical specific impulse of about 260 s, and its maximum combustion temperature is about 1900 K. On the other hand, HNP221 and HNP225 demonstrate specific impulses of 241 and 213 s, respectively, when the expansion ratio is 100:1 and the chamber pressure is 1.0 MPa [35,66-68].

# 3. Development of H<sub>2</sub>O<sub>2</sub> and HAN Green Monopropellants

Finding substitutes for the most widely used rocket fuel, hydrazine and some of its derivatives, notably Unsymmetrical Dimethylhydrazine (UDMH) and Monomethylhydrazine (MMH), is the main goal of research and development (R&D) in the field of green propellants [69–71]. These compounds' intrinsic high toxicity and related risks not only make handling and management challenging but also result in substantial expenses. This requires that safety and security procedures be followed to the letter [72,73]. Due to its detrimental effects, hydrazine was listed as a Substance of Very High Concern (SVHC) by the European Union in 2011 [72,74] and is recognized as a dangerous substance in the majority of countries worldwide [38,75,76]. Although REACH has not yet implemented explicit steps to outlaw hydrazine, its use is predicted to increase in the future and is projected to have a substantial effect on the space propulsion sector [62]. This environment offers a strong motivation to develop green propellant research in order to find appropriate substitutes [38,69,70]. Furthermore, less hazardous substances that maintain excellent propulsive performance even when held at room temperature are referred to as "green propellants" [62,64]. Although most non-hydrazine propellants are now frequently referred to as "green", it is crucial to remember that this phrase actually refers to "greener" propellants, which are safer but still need to be used with the appropriate safety procedures [70]. Owing to their widespread use in recent times, this mini-review has opted to focus exclusively on  $H_2O_2$  and HAN as GLPs, despite the large number of developed green propellants available.

#### 3.1. $H_2O_2$ Composition as Monopropellant

High-Test Peroxide (HTP) is marketed as a high-density monopropellant alternative that is safe for the environment. It provides a specific impulse of up to 180 s in vacuum when using 98% HTP, but its efficiency is marginally lower than that of hydrazine. However, HTP is a more effective and economical option because of its greater density-specific impulse when compared to hydrazine systems. This is especially important for relatively small spacecraft platforms where budgetary constraints, size restrictions, and mechanical design sometimes take precedence over the desire for a higher specific impulse [77].

Resilient and cost-effective satellite propulsion technologies are becoming more and more preferred as orbital launch prices continue to drop, even if they lead to a possibly larger total mass. The propulsion of HTP monopropellant thrusters can be achieved with either catalytic decomposition [78,79] or thermal decomposition [80]. HTP is becoming a more viable alternative for spacecraft and rocket RCS due to its cost benefits over most liquid monopropellants and the rising operational and safety-related costs connected with hydrazine.

## 3.2. Available Catalysts for H<sub>2</sub>O<sub>2</sub> Propellant Decomposition

As a possible GLP, heterogeneous catalysts were created to completely degrade  $H_2O_2$ . We go over the most recently developed systems, {HTP + catalysts}, in this part.

First, oxide compounds were created without noble metals that were modeled using computationally complicated (CC) principles. These compounds were created by undergoing high-temperature solid-state reactions on commercially available, pure precursor oxide powders, which produced the decomposition of 30–50 weight percent  $H_2O_2$ . In addition to the obvious benefit of using well-established, non-toxic, and efficient catalytic agents such as ZnO, CuO, MgO, CaO, and MnO<sub>2</sub> oxides [81], we also compared the performance of these catalysts to a commercial counterpart that included 5% Pd on alumina pellets produced by Alfa AESAR (i.e., Figure 1). The cylinder-shaped  $Al_2O_3$ -based pellets that make up this industrial catalyst have a specific surface area of about  $1.1 \text{ m}^2 \text{ kg}^{-1}$  [81].



**Figure 1.** Catalytic chamber filled of commercial  $Pd/Al_2O_3$  pellets. Reproduced from [81] with permission under OA Creative Commons Attribution-Non Commercial 4.0 International License (CC BY-NC 4.0).

For the decomposition of hydrogen peroxide, a manganese oxide  $(MnO_2)$ -based catalyst was used. Palladium (Pd) doped on a commercial alumina  $(Pd/Al_2O_3)$  catalyst served as a promoter to increase the catalytic reactivity of  $MnO_2$ . Furthermore, bimodal-type1/8-inch alumina pellets from Alfa Aesar in the U.S. were used to create the catalytic substrate. The Brunauer–Emmet–Teller (BET) surface area of these pellets is roughly

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255 m<sup>2</sup> g<sup>-1</sup>. This catalyst was remarkably shown to be able to decompose ninety weight percent of  $H_2O_2$  [81].

 $MnO_2$  is a very powerful catalyst for the decomposition of  $H_2O_2$ , responsible for decomposing down 90% of the gas [82]. As a result,  $MnO_2$  with an alumina support was chosen as the catalyst in this investigation. The process for preparing the catalyst was taken from An et al. [83].

As shown in Figure 2, two different catalysts were used to obtain a 95 weight percent decomposition of  $H_2O_2$ :  $MnOx/\gamma-Al_2O_3$  and MnOx/lanthanum-doped alumina ( $La/Al_2O_3$ ). The purpose of this selection was to offer a more thorough understanding of catalyst bed design. According to the study, the  $MnOx/La/Al_2O_3$  catalyst had a mechanical strength that was almost 57.7% more than the  $MnOx/\gamma-Al_2O_3$  catalyst in bulk crushing tests. Because of the increased mechanical robustness that results from lanthanum being incorporated into the alumina pellets, it is envisaged that the  $MnOx/La/Al_2O_3$  catalyst will help to minimize changes in pellet distribution within the catalyst bed during fire experiments [84].



**Figure 2.** Prepared catalysts (**left**:  $MnOx/La/Al_2O_3$ ; **right**:  $MnO_x/\gamma-Al_2O_3$ ) [84]. Reproduced from [84] with Springer Nature's permission.

In a stainless steel reactor, cobalt nitrate, manganese nitrate, and urea were carefully mixed with the bare minimum of distilled water while being stirred by magnets. The exact values were selected in order to determine a 1:2 cobalt-to-manganese molar ratio. In addition, two more sets of samples with cobalt-to-manganese molar ratios of 1:1 and 2:1 were carefully constructed. These catalytic preparations were then used to decompose thirty weight percent of  $H_2O_2$  [85].

Two catalysts were employed in the decomposition of 98%  $H_2O_2$ . Actually, 5% by mass of catalytic active phase content is a common, commercially accessible product of platinum (Pt) supported on  $\gamma$ -alumina carrier [86]. The second catalyst, MnO<sub>2</sub> (silica-doped  $\alpha$ -alumina supported), produced by the Łukasiewicz Institute of Aviation, is described in detail in references [78,86,87]. It is shown in Figure 3.



**Figure 3.** MnO<sub>2</sub> catalyst, supported on  $\alpha$ -alumina: (a) pre-test view and (b) post-test condition [86].

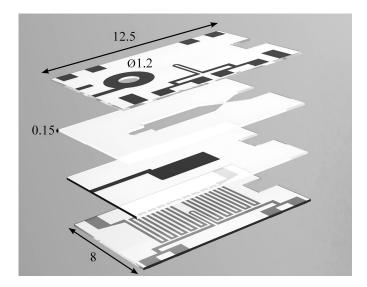
The effective testing of CoMn-based oxides with a spinel structure as catalysts for hydrogen peroxide decomposition was reported by Bispo et al. [85]. Because of the creation of free sites on the surface, materials with a high cobalt content in the octahedral interstices in particular have increased catalytic activity [88,89]. With their different oxidation states, cobalt and manganese offer excellent support for redox reactions and show promise for catalytic applications such as  $H_2O_2$  decomposition. The self-combustion synthesis process is preferred due to its controllability and simplicity. It is commonly used for the creation of oxides, including spinels. Significantly, synthetic parameters influence factors such cation distribution in tetrahedral and octahedral positions, purity, crystal size, morphology, and, ultimately, catalytic activity, which all have an impact on the morphological and structural properties of the products. The goal of this research is to determine the ideal shape, structural configuration, and chemical composition for better  $H_2O_2$  decomposition catalysts. It emphasizes the need to optimize synthesis parameters for efficient material production. As a result, the research explores the composition, structure, and attributes of CoMn-spinels as well as how they affect catalytic performance [85].

In order to decompose cold  $H_2O_2$  on its own, Maia et al. [90] presented an extruded material made from a bulk catalyst consisting of oxides of manganese and cobalt. The catalyst was carefully made by co-precipitating aluminum, manganese, and cobalt nitrates (Sigma-Aldrich) in a room temperature  $Na_2CO_3$  solution while adding a NaOH solution to keep the pH at 10. The 4:1:1 mole ratio (Co:Mn:Al) was used. Following filtering, washing, drying, and maceration, the final product was processed. The powder was then peptized using an  $HNO_3$  solution, and it was then extruded, dried on a burner, and heated to 900 °C for calcination. The final product had a cylindrical shape and was around 2 mm in diameter and 3 mm in length.

Khaji et al. [18] discovered that both qualitative and quantitative research was performed on the decomposition of 50 wt.%  $\rm H_2O_2$  as a monopropellant. This required altering the flow rate (15–55  $\rm \mu L~min^{-1}$ ), changing the catalyst (between silver (Ag) and platinum (Pt)), and regulating the working temperature (115–300 °C). The Ag catalyst showed improved stability, with Pt proving even more stable, as compared to a reference device without a catalyst, which showed unstable behavior due to limited decomposition. Furthermore, Pt was discovered to be slightly more successful in encouraging decomposition. Pt and Ag showed slightly different values quantitatively when it came to the amount of power needed to keep the temperature constant. Additionally, the study effectively demonstrated novel techniques for in situ Ag electroplating and the creation of a porous Pt bed (i.e., Figure 4). The platinum surfaces that are porous and non-porous have a greater effective surface area than the surface that is electroplated with silver [18].

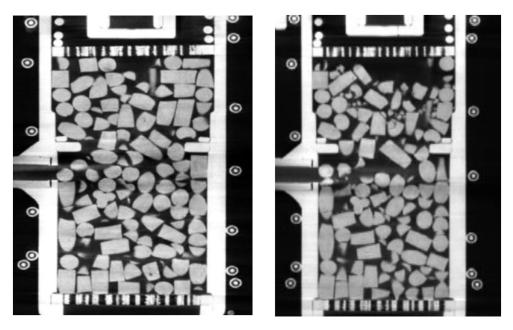
In their investigation, Ryan et al. [91] used ceria pellets, which were cylindrical in shape and measured roughly 1.4 mm in diameter and 6 mm in length, as a catalyst. Manganese oxides (MnOx) in an active phase were applied to these pellets. Previously, this specific catalyst was created and tested in a 20 N monopropellant thruster using 87.5% HTP with success [92].

Under sea level air conditions, the Mk 0 thruster was used for the tests. Because of the large nozzle area ratio, thrust and particular impulse measurements are therefore not covered. The thruster was run at inlet pressures (Pin) between 5.5 and 25 bar, which is representative of the circumstances the device encounters on a satellite platform while it is in blow-down mode. It was possible to achieve steady-state conditions with each run lasting 180 s [91].



**Figure 4.** An exploded view of the thruster design, arranged from bottom to top. Starting from the bottom, there is the floor layer housing the heater and temperature sensor. The catalytic layer is located above it, and the chamber wall layer, which includes the nozzle, comes next. The connecting pads, temperature sensor, and propellant inlet are all located on the upper, or lid, layer (noticeably creating a loop in the center). It is crucial to remember that the bottom layer is reversed in this illustration, so that the heater is actually pointing down. All measurements are given in millimeters and are given before the sintering process, which causes the component to shrink by around 20% [18].

Additionally, Ryan et al. [91] investigated a different commercially accessible catalyst material made of  $\gamma$ -alumina particles covered in platinum. Despite their asymmetrical form, these particles were far smaller than the cylindrical ceria pellets that were previously in use, with an average diameter of 1.2 mm. It was anticipated that this size reduction would increase the packing density inside the bed, and CT scans supported this theory. A 10% improvement over the ceria-based catalyst was shown by the void fraction of 0.42 with the smaller  $\gamma$ -alumina-based catalyst, as shown in Figure 5 of the analysis of the collected images.



**Figure 5.** CT scan of ceria-based catalyst before (**left**) and after (**right**) testing [91]. Reprinted from Ref. [91] with permission from AIAA.

Apart from obtaining a larger surface area with these smaller particles, it is expected that the higher packing density will hinder particle motion in the bed, which could lead to less mechanical damage to the catalyst pellets [91].

Iron oxide is also considered for  $H_2O_2$  decomposition, as discussed in the study conducted by Lin and Gurol [93] and Molamahmood et al. [94]. The research focuses on the heterogeneous catalytic reactions of  $H_2O_2$  with granular-sized goethite (R-FeOOH) particles in an aqueous solution under various experimental conditions [93]. The granular goethite was purchased from Aldrich Chemical Co. and has a size range of 0.2–0.6 mm (30–80 mesh). These particles were produced using proprietary material to bind the colloidal goethite particles. The experimental evidence suggests that the goethite particles may play an important role in the fate of  $H_2O_2$  in surface and seawater. Sunlight or direct mediation by aquatic Fe (II and III) and other metal ions does not appear to be necessary for the reactions to occur.

However, Molamahmood et al. [94] investigated six iron minerals (hematite, magnetite, maghemite, goethite, feroxyhyte, and ferrihydrite) for  $H_2O_2$  decomposition by analyzing the normalized kinetic rate constants of  $H_2O_2$  decomposition. The results show that  $H_2O_2$  decomposition over iron minerals is a surface-related heterogeneous process. Hematite and goethite are the most promising minerals for environmental cleanup in terms of reactive oxygen species (ROS) production, as their  $H_2O_2$  utilization efficiency for benzoic acid (BA) degradation is the highest among the six iron minerals. Magnetite and maghemite are highly active for both  $H_2O_2$  decomposition and  $O_2$  production at neutral and basic pH.

#### 3.3. HAN Composition as Monopropellant

In the past, the U.S. Army launched a study called LP1845 that used HAN as a liquid cannon propellant. Water, TEAN, and HAN were the ingredients of the aqueous solution [95,96]. A somewhat modified version, LP1846, was then created, consisting of water, TEAN, and HAN (with 60, 20, and 20 weight percent, respectively) (i.e., Table 1). In comparison to LP1845, LP1846 demonstrated better propulsive performance and ignitability. Due to the intense development process that it went through, LP1846 was later reclassified as XM-46 [97,98]. Following the reference given by Ferguson et al. [99], they created a combination that had the same composition as reference [100], consisting of 70.1 wt.% HAN, 15.0 wt.% water, and 14.9 wt.% methanol. With a strand burner operating at different pressures, they carried out an extensive investigation on the combustion properties of this mixture. In a similar vein, Amrousse et al. created ternary liquid monopropellants by combining HAN with methanol/water and ethanol/water, as documented in [101]. They investigated factors such as the beginning decomposition temperature and how various solvents affected the reactivity of HAN solutions. A more modern formulation, designated AF-M315E, was developed by the U.S. Air Force Research Laboratory. It is composed of HAN, 2-hydroxylethylhydrazinium nitrate (HEHN), and water [54,61,102]. A summary of various HAN-based monopropellant formulations with the weight percentages of each of their constituent components is given in the following table:

| <b>Table 1.</b> Different HAN-based mone | opropellant formulations | [62,102–104]. |
|--|--------------------------|---------------|
|--|--------------------------|---------------|

| Propellants    | HAN-Based (wt.%) | Additives (wt.%) |                                    |
|----------------|------------------|------------------|------------------------------------|
| LP-1845        | HAN = 63.2       | TEAN = 20        | $H_2O = 16.8$                      |
| LP-1846        | HAN = 60.8       | TEAN = 19.2      | $H_2O = 20$                        |
| HAN-269-MEO-15 | HAN = 69.7       | MeOH = 14.8      | $AN = 0.6$ and $H_2O = 14.9$       |
| SHP-163        | HAN = 73.6       | MeOH = 16.3      | $AN = 3.9 \text{ and } H_2O = 6.2$ |
| AF-M315E       | HAN = 44.5       | HEHN = 44.5      | $H_2O = 11$                        |

#### 3.4. Available Catalysts for HAN Propellant Decomposition

Several catalysts were developed and evaluated to decompose HAN-based monopropellants for thruster applications. These catalysts performed exceptionally well in fire tests and thermal analysis.

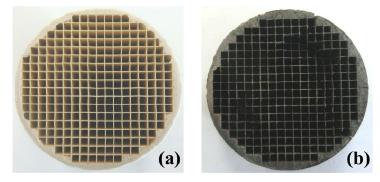
Agnihotri and Oommen used the co-precipitation technique to create cobalt-doped ceria catalysts. The effectiveness of these catalysts was evaluated by contrasting them with an iridium-supported  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst that was made by repeated wet impregnation. The predecessor of iridium metal was iridium chloride. After the procedures of drying and impregnation, the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> pellets were calcined [105].

The Pt/Al<sub>2</sub>O<sub>3</sub>Si catalyst was produced by Courthéoux et al., as described in reference [106]. Using the sol–gel method, they produced silicon-modified alumina supports by starting with silicon tetraethoxide (Si(O-C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) as the precursor for the silicon doping element and aluminum tri-sec-butoxide (Al(O-CH(CH<sub>3</sub>)-C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>) as the precursor for aluminum [107]. Using the micro-segmented flow synthesis approach, Bao et al. synthesized multi-walled carbon nanotubes (MWCNTs) into multi-walled carbon nanotube–polyvinyl alcohol (MWCNT-PVA) microspheres with a particle size comparable to binder [108,109].

Amrousse et al. studied two types of catalysts: honeycomb catalysts manufactured to order and commercially available granular Shell 405 (36%  $\rm Ir/Al_2O_3$ ; grain size = 25  $\mu m$ ), also known as S405 (i.e., Figure 6). The goal was to use iridium-based honeycomb catalysts with square channels (i.e., Figure 7) to replace the S405 catalyst, which deactivated in high-temperature combustion firings and lower experimental costs [110].



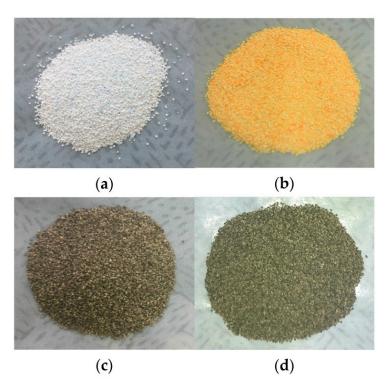
Figure 6. S405 catalyst (30% Ir/Al<sub>2</sub>O<sub>3</sub>) [110]. Reprinted from Ref. [110] with permission from Elsevier.



**Figure 7.** Honeycomb cross: (a) fresh cordierite and (b) after deposition of iridium [110]. Reprinted from Ref. [110] with permission from Elsevier.

The Pt/Barium hexaaluminate (BHA) catalyst was prepared by Kang et al. [111] using a wet impregnation method, as shown in Figure 8. The sol–gel technique is usually used to

create hexaaluminate catalyst supports. However, choosing the right binding agent and pelletization technique for hexaaluminate powder is a complex difficulty in the hexaaluminate production process. This is because hexaaluminate has inherent properties that make it extremely resistant to sintering and require certain sintering procedures [112–115].



**Figure 8.** Pt/Barium hexaaluminate (a) before Pt doping, (b) after impregnation, (c) after calcination, and (d) after reduction [111].

# 4. HAN and H<sub>2</sub>O<sub>2</sub> as Monopropellant Thrusters

Here, we have included a cross-sectional illustration of a monopropellant thruster that can run on  $H_2O_2$  or HAN. The monopropellant is compressed with inert gas (usually argon or nitrogen) and kept in a special tank. The catalyst bed is typically preheated. A mass flow meter and a solenoid valve are used to introduce a constant mass flow rate into the catalyst bed, as shown in Figure 9.

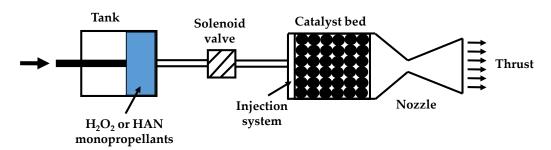
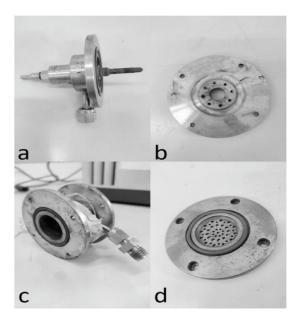


Figure 9. Section view of H<sub>2</sub>O<sub>2</sub> or HAN monopropellant thrusters.

# 4.1. $H_2O_2$ Monopropellant Thruster

Figure 10 shows the tiny experimental thruster configuration that Cassese et al. designed. A pressurized tank filled with  $N_2$  at a starting pressure of 20 MPa is part of this configuration. Moreover, a second 2 L tank holding an 87.5% concentrated  $H_2O_2$  monopropellant is present. An electronic Coriolis flow meter/regulator is used to precisely manage the propellant's mass flow rate.

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**Figure 10.** Picture of catalytic decomposition system components. (a) Glow plug-injection plate support flange. (b) Eight-hole injection plate. (c) Catalytic chamber. (d) Pellet containment plate. Reprinted from [116] with permission.

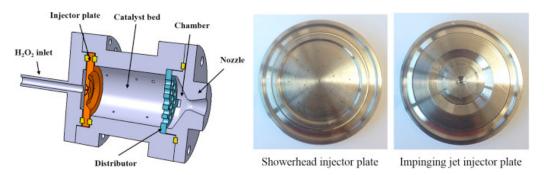
The catalytic chamber contains a stainless steel cylinder with a diameter of 25 mm and length of 36 mm. A catalytic bed is loosely packed inside this chamber. With a power input of up to 60 W, a standard diesel glow plug is used to preheat the catalytic bed right before propellant injection. A gauge pressure transducer (Setra mod. C206, referenced to 1 atm) and a K-type thermocouple are used to measure the temperature and pressure inside the catalytic chamber. Finally, a load cell is connected to the test bench, where the engine is safely positioned for thrust measurement [81].

The experiment exhibited the potential to promptly achieve stable operating conditions by avoiding delays and restricting propellant usage when conditions diverge from the usual specifications. As a result, the payload size can be decreased in relation to the amount of fuel needed to complete the trip. Strong reasons were presented, indicating that the shift from precious metal-based catalysts to a new class of oxide catalysts that are safe, eco-friendly, easily scalable, and do not contain noble metals is now feasible [81,116]. To investigate the response properties of a  $H_2O_2$  monopropellant thruster when employing various catalytic reactivities, Jo created two unique thruster configurations. With the aid of  $MnO_2$  and a mixture of  $MnO_2$  and PbO catalysts, these reactivities were evaluated. With minor differences in their aspect ratios, especially set at 1.0 and 1.95, both thrusters were meticulously built. However, the catalytic bed volumes in both arrangements were the same, at 12.25 cm<sup>3</sup>. A showerhead-style injector with 15 0.4 mm diameter orifices was used in both thruster configurations. Hydrogen peroxide could be precisely delivered to the catalytic reactor thanks to this injector's direct connection to the catalyst bed [117].

It was discovered that the catalyst used to decompose H<sub>2</sub>O<sub>2</sub> has an impact on the response characteristics, including the time it takes the thruster to reach its peak performance and the tail-off time, which is the point at which performance returns to baseline. Notably, the tail-off period is dramatically shortened when MnO<sub>2</sub> is replaced with a mixture of MnO<sub>2</sub> and PbO. The MnO<sub>2</sub>-mixed PbO catalyst shows a distinct advantage in damping pressure oscillations over a wide range of design parameters, such as feeding pressure and the aspect ratio of the catalytic bed, in terms of preserving chamber pressure stability [117].

A monopropellant thruster with a thrust of 50 N was created at a scale by Kang et al. Their main goal was to look at how the catalyst bed's properties were affected by various

injection patterns for 90% H<sub>2</sub>O<sub>2</sub>. A cross-section of the monopropellant thruster, showing the injector plates, is shown in Figure 11.



**Figure 11.** Cross-sectional drawing of 50 N scale monopropellant thruster and front views of injector plates. Reprinted from Ref. [118] with permission from Elsevier.

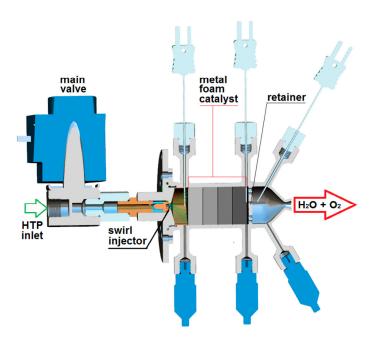
A specified mass flow rate of around 39.1 g s $^{-1}$  and a chamber pressure of 2 MPa are part of the thruster's design specifications. The thruster's adiabatic decomposition temperature can reach an astounding 700–750 °C. The dimensions of the catalyst bed are 40 mm in length and 27 mm in diameter. This thruster illustrated in Figure 11 is a noteworthy example of an engineering model because of how simple it is to assemble, thanks to the flange joints that attach all of the parts. Furthermore, it is easy to change the injector plate if needed [118].

It is possible to reduce catalyst bed and performance variations. Additionally, by effectively utilizing the pellets' whole active surface area during the atomization process, the size of the catalyst bed can be reduced. However, it is important to remember that the impinging jet injector's prolonged response time makes it less suitable for using a thruster in pulse mode [118]. As shown in Figure 12, Surmacz et al. constructed a  $H_2O_2$  thruster that operates at a pressure of 1 MPa. With a nominal mass flow rate of 15 g/s and a chamber pressure of 1 MPa, this thruster was painstakingly designed. The catalyst bed's dimensions 50 mm in length and 26 mm in diameter were carefully chosen, yielding a nominal aspect ratio of 1.9. A nominal bed loading of  $28 \text{ kg s}^{-1} \text{ m}^{-2}$  was determined. Using a swirl injector, which produced a 120-degree full-cone spray pattern that effectively coated the catalyst's front surface, the propellant was introduced into the catalyst bed with efficiency. Notably, the catalyst chamber's useful length was constrained to 42 mm in its current arrangement, resulting in a reduced aspect ratio of 1.6 [119].

The NiCrAl/Mn<sub>x</sub>O<sub>y</sub> catalyst's hot fire test series provided priceless information for assessing its applicability for 98%  $\rm H_2O_2$ -based propulsion systems. The catalyst's ignition characteristics, whether started from a cold start or a preheated bed, were experimentally validated. Investigations into both pulse mode and continuous operating modes were conducted in-depth. The efficiency of characteristic velocity showed that the catalyst bed performed remarkably well; it typically exceeded 96%. It is reasonable to assume that full propellant decomposition was attained during these experiments given the significant heat dissipation via the nozzle walls and case [119].

The performance characteristics of a new mixed oxide bulk catalyst intended for  $H_2O_2$  decomposition were studied by Maia et al. [90]. A 2 N thruster with modules that included different chambers, nozzles, and ring adapters manufactured from 316 stainless steel was used for the tests. Three chamber modules were designed in order to adjust the catalytic bed's proportions. Two nozzles and many rings of varying widths and lengths were also made in order to keep the catalytic beds in place. The thruster's theoretical performance was calculated using the NASA-CEA rocket performance code [120]. At 600 m altitude, where the tests were conducted, a nozzle expansion ratio of 1.45 and a chamber pressure of

5 bar were used to adjust the nozzle. The computed specific impulse was  $1040 \,\mathrm{m \ s^{-1}}$ , the theoretical characteristic velocity was  $940 \,\mathrm{m \ s^{-1}}$ , and the ideal thrust coefficient was 1.106, assuming frozen flow with  $90\% \,\mathrm{H}_2\mathrm{O}_2$ . Thermocouples and pressure transducers were positioned carefully before, after, and beside the catalytic bed. A graphical user interface created with LabView software was used to monitor and manage the testing, and a  $5 \,\mathrm{N}$  load cell was used to measure thrust [90].



**Figure 12.** Thruster-like test setup configuration [119].

Three microthrusters were produced and characterized, as demonstrated by Khaja et al. [18]: a reference sample with no catalyst, a microthruster with an Ag electroplated catalytic bed, and one with a Pt catalytic bed. Furthermore, discrete catalyst metallization samples as well as non-porous platinum samples were generated for microscopic examination. In addition, two lidless thruster chips (the uppermost layer in Figure 13) were created, one with an Ag bed and the other with a Pt bed, in order to perform cyclic voltammetry [18].



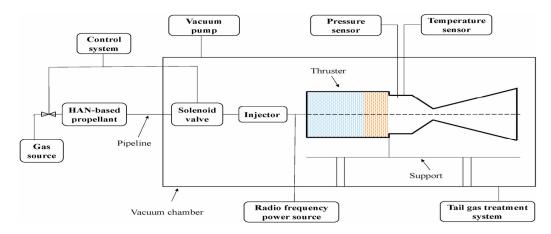
Figure 13. Assembled Mk 0 thruster [91].

Ryan et al. [90] used an HTP propellant delivery apparatus to do atmospheric tests at sea level. This previously built apparatus was used to test HTP thrusters in the 20–50 N range, both hybrid and monopropellant [92]. Although the Mk 0 and Mk 1 thrusters were

tested at the facility originally, it was determined that small thrusters in the 0.2 to 1 N range could not be evaluated there. As a result, a new laboratory was built especially for testing HTP rockets in this lower thrust range. It included propellant delivery systems, a thrust stand, an exhaust extraction system, and data collecting and control systems. Two Tedea-Huntleigh Model 1042 and Model 1041 load cells for continuous thrust and propellant mass measurement were among the setup's key components. A 30% nitric acid concentration was used to passivate the propellant tank in the nitrogen-pressurized propellant distribution system, which has a 3.8 L 316 L stainless steel tank. All components were cleaned in accordance with Swagelok "Special Cleaning and Packaging" (SC-11) requirements. The propellant mass flow rate was determined using a Bronkhorst small Cori-Flow flowmeter. The pressurization bang-bang control system was made easier to operate by the National Instruments LabView data acquisition (DAQ) system. During different test campaigns, data were captured at rates varying from 50 to 400 samples/s. To reduce aliasing errors, datasets were down-sampled to a rate of 0.05 s (20 Hz). Gems Sensors Series 3100 strain gauge pressure transducers and TC Direct tiny Type K thermocouple probes were used to measure pressure and temperature at key points on the thruster and rig [91].

#### 4.2. HAN Monopropellant Thruster

A 150 N thruster driven by HAN was placed in a vacuum chamber with a pressure of 50 Pa during the experiment depicted in Figure 14. A vacuum pump was used to guarantee that the thruster's exhaust gasses were removed. A customized gadget was used for real-time monitoring in order to continuously track and maintain the vacuum chamber pressure within the designated range of 50 Pa. Furthermore, sensors mounted on the thruster itself provided pressure and temperature readings of 1.19 MPa and 1373 K, respectively [121].



**Figure 14.** The thruster-like test setup configuration [121]. Reproduced from [121] with Elsevier permission.

Guan and colleagues discovered that altering the porosities of the pre- and post-catalytic beds had a consistent effect on the thruster's operational behavior. Increased flow resistance and a larger surface area of contact between the propellant and the catalytic bed were the outcomes of decreasing the porosity of the catalytic bed. This led to the promotion of more effective combustion and catalytic decomposition processes. Furthermore, optimizing the post-catalytic bed's porosity helped to improve the thruster's combustion characteristics [121].

According to JAXA (Japan), a number of static firing experiments were carried out using the thruster and SHP163 propellant as part of the process of modifying an HAN-based monopropellant for use in a thruster [122,123]. The catalytic ignition system that was employed followed the standard procedure for hydrazine thrusters. The catalytic

thruster configuration was placed inside a vacuum chamber, as seen in Figure 15. In order to produce thrust during testing, the propellant was added to the thruster's preheated catalyst, which started the combustion process.



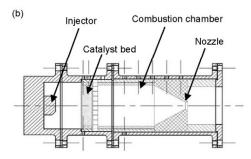


Figure 15. Catalytic thruster. (a) External view. (b) Cross-section [123].

Katsumi and Hori said the research and development (R&D) efforts relevant to SHP-163 and Green Propulsion Reaction Control System (GPRCS) were carefully investigated, with a focus on presenting the successful demonstration test of the GPRCS in space. There is fierce rivalry among new green propellant technologies in the worldwide scene. However, GPRCS's remarkable performance on the RAPIS-1 satellite should greatly increase the technology's acceptance in a number of upcoming space projects [123].

A monopropellant thruster using HAN/HN was presented by Fukuchi et al. [124]. They used a propellant valve and a 1 N class thruster, which had the same specs as a hydrazine thruster, to perform a hot firing test. Their data collection was restricted to pressure and temperature readings because it was difficult to measure thrust directly. The authors used the same protocol in this test as they would have with propellant containing hydrazine. To be more precise, they warmed a catalyst to 200  $^{\circ}$ C before running the test in continuous mode and pulse mode (0.1 s injections in 1 s cycles). The results of the hot firing tests using both 1 N and 20 N thrusters, they said, show that this monopropellant consistently displays features of ignition and combustion [124].

The setup for a 1 N class thruster was created by Kakami et al. [58], with the goal thrust and thrust chamber pressure set at 1 N and 0.4 MPa, respectively. The selected thrust chamber pressure was made in an effort to overcome the difficulties of maintaining arc discharge at high back pressures. Based on the above thrust values and theoretical specific impulse, a 1.7 mm throat diameter was determined. Compared to conventional space propulsion engines, the nozzle expansion ratio was comparatively modest because all experiments were carried out at atmospheric pressure.

Two different types of thrusters were prototyped as part of the investigation. Discharge plasma is injected into the thrust chamber from its side in the side arcjet configuration. On the other hand, the opposite arcjet type had an arcjet oriented in the opposite direction of the SHP163 droplets that were injected. Since impingement-type injectors may generate a fan-shaped liquid film for more viscous propellants, prototypes used a coaxial-type injector because of its special qualities, where liquid propellant atomization begins beneath the injector outlet. Furthermore, compared to impingement-type injectors, the mean droplet diameter attained by coaxial-type injectors is lower. As a result, coaxial-type injectors have higher C\* efficiency than impingement-type injectors. The study used nitrogen as the coaxial injector's and arcjet's operating fluid [58].

# 5. Properties of H<sub>2</sub>O<sub>2</sub> and HAN Green Propellants

Space agencies and space research labs have focused on green propellants as alternatives to conventional toxic and hazardous fuels such as hydrazine in their hunt for more

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ecologically friendly propulsion systems.  $H_2O_2$  and HAN have shown themselves to be potential options among them. This comparative study, as shown in Table 2, examines the features of various developed  $H_2O_2$ - and HAN-based propellant formulations and how they are used in green propulsion systems compared to conventional hydrazine. We hope to shed light on the viability and benefits of these green propellants over traditional alternatives by analyzing aspects including performance, toxicity, storability, and environmental effect.

| Class    | Propellant                        | Theoretical I <sub>sp</sub> (s)<br>(Vacuum) | Density $\rho$ (g cm <sup>-3</sup> ) | Volumetric $ ho I_{sp}$ (g s cm $^{-3}$ ) | Chamber Temp.<br>T <sub>c</sub> (K) | Conditions                                      |
|----------|-----------------------------------|---|--------------------------------------|---|-------------------------------------|---|
|          | AF-M315E                          | 266   | 1.47                                 | 391                                       | 2166                                | 2.0 MPa and A <sub>e</sub> /A <sub>t</sub> 50:1 |
| HAN      | SHP163                            | 276   | 1.4                                  | 386                                       | 2401                                |   |
|          | HNP221                            | 241   | 1.22                                 | 294                                       | 1394                                | 1 MPa and $A_e/A_t$ 100:1                       |
|          | HNP225                            | 213   | 1.16                                 | 245                                       | 990                                 |   |
|          | GEM                               | 283   | 1.51                                 | 427                                       | -                                   |   |
| $H_2O_2$ | HTP 98%                           | 186   | 1.43                                 | 266                                       | 1222                                | 1 MPa and $A_e/A_t$ 50:1                        |
|          | H <sub>2</sub> O <sub>2</sub> 90% | 172.13                                      | 1.39                                 | 239.3                                     | 1019.3                              | 1 MPa and $A_e/A_t$ 40:1                        |
|          | H2O2 85%                          | 150.5                                       | 1.37                                 | 206.2                                     | 892.65                              | 1 MPa and $A_e/A_t$ 10:1                        |

**Table 2.** Performances of H<sub>2</sub>O<sub>2</sub>- and HAN-based monopropellant formulations.

When it comes to a  $H_2O_2$  propellant, the theoretical  $I_{sp}$  refers to the highest possible efficiency that can be achieved for producing thrust under vacuum conditions, taking into account variables such as the propellant's concentration, purity, and engine design. Because it has more mass per unit volume, its density has an impact on the propellant system's overall mass, which in turn affects rocket performance and design. On the other hand, volumetric describes the area that  $H_2O_2$  occupies per unit mass, which is important information to know for sizing a propulsion system and propellant tank. Furthermore, the temperature within the chamber has an impact on the decomposition of  $H_2O_2$ , which is essential for propulsion. Higher temperatures hasten this process and have an effect on thrust generation and overall performance.

Conversely, the theoretical specific impulse of HAN under vacuum indicates its maximum possible efficiency in thrust generation, which depends on various aspects such as nozzle design, combustion characteristics, and HAN concentration. As a result, similar to  $H_2O_2$ , its density affects the propellant system's mass and volume. However, HAN usually has a greater energy density, which could result in propulsion systems that are more effective. The space occupancy per unit mass of HAN is determined by its volumetric qualities, which in turn influences the size and design of the propulsion system. Ultimately, the temperature of the chamber is a critical factor in the combustion dynamics of propellants based on hydrogen atoms, which is necessary to maintain consistent combustion and maximize thrust production.

## 6. Merits and Demerits of Using H<sub>2</sub>O<sub>2</sub> and HAN as Green Propellants

In the realm of rocket propulsion,  $H_2O_2$  and HAN are regarded as "green" propellants. Their use is contingent upon certain application needs, and they possess distinct advantages and disadvantages. In this part, we discuss a few advantages of both HAN and  $H_2O_2$  propellants in rocketry.

#### 6.1. Use of HAN and H<sub>2</sub>O<sub>2</sub> Propellants in Rocketry

Both HAN and  $H_2O_2$  propellants are commonly used in rocketry because of their performance features and the fact that they use less hazardous alternatives than conven-

tional propellants. We can apply some basic propulsion chemistry concepts to connect the propellants' chemistry to performance indicators such as thrust-to-weight ratio (TWR), combustion efficiency ( $\eta$ ), and  $I_{sp}$ . Here, we demonstrate how these propellants' chemistry impacts the performance metrics.

## 6.1.1. Specific Impulse

The chemical composition and the energy released during the combustion process are critical in determining  $I_{\text{sp}}$ .

 $I_{sp} = \frac{F \cdot t}{m_{propellant}} \; = \; \frac{V_e}{g_0}$ 

where F = thrust; t = time for which propellant is burnt;  $m_{propellant}$  = mass of propellant consumed; and  $V_e$  = exhaust velocity and  $g_0$  = standard gravity (9.81 m/s<sup>2</sup>).

The propellant's energy content and the molecular weight of the combustion products determine the exhaust velocity  $V_e$ . The exhaust velocity and, thus,  $I_{sp}$  increase with increasing energy per unit mass and decreasing molecular weight of the exhaust products.

In order to further enhance  $I_{sp}$ , metal additions, also known as catalysts, are frequently employed with HAN and  $H_2O_2$ . The propellant's heat of combustion can be thought of as the energy content.

- Although HAN-based systems generally have a fair balance of high I<sub>sp</sub>, the instability
  of specific oxidizer types might occasionally result in reduced combustion efficiency.
- When H<sub>2</sub>O<sub>2</sub> is catalytically decomposed into H<sub>2</sub>O and O<sub>2</sub>, high-temperature gases are produced. Although I<sub>sp</sub> is partly constrained by the fact that it is a relatively low molecular weight product, in this instance, higher concentrations of H<sub>2</sub>O<sub>2</sub> result in superior specific impulses because of the greater quantity of gaseous products produced.

## 6.1.2. Combustion Efficiency

The efficiency with which the propellant's energy is transformed into useful work (thrust) in relation to the amount of energy lost to side reactions, unreacted fuel, or heat loss is measured by  $\eta$ .

$$\eta \ = \ \frac{Q_{actual}}{Q_{Theoretical}} \times \ 100$$

where  $Q_{actual}$  = actual energy used in the combustion process (taking into account losses and inefficiencies); and  $Q_{Theoretical}$  = theoretical energy from complete combustion of propellant.

The chemical characteristics of the fuel and oxidizer have an impact on combustion efficiency. For instance, the presence of intermediates such as nitric acid ( $HNO_3$ ) or other molecules that could cause incomplete reactions can result in reduced combustion efficiency for HAN. Careful formulation, however, can lessen these losses.

When utilized in a regulated catalytic decomposition procedure,  $H_2O_2$  has a relatively high combustion efficiency, turning the majority of the peroxide into oxygen and water vapor with few intermediates that could absorb or waste energy.

## 6.1.3. Thrust-to-Weight Ratio

A rocket engine's thrust-to-weight ratio (TWR) shows how much thrust it produces in relation to its weight. The engine's power and responsiveness increase with the thrust-to-weight ratio.

$$TWR = \frac{F}{W}$$

where F = thrust; and W = weight of the rocket (or engine, depending on context).

The engine's thrust is affected by the propellant's mass flow rate and exhaust velocity, which are both connected to the propellant's specific impulse. The energy density of the

propellant and the effectiveness of the combustion process can both have an impact on the mass flow rate.

Both HAN and  $H_2O_2$  can contribute to strong thrust, particularly in tiny rockets, if their energy characteristics and exhaust gas temperatures are taken into account.  $H_2O_2$  frequently results in extremely high exhaust temperatures. In some applications, HAN formulations can provide more control over the combustion process, leading to a more stable operation, even though they may provide a little less thrust.

## 6.1.4. Relating Chemistry to Performance

In contrast to conventional rocket propellants such as hydrazine, HAN-based propellants are frequently selected due to their high-energy content and less toxicity. Depending on the formulation, the decomposition of HAN produces a variety of chemicals, such as nitrogen, water vapor, and NO<sub>2</sub>. These gases contribute to the overall performance and lead to the exhaust gases.

- Chemistry: HAN is a potent oxidant that produces a controlled and vigorous combustion process when mixed with metals (such as aluminum) or fuels such as hydrazine.
- Effect on performance: Some intermediate species that do not contribute to thrust may reduce combustion efficiency. HAN can, however, offer efficient combustion and a strong specific impulse with appropriate composition.
- Chemistry: When catalyzed, the high-energy molecule H<sub>2</sub>O<sub>2</sub> decomposed exothermically into oxygen and water vapor.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Water vapor and oxygen, which are relatively light gases that can be released quickly, are the products of the process.

Effect on performance: The mass flow rate and the decomposition temperature have a
significant impact on the specific impulse. Because they produce more gas per unit
of mass, high concentrations of H<sub>2</sub>O<sub>2</sub> (such as 90%) result in higher I<sub>sp</sub> and better
performance. Water vapor, which is produced during the decomposition process, is
advantageous for high I<sub>sp</sub> since it has a lower molecular weight than other propellants.

# 6.2. H<sub>2</sub>O<sub>2</sub> Propellant

#### 6.2.1. Merits of H<sub>2</sub>O<sub>2</sub> Propellant

- Environmentally benign: H<sub>2</sub>O<sub>2</sub> decomposes into water and oxygen, making it a benign substance for the environment. This is in sharp contrast to certain conventional rocket propellants, which have the potential to be extremely hazardous and environmentally damaging, such as hydrazine.
- Stability: H<sub>2</sub>O<sub>2</sub> is comparatively stable and, with correct handling, may be stored for extended periods of time, unlike many other rocket propellants. Because handling hazardous goods is less risky, this is good for logistics related to both storage and transportation.
- Non-toxic combustion products: The main byproducts of the combustion of H<sub>2</sub>O<sub>2</sub> are oxygen and water. Oxygen and water are both non-toxic and present very little risk to the environment. This is especially crucial for space missions where protecting the environment and crew safety are top priorities.
- Versatility: H<sub>2</sub>O<sub>2</sub> is adaptable to diverse propulsion systems because it may be utilized
  in a range of concentrations. Adjusting the concentration of H<sub>2</sub>O<sub>2</sub> offers versatility in
  developing and improving rocket engines for various applications and performance
  needs, whether it is employed as a monopropellant or as an oxidizer in bipropellant systems.

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#### 6.2.2. Demerits of H<sub>2</sub>O<sub>2</sub> Propellant

Low specific impulse (I<sub>sp</sub>): When compared to certain other propellants that are
frequently employed in aerospace applications, H<sub>2</sub>O<sub>2</sub> has a comparatively lower
specific impulse. Given that optimizing thrust efficiency is critical in high-performance
propulsion systems, this shortcoming may limit its usefulness.

- Catalyst sensitivity: Certain materials promote the decomposition of hydrogen peroxide; therefore, choosing materials that come into touch with the propellant requires careful thought. Due to its sensitivity to catalysts, hydrogen peroxide propulsion systems might present difficulties in their design and operation. This is because unintentional catalytic reactions can result in premature decomposition and possible safety risks.
- Decomposition issues: H<sub>2</sub>O<sub>2</sub> has the potential to spontaneously decompose over time, raising stability issues for long-term use and storage. In addition to endangering the propellant's integrity, improper management of the decomposition process increases the possibility of uncontrollable responses. Stabilizers are frequently added to hydrogen peroxide compositions to overcome this problem and maintain chemical stability and shelf life. On the other hand, the addition of stabilizers could complicate propellant handling and performance improvement.

#### 6.3. HAN Propellant

#### 6.3.1. Merits of HAN Propellant

- Greater specific impulse: When it comes to specific impulse, HAN-based propellants are far superior to other propellants such as H<sub>2</sub>O<sub>2</sub>. The effectiveness of a rocket engine in converting propellant mass into thrust is measured by specific impulse. High-performance applications such as satellite deployment and space exploration benefit greatly from the higher specific impulse of HAN-based propellants, which allows rockets to reach larger velocities and payloads with the same amount of propellant.
- Enhanced capabilities and performance: The high-density impulse of HAN-based propellants enables more effective propulsion systems, resulting in improved spacecraft and launch vehicle performance. Longer operational ranges, higher payload capacity, and shorter mission durations are possible outcomes of this.
- Lower toxicity: When HAN-based propellants are used with some conventional propellants, including hydrazine-based fuels, the amount of harmful byproducts produced is decreased. As a result, the risks to the environment and human health from propellant handling, storage, and combustion are reduced.
- Reduced pollutants: HAN-based propellants help to lessen the hazardous pollutants
  emitted during rocket launches by using ecologically benign chemicals and combustion
  procedures. This is especially important for reducing the negative environmental
  effects that space exploration activities have on ecosystems and the Earth's atmosphere.
- Enhanced safety: HAN-based propellants have a lower environmental impact, which benefits the environment as well as the safety of those handling and launching rockets.
   Reductions in toxicity levels and emissions make the workplace safer and lessen the possibility of health hazards to people.

#### 6.3.2. Demerits of HAN Propellant

Corrosiveness: Because of their corrosive properties, HAN-based propellants can
present difficulties. Over time, HAN can lead to corrosion when it comes into touch
with specific materials that are frequently utilized in propulsion systems, such as
metals or polymers. To ensure compatibility with HAN-based propellants, this calls
for careful attention to detail in the design and construction of propulsion systems.

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To lessen the corrosive impacts, engineers must carefully choose materials that are resistant to corrosion or use protective coatings.

- Sensitivity: It is well known that HAN is susceptible to contamination, which may negatively impact its handling and stability qualities. Propeller integrity might be jeopardized by minute contaminants introduced during production or handling procedures. Thus, to reduce contamination and guarantee the purity of HAN-based propellants, stringent quality control procedures are necessary at every stage of the production process. To prevent exposure to contaminants, this entails keeping clean manufacturing settings, using strict testing techniques, and putting in place appropriate handling and storage measures.
- Limited experience: HAN-based formulations may not have as much operational experience or historical data as traditional propellants. Due to their short history, there may be questions about their long-term effectiveness, dependability, and suitability for current propulsion systems. It can be difficult for engineers and researchers to forecast how HAN-based propellants will behave in different operating environments and to spot certain problems that might occur with prolonged use. Therefore, in order to acquire insight into the endurance and performance characteristics of HAN-based propellants and to create confidence in their appropriateness for actual applications, a great deal of testing, simulation, and validation work is required.

## 7. Future Directives

 $\rm H_2O_2$  and HAN have been examined by physicists as possible green stimulus systems for propulsion by jet discharge in the last few decades, particularly in RCS. However, in consideration of moving these greener alternatives forward and ultimately bring ruling class to display, sure tactics and progresses must be paid consideration to.

#### 7.1. H<sub>2</sub>O<sub>2</sub> Propellant

It is essential to improve the purity and aggregation of  $H_2O_2$ . To enhance the effectiveness of monopropellants, investigators should apply two properties together. This entails taking into account the necessary security and safety procedures while attempt to use concentrations that are conventional grades (about 90%). Further inspection into new catalysts and supplements should improve overall effectiveness and catalytic decomposition. For anticipated force, impetuses that reduce or entirely eliminate the era of undesirable byproducts are essential. Moreover, further research should focus on rapport tests in rocket systems. It is critical to resolve the aforementioned questions and guarantee balance and dependability over the long haul in order to favorably involve these green stimulus systems into next scope responsibilities.

## 7.2. HAN Propellant

In conditions of HAN, the focus should be to continue reconstructing the composition of HAN propellants in order to improve their attributes. To optimize HAN's potential as an environmentally companionable propellant, it is essential to investigate differing fuel blends that work well together. Further research into sophisticated leave designs is required to increase the HAN-located propellants' manufacturability. To guarantee the favorable implementation of HAN-located formulations, it is crucial to inspect the effects of variable convert environments on their balance and reliability. Safety concerns should be top priority for engineers and analysts actively working on scope propulsion. This requires generating reliable handling codes and researching some possible risks in connection with established HAN propellants. It is fault-finding to take into account the growth of acceptable thrusters and valves for Reaction Control System (RCS) applications

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as HAN-located propellants are integrated into complete propulsion by jet discharge plans. Moreover, ongoing material impact estimates are necessary to determine what "green" HAN-located propellants are overall in relation to conventional alternatives. Finally, to redistribute HAN-based propellants, the force society must handle supervisory issues and concerns, including acquiring permissions for scope responsibilities.

## 8. Outputs and Recommendations

Because they are less toxic and have less of an effect the on atmosphere than usual propellants, HAN and  $H_2O_2$  are believed to be green propellants. The following discusses the results and advice for utilizing bureaucracy:

#### 8.1. Performance Characteristics

In fact, HAN-located propellants have a higher distinguishing drive ( $I_{sp}$ ) than conventional propellants such as hydrazine, which form bureaucracy desirable for responsibilities such as scope propulsion structures where efficiency is essential.  $H_2O_2$ , in another way, is valued for its extreme mass impulse and storability that qualifies it for long-term responsibilities and its use of place stability is detracting, containing a monopropellant for spacecraft stance control structures or in satellite force orders. Because of these qualities, two propellants together may be useful for differing room missions, which is contingent upon surplus and requirements.

## 8.2. Safety Considerations

Undoubtedly, even though propellants such HAN and  $H_2O_2$  are greener options, safety must forever come first. Both HAN and  $H_2O_2$  have oxidizing kinds that ability pose weighty risks. Strict guidelines need to be implemented when managing, storing, and moving bureaucracy to guarantee safety. This entails providing the necessary preparation for the at-risk crew, using dependable storage facilities, and complying with regulations for controlling their conveyance. Furthermore, it is necessary to engage risk assessment and alleviation measures to reduce the likelihood of accidents. The emergencies connected to these propellants may be successfully mitigated with specific security processes, enabling their dependable use.

# 8.3. Environmental Impact

Both HAN and  $H_2O_2$  have the potential to be more environmentally friendly than typical propellants since they produce fewer toxic byproducts during burning. As a result, the overall environmental effect of space missions and other uses for these propellants may be reduced. However, it is critical to carry out a thorough analysis of their environmental impact, accounting for more than just combustion byproducts. This entails analyzing the emissions linked to their manufacturing and usage, gauging the environmental impact of their manufacturing processes, and taking into account the appropriate recycling or disposal of any waste produced during their lifecycle. Stakeholders should ensure that any possible environmental advantages are maximized while limiting any negative effects on the environment by completing extensive environmental evaluations and using this information to inform choices concerning the usage of HAN and  $H_2O_2$ . Promoting sustainable practices in space exploration and propulsion technology requires a comprehensive strategy to assess the environmental effects.

#### 8.4. Compatibility and Materials Compatibility

Indeed, preserving system integrity and averting degradation or failure depends on assuring compatibility between propellants such as HAN and  $H_2O_2$  and the materials used in propulsion systems. If not correctly controlled, the distinct chemical characteristics of

both propellants may interact with certain materials to cause corrosion, deterioration, or other problems. Specialized materials or coatings might be needed to assure propellant compatibility with propulsion system components in order to remedy this. Compatibility testing, which evaluates how propellants interact with various materials under varied variables, such as temperature, pressure, and exposure time, is a crucial phase in the development and operation of propulsion systems. To maintain the long-term reliability and performance of propulsion systems using HAN and H<sub>2</sub>O<sub>2</sub> propellants, engineers can detect potential compatibility issues early in the design phase and adopt suitable mitigation steps by conducting rigorous compatibility testing. Maintaining the efficacy, safety, and efficiency of propulsion systems in space missions and other applications requires a proactive strategy.

## 8.5. Applications

HAN-based and  $H_2O_2$  propellants are both widely utilized in the aerospace industry. HAN-based propellants, known for their high specific impulse, find applications in various areas. They are particularly suitable for satellite propulsion, facilitating efficient thrust for maneuvering and orbit adjustments. Moreover, their high performance makes them appealing for integration into missile propulsion systems, enhancing range and maneuverability. Additionally, HAN-based propellants contribute to the improved performance of tactical rocket systems, offering heightened speed and accuracy. On the other hand,  $H_2O_2$  is a highly adaptable propellant that finds extensive use in the aircraft industry. It is useful for propulsion systems in spacecraft, providing thrust for orbital maneuvers and trajectory corrections.  $H_2O_2$  also serves as fuel for Auxiliary Power Units (APUs), which makes it easier to generate power for various spacecraft systems while they are on board. Furthermore, it provides dependable and small-footprint propulsion for tiny thrusters in spaceship attitude control systems by acting as a monopropellant. These many uses highlight the adaptability and performance benefits of hydrogen peroxide- and HAN-based propellants in enhancing satellite technology, space exploration, and defense systems.

## 8.6. Advancements and Research

Propulsion systems, in general, as well as HAN- and  $\rm H_2O_2$ -based propellants, perform better and are more stable and safe because of ongoing research and improvements in the field. The following are some crucial areas of attention:

- Enhancements to performance: Scientists are investigating methods to improve the specific impulse and combustion efficiency of HAN- and H<sub>2</sub>O<sub>2</sub>-based propellants. Optimizing formulas, additives, or combustion processes may be necessary to attain increased thrust levels and improved efficiency.
- Improvements in stability: Work is being conducted to make HAN- and H<sub>2</sub>O<sub>2</sub>-based propellants more stable during operation and storage. This entails improving production procedures to yield more reliable and stable propellant formulas, as well as creating stabilizers or additives to lessen decomposition reactions and increase shelf life.
- Safety improvements: The goal of research is to make handling, storing, and transporting HAN- and H<sub>2</sub>O<sub>2</sub>-based propellants safer. To reduce risks or prevent accidents, this may entail creating better handling protocols, creating safer storage containers, or adding additional safety measures to propulsion systems.
- Developments in additive manufacturing: Often referred to as 3D printing, additive
  manufacturing opens up new possibilities for the creation and design of propulsion
  system components. Scholars are investigating the potential of additive manufacturing
  processes to yield lighter and more intricate parts, hence enhancing propulsion system
  efficiency and performance.

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 Applications of nanotechnology: Nanotechnology has the potential to improve the characteristics of propellants and propulsion systems. Scholars are examining the potential use of nanomaterials in HAN- and H<sub>2</sub>O<sub>2</sub>-based propellants to boost thermal stability, increase energy density, and improve combustion efficiency.

Developments in material science: New materials with enhanced compatibility, durability, and performance qualities for use in propulsion systems are being created thanks to advances in material science. This includes investigating novel alloys, coatings, and composite materials that can survive the abrasive conditions involved in propulsion operations.

Scientists and engineers hope to enable future space exploration, satellite technology, and defense applications by developing more environmentally friendly, dependable, and efficient propellant systems through cutting-edge research and utilizing these improvements.

#### 8.7. Regulatory Compliance

When working with propellants such as HAN and  $H_2O_2$ , regulatory compliance is essential because of their possible risks and environmental implications. The following are important considerations for regulatory compliance:

- Rules and guidelines: For the use, handling, and transportation of propellants such as HAN and H<sub>2</sub>O<sub>2</sub>, a number of regulatory entities, including federal agencies and international organizations, provide rules and guidelines. The aforementioned policies are designed to guarantee safety, safeguard the environment, and adhere to global norms.
- Particular guidelines for using "green" propellants: "Green" propellants, such as HAN and H<sub>2</sub>O<sub>2</sub>, are intended to have a smaller environmental impact than conventional propellants. Regulatory organizations may have particular guidelines or recommendations for their use. These specifications could include methods for certification, testing, or reporting that show adherence to environmental laws.
- Regulation observance: Strict adherence to pertinent rules and norms is necessary for all companies and entities involved in the development, production, handling, and transportation of HAN- and H<sub>2</sub>O<sub>2</sub>-based propellants. This includes putting in place the proper safety procedures, carrying out the requisite testing and documentation, and securing any licenses or approvals from law enforcement.
- Constant monitoring and adherence to increasing regulatory requirements: Adhering
  to regulations necessitates ongoing monitoring and effort rather than a one-time
  effort. To ensure compliance, organizations should stay up to date on any revisions or
  modifications to regulations and modify their procedures as necessary.
- Cost considerations: Despite their possible environmental advantages, it is imperative that propellants such as HAN and H<sub>2</sub>O<sub>2</sub> be widely adopted for a number of reasons. First off, the pricing of these propellants is heavily influenced by the cost of the production techniques used, with developments having the potential to promote more affordable manufacturing techniques. Second, taking sourcing and processing into account, the cost and availability of raw materials needed for production affect overall cost-effectiveness. Thirdly, economies of scale are crucial, since higher production quantities frequently result in cheaper costs per unit. Logistics, transportation, and infrastructure costs are also essential, with effective networks reducing distribution costs. Costs are also shaped by competitive price dynamics, which are impacted by market demand and tactics. Furthermore, it is critical to assess the whole cost of ownership, which accounts for upkeep and disposal. Stakeholders can improve the cost-effectiveness of HAN- and H<sub>2</sub>O<sub>2</sub>-based propellants and establish them as competitive options in the aerospace sector and beyond by carefully evaluating and addressing these cost aspects.

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## 9. Conclusions

In this review paper, we have provided an updated overview for propulsion engineers and space researchers within the field of chemical propulsion. We focused on recent developments, designs, and potential applications of H<sub>2</sub>O<sub>2</sub> and HAN as Green Liquid Propellants (GLPs) for satellite Reaction Control Systems (RCSs). The utilization of both monopropellants offers numerous advantages for space agencies and aerospace organizations. Our exploration began with defining various compositions of both H<sub>2</sub>O<sub>2</sub> and HAN, highlighting their potential as environmentally friendly green propellants. Additionally, we discussed the predominant catalysts employed in Reaction Control Systems utilizing H<sub>2</sub>O<sub>2</sub> and HAN. Various forms, including powders, pellets, spheres, and honeycombs, serve as catalytic support due to their favorable textural and porous characteristics. These activated catalysts were then applied across a range of thruster classes. Numerous directives were issued to improve the efficiency, safety, and stability concerns related to the practical application of environmentally friendly propellant systems. Ultimately, the decision between H<sub>2</sub>O<sub>2</sub> and HAN hinges on the particular needs of the propulsion system, considering factors such as performance, environmental impact, safety, and operational considerations. Each propellant presents distinct advantages and challenges, and continuous research endeavors seek to overcome some of the limitations associated with these eco-friendly propellants.

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#### **Abbreviations**

AF-M315E Air Force Monopropellant 315E
AFRL Air Force Research Laboratory
ADN ammonium dinitramide
AN ammonium nitrate

AN ammonium nitrate
BHA Barium hexaaluminate

BA benzoic acid

BET Brunauer–Emmet–Teller

CEA Chemical Equilibrium with Applications

η Combustion EfficiencyCC Computationally ComplexDEAN Diethyl Hydroxylamine

DEHAN Diethyl Hydroxylammonium Nitrate
EILs Environmentally Ionic Liquids
EDTA Ethylene Diamine Tetraacetic Acid

Ve exhaust velocity

GLY Glycerol

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GLPs Green Liquid Propellants

GPIM Green Propellant Infusion Mission

GPRCS Green Propellant Reaction Control System
HNP High-performance Non-detonating Propellant

HTP High-Test Peroxide

N<sub>2</sub>H<sub>4</sub> hydrazine

HN hydrazinium nitrate H<sub>2</sub>O<sub>2</sub> hydrogen peroxide

HPAS Hydrogen Peroxide Aqueous Solutions HEHN hydroxyethyl hydrazinium nitrate HAN Hydroxylammonium Nitrate

XM46 Hydroxylammonium Nitrate-based propellant

HILs hypergolic ionic liquids

ISAS Institute of Space and Astronautical Science
JAXA Japan Aerospace Exploration Agency

LGP Liquid Green Propellant

LO<sub>x</sub>/LH<sub>2</sub> Liquid Oxygen/Liquid Hydrogen

MEO methanol

MMH Monomethylhydrazine

MWCNTs multi-walled carbon nanotubes

NASA National Aeronautics and Space Administration

NA nitric acid PVA polyvinyl alcohol

RAPIS-1 Rapid Innovative Payload Demonstration Satellite 1

RCS Reaction Control of Satellites ROS reactive oxygen species

REACH Registration, Evaluation, Authorization, and Restriction of Chemicals

R&D research and development RPA Rocket Propulsion Analysis

SHP163 Sei-Hori Propellant (16.3% of methanol)

S405 Shell 405 (36%Ir/Al<sub>2</sub>O<sub>3</sub>) catalyst

Isp specific impulse

SVHC Substances of Very High Concern

TWR thrust-to-weight ratio TEAN triethylammonium nitrate

U.S. United States

UDMH Unsymmetrical Dimethylhydrazine

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