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Review

Review of Alternative Sustainable Fuels for Hybrid Rocket Propulsion

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Abstract: Hybrid rockets using specific oxidizer–fuel combinations are considered a green alternative to current propulsion systems, as they do not release very toxic or polluting exhausts, but only much less harmful substances such as carbon monoxide/dioxide and soot. However, in a long-term vision where space access and rocket transportation become a daily routine all around the world, the simple use of current green propellants could begin to become insufficient if the rest of the industry already follows much stricter rules, which are expected to tighten significantly in the future, thereby making emissions from rocket flights no more negligible. In this paper, the possible use of alternative sustainable solid fuels for hybrid rockets that are not derived from fossil fuels and are ideally carbon neutral is investigated and discussed based on the available data in the hybrid literature and on the literature related to renewable fuels in general. Even if this topic is apparently far away from the current necessities, as hybrid propulsion is not yet operational, it is paramount to consider a long-term vision and associated research efforts to make sure that the potential hybrid propulsion introduction to the commercial market is more than a simple flash in the pan, but offers a solid opportunity.

Keywords: hybrid rockets; alternative fuels; sustainable fuels

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Citation: Barato, F. Review of Alternative Sustainable Fuels for Hybrid Rocket Propulsion. *Aerospace* **2023**, *10*, 643. https://doi.org/10.3390/aerospace10070643

Academic Editors: Jongshinn Wu and Hui Tian

Received: 7 May 2023
Revised: 26 June 2023
Accepted: 15 July 2023
Published: 17 July 2023

1. Introduction

In recent times, there has been a great deal of focus regarding green technologies, as pollution and climate change have become a hot topic in the media. The rocket and space business have also been affected by this trend. However, thanks to the really small size of the industry and due to the difficulties related with rocket science and space technology, this sector has always followed a special paradigm, one which is much more relaxed compared to the conventional industry. In fact, the chemicals used in space propulsion have often been toxic, carcinogenic, and corrosive, such as, for example, storable liquid propellants including hydrazine and the mixed oxides of nitrogen. The solid propellants used in launch vehicles emit hydrochloric acid due the ubiquitous use of ammonium perchlorate oxidizers and the release of alumina particles from metallized fuel. After decades of relative stagnation, in recent years there has been a spectacular surge of interest towards multiple activities in space, both from governmental and commercial entities, with the birth of the so-called New Space Economy [1–5]. This boost has been possible thanks to several factors, which in particular include increased competition, new manufacturing technologies, miniaturization, reduced launch costs and higher availability, the proliferation of small satellites, and the rise of very large constellations in low earth orbit. The predicted number of satellites to become operational in the next decade is estimated to be higher than all the satellites produced in the previous space history combined. For these reasons, the number of launches is foreseen to grow exponentially in the following years. Moreover, new businesses such as suborbital/orbital space tourism are projected to start full operation and sustained growth, together with the commercialization and expansion of current activities that include, for example, Earth observation, communication, microgravity research/manufacturing, and many others. Many are even predicting the possibility of frequent and affordable point-to-point suborbital space travel [6–23]. In this context, the space propulsion industry, particularly the New Space one, is shifting away from the old conventionally used chemicals in order to reduce costs, time, and environmental impact, thus trying to mimic the other terrestrial industrial fields in the means of production. In this regard, hybrid propulsion has several potential advantages that could favor this trend [24–27]. Hybrid rockets can use green propellants, mainly hydrocarbon solid fuels coupled with oxidizers such as liquid oxygen, hydrogen peroxide, or nitrous oxide, which are widely available chemicals. These combinations do not release very toxic or polluting exhausts, but only much less harmful substances like water vapor, carbon monoxide/dioxide, unburnt hydrocarbons, and soot. Moreover, hybrid rockets are suitable to be produced in an industrial manner, as already pioneered by the American Rocket Company (AMROC) in the 1980s. This is in contrast with large solid propulsion that is a batch process only made possible by few specialized large companies (e.g., Northrop Grumman, Safran, IHI Corporation, Avio ...). Hybrid rockets are non-explosive in nature, as the oxidizer and fuel are not inherently mixed as is done in solid propulsion, thereby facilitating production and operations. Furthermore, they are less sensitive to tiny cracks and temperature, thus contributing to high reliability at frequent launch rates.

Space shuttle solid rocket boosters (SRBs) were nominally reusable, but their complex refurbishment tends to exclude solid propulsion from the reusable technologies. As already mentioned, current solid rockets are heavily polluting. Green oxidizer replacements such as ammonium nitrate, ammonium dinitramide, and hydrazinium nitroformate [28] have been under study for a while, but it seems that there are no current plans for upscaling. For these reasons, it is highly probable that the European Ariane 6 and the American United Launch Alliance (ULA) Vulcan will be the last newly developed major launch vehicles to use solid rocket boosters in the future, while some smaller launch vehicles could continue to be developed with this technology, thus borrowing know-how from the military ballistic missile field, particularly in China [29] and India [30].

Liquid propulsion, on the other hand, is having a huge development in recent years. While in the past, a typical cryogenic propulsion system was generally considered to be much more expensive on a thrust basis compared to a solid one (e.g., Shuttle RS-25 [31,32] vs. SRBs [33]), New Space companies now claim to have drastically reduced costs thanks to several manufacturing improvements, particularly through the use of additive manufacturing [34]. Liquid rockets can also be green, as they can use the same oxidizers as hybrids, together with analogous hydrocarbon fuels (e.g., Rocket Propellant-1, RP-1) or even better ones such as methane or hydrogen. Moreover, the modern (shuttle excluded) reusability of liquid propulsion has been demonstrated by SpaceX and is being pursued by many other players [35–43]. Thus, liquid propulsion seems to be the baseline for the future of space transportation.

Compared to liquids, hybrid rockets have nominally half the plumbing, but generally, their architecture is even simpler, particularly as they are frequently ablatively cooled, while liquid engines are more often regeneratively cooled [44]. The solid fuel cannot spill and is much more difficult to ignite and burn than a liquid fuel. For these reasons, hybrid propulsion is gaining tremendous popularity for small sounding rockets.

Several issues have always hindered hybrid rockets from reaching operational status, but this topic is out of the scope of this paper, and an extensive literature is already available e.g., [24–27,45–49]. At the moment, a few companies have serious plans to develop hybrid launch vehicles, such as HyImpulse (Neuenstadt am Kocher, Germany) [50], Gilmour Space Technologies (Helensvale, Australia) [51], INNOSPACE (Sejong-si, Republic of Korea) [52], TiSPACE (Taiwan) [53], DeltaV (Turkey) [54–56], and NAMMO (Raufoss, Norway) [57], while many others have similar ambitions but are still behind in large scale development (Equatorial Space Systems [58], Vaya Space [59], Hybrid Propulsion for Space [60] ...). Even if hybrid propulsion development is more focused on low production costs than reusability, it is possible to claim that much of the propulsion system can be conceived as reusable with the fuel/thermal protection cartridge as well as the nozzle parts that need refurbishment. Hybrids promise to provide increased reliability, shorter schedules, and lower costs compared to liquids. These aspects could be more and more important in the future if the number of launches should increase significantly. Typical current launchers' failure rates are around a few percent, which is orders of magnitude higher than what is acceptable for the other industries. If the launch business should expand exponentially, these numbers cannot be tolerable anymore and should be drastically reduced. In this regard, hybrids are often claimed to be a potential game-changer, even if the actual proof has not been possible to fully demonstrate yet.

2. Preliminary Assessment

Coming back to the original discussion, in a long-term vision where space access and rocket transportation become a daily routine all around the world, the difference in the green definitions between the space industry and other fields could be lifted, and the simple use of the of current green rocket propellants could begin to be not enough if the rest of the industry today already follows much stricter rules, which are expected to tighten significantly in the future, thereby making emissions from rocket flights no more negligible. In fact, many countries and stakeholders have proposed to enforce robust long-term (mainly carbon) emission reduction goals for 2050 (and beyond) that are consistent with the two different but related global warming limits: holding warming below a 2 °C increase above pre-industrial levels and reducing global warming below 1.5 °C by 2100. According to the recommendations, global energy and industry CO_2 emissions should reach zero around 2050 [61].

It is important to briefly highlight here that combustion emissions are strictly related to two very different issues: **global warming** and **pollution**, which have different effects but with the general media and public opinion often confusing the two.

Some space companies are already claiming to take into consideration the rocket emission aspect beyond the basic green definition, for example, Orbex (Forres, UK) [62], which is developing the prime liquid launch vehicle using bio-propane produced from renewable feedstocks such as plant and vegetable waste supplied by Calor, a major UK supplier; or bluShift Aerospace (Brunswick, ME, USA) [63], which is developing the hybrid rocket powered Red Dwarf launch vehicle, which uses a proprietary bio-derived solid fuel claimed to be renewable, carbon-neutral, clean burning, and biodegradable.

It is thus worth checking if these claims have a real meaning or if they have more of a marketing purpose (at least for now). To do so, only a rough order of estimated magnitude is sufficient. First of all, considering the different oxidizer options, only three green chemicals are widely available: liquid oxygen (LOX), nitrous oxide (N_2O), and hydrogen peroxide (H_2O_2). The first two are available in their pure form, while the latter is produced in a water solution, and the vast majority are not already at propulsion concentrations. Combustion with a typical solid hydrocarbon such as paraffin wax or polyethylene mainly releases water and carbon dioxide (Table 1), with significant quantities of carbon monoxide and unburned hydrocarbons, particularly for fuel-rich mixture ratios.

Table 1. Typical major hybrid rocket exhaust emissions for green oxidizers burned with solid hydrocarbon fuels (mass fraction, %).

Oxidizers/ Chemical Species	LOX	H_2O_2	N_2O
H_2O	21	60	9
CO_2	29	23	14
CO	26	7	10
O_2	13	5	4
O	3	0	1
OH	7	4	2
N_2	0	0	56
NO	0	0	2
others	1	1	2
Sum	100	100	100

In the case of nitrous oxide, a large quantity of inert nitrogen is present with minor quantities of harmful nitrogen oxides, thus making it slightly more polluting. Moreover, nitrous oxide is a very powerful greenhouse gas, approximately 300 times more powerful than carbon dioxide, so, if used extensively, it is important to carefully minimize its release during operations (e.g., filling/venting). The results in Table 1 have been calculated at 40 bar of chamber pressure and at the respective mixture ratio corresponding to each maximum specific impulse [64], and they will change somewhat with different inputs.

Oxygen combustion emits more carbon emissions on a kg basis compared to the other two; however, due to its high specific impulse (around 10–15%), less propellant mass is required [25–27]. A balanced comparison is out of the scope of this paper. The selection of the fuel can also contribute to different levels of carbon emission, both directly (emission per kg of propellant) and indirectly (higher/lower propellant mass due to lower/higher performance, respectively). It is worth noting that all hydrocarbon fuels (paraffin wax, PE, HTPB ...) tend to have nearly equal performance [64]. Other common solid materials that contain other molecules (such as sorbitol, ABS, PMMA, PVC etc.) generally provide equal or, more often, lower performance. Only exotic fuels or energetic additives can provide performance benefits compared to hydrocarbons, but they come with significant drawbacks, not only from a pollution point of view. What this paper wants to point out is that emissions will become, in the future, another major point to take into consideration in the classical propellant combinations trade-off analyses.

For the sake of an initial order of magnitude assessment, the typical total carbon emissions of launch vehicles burning hydrocarbons can be considered between 25–70% of the initial propellant mass, depending on the oxidizer–fuel combination and mixture ratio.

Total carbon emissions per year are around 40 billion tons [65–72]. The transportation field constitutes around 21% of that. The aviation industry is responsible for 12% of the transportation emissions, which corresponds to 2.5% of the total emissions, i.e., around one billion tons per year. There are 40 million flights per year (i.e., around 100,000 per day). The average flight time is around 2 h, with a carbon emission of 26 tons. It is worth noting that nearly $\frac{3}{4}$ of the mass of the carbon dioxide emitted by an air-breathing engine is the oxygen taken from the atmosphere. Thus, contrary to rocket engines, the total emitted carbon dioxide mass is higher than the propellant (i.e., fuel) stored on board (theoretically around three times).

In 2022, there have been 178 launches [73]. The most-employed launch vehicle has been the SpaceX Falcon 9, which has around 400 tons of propellant and has been launched 60 times last year [35].

In order to assess the problem of rocket emissions, three hypothetical launch vehicles are considered here: a 40 t propellant one, representing a possible generic small launch vehicle (Table 2), a 400 t one (such as the F9, Table 3), and finally a 4800 t one, similar to SpaceX Starship/Super Heavy [7] (Table 4). For the sake of simplicity, carbon emissions have been considered equal to 50% of the propellant mass. It is worth noting that, in reality, the payload efficiency (and consequently the emission efficiency) is higher for the 400-ton launch vehicle compared to the small launcher (around 4% vs. 1% [35]), while the Starship is proportionally less efficient for its massive size (2–3% [7]), probably due to its particularly full reusability features (such as stainless steel design). As a sideline note, reusable launchers, particularly using retro-propulsion for the reentry and landing, are slightly more polluting (as emissions) on a payload basis (roughly 40% for a F9) compared to their equivalent expandable versions [35]. However, we cannot neglect that the expendable launchers drop large pieces of hardware on the Earth, which are almost always not recovered.

The emissions of the three classes of launch vehicles have been compared with the total aviation emissions as a function of the foreseen launch rate. Moreover, to take the future regulation restrictions into account, four scenarios have been considered: one with the current situation and the others where the decarbonization of the aviation industry reaches 90%, 95%, and 99% of today values, respectively.

Table 2. Relative launcher CO_2 emissions (space launch/aviation, %). 40-ton propellant launch vehicle.

Aviation Decarbonization Level/ Launches per Year (Day)	0% (Current)	90%	95%	99%
30 (1 every 10)	0.00	0.00	0.00	0.01
300 (1)	0.00	0.01	0.01	0.06
3000 (10)	0.01	0.06	0.12	0.58
30,000 (100)	0.06	0.58	1.15	5.77

Table 3. Relative launcher CO_2 emissions (space launch/aviation, %). 400-ton propellant launch vehicle.

Aviation Decarbonization Level/ Launches per Year (Day)	0% (Current)	90%	95%	99%
30 (1 every 10)	0.00	0.01	0.01	0.06
300 (1)	0.01	0.06	0.12	0.58
3000 (10)	0.06	0.58	1.15	5.77
30,000 (100)	0.58	5.77	11.5	57.7

Table 4. Relative launcher CO_2 emissions (space launch/aviation, %). 4800-ton propellant launch vehicle.

Aviation Decarbonization Level/ Launches per Year (Day)	0% (Current)	90%	95%	99%
30 (1 every 10)	0.01	0.07	0.14	0.70
300 (1)	0.07	0.70	1.39	6.96
3000 (10)	0.70	6.96	13.9	69.6
30,000 (100)	6.96	69.6	139	696

From the previous tables, it is possible to infer some basic but important conclusions. The actual impact of launch vehicles emissions is completely negligible. For the medium launch vehicle, emissions reach a few percent only for 90–99% of the decarbonization levels and an astonishing 10–100 launches per day, which is 20–200 times the levels of the actual market. The total payload released into orbit will be in the order of 45 thousand tons (in LEO). It is difficult to envision such a huge increase in the mass into orbit. Regarding the small launcher, emissions reach a few percent only for 95–99% of the decarbonization levels and at least 100 launches per day. A total of 100 launches per day, considering an average payload of 1–2 small satellites of few hundreds kg, means a full mega constellation launched in a single year! It is difficult to think that such a large number of satellites would be put into orbit only by small launchers. To be certain, problems with orbital debris, as well as traffic management both in space and in the atmosphere, the availability of launch complexes and safety ranges would hit the market hard well before reduced carbon emissions are realized. Regarding the Starship, the warning threshold is reached in advance thanks to its high-propellant mass, which is still an incredibly large number of launches (particularly for its size), and deep decarbonization levels of the aviation industry are required. The only way this could occur would be to use the rocket launch vehicle for aircraft-like transportation, such as the nowadays often-cited point-to-point suborbital space travel. Proponents claim that this is possible thanks to dramatic cost reductions related to reusability and improved safety provided by technology development [7]. However, it is worth noting that modern aviation had less than two accidents per million flights in 2020 [74,75] compared with more than one out of 100 by typical rocket launchers [76]. The Airbus A380 has been certified after five planes flew more than 2000 flying hours in total [77]. It seems that the rocket industry is far from guaranteeing such levels, and it is probably only ready for the less-regulated space tourism market. A plane such as the Boeing 747 consumes approximately 150 tons of fuel for a 10 h flight [78], while the Starship will require an order of magnitude more of fuel for a single trip [7]. Even if the challenging full reusability target is met, it is really difficult to achieve the same level of reliability and costs. It is interesting to remember that the supersonic Concorde flew, on average, around 2000 flights per year [79–86]. The price of the ticket was approximately around 10k USD adjusted for inflation. This is still an order of magnitude less than the price of a ticket for a flight on Virgin Galactic SpaceShipTwo [87], even if prices are allegedly predicted to decrease significantly as commercial operations start to become routine. At the moment, there are slightly more than 200.000 ultra-wealthy individuals, i.e., with more than 30 million USD in net worth [88–91]. More than 56 million people are millionaires. The potential consumers are there. A total of 3000 flights per year would correspond, for instance, to one flight a day from ten different spaceports at the same time. A total of 30,000 flights per year would correspond, instead, to one flight a day from 100 different locations all around the world. However, the SpaceShipTwo is a much smaller vehicle, and its carbon emissions are estimated to be around 1.7 tons per flight, which will be negligible in every previous scenario [92]. As another side note, interestingly enough, the carbon emissions of the White Knight Two carrier are much higher, around 27 tons, as its flight time is around two hours compared with 60 s for the rocket and because, as already pointed out, in an air-breathing engine, carbon emissions are much higher than the amount of consumed propellant stored onboard (i.e., only the fuel).

Based on current trends and previous evaluations, carbon emission concerns are not an issue, as confirmed by several reports [93–103] and the impact assessments from various authorities [92,104]. However, if space activities grow significantly, it is possible that an indirect impact could come from regulations by local authorities, sometimes pushed by environmental groups or other entities, particularly in case of new commercial spaceports located relatively near to inhabited areas or natural habitats. In this case, pollution can be considered as a more important issue than global warming.

Another pressure for change could come from lobbying by other sectors such as the aviation industry, particularly if the rocket business starts to be seen as partially in competition with them (particularly in the case of point-to-point suborbital space travel) or simply by the scarcity of raw materials or increased prices due to the dismissal of the same chemicals by the other industries (such as in the case of hydrazine in the space business). In this regard, it is helpful to evaluate if hybrid propulsion can face these potential future issues, particularly as the technology is still not operational, so it would be not wise to invest money to field a technology that is at risk of being phased out soon afterwards.

Local environmental regulations regarding pollution and noise tend to not affect emissions released above a certain altitude; for example, airplane operations in the USA at or above 3000 feet (914 m) above ground level (AGL) are considered a categorical exclusion for the modeling of local air quality impacts as defined by the U.S. Environmental Protection Agency (EPA) [105]. Consequently, the air launch of rockets is a good way to avoid ground restrictions.

From the Aerospace Corporation report [93], it is important to underline that the major source of concern is considered to come from chlorine (by solid rockets), alumina (again by solid rockets, but potentially also hybrids), soot particles (mainly but not restricted to solids, hybrids, and kerosene liquid engines), and their not well known interactions with the ozone layer. Other minor constituents of the plume such as hydrogen oxides and nitrogen oxides could also affect ozone concentrations in the atmosphere. It is worth noting that nitrogen oxides can be produced indirectly by all propellant combinations through the thermal heating of the atmosphere, particularly for over-expanded plumes [103].

Again from [93], particles accumulate in the stratosphere in distinct layers and intercept incoming solar radiation. The lifetime of small particles injected into the stratosphere can be as long as four years. The energy from the intercepted solar flux warms the stratosphere, thereby indirectly adding to ozone loss by accelerating ambient-ozone-destroying reactions and producing a negative radiative forcing that cools the Earth's surface. Rocket emissions, therefore, act in the same manner as geoengineering schemes to counteract the warming from greenhouse gases. However, geoengineering is controversial, and there is no formal policy regarding its deployment. Moreover, ozone depletion has been the reason for banning specific substances such as chlorofluorocarbons (CFC), so rocket emissions could come into scrutiny in the future.

In any case, the interaction of rocket emissions with the atmosphere is still a very complex and not well understood topic, with models and predictions giving widely uncertain and sometimes contradictory results [93–103]. In particular, as will be more evident in the following, radiation forcing and other effects produced by **soot emissions** are the critical aspects that needs to be better interpreted and quantified when evaluating the impact of hybrids compared to liquid technology.

The first lesson learned is that, for commercial Earth applications (not deep space or military), the use of metals or other solid additives that exit the nozzle as particles and leave a visible trail, which is often used to improve the hybrid propellant density impulse, is not favorable. Moreover, the neat fuel should cover the walls of the combustion chamber as much as possible, while the thermal protections should release as few particle and toxic gases as possible. Finally, combustion should be as efficient as possible and should use the least amount of fuel as possible. The last two aspects go on par with an increase in performance, so they are in synergy with usual development efforts but come at the price of higher development difficulties, for example regarding limiting nozzle erosion due to higher temperatures and the higher presence of oxidizing species. Research into affordable high temperature/oxidation-resistant lightweight green ceramic materials is thus favorable to limit both erosion and particle/toxic emissions.

The engine architecture also has a tremendous impact on emissions. For example, the SpaceX gas generator cycle Merlin engine of the Falcon 9 produces a large amount of soot from the fuel-rich exhaust of the turbopump unit (Figure 1). Staged combustion engines, tank pressure, electric pump feeding, and clean gas generators (e.g., Soyuz H_2O_2 units) should provide much better emissions.

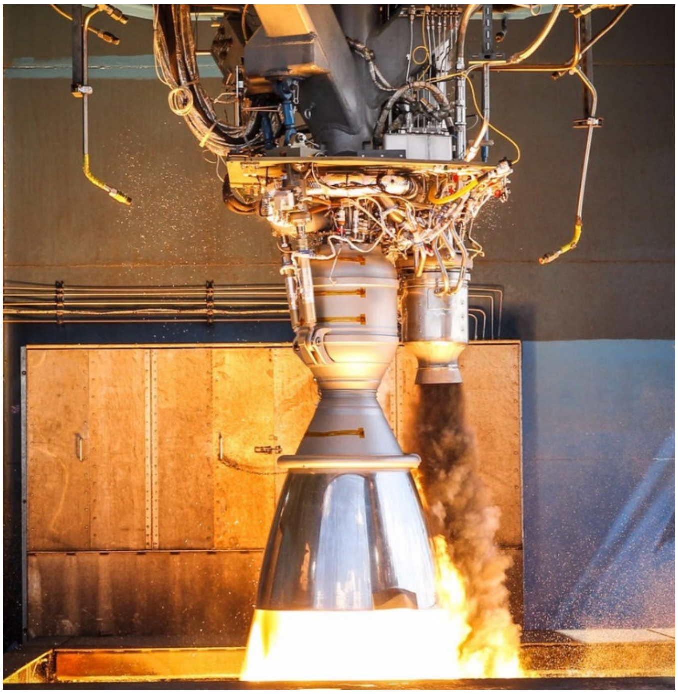

Figure 1. Firing test of a SpaceX Merlin 1D engine at SpaceX premises. The soot emissions of the fuel-rich gas generator are clearly visible on the right. From SpaceX.

A typical qualitative example of different exhausts' behaviors is the visual comparison between the plume of the SpaceShipTwo test flights performed with the HTPB-based motor (Figure 2), which presented a significant black smoke trail [106], and the Nylon-based one (Figure 3), which, on the contrary, presented a much cleaner flame [107]. We do not know if the effect is due only to the fuel itself or also to different motor configurations, combustion efficiencies, and/or mixture ratios (considering that they have been developed by different teams as well [108–110]). Moving forward, the hybrid exhausts characteristics should be more carefully taken into account in the future.

Figure 2. VSS Enterprise third rocket powered flight. Note the relatively smoky plume of the HTPB-based hybrid rocket motor. From Virgin Galactic trough The Telegraph [106].

Figure 3. VSS Enterprise fourth rocket powered flight. Note the relatively clean plume of the Nylon-based hybrid rocket motor. From National Transportation Safety Board (NTSB) [107].

In any case, the non-premixed turbulent diffusive flame of hybrid rockets [111–122], burning a solid material, could probably never compete with the best liquid engines burning liquid methane, or even less with liquid hydrogen. Additionally, methane-fueled engines can be expected to emit, uniquely, potentially significant amounts of hydrogen oxides (HOx) into the stratosphere [93].

Based on previous considerations, of all the pollutants and soot emissions seem to be the inherent Achilles heel of hybrids when compared with modern and future liquid engines, as they have a significant environmental impact and apparently cannot be reduced at the same level. At the moment, most of the hybrid development is focused on sounding rockets [123,124], small launch vehicles [125–127], and suborbital spaceships [87,92], which hold only a few tons of propellant or a few dozen tons at maximum, and they release a relatively modest total amount of soot compared with larger launch vehicles that burn hundreds of tons of propellant per flight.

Anyway, internal fluid dynamic design aside, it is possible to state that some fuels inherently burn more cleanly than others. HTPB has been a workhorse in hybrid rocket research and development, which has been borrowed from solid propulsion, together with its casting process. However, it seems to not be the ideal fuel when it comes to wide availability, the ease of mass production in a simple industrial environment, and pollution. Thermosets and elastomers often do not burn cleanly and do not allow for the possibility of melting and recycling production waste. In this regard, commodity plastics such as polypropylene and polyethylene [128], which are the two most widely used thermoplastics, seem to be a better choice. Paraffin wax is also an important candidate, particularly because it also has a high regression rate [129–137]. Other plastics such as polystyrene (PS) and polyvinyl chloride (PVC) release toxic gases (styrene and chlorine, respectively) when burnt [138–140]. Nylon and polyurethane (PU) have also been found to release hydrogen cyanide [141]. Poly (methyl methacrylate) (PMMA) has been used extensively in past hybrid research [113–121]. Polycarbonate and acrylonitrile butadiene styrene (ABS) are two plastics that have been also proposed and, particularly with the latter, have been investigated for hybrid propulsion, as they are also suitable (together with some others) for production by modern flexible technologies such as 3D printing [142–146].

Based on the previous considerations, there is a large variability in emissions between different hybrid solutions, so if limiting pollution is set as a requirement, this ends up having a huge impact on hybrid motor design. Therefore, it is better to keep this in mind during current development efforts and trade-offs before emission regulations will come into play in the future.

An environmental advantage of hybrids is that it is not possible to release the fuel through spill or evaporation, contrary to liquid fuels. Methane released during evaporation of the cryogenic liquid is a powerful greenhouse gas if vented in the atmosphere (80 times more than carbon dioxide on a twenty years scale [147,148]). RP-1 spills can hurt the environment, and this is one of the reasons sometimes that ethanol is preferred instead. Finally, the increased safety of hybrid solid fuels makes it more difficult for them to catch fire or lead to an explosion, thereby making hybrid propulsion easier to integrate with the surrounding environment.

In the following chapter, some possible paths for future sustainable hybrid fuel production are discussed.

3. Sustainable Hybrid Fuels

First of all, in order to be affordable and sustainable (in a broader meaning), a fuel should be available in significant quantities at a reasonably low price. Hybrid rockets have been demonstrated to be able to burn a very large multitude of solid materials, including lard and food such as salami and pasta. However, for practical operational systems, the choice is more complicated and restricted. Compared to industrial applications and stationary power plants, there are some specific problems with burning fuels for rocket propulsion: First, the exhausts are released directly into the atmosphere without any possibility of filtering, purification, or capture. Secondly, the requirement for very high performance (e.g., specific impulse, density, regression rate, thermo-mechanical properties . . .) significantly limits the practical fuel material choices and composition.

In this respect, three main paths toward sustainability have been identified, which are not mutually exclusive. The first one is to use recycled plastics that have been originally produced for other applications. The second possibility is the use of natural or bio-derived fuels. The final option is the production of synthetic fuels from renewable resources.

3.1. Plastic Recycling

Plastic recycling is the reprocessing of plastic waste into new and useful products. When executed properly, this practice has the potential to diminish reliance on landfills, preserve resources, and safeguard the environment against plastic pollution. Despite the growing trend of increasing recycling rates, they still fall considerably short of what is technically achievable, primarily due to economic factors. In 2015, the global recycling rate stood at 19.5%, with 25.5% being incinerated and the remaining 55% being mainly deposited in landfills [149–155].

More than 90% of plastic waste consists of thermo-softening polymers, which can be melted and reformed into new items through a process called mechanical recycling. This practice is the most widely used form of recycling globally. Its prevalence is attributed to its simplicity, cost-effectiveness, and lower carbon footprint compared to other methods. However, the quality of the recycled polymer can be diminished due to factors such as polymer degradation and the accumulation of impurities, which restricts its usefulness and effectiveness. Technological solutions exist for many of these issues, although they come at a financial expense [149–155].

Nonetheless, this could be a relatively minor issue for the rocket industry, where the cost of the propellant is often almost negligible compared with the other expenses. Moreover, the fuel mass in a hybrid rocket burning a typical hydrocarbon such as HDPE or paraffin is only around 30% of the total propellant mass in an oxygen-based system (mixture ratio around 2–3) and less than 15% in a hydrogen peroxide or nitrous-oxide-based motor (mixture ratio around 6–8). On the contrary, in rocket propulsion, particularly for the most demanding applications, the quality and consistency of the fuel grain characteristics is of paramount importance. Moreover, as emissions are considered here, the purity of the final product that has to be burnt greatly affects the exhaust composition.

When plastic is recycled in open-loop recycling (also called downcycling), the quality of plastic is progressively diminished with each recycling cycle. This is the main solution that is adopted, as the only industrial successes of closed-loop or primary recycling have been with PET, polyethylene terephthalate, and bottles [155]. More than 50% of all plastic produced and plastic waste is made up of polyolefins (HDPE, LDPE, PP, and much less PS). HDPE is accepted at most recycling centers in the world, as it is one of the easiest plastic polymers to recycle. ESE World B.V. carried out a test to demonstrate that HDPE can be recycled at least 10 times [156]. ESE found that the plastics injection molding and shredding techniques do not alter the material properties over the entire period of reuse. In order to meet the strict quality requirements of rocket propulsion and to also minimize the unwanted collateral emissions, it is possible that batches of recycled fuel plastic could be melted and purified further before casting the solid grain.

Feedstock recycling offers an alternative approach to mechanical recycling by converting waste plastic back into its original chemical components (monomers). These monomers can then be polymerized again to create fresh plastic, thereby theoretically allowing for nearly infinite recycling. However, in practice, feedstock recycling is significantly less common than mechanical recycling. Its implementation is limited due to the lack of reliable industrial-scale depolymerization technologies for all types of polymers and the higher equipment costs involved. While commercially viable depolymerization of PET, PU, and PS exists to some extent, the feedstock recycling of polyolefins, which account for nearly half of all plastics, is much more limited.

Almost all the plastic cited in advance can be recycled in one way or another. A special mention goes to ABS. ABS has very good mechanical properties and has been shown to have a combustion performance analogous to HTPB. ABS finds great application in the production of products through the use of rapid prototyping machines and production techniques such as FDM (fluid deposition modeling). For this reason, several researchers advocate the use of ABS in hybrid propulsion in order to exploit the advantages of this manufacturing technique, in particular the flexibility in the grain design shapes. ABS is assigned the number 7—"Other Plastics"—recycling code. Most municipalities do not recycle number 7 (contrary to HDPE, which uses code number 2). Instead, a very large percentage of these "Other Plastics" wind up in landfills. Nowadays, ABS recycling is limited to industrial froth floatation and injection molding units. ABS is relatively easy to recycle, so it is possible that, in the future, recycling efforts will expand as the market of 3D printing will continue to grow [157]. However, ABS mechanical properties tend to degrade more rapidly with the number of re-cycles than HDPE.

In general, the mixing of virgin plastic and recycled plastic is a way to obtain intermediate properties and still partially improve the sustainability of the material.

Despite the inability of thermoset polymers to be re-melted, advancements have been made in mechanical recycling techniques for these materials. Typically, this process entails breaking down the material into small crumbs, which can subsequently be combined with a binding agent to create a new composite material. For instance, polyurethanes can undergo recycling to become reconstituted crumb foam. Similarly, tire recycling produces crumb rubber that can be utilized as an aggregate. While there have been developments in devulcanization technologies to facilitate the recycling of rubber waste, only a limited number of these methods hold commercial significance.

For the reasons exposed in this paragraph and in the previous chapter, **thermoplastic fuels**, in particular **polyethylene**, **polypropylene**, and **paraffin wax**, are by far preferable as potential sustainable hybrid fuels, as they are the most abundant, clean, and easy to recycle.

Nevertheless, the firing of recycled plastic in a hybrid rocket does not avoid the emissions due to the combustion. However, the hybrid rocket can be thought of as a sort of incinerator, thus eliminating material potentially directed to landfill. Conventional industrial ground incinerators can be considered much better in a one-to-one comparison thanks to their specific design, large size, and filtering/purification units, but the hybrid rocket is providing a capability (rocket propulsion) that will require something to burn anyway, so in this way it can provide an added contribution to the reduction of waste without requiring the further extraction of fossil fuels.

In this respect, in addition to a tight control of the fuel supplies and a careful attention to obtaining clean burning (or as clean as possible) to keep polluting emissions at a minimum, in order to completely eliminate fossil fuels as the primary source, it is necessary to resort to one of the two following solutions.

3.2. Bio-Derived Fuels

A bio-derived fuel is produced through contemporary processes from biomass, rather than by the very slow geological processes involved in the formation of fossil fuels, such as oil. Thanks to photosynthesis, the energy for the growth of plants is taken by the Sun, and the carbon is absorbed from the carbon dioxide in the atmosphere. Thus, ideally, biofuels are carbon neutral, as the amount of carbon released by combustion is the same as that absorbed during the plant lifetime. In reality, the collateral works tend to make the equation less perfect, even if the use of renewable resources for the energy required by cultivation activities help improve the balance [158,159].

Bio-polyethylene (PE) can be produced by synthesizing the ethylene monomer via the dehydration of bioethanol obtained from glucose [160]. The glucose can be obtained from different biological feedstocks, such as sugar cane, sugar beet, starch crops coming from maize, wheat, or other grains and lignocellulosic materials. In 2010, on a commercial scale, the first companies to produce bio-PE have been the Brazilian company Braskem and the joint venture between Dow and Crystalsev. Dow is the second largest chemical manufacturer in the world, while Crystalsev is the major Brazilian ethanol producer. Furthermore, the chemical companies Solvay, Nova Chemicals, and Petrobras are in the bio-PE market, wherein they contribute to the production of about 20% of the world's bio-based plastics production. At the beginning, bio-ethylene production was not considered to be cost-competitive when compared with petrochemical-derived ethylene, but, starting from 2008, the price of one barrel of ethanol derived from sugar cane has become competitive with the price of one barrel of crude oil (about 115 USD versus 80 USD in 2020, where 1 L = 0.0085 barrel). The price of 1 kg of bio-PE is about 30% higher than petrochemical PE [160].

PS, epoxy resins, and rubbers such as ethylene propylene diene monomer rubber (EPDM) could be further bio-based candidates for the use of bio-based ethylene. (Reinforced) EPDM is a typical solid rocket thermal protection, and epoxy resin can be used in thermal protections and structural parts made out of composite materials.

Bio-PP could be obtained from biological resources through the butylene dehydration of bio-isobutanol obtained from glucose and subsequent polymerization. With respect to the production of bio-PE, the process followed to obtain bio-PP has been less explored, which explains why bio-PP has not yet been commercialized.

Bio-PU can be produced from soybean (polyol)-based pre-polymers [161]. Two types of polyurethane were synthesized in Brazil for testing in hybrid rockets [162]; one was plasticized with a mineral oil, and the other was created with castor oil; the second was also later mixed with paraffin wax particles.

Stearic acid (formula $CH_3(CH_2)_{16}CO_2H$) obtained from palm oil can also be considered as a natural additive to paraffin wax [163] due to their similar characteristics (density, melting point, viscosity, hydrogen–carbon ratio of two . . .).

Another very interesting natural fuel is **beeswax** [164–170]. Beeswax (cera alba) is a natural wax produced by honeybees of the genus Apis. Worker bees use the beeswax to build honeycomb cells. Chemically, beeswax consists mainly of esters of fatty acids and various long-chain alcohols. Beeswax is edible, has similarly negligible toxicity to plant waxes, and is approved for food use in most countries.

Beeswax is a tough wax formed from a mixture of several chemical compounds. An approximate chemical formula for beeswax is $C_{15}H_{31}COOC_{30}H_{61}$. This means that the carbon-to-hydrogen ratio is around two, such as for a typical hydrocarbon fuel (HDPE, paraffin wax, kerosene . . .). The oxygen content is less than 5%. Its main constituents are palmitate, palmitoleate, and oleate esters of long-chain (30–32 carbons) aliphatic alcohols. Beeswax has a relatively low melting point range of 62 to 64 °C. The flash point of beeswax is 204.4 °C. The specific gravity of beeswax at 15 °C is from 0.958 to 0.975 [164–170].

The use of beeswax in hybrid propulsion has been investigated by several researchers, as its properties (thermomechanical, melting point, viscosity, energy content, and elements composition) are very similar to those of paraffin wax, including the high regression rate due to the entrainment of liquid droplets from its low viscosity melted surface layer (liquefying fuel behavior). Mixtures of beeswax with different additives (aluminum, ethylene-vinyl-acetate, charcoal . . .) have been tested in order to improve impulse density and/or mechanical properties. Centrifugal casting of beeswax grain, again in analogy with paraffin wax, has also been studied [170].

The annual production of beeswax reached 66,000 tons in 2019, with the top producer being India at 25,700 tons, followed at a distance by Ethiopia, Argentina, Turkey, and South Korea at 5800, 4900, 4700, and 3800 tons, respectively [171]. To put this into perspective, the fuel mass of the SpaceShipTwo is around one ton. A total of 300 launches per year will require less than 0.5% of the annual production of beeswax. A total of 3000 launches per year will require less than 5% of the current annual production. Scaling up the production of beeswax does not require building complex infrastructures.

BluShift Aerospace is developing fully modular hybrid rocket motors, which are referred to as MAREVLs (Modular Adaptable Rocket Engines for Vehicle Launch). Over the last five years, bluShift has been developing a very specific hybrid rocket motor that has some particular advantages [63]. The proprietary hybrid fuel that bluShift has been testing is claimed to be 100% bio-derived, to be carbon neutral, and to not contribute to a net gain in greenhouse gases. Moreover, the wax-based fuel that bluShift uses is claimed to have a high enough regression rate that fuel grains can be left with a simple single fuel port.

The mixing of biofuels with analogous/compatible fossil fuels, which is already performed in the automotive industry and, to a lesser extent, in the aviation sector, is an intermediate path to improve sustainability before a full satisfactory substitution is available.

To conclude this section, it is possible to affordably obtain bio-derived sustainable solid fuels with equal or similar properties to the currently used hybrid fuels such as PE and paraffin wax.

3.3. Synthetic Fuels

In the broadest definition, a synthetic fuel is a fuel that is not derived from natural occurring crude oil, but is obtained from either **syngas**, a mixture of carbon monoxide and hydrogen, or a mixture of carbon dioxide and hydrogen. The balance of the reactants is controlled through the water–gas shift reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2.$$

The syngas could be derived from the **gasification** of solid feedstocks, such as coal or biomass, or by the **reforming** of natural gas.

During gasification, the coal is blown through with oxygen and steam (water vapor) while also being heated (and in some cases pressurized). It is essential that the supplied oxidizer is insufficient for the complete oxidation (combustion) of the fuel. During the reactions mentioned, oxygen and water molecules oxidize the coal and produce a gaseous mixture of carbon dioxide (CO_2), carbon monoxide (CO), water vapor (H_2O), and molecular hydrogen (H_2).

Steam reforming or steam methane reforming is a method for producing syngas through the reaction of hydrocarbons with water. Commonly, natural gas is the feedstock. The main purpose of this technology is hydrogen production. The reaction is represented by this equilibrium:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2.$$

The reaction is strongly endothermic. Today, the steam reforming of natural gas produces most of the world's hydrogen.

A common method for refining synthetic fuels includes the **Fischer–Tropsch** conversion [172]. The Fischer–Tropsch process involves a collection of chemical reactions that convert a mixture of carbon monoxide and hydrogen or water gas into liquid or solid hydrocarbons. These reactions occur in the presence of metal catalysts, typically at temperatures of 150–300 °C and pressures of one to several tens of atmospheres. The Fischer–Tropsch process involves a series of chemical reactions that produce a variety of hydrocarbons, ideally having the formula C_nH_{2n+2}. The more useful reactions produce alkanes as follows:

$$(2n + 1)\ H_2 + n\ CO \rightarrow C_nH_{2n+2} + n\ H_2O,$$

where n is typically 10–20 for the production of liquid fuels (jet fuel, diesel fuel), but it is higher for solid waxes and around 3–4 for liquefied petroleum gas (LPG, mostly propane C_3H_8 and butane C_4H_{10})

Most of the alkanes produced tend to be straight-chain and suitable as diesel fuel. In addition to alkane formation, competing reactions yield small amounts of alkenes, as well as alcohols and other oxygenated hydrocarbons. In the process, lighter hydrocarbons are produced from the heavier ones by hydrocracking. Hydrocracking is a catalytic cracking process that is assisted by the presence of added hydrogen gas. Cracking is the process of breaking a long chain of hydrocarbons into short ones by the breaking of carbon–carbon bonds in the precursors.

Sasol Performance Chemicals, which produces the SASOL 0907 microcrystalline wax that is already used by several researchers in hybrid propulsion [173–178], is also one of the world leaders in the large-scale commercial application of proprietary technology for the production of synthetic Fischer–Tropsch (FT) waxes [172].

These synthetic waxes are made in a controlled environment using carbon monoxide and hydrogen as the feedstock to produce saturated, straight-chain hydrocarbons of consistently high purity and quality. The very linear molecular structure of the wax results in many desirable properties.

One significant advantage of synthetic fuels compared to the classical ones is the much higher purity of the product, which is beneficial both in keeping at minimum the unwanted secondary emissions and also in controlling/tailoring the physical/chemical properties of the solid fuel grain.

However, today the original constituents of the wax are still predominantly derived from fossil fuels, but if they are obtained by different cleaner methods, synthetic fuels could represent a possible path toward sustainability. In this regard, there are two main methods for making carbon-based sustainable synthetic fuels [179]:

1. **Electro-fuels** (e-fuels) made using captured carbon dioxide in a reaction with hydrogen, which are generated by the electrolysis of water;

2. **Synthetic biofuels** made through the chemical or thermal treatment of biomass or biofuels.

In the first case, the so-called green hydrogen can be obtained from water electrolysis using electricity produced from renewable resources, while the carbon content can derive from CO_2 removed from the atmosphere.

The second option is strictly related to the discussion on the previous section about biofuels, as the original sources belong to the same category. A distinction can be made depending on if the final product is obtained through chemical (catalytic conversion, synthesis) or biological processes (fermentation, anaerobic digestion). Regardless, as the full production path requires several steps, it is possible for both kinds of processes to occur at different points in the production chain.

Biomasses are already a renewable resource that can be used for gasification. Natural gas used in reforming can be replaced by biogas. Biogas is produced from the decomposition of organic materials. These residues are placed in a biogas digester in the absence of oxygen. With the help of a range of bacteria, organic matter breaks down, thus releasing a blend of gases: 45–85 vol% methane and 25–50 vol% carbon dioxide. This natural process, also called anaerobic digestion (AD), has long been used to leaven bread and brew beer. The output is a renewable gas which can be used for multiple applications. By upgrading biogas, biomethane is obtained. This purified form of raw biogas can be used as a natural gas substitute: CO_2, H_2O, H_2S, and other impurities are removed during biomethane production, thus leaving a high-caloric, pure gas.

Other ways of producing sustainable synthetic fuels are also available. In any case, if all the carbon present in the synthetic fuel is extracted from the atmosphere, either directly (artificial carbon dioxide removal) or indirectly (bio-sequestration through biomass growth), the combustion of the fuel turns out to be ideally carbon neutral. Obviously, the production of the fuel should employ renewable energy to maintain the balance of emissions.

Synthetic fuels are currently more expensive than fossil fuels and biofuels, but costs are expected to decrease in the future. Moreover, as mentioned before, fuel costs currently have an almost negligible impact on the whole expense of space operations. Even with advances in reusability, it is safe to assume that the impact will always be lower compared to the aviation sector. Therefore, the space sector could exploit the much larger pressure for the change and market size of the aviation industry. Because of the extreme sensitivity of flight performance on the weight, the fuel energy density is critical for the aeronautical field. Moreover, the huge complexity of the aeronautical certification process makes new alternative technologies more problematic to introduce. For these reasons, the field of aviation is pursuing the research on alternative fuels under the acronym of **SAF** (**sustainable aviation fuel**), which has been conceived as a drop-in replacement to currently used fossil fuels [180–198]. Again, the mixing of synthetic fuels with classical fuels (or even biofuels) can be thought as a possible transitory path toward full sustainability. In fact, in aviation, SAFs are already used in blends (up to 50% of the fuel), and tests are currently being carried out with 100% SAF [193–198].

Synthetic fuels usually require more energy to be produced compared with biofuels (unless in the latter, artificial light is used instead of the Sun), but with much less time and land surface (unless some of the constituents are also bio-derived).

The utilization of concentrated solar energy to directly provide the heat for certain steps of the production of synthetic fuels in a thermochemical reactor seems to be a promising solution to dramatically improve the energetic efficiency and sustainability of the process, and it is already under development [199–201], particularly for the aviation sector, where, as already mentioned, battery energy storage and hydrogen fuel cells still have a long way to go as alternatives to liquid fossil fuels.

To conclude, synthetic fuels have the concrete possibility to provide a sustainable, cleaner, and even higher-performing alternative to current fossil fuels for hybrid rocket propulsion.

4. Conclusions

After a period of relative stagnation, the space business is now expanding dramatically, being particularly led by the New Space Economy and its players. For routine access to space, low costs, high reliability, safety, and environmental friendliness are the key to success. Hybrid rockets have the potential to provide all these features to a greater extent than ever before. In the long term, the commercial space industry could face more restricted environment regulations, so it is important to analyze the possibility for the further improvement of rocket emissions.

It has been shown that carbon emissions from access to space will remain negligible in the coming years in almost all possible scenarios. Pollution from exhaust particles/soot is a much higher but still not a well understood concern. In any case, it is not guaranteed that an expanding rocket business will continue to be granted different (more relaxed) rules compared to the other industrial fields, so it is important to be prepared for future restrictions, particularly at local levels in privately owned/controlled sites. The air launch of rockets can mitigate some of these restrictions.

Hybrid rockets have much better exhausts than conventional solid rockets; moreover, they have some environmental advantages compared to liquids, but they generally cannot match the best-in-class emission levels of liquid propulsion. Nevertheless, it seems that, with the right tricks, which will also improve performance, hybrid emissions could be brought under sufficient control. Some suggestions include the following: using a neat fuel without additives that produce solid particles, running at an optimum mixture ratio and high combustion efficiency, using non-eroding ceramic inserts and green thermal protections, limiting the amount of ablative thermal protections, and lining the chamber with the fuel as much as possible.

Numerous kinds of plastics release undesirable toxic gases during combustion; in this regard, the most promising fuels both from an environmental and performance point of view are pure hydrocarbons such as PE, PP, and paraffin wax. To improve hybrid fuel sustainability, three solutions that are not mutually exclusive have been identified.

The first one is the use of recycled plastics. It has been shown that both thermoplastic and thermosetting material can be reused, but the latter are much more convenient to recycle for the production of solid fuel grains. Considering their performance and ease of reuse, polyethylene, polypropylene and paraffin wax are again considered as the best candidates, with other plastics as secondary options. Great care should be given to the quality of the final material that is (re)used for the realization of the solid grains, and some further purification steps are probably necessary, but the added cost is more tolerable in the space business compared to other industries. However, as the fuel is burned definitively, the release of greenhouse and/or polluting gases cannot be avoided.

The second, a more effective possibility is the use of bio-derived fuels, with the most investigated up to now in hybrid propulsion being natural beeswax for its strong similarity with paraffin wax. Bio-PE is also another promising candidate, as it is already commercially available at moderate costs.

Finally, the third option considers the use of synthetic fuels produced from renewable resources. Synthetic fuels are made in a controlled environment using carbon monoxide and hydrogen as the feedstock, thereby producing saturated, straight-chain hydrocarbons of consistently high purity and quality, generally trough the Fischer–Tropsch process. One significant advantage of synthetic fuels compared to the classical ones is the much higher purity of the product, which is beneficial in both keeping at minimum the unwanted secondary emissions and also in controlling/tailoring the physical/chemical properties of the fuel grain for better repeatability and performance.

Based on the analyses and results provided in this paper, current hybrid rocket research for commercial applications should be focused on neat fuels such as PE, PP, and paraffin wax without particle-producing additives, not only for they already-known interesting propulsive characteristics, low costs, and large availability, but also because they are the most straightforward replacements to an analogous sustainable fuel in the near future, thus exploiting strong synergies with the aviation sector. Moreover, more research and attention on hybrid rockets soot emissions is strongly recommended.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Conflicts of Interest: The author declares no conflict of interest.

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