

Review

# Test Activities on Hybrid Rocket Engines: Combustion Analyses and Green Storable Oxidizers—A Short Review

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**Abstract:** Hybrid rocket engines (HREs) offer a low-cost, reliable, and environmentally friendly solution for both launch and in-space applications. Hybrid propellants have been identified as green thanks to their use of non-toxic, non-carcinogenic oxidizers. Of particular relevance are storable oxidizers, namely high-concentration ( $\geq 90$  wt.%) hydrogen peroxide (HP,  $H_2O_2$ ) and nitrous oxide ( $N_2O$ ). This work provides a survey of experimental activities based on  $H_2O_2$  and  $N_2O$  for hybrid rocket propulsion applications. Open literature data are completed with original thermochemical calculations to support the discussion.

**Keywords:** green propellants; storable oxidizers; hybrid rocket engine; hydrogen peroxide; nitrous oxide; combustion; environmental impact; greenhouse effect; launch system; in-space propulsion

## 1. Introduction

In the field of thermochemical propulsion, a propellant is defined as *green* if it has characteristics of low (if any) toxicity and easy and safe transportation and handling. In addition to this, a green propellant should provide the lowest possible emission levels during its lifecycle, from production and storage to the interaction of its exhaust combustion products with the external environment. Interest in green propellants has been furthered by ever-deeper environmental responsibility and requirements for a reduction in humanity's impact on environment. The development of green propellants is fostering advances in thermochemical propulsion. In this latter field, the major causes of environmental impact can currently be identified as: (i) ammonium perchlorate (AP) in solid propellant propulsion systems; and (ii) hydrazine/hydrazine-derived liquid propellants. The former raises environmental concerns due to the presence of HCl in its exhaust, as well as the possible influence of condensed combustion products (CCPs) on ozone depletion [1–4]. Propellants based on hydrazine and nitrogen tetra-oxide require complex (and expensive) handling procedures, with criticalities in cases of accidental release or emergency dumping [5–7].

Hybrid rocket engines (HREs) are typically presented as having a low environmental impact and being safe propulsion systems [8]. HREs usually burn solid hydrocarbon fuel with a liquid oxidizer (gaseous oxidizers are considered in lab- and small-scale applications). Therefore, the main exhaust products of HREs are CO,  $CO_2$ , and  $H_2O$ . The environmental impact reduction of HREs has been evaluated by contrasting them with the toxic and polluting emissions of AP-based solid rocket motors and the hazardous handling of hydrazine-based propellants. The high safety of HREs is due to their use of inert fuel grains during manufacture and transportation, and to their tolerance to grain cracks thanks to their peculiar combustion behavior. The combustion of conventional (polymeric) fuels as hydroxyl-terminated polybutadiene (HTPB) shows slow regression rates, therefore limiting the thrust produced by HREs with simple grain geometries (i.e., single, central port cylindrical grains). This is a critical point for the implementation of HREs in launch systems. Liquefying fuels offer a faster solid-fuel regression rate ( $r_f$ ) than polymeric



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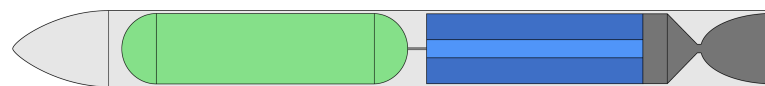
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formulations [9,10]. However, these fuels suffer from unsuitable thermomechanical properties [11]. Currently, HREs are typically conceived for small and medium launch vehicles, space tourism, and in-space propulsion applications [12,13]. Liquid oxygen (LOX) is the most performing oxidizer in terms of theoretical specific impulse and  $r_f$  performance [14]. However, because it requires low temperatures (90 K), LOX complicates the overall HRE design while limiting system storability and requiring relatively complex fluidic line design (injection/atomization and grain ignition). The use of storable oxidizers reduces some of the critical points related to the use of cryogenic liquids for both launch and in-space applications. Oxidizers such as  $N_2O$  and  $H_2O_2$  (at different concentrations) offer interesting features such as exothermic decomposition (with the possibility of a simplified design of the engine ignition system) and relatively high oxygen content. This work provides a review of the open literature dealing with the analysis and testing of storable propellants in HRE development, with a focus on liquefying fuels. Analyses and studies are critically discussed to provide readers with a green perspective on HREs. Highlighting the role of liquefying fuels, and, in particular, of paraffin-based fuels is a choice based on the overall relevance of these fuels for both launch and in-space applications, and on their theoretical flame temperature/specific impulse performance, which shows no significant difference to conventional fuels such as HTPB [14]. In the discussion, fundamental aspects of hybrid rocket combustion are introduced first. Then, after a short presentation of the most relevant physical properties of storable oxidizers and a short analysis of thermochemical performance of propellants of interest, combustion tests of  $N_2O$  and  $H_2O_2$  with solid fuel are reviewed.

Finally, conclusions are presented, together with some recommendations for future developments.

## 2. Hybrid Rocket Combustion

The Figure 1 shows the conventional configuration of an hybrid rocket engine. Pioneering efforts in the study of solid-fuel combustion in HREs began in the first half of the 20th century. Altman and Holzman [14] offer a comprehensive review, covering hybrid propulsion milestones from its inception to the most recent achievements. Interestingly, earlier efforts in hybrid propulsion used  $N_2O$  (Andrussow, Lutz, and Noggerath at I.G. Farben in 1937), and  $H_2O_2$  (Moore and Berman at General Electric from the late 1940s to the mid-1950s) [14].



**Figure 1.** Simplified scheme of HRE with conventional configuration: the (liquid/gaseous) oxidizer tank is shown in green, while the solid-fuel grain (with a single central port perforation) is in blue.

The following subsections provide: (i) a discussion of the fundamentals of hybrid rocket combustion, starting from early studies on conventional fuels and covering the most recent efforts; (ii) combustion enhancement techniques; (iii) an introduction to some peculiarities of HREs, such as soot production and, in particular, the oxidizer-to-fuel ratio (O/F) shift effects; and (iv) a brief review of environmental studies in the rocket industry. Treatment in this section is mainly conducted considering gaseous oxygen as an oxidizer, as per lab- and small-scale activities typical of early fundamental studies. However, when  $N_2O$  and  $H_2O_2$  combustion is encountered in references dealing with the topics (i)–(iv), a discussion of the relevant publications is performed in Section 3.

### 2.1. Fundamentals

The combustion of conventional fuels occurs in a boundary layer created by an oxidizer stream over a condensed phase surface. Vaporized fuel diffuses from a regressing surface to an atomized/gaseous oxidizer flow. A diffusion flame transfers heat into a condensed phase by convection and radiation. Mass blowing from the grain surface hinders the convective

heat transfer (i.e., blockage effect). Radiation heat transfer from gaseous combustion products exerts a limited influence on the combustion process of non-metalized fuels. For conventional fuels, the  $r_f$  is relatively slow. Marquardt and Majdalani [15] provide a review of turbulent boundary layer combustion models. In the field of HRE combustion modeling and analysis, the early efforts of Marxman and co-workers [16–18] still play a central role. A series of efforts toward detailed analyses was made by the Pennsylvania State University research group and is well presented by the authors in [8]. In HRE combustion, the regression rate is related to the total (i.e., propellant) mass flux ( $G$ ) by a power-law relationship, as follows:

$$r_f = a_r G^{n_r} \quad (1)$$

with  $n_r = 0.8$  for a purely turbulent convective heat-transfer regime. Equation (1) is typically used in a slightly different form, considering the oxidizer mass flux ( $G_{ox}$ ) as the controlling parameter. In actual testing conditions, the  $n_r$  exponent shows differences regarding the purely convective regime, with values in the range 0.6–0.8 [8]. This is partially due to the influence of radiation heat transfer that is possibly caused by: (i) fuel-rich O/F, implying the presence of highly emitting soot particles; and (ii) relatively low total (or oxidizer) mass fluxes yielding reduced convective heat transfer. Discussion on the impact of radiation heat transfer in lab-scale HREs with pure hydrocarbon fuels has been led by Strand et al. [19], Chiaverini et al. [20], and Estey et al. [21]. It is worth noting that with reduced  $G$ , the impact of radiation can be significant, yielding an  $r_f$  dependence on combustion-chamber pressure  $p_c$  (indeed, on  $p_c \cdot D$ , with  $D =$  port diameter). Combustion pressure effects on  $r_f$  are also possible for high  $G$  values when chemical kinetics starts playing a significant role. Finally, a diffusion flame implies relatively low combustion efficiencies due to difficult oxidizer–fuel mixing. This possibly affects the emissions of HREs, unless specific correcting actions/designs are pursued. Advanced studies for HRE development tackle issues related to slow  $r_f$  and combustion efficiency.

## 2.2. Studies on Combustion Performance Enhancement

Combustion performances of HREs include: (i) the  $r_f$ ; and (ii) the combustion efficiency. Although high-enough combustion efficiencies are pursued in both launch systems and in-space applications, the research for faster  $r_f$  is typical of the access to space systems. The following treatment focuses on  $r_f$  enhancement first. Then, efforts for higher combustion efficiencies are presented.

Several techniques have been proposed for the  $r_f$  enhancement of conventional fuels. These include (in non-chronological order of development): (i) the use of liquefying fuel formulations; (ii) solid-fuel loading with high-energy-density fuels as metal and hybrid powders; (iii) the implementation of exotic oxidizer-injection methods; (iv) heat-transfer increase by the alteration of grain surface roughness and port shape. Recent reviews of the topic have been carried out in [11,22–27].

The use of AP (or other oxidizers) as an additive for ballistic performance enhancement has been proposed too [25,26]; however, this solution is not considered in detail in this review due to its implications for the effects of Cl on the exhaust, or the possible detriment of intrinsic HRE safety. Focusing on  $r_f$  and combustion efficiency enhancement, the following discussion does not consider multiport configurations, where high thrust levels are pursued by increasing the regressing surface area. The reason behind this choice is that the method has been widely investigated in the past, demonstrating volumetric efficiency criticalities, despite some relevant results in terms of generated thrust [28].

Liquefying formulations offer enhanced  $r_f$  thanks to the entrainment mass transfer of the melted fuel. In these kinds of fuels, grain melts under the enthalpy transfer from the flame. Depending on the pressure regime, the surface layer (liquid at subcritical conditions, fluid in the supercritical regime) is unstable under the shear action of the propellant stream: the behavior is connected to the surface-layer low viscosity (and, in subcritical conditions, surface tension) [9,10,29,30]. As a result of the low stability, the melted fuel is sprayed into the propellant stream. Therefore, this mechanism provides an additional contribution to the

surface vaporization regression. Originally reported in [31], the entrainment mechanism was first justified and detailed in [9,10].

A detailed analysis on entrainment in hybrid rocket engines is reported by the authors in [29,30,32,33]. Entrainment provides mass transfer from the regressing grain without contributing to convective heat-transfer blockage. Therefore,  $r_f$  of up to four times that of conventional formulations can be achieved [9,30,34–39]. Paraffin waxes are a class of liquefying fuels of particular interest thanks to their availability and ease of handling. The poor mechanical properties of pure paraffin require improvements before they are suitable for operating conditions during launch and in-space operations. Blending wax with thermoplastic polymers is the strategy commonly pursued for this purpose [11,25,35–38,40–43]. Such a reinforcement, as well as the use of HTPB (or another thermosetting matrix) [44,45], produces significant effects on the mechanical response of fuel only for relatively high blending-polymer mass fractions. This high-polymer load implies a reduction in entrainment mass transfer due to increased melt fuel viscosity. Evaluation of the  $r_f$  dependence on the melt fuel viscosity is reported in [38,40–43].

The achieved results show  $r_f \propto \mu^n$ , with  $n$  in the range  $-0.2$  to  $-0.3$ . Recently, an innovative method for fuel-grain reinforcement has been proposed [46]. The method exploits 3D printing to generate cellular structures that are embedded in the paraffin–fuel matrix. The structure provides mechanical reinforcement, therefore preventing (or limiting) paraffin blending [46,47]. Results for a gyroid structure printed in acrylonitrile butadiene styrene (ABS) with a 15% infill and embedded in a microcrystalline wax matrix show a yield strain increase of 213%, with the grain mechanical behavior turning from brittle to ductile. For the same matrix, the embedded ABS structure promotes  $r_f$  increases in the range of 60 to 90% (depending on reinforcement infill).

In HRE applications, solid-fuel loading with energetic additives has  $r_f$  (and the mass burning rate) enhancement as the main driver [11,22,23,48,49]. In contrast to solid rocket motors, metal and metal hydride powders show no marked increase in the theoretical specific impulse of HREs. Such a result is well discussed in [50,51], where experimental data considers oxygen as the oxidizer.

In particular, focusing on Al powders, the active metal content of the energetic filler has nearly no impact on the theoretical specific impulse of HRE [51]. When considering metal fuels for performance enhancement, a correct evaluation of the possible drawbacks should be pursued (i.e., two phase-flow losses due to CCPs). These considerations are complicated by the lack of detailed analyses in the open literature: no experimental investigations on the particle size and size distribution of condensed products from the combustion of HREs are available (though some considerations can be inferred from the experience on solid rocket motors [52,53]). However, in HREs, in contrast to solid rocket motors, particles are added with small mass fractions, with a limited impact on the (expected) condensed species' mass fractions [50,51]. In conventional formulations, the accumulation of partially oxidized metal at the regressing surface has been identified as a limiting factor for regression rate enhancement [23,48]. Recent studies on the combustion behavior of metalized fuel formulations show limited performance enhancement for conventional formulations, typically  $<60\%$ , featuring oxidizer mass flux dependence [54–56]. Experimental analyses considering paraffin-based fuels (in particular, paraffin–polyethylene blends) are reported in [57].

In this latter work, the use of micron-sized Al (nominal particle size in the range 10 to 20  $\mu\text{m}$ ) in paraffin blends provided faster  $r_f$  than for its non-metalized counterpart. However, under the investigated conditions (GOX,  $G_{ox} = 100 \text{ kg/m}^2\text{s}$ ), the percentage  $r_f$  enhancement achieved by a 25 wt.% metal load of a 10 wt.% polyethylene blend is within the previously reported range, with pure paraffin outperforming compared to the metalized blends.

Swirl and vortex flow injection enables  $r_f$  enhancement [58–60], increases combustion efficiency [36,61–63] and reduces the pressure oscillations/low-frequency instabilities observed in small-scale engines [8,58,59]. The main limitations of this approach are related to

swirl decay along the fuel grain due to viscous dumping [8,58,61,64]. For in-space applications, this issue can be addressed with non-conventional engine configurations, such as the exotic vortex flow pancake (VFP) [36,63,65]. The VFP features a length-to-diameter ratio  $< 1$ , thus limiting vortex intensity losses along the combustion chamber while offering high combustion efficiencies ( $\sim 99\%$  in terms of characteristic velocity).

Focusing on conventional engine geometry, according to the data reported in [59,60],  $r_f$  increases of up to 270% are achieved for a swirl geometrical number of 19.4 and classical fuel.

A scaling analysis for swirl injection is presented by Paccagnella et al. [61]. Swirl injection effects on the ballistic response of solid fuels are investigated in [66–68]. Although general comments presented for conventional fuels are confirmed by these analyses, in [67] the authors highlight how the sensitivity of wax fuel to swirl injection results is stronger than that of conventional compositions.

An interesting combination of swirl and standard injection is proposed in the A-SOFT (altering-intensity swirling-flow-type) HRE [69–71]. This peculiar engine is under development, and proposes a tailoring of the injection conditions to control thrust at an optimal oxidizer-to-fuel-mass ratio while achieving relatively fast regression rates with a fixed motor configuration.

Enhanced fuel–oxidizer mixing can be promoted by special grain configurations and devices. Effects on the combustion efficiency of diaphragms are discussed by Grosse [72]. In this work,  $N_2O$  is considered to be an oxidizer: these results are discussed in detail in Section 3. Exotic grain configurations with a single central port with helical geometry [27,73] and engines with peculiar grain segmentation [74,75] have been proposed for enhanced combustion performance. For the former, a series of experimental data on ABS combustion is available, while, for the latter, the open literature reports no regression rate or combustion efficiency data. In [27], helical port geometry favors  $r_f$  enhancement thanks to: (i) increased skin friction; and (ii) the reduction of wall-blowing using centrifugal effects induced by the helix pitch. Regression rates of up to four times those of conventional port configurations were achieved using this method for 3D-printed ABS grains. As clarified by the engineering model developed by the authors in [73], 75% of the overall regression rate enhancement is due to the increased skin friction, with 25% of the performance gain being due to the reduced wall-blowing. Unfortunately, during combustion, grain consumption gradually erases the helical configuration of the port, reducing the  $r_f$  enhancement [27].

### 2.3. The O/F Shift, Condensed Combustion Products, and Soot

In typical HRE configurations, the overall  $O/F(t)$  changes over time. This effect is due to  $r_f(G_{ox})$  and the regressing surface evolution during the combustion. For a cylindrical grain with a single central port perforation,  $O/F(t)$  increases in time for  $n_r > 0.5$  (with neutral and regressive behaviors being related to  $n_r = 0.5$  and  $n_r < 0.5$ , respectively). As a result of the O/F shift, the specific impulse of the system changes during engine firing. The phenomenon is well known, though few studies have focused on its effects on engine performance. A discussion on the influence of O/F shift on performance is reported in [76]. This analysis includes data from different single- and multiport configurations [76]. Results show how the cylindrical grain with single-port perforation exhibits no significant performance detriment during burning due to the O/F shift in terms of combustion efficiency. However, the phenomenon must be taken into account during engine design, since suitable time-averaged O/F should characterize the firing.

The open literature lacks detailed studies on the impact of CCPs on the actual gravimetric specific impulse values. However, solid-fuel formulations typically show limited additive mass fractions (in particular, in the case of entrainment-producing compositions, where the energetic filler typically increases the melt fuel viscosity [77]). Therefore, a limited impact of CCPs on the expansion process of loaded HRE propellants is expected. Similarly, the use of a relatively small additive mass fraction suggests limited environmental effects, such as ozone depletion mechanisms fostered by metal oxides.



Soot formation is a critical aspect of HRE combustion. However, the open literature lacks detailed studies offering an assessment/estimation of its impact on actual systems. Considering the O/F shift, and the peculiar combustion mechanism of HREs, the fuel may burn in fuel-rich conditions favoring soot formation. Detailed analyses on this point depend on the specific system/operating conditions under scrutiny, and cannot be generalized. Although soot formation is a kinetically driven phenomenon, thermochemical equilibrium also foresees the possible insurgence of condensed carbon from fuel combustion when the carbon-to-oxygen ratio exceeds unity, as reported by De Luca et al. [12]. A recent analysis of the impact of oxygen concentration effects on soot production is discussed by Aphale et al. [78]. In this study, the analysis focuses on polymethyl methacrylate burning under different oxygen concentrations spanning from 17% to 100%. The final aim of the study reported in [78] is an evaluation of the impact of radiation heat transfer on  $r_f$ . Under the investigated conditions, soot production is observed to increase with increasing oxygen mass fraction up to 45% O<sub>2</sub>, with a subsequent decrease. Under these circumstances, the radiation heat transfer monotonically increases, due to flame temperature enhancement, with increasing oxidizer content. Few studies have tackled the problem of exhaust plume analysis for HREs [79]. In addition to this, the open literature offers scarce investigations (if any) of the after-burning effects of HRE plumes.

#### 2.4. Environmental Impact

Air pollution is defined as the change in the natural composition of atmosphere. In this sense, combustion processes have a strong impact. In the troposphere, thermochemical rocket emissions are negligible compared with aviation and the other sources [80–82]. On the other hand, they are the only cause of pollution at higher altitudes. Thus thermochemical rocket propulsion is fully responsible for the human impact on the stratosphere. In the upper atmosphere, rocket combustion may affect the stratosphere equilibrium mainly in two ways: (i) the greenhouse effect; and (ii) ozone-layer breakdown.

The former is caused by the response of molecules to short-wave radiation (by the Sun) and long-wave radiation (infrared, by the Earth). Greenhouse gases are transparent to short waves but tend to absorb longer waves. Atmospheric gases responsible for this effect are water vapor (H<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>), and ozone (O<sub>3</sub>). Normally, if annual global radiated energy is equal to the level of solar energy absorbed, the Earth's temperature is in global equilibrium. The artificial introduction of more CO<sub>2</sub> and H<sub>2</sub>O or of nitrogen oxides (NO<sub>x</sub>), CO, CH<sub>4</sub>, UHC, and soot might alter this equilibrium [83].

Ozone can be found all over the atmosphere, but it has its maximum concentration between an altitude of 25 and 35 km [83]. There, the thick O<sub>3</sub> layer acts as a solar ultraviolet (UV) radiation filter. Ozone is an unstable gas formed by the chemical reaction of O<sub>2</sub> and O chemical in which, under nominal atmospheric conditions, the direct and reverse reactions are in equilibrium. The introduction of chlorine and bromide compounds, as well as N<sub>2</sub>O and NO<sub>x</sub>, which act as catalysts in ozone depletion, alter this equilibrium, causing the so-called "ozone hole" phenomenon.

The effects of chemical rockets on the environment have already been investigated during the Space Shuttle program [84–86] and were later reviewed by the authors in [4]; many issues have been addressed. The Space Shuttle's major chemical products at the nozzle exit were: (i) HCl, Al<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>, H<sub>2</sub>O, CO, and CO<sub>2</sub> for the solid rocket boosters (typical solid fuel); and (ii) H<sub>2</sub> and H<sub>2</sub>O for the main engines working with LOX and liquid hydrogen (LH<sub>2</sub>). A model to analyze the effects of exhaust gases reacting with the atmosphere is reported in [87]. Results highlighted the danger of the use of Cl in rockets for ozone depletion. However, LOX/LH<sub>2</sub> green products also react when mixed at high temperatures with the surrounding atmosphere. This reaction leads to the production of nitric oxide, responsible for O<sub>3</sub> dissociation. However, this amount of NO is negligible compared to the direct introduction of chlorine [87]. Results suggest a deeper investigation into atmosphere interaction with exhaust plume gases when operating hybrid rocket

engines (usually operating at a high O/F ratio) employing  $N_2O$  or  $H_2O_2$  as oxidizers. Studies about this topic are not currently present in the literature.

Due to the relatively recent diffusion of hybrid engines, few studies are available about their environmental impact. Discussion from [88] yields to consider HRE direct emissions as less impacting than other rocket engines when focusing on the greenhouse effect.

Whitmore et al. [79] carried out a comparison between hydrazine ( $N_2H_4$ ) and the ABS-gaseous oxygen (GOX) propulsion system's plume species. For the hybrid engine, dominant combustion products at the nozzle exit are CO,  $CO_2$  and  $H_2O$  when operating at an equivalence ratio range of  $1.35 < \Phi < 2.25$ , with negligible production of C(gr). CO is characterized by little contamination risk, and  $CO_2$  and  $H_2O$  mass concentrations vary between 10 and 35%. The contamination potential is relevant, but the hybrid engine results cleaner than hydrazine, which is characterized by condensable species varying from 40 to 50% mass concentrations.

A study on the emissions from the mission profile of a LOX/paraffin three-stage hybrid launcher is reported in [82]. The NASA-CEA code is used for the analysis. Considering the methods implemented in [82] improvements in the emission functions developed in [88] were achieved. Combustion products at the nozzle exit are obtained as a function of the trajectory without requiring the hypothesis of pollution distribution along atmospheric altitude [82]. In [82], Al impact is not accounted for since it is not present in the fuel, greatly lowering the environmental impact [88]. Carbon soot is neglected because it is obtained only for  $O/F < 1.2$  (far from operating conditions). Major mass fractions are obtained for CO,  $CO_2$ , and  $H_2O$ . The instantaneous radiative force (iRF) for the latter two is computed using models formulated by the authors in [88]. The carbon footprint (CFP) is computed from the global warming potentials (GWP). CO and  $CO_2$  are the only two major gases with a  $GWP \neq 0$ , with  $GWP_{CO_2} = 1$  and  $GWP_{CO} = 3$  [81]. Results show a total  $CFP = 6636$  kg, an  $iRF_{CO_2} = 4.9 \cdot 10^{-12}$  mW/m<sup>2</sup>, and an  $iRF_{H_2O} = 1.0 \cdot 10^{-8}$  mW/m<sup>2</sup>. A  $-25\%$  CFP and  $-10\%$  iRF can be achieved by a  $-10\%$  payload mass reduction [82].

Further studies should move in the direction of expanding the plume-atmosphere interaction developed in [87] to hybrid rocket engines, to understand their effect on ozone depletion, especially when using  $N_2O$  as an oxidizer. Additionally, if considering the results of in [82] and the results reported in the Section 3, a deeper investigation of the impact on radiation forces when using  $H_2O_2$  as an oxidizer should be conducted.

### 3. Green Storable Oxidizers

When pursuing high performance in terms of  $r_f$  and specific impulse, LOX has always been an attractive opportunity for HRE designs. The most powerful HRE to date (rated 1.1 MN thrust) was designed and built by the American Rocket Company (AMROC) using the aforementioned oxidizer and HTPB as fuel [28]. Recently, HyImpulse, a German start-up developing sounding rockets and planning the development of a three-stage launch vehicle for the orbit insertion of payloads of up to 500 kg, is considering LOX for its applications. A 75 kN demonstrator, HyPLOX75, was successfully fired in a static test in September 2020 [89]. As a side advantage in the small- to large-scale applications, LOX burning behavior can be related to a variety of lab-scale datasets employing gaseous oxygen as the oxidizer. However, the use of LOX requires complex handling and implementations, due to its cryogenic nature. Trends in the propulsion market regarding the possible exploitation of HREs in small- to medium-size launchers promote interest in storable oxidizers such as hydrogen peroxide [90,91] and nitrous oxide [90]. Therefore, the open literature research and relevant operating realizations identify  $N_2O$  and  $H_2O_2$  as the current candidates for affordable hybrid propulsion systems [92–94]. Historically, other storable oxidizers have been investigated for HRE applications, such as nitrogen tetroxide ( $N_2O_4$ ), nitric acid ( $HNO_3$ , NA), and red-fuming nitric acid (RFNA). However, presently, these reactants are not considered in the perspective of commercial applications due to them raising significant environmental concerns [14].

Table 1 presents an overview of the most relevant properties of cryogenic and storable oxidizers. For hydrogen peroxide, two different concentrations are considered: 90 wt.% and

98 wt.%. As reported by Whitmore [95], the use of H<sub>2</sub>O<sub>2</sub> with a concentration >90 wt.% makes the definition of a green propellant only slightly applicable (see also [96]). However, high concentrations of hydrogen peroxide are typically accepted as green reactants.

Thermochemical computations are hereby reported as connections between Sections 2 and 3. The analysis takes into account paraffin wax, widely considered in lab- and small-scale testing, burning with storable oxidizers. The presented data include the reference case of a cryogenic oxidizer.

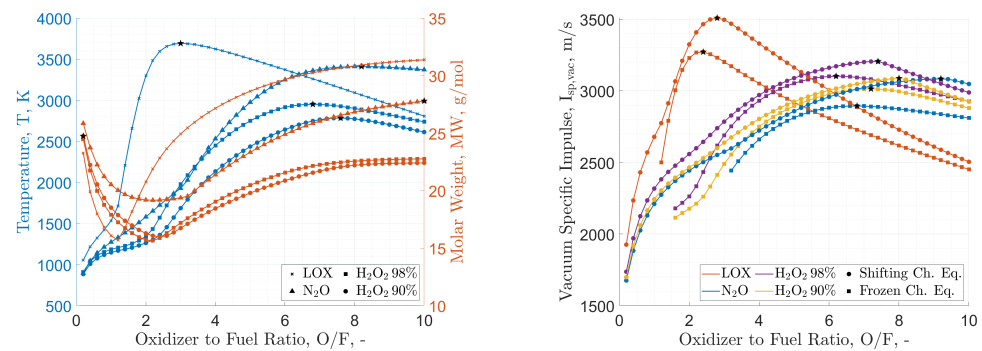
Figure 2 provides a comparison of specific impulse performances between cryogenic and storable oxidizers. The reported data shows the reduced gravimetric specific impulse performance of H<sub>2</sub>O<sub>2</sub> and N<sub>2</sub>O compared to LOX. Data from Table 1 show the attractive density of H<sub>2</sub>O<sub>2</sub> over N<sub>2</sub>O and LOX. This feature, together with the higher gravimetric specific impulse, suggests a better suitability of this oxidizer over nitrous oxide when the final application requires high volumetric efficiency. However, both storable oxidizers provide the possibility of HREs with equivalent or superior performance compared to AP-based solid propellants, whose theoretical specific impulse in the same conditions of the data reported in Figure 2 is in the range of 1952 m/s to 3092 m/s for a typical commercial formulation with 68 wt.% AP, 18 wt.% micron-sized Al, and 14 wt.% HTPB. Focusing on the possible use of HREs in in-space applications, the peak values of the gravimetric specific impulse are comparable with those of hydrazine–nitrogen tetroxide storable propellants (in the range of 1556 m/s to 2296 m/s under similar operating conditions). In contrast to LOX-based systems, HREs based on N<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> feature relatively small variations of the gravimetric specific impulse over a relatively wide range of O/F (see Figure 2). However, for these systems, as well as for the cryogenic counterpart, it is possible to observe a specific impulse performance change when passing from fuel-rich to fuel-lean mixture ratios. Figure 3 provides an evaluation of the impact of this O/F shift on the emissions (as evaluated from a thermochemical equilibrium code). As discussed in Section 3, H<sub>2</sub>O<sub>2</sub> and N<sub>2</sub>O gravimetric specific impulse performances are not significantly affected by the addition of energetic additives. This is testified by the data reported in Figure 4, where Al is taken as the reference material, and in Table 2, where different additives are contrasted for a 10 wt.% load. The faint influence on the maximum specific impulse (with a corresponding small shift of the O/F at which the maximum performance is achieved) is accompanied by the presence of a small fraction of CCPs (typically <5 wt.%). Such a result suggests that solid-fuel loading with energetic additives should be considered as a strategy for regression rate tailoring, together with the possible implementation of non-conventional oxidizer-injection methods.

**Table 1.** Physical properties of storable oxidizers [71,97,98].

Property	HP 90 wt.%	HP 98 wt.%	N <sub>2</sub> O	LOX
Active O <sub>2</sub> content [%]	42	46	36	100
Boiling point @ 1 atm [K]	414	422	185	90
Freezing point @ 1 atm [K]	261	270	182	54
Density @ <sup>a</sup> 293 K, 1 atm [g/cm <sup>3</sup> ]	1.395	1.431	0.786 <sup>b</sup>	1.141 <sup>c</sup>
Vapor pressure @ <sup>a</sup> 293 K [Pa]	200	133	5.0 × 10 <sup>6</sup>	9.9 × 10 <sup>4</sup> <sup>c</sup>
Molar mass [g/mol]	32.4	33.7	44	32
Decomposition Temperature @ 2.0 MPa [K]	1029	1225	1907	N.A.

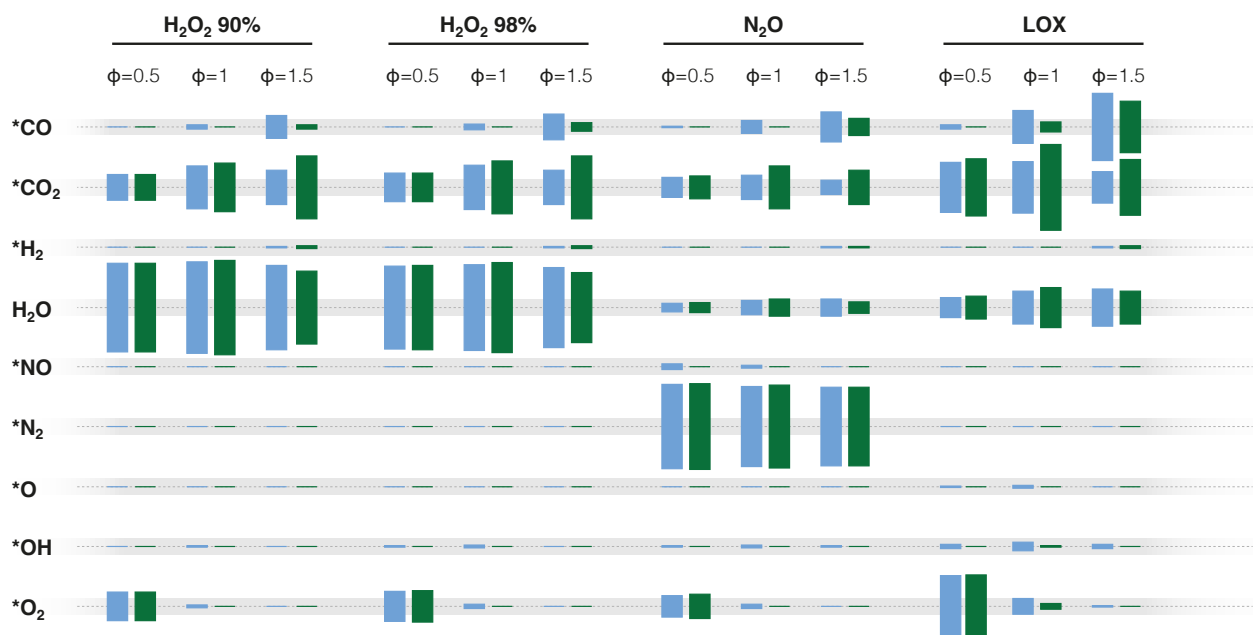
<sup>a</sup> Except where marked differently. <sup>b</sup> Liquid, @ 5.0·10<sup>6</sup> Pa (vapor pressure). <sup>c</sup> Liquid, @ 90 K (boiling temperature).



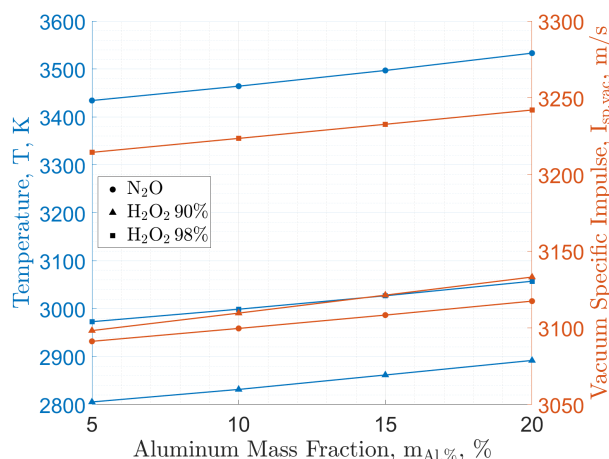


**Figure 2.** Cryogenic and storable oxidizers, theoretical performance by NASA-CEA code: adiabatic flame temperature and molar mass in the combustion chamber (left), vacuum specific impulse at exhaust (right). Paraffin-wax fuel ( $C_{50}H_{102}$ , heat of formation  $-1438.2$  kJ/mol [72]). Calculations are performed for: (i) combustion-chamber pressure,  $p_c = 7.0$  MPa, (ii) shifting chemical equilibrium and frozen chemical equilibrium (freezing @ throat), (iii) supersonic exhaust-to-throat-area ratio of 40. Maxima are highlighted by stars.

Legend: ■ Frozen Ch. Eq. ■ Shifting Ch. Eq. ■ 11% total combustion products



**Figure 3.** Exhaust composition from NASA-CEA for paraffin ( $C_{50}H_{102}$ , heat of formation  $-1438.2$  kJ/mol [72]) burning with different oxidizers at equivalence ratios ( $\Phi$ ) in the range 0.5 to 1.5. Calculations are performed for: (i) combustion-chamber pressure,  $p_c = 7.0$  MPa; (ii) shifting chemical equilibrium and frozen chemical equilibrium (freezing @ throat); and (iii) supersonic exhaust-to-throat-area ratio of 40. \* NASA-CEA thermodynamic properties fitted to 20,000 K.



**Figure 4.** Paraffin fuel ( $C_{50}H_{102}$ , heat of formation  $-1438.2$  kJ/mol [72]) burning with storable oxidizers: theoretical performance by NASA-CEA. Maximum adiabatic flame temperature and vacuum specific impulse at exhaust for increasing energetic additive mass fraction, with Al as a case study. Calculations are performed for: (i) combustion-chamber pressure,  $p_c = 7.0$  MPa; (ii) shifting chemical equilibrium; and (iii) supersonic exhaust-to-throat area ratio of 40.

**Table 2.** Maximum vacuum specific impulse of paraffin fuel ( $C_{50}H_{102}$ , heat of formation  $-1438.2$  kJ/mol [72]) loaded with 10 wt.% of different energetic additives. Corresponding oxidizer-to-fuel ratio and condensed combustion product mass fraction are reported. Calculations are performed for: (i) combustion-chamber pressure,  $p_c = 7.0$  MPa; (ii) shifting chemical equilibrium; and (iii) supersonic exhaust-to-throat area ratio of 40.

Additive	Oxidizer								
	N <sub>2</sub> O			HP (90 wt.%)			HP (98 wt.%)		
	I <sub>sp,vac</sub> m/s	O/F -	CCPs wt. %	I <sub>sp,vac</sub> m/s	O/F -	CCPs wt. %	I <sub>sp,vac</sub> m/s	O/F -	CCPs wt. %
-	3083	9.2	0	3087	8.0	0	3206	7.3	0
Al	3100	8.3	2.0	3110	7.4	2.2	3224	6.7	2.3
Mg	3091	8.3	2.9	3102	7.4	1.5	3215	6.7	1.1
AlH <sub>3</sub>	3106	8.5	1.7	3116	7.6	1.9	3231	6.9	2.0
MgH <sub>2</sub>	3091	8.5	1.5	3101	7.5	1.3	3215	6.8	0.9
LiAlH <sub>4</sub>	3099	8.5	1.4	3111	7.6	1.5	3225	6.9	1.6

### 3.1. Nitrous Oxide

At ambient temperature, N<sub>2</sub>O is liquid when stored at vapor pressure (see Table 1). In the following discussion, this is the default considered condition. Nitrous oxide features a high vapor pressure, with two main operating drawbacks: (i) a relatively low density; and (ii) a strong greenhouse impact (two orders of magnitude stronger than that of CO<sub>2</sub> [99]). The density of this liquid oxidizer is 30% lower than that of LOX (see Table 1). At the system level, the low volumetric efficiency of N<sub>2</sub>O is partially mitigated when exploiting its high vapor pressure for self-pressurization.

Nitrous oxide exothermic decomposition into N<sub>2</sub> (~66 wt.%) and O<sub>2</sub> (~34 wt%) yields flame temperatures in the region of ~1900 K (see Table 1). Thermal decomposition of the oxidizer occurs at temperatures of around 793 K, while a list of the possible catalysts for N<sub>2</sub>O decomposition is given in [100–103]. Further considerations on N<sub>2</sub>O physical properties are included and referenced in [104].

Nitrous oxide is one of the most commonly used oxidizers in HREs at the lab- and small scale (in particular, when dealing with sounding rockets). Moreover, it is the oxi-

dizer selected for one of the most relevant HRE realizations to date, namely the SpaceShipOne suborbital vehicle [14].  $N_2O$  is widely used in relatively small systems since the cost-effectiveness trade-off, along with its high safety compared with other oxidizers, is favorable [105]. From the propulsion system design viewpoint,  $N_2O$  high vapor pressure (Table 1) allows the self-pressurization of the oxidizer. Therefore,  $N_2O$  offers the possibility to eliminate the additional weight, complexity, and cost of the pressurization system. The peculiarities of nitrous oxide decomposition are reviewed in [106].

Given the wide use of nitrous oxide in experiments and small-scale firings, a large  $r_f(G_{ox})$  dataset exists. Table 3 provides an overview of the relevant results from the literature, considering the power-law fitting of the regression rate of Equation (1).

A wide series of lab-scale testing and hybrid sounding rockets were designed and implemented by Stanford University-related research groups [107–116]. The typical fuels considered in these efforts were paraffin wax and paraffin-based formulations.

In 2004, Van Pelt et al. [107] used paraffin with a  $N_2O$  oxidizer to launch a four-inch sounding rocket to nearly 1830 m. Then, in 2005, McCormick et al. [110] used paraffin loaded with 40 wt.% Al burning in  $N_2O$  to launch a 3 in (7.5 cm) sounding rocket to nearly 3050 m (10,000 ft).

Later, between 2006 and 2007, Lohner et al. [108] and Doran et al. [109] provided  $r_f$  data for  $N_2O$  in combination with conventional fuels (HTPB, PMMA, HDPE) and exotic formulations (SP1A—a paraffin wax, and Sorbitol—a sugar alcohol with chemical formula  $C_6H_{14}O_6$ ). These lab-scale firings included the testing of metalized fuel formulations including micron-sized Al (nominal size 2  $\mu m$ ). Different Al loads (5 to 20 wt.%) were mixed with the fuels to observe the effects on the  $r_f$ . Experimental data from these two studies are not reported in Table 3: the authors did not report any  $r_f(G_{ox})$  [108,109]. However, as discussed in [109], for HTPB, Al addition at 5 wt.% has a small effect on  $r_f$ , while a 10 wt.% promoted a more sensible effect. For Sorbitol, Al load exhibited no marked influence on the fuel consumption rate. On the other hand, the relatively large data-scattering of SP1A prevents any consideration of the outcomes when loaded with 10 and 20 wt.% Al, under the investigated conditions. Similar considerations hold for the data discussed in [117]. This latter study considers  $N_2O$  and its mixtures with  $CO_2$  for an HRE-based Mars Ascent Vehicle presenting non-metalized and metalized paraffin-based fuel data together with  $r_f(G_{ox})$  of SP1A and SP7A formulations from Stanford. No details have been given on the selected paraffin, and the selected Al features a (nominal) particle size of 2  $\mu m$ . Although the focus of the work discussed in [117] is on the effects of  $CO_2$  on the HRE combustion performance, the reference briefly analyze the behavior of the tested liquefying fuels in  $N_2O$ . No clear trend is noted when contrasting the non-metalized paraffin with the 40 wt.% Al-loaded counterpart over the  $G_{ox}$  range from 130 to 230  $kg/(m^2s)$ .

In 2006, NASA, in collaboration with Stanford University and the Space Propulsion Group (SPG), launched a project to develop a 100 km nitrous oxide–paraffin hybrid rocket vehicle (named Peregrine) to carry a 5 kg payload to > 100 km altitude [111]. The ground-test facility for Peregrine is detailed in [112], while Doran et al. [114] and Zilliac et al. [115] discuss details for the static firing tests of the engine. Efforts toward combustion efficiencies of around 95% are reported in these publications, with a limited discussion on the solid-fuel ballistics, but with relevant information on combustion instabilities.

In 2012, a rocket student team from Stanford University designed a medium-scale hybrid rocket using paraffin fuel and Nytrox (a mixture of oxygen and  $N_2O$ ) [116]. Two ground firing tests were performed to evaluate the performance of the engine, with nitrous oxide replacing the original oxidizer. A discussion of Nytrox follows at the end of this Section.

European efforts for  $N_2O$ -based sounding rockets include the results from the HEROS (Hybrid Experimental Rocket Stuttgart) project [105], a project exploiting paraffin-based fuel that achieved three successful launches over four years of the project's duration, and the activities of the Delft Aerospace Rocket Engineering (DARE) of TU Delft [118–123]. In the most recent DARE activities, a  $N_2O$ -Sorbitol propellant combination has been developed.

Nitrous oxide was used by Lee and Tsai [124] to characterize the burning behavior of 50% paraffin wax + 50% HTPB mixture fuel (known as 50P). Under the investigated conditions, the performance of the hybrid rocket was reported to be similar to the gaseous oxygen case in terms of  $r_f$  values (providing the  $r_f(G_{ox})$  shown in Table 3), though the use of  $N_2O$  as an oxidizer yielded lower specific impulse.

A 1 kN lab-scale HRE has been exploited by Grosse [72] to study the effect of diaphragms on combustion efficiency and the regression rate of the same. The tested diaphragms differ in geometry (featuring one and four perforations) and were placed at different locations along the fuel grain. Taking as baseline the performance of the grain without diaphragms, under the investigated conditions presented in [72], the  $r_f$  downstream of the diaphragm at the 33%-grain length position featured a 40% increase at 250 kg/(m<sup>2</sup>s) for the one-hole diaphragm. Such a performance enhancement reached an 84% increase at 180 kg/(m<sup>2</sup>s) for the four-hole diaphragm. Interestingly, positioning the four-hole diaphragm at 24% or 33% of the overall grain length produced the same combustion efficiency as the case where the insert is located at the grain end (before the aft-combustion chamber, which is the conventional location for such a device). In all these cases, the specific impulse of the system reached values close to 2021 m/s. The gain compared to the case without a diaphragm is estimated to be around 12% [72]. Enhanced propellant mixing and heat transfer justify the interesting and organically discussed results presented in [72]. This work was then extended by Bettella et al. [125], with a good agreement of the achieved results from the lab to intermediate scale.

The ballistic response of paraffin-based blends was investigated by Liu et al. [30] with both GOX and  $N_2O$ . In the study, a fuel blend (65P in Table 3) composed of paraffin (65 wt.%), PE (4 wt.%), HTPB (15 wt.%), Al (10 wt.%), Mg (5 wt.%), and  $Cu_2Cr_2O_5$  (1 wt.%) was investigated for regression rate determination in a lab-scale engine with an injection swirl geometrical number of  $SN_g = 6.83$ . No details are given in the paper about the metal powder particle sizes. In this study, the  $r_f(G_{ox})$  of Equation (1) yields a larger  $n_r$  value for GOX than  $N_2O$ . Such a result is justified by Liu et al. when considering the high oxidation capacity and the lower heat required during the injection of this oxidizer compared with the  $N_2O$ . Under the operating conditions tested in [30], the  $r_f$  of the 65P formulation exhibited no significant differences between the two oxidizers. The typical gasification surface profile observed with swirl injection, with a pit in the proximity of the oxidizer inlet [36,61–63], characterizes the post-firing grains of this study.

The effects of oxidizer-injection geometry on the performance of a 1 kN paraffin/ $N_2O$  HRE was investigated in [126]. Showerhead, hollow-cone, pressure-swirl, and vortex injectors were compared. The fastest  $r_f$  was achieved with a vortex injector. The results are due to the higher residence time promoted by the vortex flow, together with higher mass fluxes reached in operations with this injector configuration. The evaluation of different showerhead injection systems is reported by the same research group [127]. In this work, the same engine and propellant composition employed by the authors in [126] is considered. Showerhead injectors with injection holes were tested in the range 0.8 to 1.8 mm for several channels spanning from 71 to 11. The injector with the smallest orifice size showed the fastest regression rate and produced the  $r_f(G_{ox})$  power-law approximation reported in Table 3. This injector also provided the highest efficiencies in terms of characteristic velocities, with values in the range 85% to 95%, with a  $G_{ox}$  dependence (the higher the mass flux, the higher the efficiency).

The same microcrystalline paraffin wax that was tested by Grosse [72] was used as fuel in a vortex flow HRE with 1 kN thrust presented by Bellomo et al. [128]. The work discusses experimental results studying the effects of tangential vortex oxidizer injection, evaluating different pre- and post-combustion-chamber configurations. Vortex injection effects are contrasted with the standard (axial) flow case. Vortex injector details given by the authors in [128] show a configuration with six inlets with a diameter of 1.2 mm, and an injector channel of 25 mm. The latter diameter coincides with the grain port diameter in the absence of a pre-combustion chamber. Vortex injection decreased pressure oscillations compared to

the axial case from 7% to 4%. At the same time, a 40% regression rate increase was achieved, for a reported  $a_r$  enhancement of 67% ( $n_r$  being arbitrarily set to 0.5 in this study, given the neutral trend of  $p_c(t)$ ). Using diaphragms, the reported  $r_f$  enhancement was in the region of 6%. Combustion efficiency reached 96% when combining the vortex injection with a diaphragm at the end of the grain. The achieved results proved: (i) the impact of propellant mixing before expansion; and (ii) the stronger impact on  $r_f$  enhancement of vortex injection compared to the use of diaphragms.

Nardozzo et al. [129] used  $N_2O$  as an oxidizer to conduct counterflow diffusion flame experiments with HTPB fuel. These tests aimed to investigate the effect of pressure on the  $r_f$  of hybrid fuels. The fuel  $r_f$  was found to slightly increase for increasing chamber pressure. This result contrasts with what was achieved by the authors in [55], where HTPB showed  $r_f \propto 1/p_c$ . However, this different behavior could be due to the use of a different oxidizer (GOX) or the loading of metal in the fuel.

A comparison between the ballistic response of HTPB-based fuels burning in gaseous  $O_2$  and  $N_2O$  was reported by Carmicino et al. [130]. In the same work, the  $r_f$  of metalized HTPB formulations are contrasted with those of paraffin-based fuels. Tests were performed in an HRE with a showerhead injector and grains with single-port perforation. Non-metalized HTPB showed no  $r_f$  dependence on the oxidizer tests. The addition of micron- and nano-sized Al to HTPB (with mass fractions of 3 and 12.8%) promoted regression rate and mass burning rate enhancements for tests in  $N_2O$ . As reported in the original paper, this result features good agreement with other relevant literature data on HDPE combustion with the same oxidizers [108,131]. Micron-sized Al is a spherical powder with a mean diameter in the range of 6.5 to 8  $\mu m$ . The nanometric powder is produced by electrical explosion of wires and features a particle size of 100 nm. The average regression rate enhancement for micron-sized Al was 25% over the non-metalized HTPB for oxidizer mass flux of 100  $kg/(m^2s)$ . Under the conditions tested by the authors in [130], the performance of nano-sized Al exhibited similar results to the coarser Al counterpart. The paraffin-based fuel formulation tested by Carmicino et al. is a blend of macrocrystalline paraffin wax with 15 wt.% styrene polymer [35,36]. Paraffin-based formulation enabled an 80% regression rate increase over the metalized HTPB in the test conditions analyzed by the authors in [130]. As discussed by Carmicino et al., this result is possibly affected by the relatively low mechanical properties of the blend, causing solid-fuel sliver detachment.

Nyrox is a mixture of liquid  $N_2O$  and oxygen. The two gases are highly miscible in liquid phase. A detailed theoretical investigation of Nyrox is presented by the authors in [132].

Since vapor-phase  $N_2O$  can experience rapid thermal decomposition [133], Nyrox can be implemented to reduce such risk [95]. The maximization of the oxygen dilution in nitrous oxide requires a storage condition at 273 K of 0.9 MPa (higher than the corresponding  $N_2O$  vapor pressure). A discussion on the ignition and combustion of electrical arc-ignited 3D-printed ABS fuel grains burning with  $N_2O$  and gaseous oxygen is reported in [95,134,135]. In particular, in these latter works Nyrox 87 (87 wt.%  $N_2O$ , with 13 wt.%  $O_2$ ) is used as an oxidizer in comparison with oxygen.

From data given by in [95], the Nyrox 87-ABS regression rate is moderately lower than for GOX/ABS (−25%). This result is primarily due to the reduced flame temperature and the associated heat transfer from the flame zone to the fuel surface. However, under the investigated conditions presented in [95], the  $r_f$  of Nyrox 87-ABS is nearly doubled compared to the  $N_2O$  case. Despite its acceptable performances, the Nyrox/ABS propellants exhibit mean ignition latencies that are significantly larger than for gaseous oxygen: 0.9 s versus 0.3 s [95]. However, in actual systems, these delays could have a limited impact when considering relatively long firing times. Multiple prototype ground-test units with thrust levels varying from 4.5 N to 900 N have been developed and tested by Whitmore et al. [95,134,135].



**Table 3.** Regression rate vs. oxidizer mass flux data of solid fuels with N<sub>2</sub>O as an oxidizer [see Equation (1)]:  $a_r = [\frac{mm}{s} / (\frac{kg}{m^2s})^{n_r}]$ , with  $G_{ox} = (\frac{kg}{m^2s})$ , except where otherwise stated.

Fuel	$a_r$	$n_r$	Ref.	Notes
SP-1a (Paraffin Wax)	0.155	0.50	[136]	
	0.178	0.50	[107]	
SP-7	0.078	0.545	[117]	
Sasol 0907 w/o diaphragm	0.132	0.56	[72]	Commercial paraffin wax (microcrystalline): congealing point 356–367 K, assumed as C <sub>50</sub> H <sub>102</sub> .
Sasol 0907 w 1-hole diaphragm, pre-grain	0.162	0.49	[72]	
Sasol 0907 w 1-hole diaphragm, post-grain	0.539	0.36	[72]	
Sasol 0907 w 4-hole diaphragm, pre	0.145	0.54	[72]	
Sasol 0907 w 4-hole diaphragm, post	0.293	0.52	[72]	
Paraffin	0.159	0.784	[127]	$46 \frac{kg}{m^2s} < G_{ox} < 51 \frac{kg}{m^2s}$
50P	0.115	0.504	[124]	Fuel formulation with 50 wt.% Paraffin + 50 wt.% HTPB $125 \frac{kg}{m^2s} < G_{ox} < 475 \frac{kg}{m^2s}$
65P	0.088	0.395	[30]	Fuel formulation with 65 wt.% Paraffin + 15 wt.% HTPB + 4 wt.% PE + 5 wt.% Mg + 10 wt.% Al + 1 wt.% Copper Cromite $91 \frac{kg}{m^2s} < G_{ox} < 242 \frac{kg}{m^2s}$
Paraffin + SEBS-MA	0.072	0.77	[36,130]	Macrocrystalline wax, 15 wt.% SEBS-MA $30 \frac{kg}{m^2s} < G_{ox} < 100 \frac{kg}{m^2s}$
Sorbitol	0.286 <sup>a</sup>	0.310 <sup>a</sup>	[108]	$4 \frac{g}{cm^2s} < G_{ox} < 15 \frac{g}{cm^2s}$
	0.198 <sup>a</sup>	0.325 <sup>a</sup>	[108]	$5 \frac{g}{cm^2s} < G_{ox} < 14 \frac{g}{cm^2s}$
HTPB	0.417 <sup>a</sup>	0.347 <sup>a</sup>	[109]	$5 \frac{g}{cm^2s} < G_{ox} < 23 \frac{g}{cm^2s}$
	0.008	0.77	[95]	$5 \frac{g}{cm^2s} < G_{ox} < 50 \frac{g}{cm^2s}$
HDPE	0.020	1.09	[36]	Vortex flow pancake (VFP) HRE operating in fuel-rich conditions. $4.5 \frac{g}{cm^2s} < G_{tot} < 7.5 \frac{g}{cm^2s}$
	0.104 <sup>a</sup>	0.352 <sup>a</sup>	[108]	$2.5 \frac{g}{cm^2s} < G_{ox} < 25 \frac{g}{cm^2s}$
	0.248 <sup>a</sup>	0.331 <sup>a</sup>	[109]	$2.5 \frac{g}{cm^2s} < G_{ox} < 27.5 \frac{g}{cm^2s}$
PMMA	0.013	0.875	[137]	$77 \frac{g}{cm^2s} < G_{ox} < 191 \frac{g}{cm^2s}$
	0.111 <sup>a</sup>	0.377 <sup>a</sup>	[108]	$2.5 \frac{g}{cm^2s} < G_{ox} < 27 \frac{g}{cm^2s}$
	0.284 <sup>a</sup>	0.335 <sup>a</sup>	[109]	$2.5 \frac{g}{cm^2s} < G_{ox} < 30 \frac{g}{cm^2s}$
ABS	0.007 <sup>b</sup>	0.80 <sup>b</sup>	[95]	$5 \frac{g}{cm^2s} < G_{ox} < 50 \frac{g}{cm^2s}$

<sup>a</sup>  $r_f = [\frac{mm}{s}]$ ,  $G_{ox} = [\frac{g}{cm^2s}]$ . <sup>b</sup>  $r_f = [\frac{cm}{s}]$ ,  $G_{ox} = [\frac{g}{cm^2s}]$ .

### 3.2. Hydrogen Peroxide

Hydrogen peroxide is a green oxidizer, liquid at ambient temperature. In contrast to pure nitrous oxide,  $\text{H}_2\text{O}_2$  is not used in its pure form, but is typically blended in a water solution to reduce hazards in case of accidents. Usually,  $\text{H}_2\text{O}_2$  self-decomposes at a rate of  $\sim 1\%$ /year. Reduced rates are observed for high concentrations [94]. Currently, technologies allow the refinement of high-purity concentrations (99.99%), referred to as high-test peroxide (HTP). However, only concentrations up to 98% have been tested and implemented in sounding rockets. HTP has an active  $\text{O}_2 > 125\%$  compared to  $\text{N}_2\text{O}$ , and its density is superior to LOX (Table 1). Specific impulse is slightly better than nitrous oxide, but  $\text{H}_2\text{O}_2$  is characterized by a decomposition that leads to relatively low temperatures, with  $1000 \lesssim T \lesssim 1200 \text{ K}$  (Table 1). A promising feature of hydrogen peroxide lies in the use of its catalytic decomposition to reach auto-ignition temperature inside the combustion chamber and to start combustion without requiring an igniter. Except for the last reference, all the authors reported in Table 4 adopt this system. An alternative solution to the use of an external device (igniter) and a catalytic bed has been proposed by Whitmore et al. [138], by exploiting electrostatic fields stored in ABS fuel layers.

Focusing on exhaust plume composition as observed by equilibrium thermochemistry reported in Figure 3, high concentrations of  $\text{H}_2\text{O}_2$  result in lower CO and  $\text{CO}_2$  levels than LOX and  $\text{N}_2\text{O}$  oxidizers. However,  $\text{H}_2\text{O}$  significant emission could cause an environmental impact in the form of instantaneous radiative force (see Section 2.4).

Due to the lower accessibility and more difficult management of hydrogen peroxide compared to nitrous oxide, its application is not widely used. Although the latter is adopted by most of the student rocket groups working with HREs (Skyward Experimental Rocketry, Aris Space, HyEnd, PoliWRocket, DARE, etc.), there are no records of using  $\text{H}_2\text{O}_2$ . Among space companies, Gilmour Space Technologies is working on a three-stage hybrid rocket based on hydrogen peroxide as an oxidizer (Eris rocket) [139]. The Łukasiewicz Research Network—Institute of Aviation in Warsaw has designed ILR-33 Amber, a multistage using HTP and HDPE [140]. NAMMO Space works with 87.5%  $\text{H}_2\text{O}_2$  and HTPB with its Nucleus Sounding Rocket [141].

Hydrogen peroxide was and is widely investigated due to its attractive properties as an oxidizer in HREs. An intensive literature review of the use of HTP in hybrid rocket engines was performed by Okninski et al. [13,94]. Table 4 is a review of the collection made in [94], extended with further developments on the topic from the past two years.

In the past two years, new studies have been published. Granado et al. [142] designed an algorithm to simulate the operational life of a hybrid rocket engine at different conditions and configurations. Results were compared with experimental data obtained from their engine, HYCAT, which operates with 87.5%  $\text{H}_2\text{O}_2$  and HDPE.

Glaser et al. [137] studied a cylindrical discrete divergent–convergent fuel-grain configuration to decrease the O/F shift and enhance fuel–oxidizer mixing. Tests were performed with  $\text{N}_2\text{O}$  as well as with  $\text{H}_2\text{O}_2$  and HDPE (in two different facilities). Nitrous oxide global average regression rate fits the formula  $r_f = 0.013 G_{ox}^{0.875}$ , and  $\text{H}_2\text{O}_2$  was tested on the HYCAT engine (the same as the previous reference) obtaining  $r_f = 0.0003 G_{ox}^{1.32}$ . The latter engine showed a local  $r_f$  increase higher in the backward-facing steps than in forward-facing steps, in contrast to the  $\text{N}_2\text{O}$  engine. This different behavior probably lies in the different fuel lengths of the motor. Hydrogen peroxide performance with this fuel configuration surpasses the results found in [142], where the same motor with an axial grain shape was used.

Researchers at the Beihang University carried out an intensive investigation of hydrogen peroxide with a 95% concentration. Meng et al. [143] have studied the effects of adding aluminum and aluminum hydride to HTPB when using 95%  $\text{H}_2\text{O}_2$ . Zhao et al. [144] have worked with 98%  $\text{H}_2\text{O}_2$  and PE, exploring thrust throttling. This was achieved by combining a flow-oriented throttleable injector cooperating with a cavitating controllable venturi. This movable injector, designed to drastically reduce the pressure drop among all operating conditions, worked stably during cold flow tests and after ignition. Zhu et al. [145]

have proposed an efficient design optimization method, considering random and interval uncertainties to conduct uncertainty analysis and optimize the design of a hybrid rocket motor with mixed uncertainty. Verification of the method was performed by firing an eco-friendly, non-toxic, and high-performance combination of 98% H<sub>2</sub>O<sub>2</sub> and HTPB. Meng et al.'s most recent publication [146] focuses on simulating combustion surface regression through a numerical model powered by a Butterworth filter. The validation was performed through a firing test based on 98% HTP and HTPB. Wei et al. [147] carried out a deep numerical investigation to study a three-dimensional regression rate of an HRE single-port wagon-wheel fuel grain. A great contribution to the analysis was given by the computed tomography and image processing of the burnt grain. Tests were performed with 98% H<sub>2</sub>O<sub>2</sub> and HTPB.

Yun et al. [148] used 90% hydrogen peroxide along with HDPE to study the influence of port diameter and the length of solid fuel on the performances. Characterization was based on the ratio of nozzle throat area to fuel port area (*J*) for the port diameter, and the ratio of grain length to port diameter (*l*) to design the fuel length. When  $0.3 < J < 1$ ,  $200 < G_{ox} < 500 \text{ kg}/(\text{m}^2\text{s})$ . An increase of *J* was associated with a decrease in the fuel port diameter and strongly influences the regression rate. Optimum performance corresponded to  $0.4 < J < 0.6$ . An increase in *l* corresponded to an increase in combustion efficiency  $\eta_{c^*}$ , and O/F decreased, with the best results achieved for *l* = 20.

**Table 4.** Regression rate vs. oxidizer mass flux data of solid fuels with H<sub>2</sub>O<sub>2</sub> as oxidizer [see Equation (1)]:  $a_r = [\frac{mm}{s} / (\frac{kg}{m^2s})^{n_r}]$ , with  $G_{ox} = (\frac{kg}{m^2s})$ , except where otherwise stated. Ignition is through the catalytic bed and engines are characterized by a radial architecture, except where differently specified.

H <sub>2</sub> O <sub>2</sub> Conc.	Fuel	a <sub>r</sub>	n <sub>r</sub>	Ref.	Notes <sup>a</sup>
84%	Paraffin	0.0344	0.9593	[149]	$111 \frac{kg}{m^2s} < G_{ox} < 162 \frac{kg}{m^2s}$
85%	LDPE	0.0061	0.78	[150]	$70 \frac{kg}{m^2s} < G_{ox} < 211 \frac{kg}{m^2s}, 0.69 \text{ MPa}$
		0.0294	0.52		$70 \frac{kg}{m^2s} < G_{ox} < 211 \frac{kg}{m^2s}, 1.38 \text{ MPa}$
		0.0419	0.49		$141 \frac{kg}{m^2s} < G_{ox} < 492 \frac{kg}{m^2s}, 2.76 \text{ MPa}$
87.5%	HDPE	0.0066	0.8159	[142]	$150 \frac{kg}{m^2s} < G_{ox} < 400 \frac{kg}{m^2s}$
87.5%	HDPE	0.0003	1.32	[137]	Axial with discrete divergent–convergent grain $150 \frac{kg}{m^2s} < G_{ox} < 400 \frac{kg}{m^2s}$
87.5%	PE	0.0446	0.3288	[151]	Vortex end-burning configuration
88%	PE	0.0072	0.8	[152]	$155 \frac{kg}{m^2s} < G_{ox} < 400 \frac{kg}{m^2s}$
90%	PE	-	0.45	[153]	Single-port, rod-and-tube, telescope geometry
90%	HTPB	0.0402	0.5623	[154]	$109 \frac{kg}{m^2s} < G_{ox} < 255 \frac{kg}{m^2s}$
90%	Paraffin blend	0.279 <sup>a</sup>	0.732 <sup>a</sup>	[155]	Fuel formulation with 50 wt.% Paraffin + 20 wt.% PE wax + 18 wt.% EVA + 10 wt.% SA + 2 wt.% Carbon
90%	HTPB + 60 wt.% Al	0.014 <sup>b</sup>	0.7 <sup>b</sup>	[156]	$116 \frac{kg}{m^2s} < G_{ox} < 320 \frac{kg}{m^2s}$
	HTPB + 60 wt.% Al-Mg	0.029 <sup>b</sup>	0.6 <sup>b</sup>		$148 \frac{kg}{m^2s} < G_{ox} < 298 \frac{kg}{m^2s}$

Table 4. Cont.

H <sub>2</sub> O <sub>2</sub> Conc.	Fuel	a <sub>r</sub>	n <sub>r</sub>	Ref.	Notes <sup>a</sup>
90%	DCPD	0.057 <sup>b</sup>	0.49 <sup>b</sup>	[157]	281 $\frac{kg}{m^2s}$ < G <sub>tot</sub> < 450 $\frac{kg}{m^2s}$
	HTPB	0.060 <sup>b</sup>	0.50 <sup>b</sup>		
	HTPB + 25 wt.% NaBH <sub>4</sub>	0.019 <sup>b</sup>	0.73 <sup>b</sup>		
	HTPB + 50 wt.% NaBH <sub>4</sub>	0.008 <sup>b</sup>	0.90 <sup>b</sup>		
	HTPB + 25 wt.% AlH <sub>3</sub>	0.037 <sup>b</sup>	0.65 <sup>b</sup>		
90%	Paraffin	0.145	0.5	[158]	
90%	HDPE	0.0320	0.54	[159]	231 $\frac{kg}{m^2s}$ < G <sub>ox</sub> < 409 $\frac{kg}{m^2s}$
95%		0.0074	0.75		
90%	HTPB	0.0939	0.53	[160]	
98%		0.0982	0.53		
98%	HTPB + 20 wt.% Al	0.0039	1.0433	[161]	Solid propellant igniter 75 $\frac{kg}{m^2s}$ < G <sub>ox</sub> < 170 $\frac{kg}{m^2s}$
	HTPB + 20 wt.% C <sub>14</sub> H <sub>10</sub> + 20 wt.% Al	0.0043	1.0336		
	HTPB + 28 wt.% Al	0.0267	0.7249		
	+ 10 wt.% Mg + 2 wt.% C				

$$^a r_f = \left[ \frac{mm}{s} \right], G_{ox} = \left[ \frac{g}{cm^2s} \right]. \quad ^b r_f = a_r G_{tot}^{n_r}.$$

#### 4. Conclusions and Future Developments

A renewed interest in hybrid rocket propulsion has been fostered by current efforts toward green propellants. However, these systems feature a lower maturity level when compared to solid rocket motors and liquid rocket engines. The current work provides a review of the state of the art on currently ongoing test activities regarding HREs burning solid fuels with storable oxidizers such as N<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>. In the analysis, special emphasis is given to paraffin-based fuels. The work aims to identify possible fields of research that may improve knowledge of hybrid rocket engine combustion from a greener perspective.

The work highlights some critical points surrounding the assessment of the environmental impact of HREs. First, there is a lack of detailed studies considering the impact of soot on engine emissions. Independently of the fuel considered, analysis of this aspect is relatively sparse. Similarly, improved knowledge is needed of the exhaust composition of HREs featuring metal loads. Despite the relatively low mass fraction typically considered in HREs, and in light of the relatively small mass fraction of CCPs expected in the exhaust, no open literature study provides an insight into the evolution and impact of particulates from a hybrid plume. Similarly, analyses on the exhaust plume–environment interaction is missing. These points should be addressed in further studies, to develop safer, cheaper, and greener propulsion systems.

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## Abbreviations

The following abbreviations are used in this manuscript:

A-SOFT	Altering-intensity Swirling-Flow-Type
ABS	Acrylonitrile Butadiene Styrene
AMROC	American Rocket Company
AP	Ammonium Perchlorate
CCPs	Condensed Combustion Products
CFD	Computational Fluid Dynamics
CFP	Carbon Footprint
DARE	Delft Aerospace Rocket Engineering
GOX	Gaseous Oxygen
GWP	Global Warming Potential
HDPE	High-density Polyethylene
HEROS	Hybrid Experimental Rocket Stuttgart
HP	Hydrogen Peroxide
HRE	Hybrid Rocket Engine
HTP	High-Test Peroxide
HTPB	Hydroxyl-terminated Polybutadiene
iRF	Instantaneous Radiative Force
LH <sub>2</sub>	Liquid Hydrogen
LOX	Liquid Oxygen
NA	Nitric Acid
NO <sub>x</sub>	Nitrogen Oxides
O/F	Oxidizer-to-fuel Ratio
PMMA	Polymethyl Methacrylate
RFNA	Red-fuming Nitric Acid
SPG	Space Propulsion Group
SPLab	Space Propulsion Laboratory
UV	Ultra Violet
VFP	Vortex Flow Pancake

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