

COB-2023-0414

PERFORMANCE PARAMETERS, ECONOMIC VIABILITY AND SUSTAINABILITY OF HYBRID ROCKET PROPELLANTS: A SYSTEMATIC REVIEW

Paulo Henrique Reis Brandão
Carlos Alberto Gurgel Veras
Edgar Amaral Silveira

University of Brasilia UnB - Brasília, DF, 70910-900
222106137@aluno.unb.br; gurgel@unb.br; edgar.silveira@unb.br

Abstract. Hybrid rocket propellant engines (HRPE) have been the focus of many studies o account of their potential for the Space 4.0 industry. In this context, this article conducts a systematic review on different pairs of oxidizer and fuel applied to HRPE, with special attention on performance, economic viability and sustainability. The analysis includes parameters such as regression rate, the specific impulse, mechanical properties, emissions, cost, and ease of access. The environmental impact of the propellants, such as their emissions and waste generation, is a crucial consideration in the development of environmentally friendly propulsion systems. The article also evaluates attempts to improve the performance of the propellants through the fuel blending, emphasizing the importance of sustainability in the selection of oxidizers and fuels combinations. The article’s main objective is to identify the best combination of oxidizer and fuel for the Brazilian scenario. A comprehensive literature search was conducted to achieve these objectives, and the findings were synthesized and analyzed. The InOrdinatio methodology was applied to 1739 documents obtained in the Web of Science search directory applying the following keywords: “hybrid rocket”, “propellant,” and “sustain*.” It can be inferred from the research that using fuel blends does not make significant changes in specific impulse, but can improve physical characteristics of the propellants in certain cases. A basic economic analysis was also performed for the launch system’s development, production and operation based on the best propellants combination. The findings can help researchers and engineers in the aerospace industry to design more efficient, cost-effective, and environmentally friendly hybrid rocket propulsion systems for future space missions. The review also investigates the use of high-performance hybrid rocket fuels in ramjet engines of long-range missile systems.

Keywords: : propellant, hybrid rocket, sustainability, combustion, regression rate.

1. INTRODUCTION

Hybrid rocket engines (HREs) possess distinct benefits when compared to either pure solid or liquid propellant systems. These advantages include inherent safety, straightforward mechanical design, reduced sensitivity to temperature fluctuations, the potential for throttle control, and lower costs relative to other options. Nonetheless, there are also drawbacks to consider, such as limited volumetric loading at high thrust levels, the possibility of fuel residuals, changes in mixture ratio during engine operation, and inefficiencies in combustion. One commonly cited disadvantage of HREs is their relatively low rates of regression for solid fuel, which affects their overall performances, Thomas *et al.* (2021).

Mishra (2017) states that the hybrid propulsion rocket engine is a novel engine that combines features from both solid propulsion rocket engines and liquid propulsion rocket engines in order to achieve improved performance. This engine has the capability to utilize both solid and liquid propellants, allowing for various combinations of propellant types. Among the different options, the combination of liquid oxidizer and solid propellant is the most commonly employed configuration.

Hence, the selection of fuel and oxidizer for these applications is critical to achieve a high specific impulse (Isp) that translates to better performance. It would be beneficial if the propellants possess a high-density specific impulse, as this would lead to efficient utilization of the structure and reduce the impact of structural factors. Additionally, it would be advantageous if the cost of the propellant ingredients is economically viable (Marothiya *et al.*, 2021).

DeLuca *et al.* (2013) presumed that for hybrid rocket propulsion, selecting the most optimal ingredients that have been proven effective in both liquid and solid rocket propulsion systems. The selection of a suitable liquid oxidizer plays a crucial role in designing the entire propulsion system. Fortunately, the technology associated with liquid oxidizers is well-established, thanks to the significant expertise gained over the past few decades in the field of liquid rocket propulsion. On the other hand, there is still room for improvement in solid fuel technology for hybrid propulsion. Challenges persist, including low regression rates and combustion inefficiencies, causing difficulties to carry out large-scale rocket operations. Figure 1 shows a possible configuration for a hybrid rocket system.

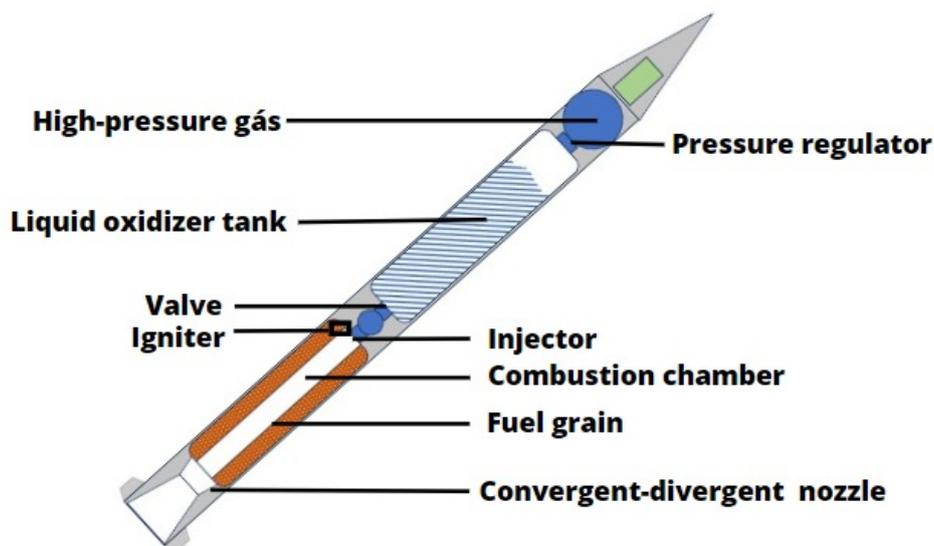


Figure 1. Hybrid rocket configuration.

2. BIBLIOMETRIC ANALYSIS

The bibliometric research methodology used was InOrdinatio, and the Web of Science was chosen as the data base. The topics in the search field were: TOPIC: ‘hybrid rocket’ OR TOPIC: ‘propellant’ AND TOPIC: ‘sustain*’. The document type selected in the bibliographic search was all documents, the publication date: All years and no filters for authors and countries.

The initial search yielded a total of 1739 documents. Following the implementation of the InOrdinatio methodology, the most relevant documents aligned with the research theme were carefully chosen, resulting in a refined list of 32 references. Subsequently, the data extracted from these selected references sourced from the Web of Science was imported into Vosviewer, a software designed for constructing and visualizing bibliometric network maps. An in-depth analysis involving co-authorship, co-occurring keywords, and co-cited references plays a essential role to determine the relationship among influential authors, pertinent keywords, and references related to the review subject. Bibliometric review results are presented in Tables 1, 2 and 3.

The most relevant authors obtained from the analysis are Merroto, Galfetti, Paravan, Deluca and Tadini with two documents and more than 60 citations. Table 2 related co-occurrence keywords will be used as a guide for choosing the paper keywords. The references from bibliography in the field of study of this paper have a considerable influence from Karabeyoglu and Whitmore whose work manly published in the Journal of Propulsion and Power.

Author	Documents	Citations
Merotto, L.	2	114
Galfetti, L.	2	67
Paravan, C.	2	67
Deluca, L. T.	2	64
Tadini, P.	2	64
Fanton, L.	1	61

Table 1. Authorship documents citations.

Keyword	Occurrences
hybrid rocket	12
combustion	9
regression rate	9
propulsion	7
fuel	6
propellant	6

Table 2. Keyword occurrences.

Reference	Citations
Karabeyoglu M.A., J Propul Power	24
Whitmore S.A., J Propul power	10
Chiaverini M.J., J Propul Power	5
Anflo K., Patent Wa	5
George P. S., Rocket Propulsion El	5
Deluca L. T., Acta Artonaut	4

Table 3. Reference citations.

Network maps created in Vosviewer of co-authorship, co-occurrence keywords and co-citation references relations are illustrated in Figures 2,3 and 4.

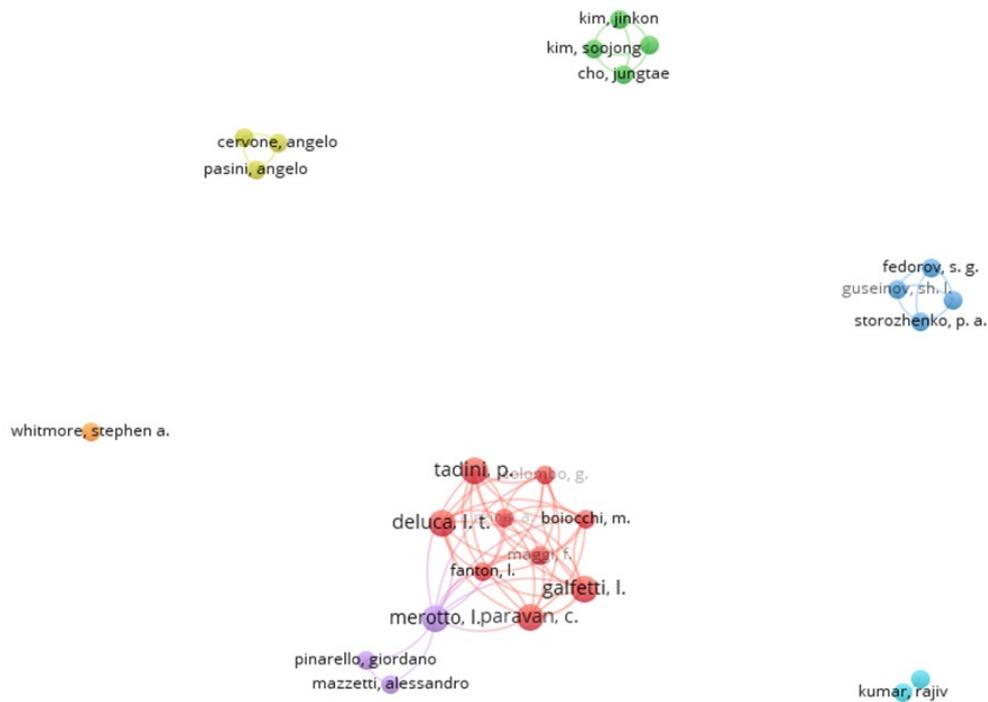


Figure 2. Co-authorship network map.

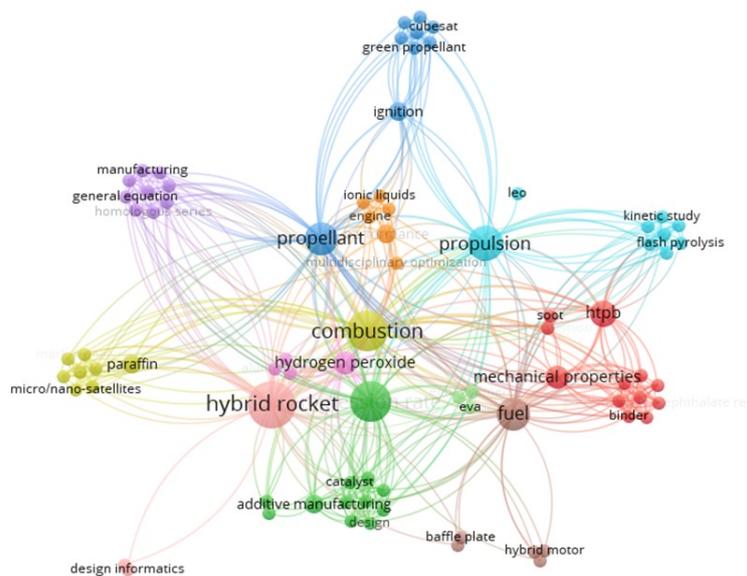


Figure 3. Co-occurrence keywords network map.

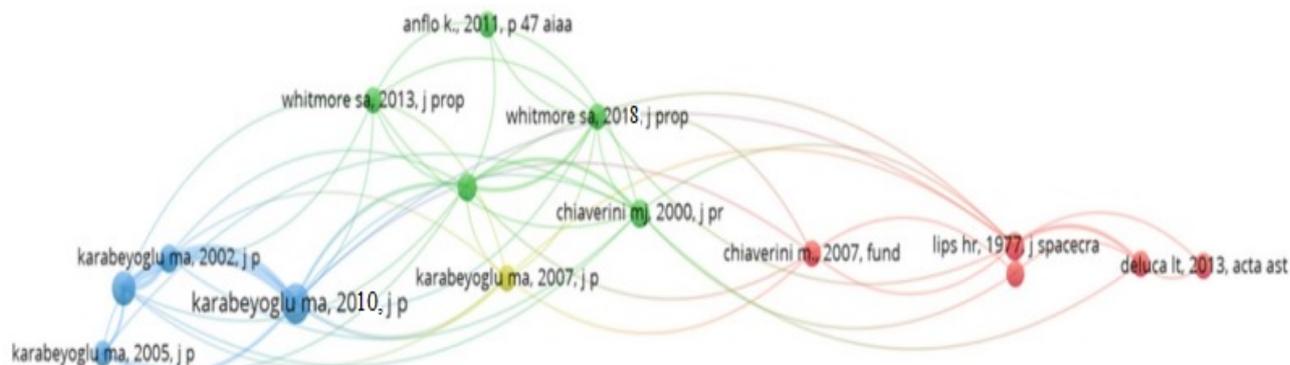


Figure 4. Co-citation references network map.

Examining the authorship connections displayed in Figure 2 reveals that out of the six author groups, five exhibit no links between them. Notably, Merotto is a bridge between two collaborative clusters. Particularly striking is the red group, which stands out as the most interlinked, featuring well-regarded authors like Tadini and Deluca, both recognized for their extensive citations within the field.

The co-occurrence keywords map, depicted in Figure 3, offers a visualization of the intricate relationships among the keywords featured. "hybrid rocket", "combustion", "propellant", and "propulsion" emerge as highlight keywords within the map.

The network map of co-cited references, as illustrated in Figure 4, provides a clear visualization of the significance and interrelationships among the chosen papers in this systematic review. Notably, the works of Karabeyoglu, Whitmore, and Chiaverini, published in the *Journal of Propulsion and Power*, stand out as pivotal and closely interconnected references within the research domain.

It's important to emphasize that the low number of citations for authors and references, identified during the bibliometric review is due to the initial choice of keywords and their alignment with the theme of the paper. After revisiting the search and utilizing only the keywords "hybrid" and "rocket," Dr. Karabeyoglu, for example, possesses 771 citations on the Web of Science and 732 on Scopus.

3. BRAZILIAN SCENARIO

Throughout Brazilian history, significant success is achieved in conducting research and development related to solid propellant motors for sounding rockets and launch vehicles. However, there has been relatively limited investment in supporting the development of liquid propellant rocket engines. The higher costs associated with these propulsion systems and the shortage of qualified human resources have resulted in delays in technological advancements in this field. As a result, Brazil's rocket propulsion industry lacks modernity and competitiveness. To overcome these challenges, the adoption of cheaper and less complex propulsive systems would require less overall development effort, thus creating greater opportunities for public financing. Keeping this in mind, the development of hybrid rocket engines (HRE) could present a competitive alternative for rocket engine development in Brazil (Bertoldi *et al.*, 2022).

In south hemispheric, Brazil was the first country to begin development in hybrid propellant technology applied to rockets and ramjets. Over the past years, several researches in this field have been conducted (Viegas and Salemi, 2000) (Santos *et al.*, 2005) (Santos *et al.*, 2006) (Da Cás *et al.*, 2012) (Shynkarenko *et al.*, 2019) (Azevedo *et al.*, 2019) (Bouziane *et al.*, 2019) (Bertoldi *et al.*, 2019).

4. OXIDIZER

Propulsive devices can be categorized into two main types: air-breathing engines and non-air-breathing engines. Air-breathing engines utilize the surrounding atmospheric air as an oxidizer to burn fuel. On the other hand, non-air-breathing engines do not rely on the atmosphere for oxidizers; instead, they carry their own oxidizers onboard the vehicle. The majority of non-air-breathing engines are commonly referred to as rocket engines or rocket motors (Mishra, 2017). This paper will approach four oxidizers that are usually used in HRP: Liquid Oxygen (LOX), Nitrous Oxide (N_2O), Hydrogen Peroxide (H_2O_2) and Hydroxyl Ammonium Nitrate (HAN).

4.1 Liquid Oxygen (LOX)

Among cryogenic liquid oxidizer propellants, liquid oxygen is extensively utilized and is considered the most common choice. Liquid oxygen has a boiling temperature of 90 K under atmospheric pressure and needs a cryogenic system. Therefore, it is crucial to properly insulate the liquid oxygen tanks and pipeline systems. To prevent moisture condensa-

tion, each liquid oxygen tank should be equipped with an external drainage system. Despite these considerations, liquid oxygen is preferred over other oxidizers due to its superior performance. Additionally, it is both noncorrosive and nontoxic in nature, Mishra (2017).

Sutton and Biblarz (2017) observed that a prevalent propellant combination utilized in large hybrid booster applications has involved pairing liquid oxygen (LOX) as the oxidizer with HTPB fuel. Liquid oxygen is a commonly employed cryogenic oxidizer in the space launch sector. It offers a favorable balance of safety, cost-effectiveness, and high performance. This hybrid propellant combination generates an exhaust that is nontoxic and relatively free of smoke, making it a desirable choice for future booster applications. Moreover, it is considered to be chemically and performance-wise comparable to LOX-kerosene bipropellant systems.

Although LOX is a good choice for various hybrid rocket propulsion applications, the use is limited by factors that can complicate vehicle operations and necessitate additional ground infrastructure. However, LOX is not considered an attractive solution for long-duration missions, such as spacecraft applications, mainly due to its cryogenic nature and the challenges associated with storing LOX in space for extended periods. (Okninski *et al.*, 2021).

4.2 Nitrous Oxide (N_2O)

The alternative to liquid oxygen is nitrous oxide (N_2O). Because its critical temperature equals 36.6 °C, it allows to store nitrous oxide in liquid phase at the ambient temperature. At 20 °C, the N_2O vapor pressure is 5.85 MPa. This feature eliminates additional pressurization devices in the oxidizer feed system if the injection is under tank blowdown (Surmacz *et al.*, 2009).

Lee and Tsai (2009) affirms that N_2O for propulsion system is versatile, for example for monopropellant in satellite attitude control, rocket ignition system and bipropellant or hybrid rockets. No matter how to apply N_2O in the propulsion system, the emergent need to utilize it to provide oxygen is that the N_2O should be decompose to release the oxygen and heat by external energy or a proper catalyst. N_2O could decompose exothermically with adiabatic decomposition temperature reaching 1640 °C, and decomposed oxygen could supply to meet the further combustion needs for a various fuels. NASA had demonstrated the large-scale paraffin fuel hybrid rocket firing test with N_2O as the oxidizer, and the results indicated that the regression rate and combustion rate are in the same trend and consistent with the cases by using gaseous oxidizer (GOX).

Although N_2O has some disadvantages in the choice of properties as the propellant combination and the production and transportation costs are relatively high, considering the practical situation, without the need to reduce the temperature, N_2O can be liquefied at room temperature and easy to carry into the rocket engine, which also has good controllability as an oxidizer. Therefore, it has broad application prospect in the hybrid rocket engine. Many domestic and foreign research institutions are conducting technical researches in hybrid engine, mostly using N_2O as oxidizer (Tadini *et al.*, 2017).

4.3 Hydrogen Peroxide (H_2O_2)

Hydrogen peroxide (H_2O_2) serves as an accessible oxidizing agent, and its production is environmentally friendly, posing no toxic or polluting risks. In the combustion chamber, hydrogen peroxide and the fuel undergo catalytic decomposition to initiate the desired chemical reaction which requires an efficient catalytic device for this process. A notable advantage of H_2O_2 is that it remains in liquid form even without external pressure or cooling, rendering it safe and suitable for various small-scale hybrid rocket engines, especially sounding rockets near the Earth space, Tadini *et al.* (2017).

During the 1990s, researchers globally explored the potential of hydrogen peroxide for various propulsion applications, predominantly utilizing concentrations ranging from 87.5% to 98%. In the context of hybrid propulsion systems, the initial applications of hydrogen peroxide date back to 1950 when the General Electric Company conducted tests using 90% hydrogen peroxide in combination with polyethylene fuel. These tests involved over 500 firings and demonstrated thrust levels reaching approximately 89 kN (Wernimont *et al.*, 1999).

High Test Peroxide (HTP) at a concentration of 98% ensures safe handling, but it is essential to take specific precautions to avoid any contact between HTP and organic substances. The utilization of 98% HTP in hybrid rocket propulsion provides the benefit of enhanced performance compared to lower concentrations. This makes it an efficient and effective option for space transportation (Okninski *et al.*, 2021).

4.4 Hydroxyl Ammonium Nitrate (HAN)

Hydroxyl ammonium nitrate (HAN) is a salt derived from the combination of hydroxylamine and nitric acid. It is also referred to as hydroxylamine nitrate (NH_2OHNO_3). In its pure state, HAN appears as a colorless and hygroscopic solid. However, when dissolved in water, it transforms into a colorless and odorless liquid. Due to its ease of decomposition, especially in the presence of a catalyst during exothermic chemical reactions, HAN holds potential for use as a monopropellant in liquid-propellant rocket engines (Mishra, 2017).

According to Amrousse *et al.* (2017), HAN has been pursued as a liquid gun and rocket propellant due to its advantages

over conventional propellants. It is the main ingredient in the propellants for regenerative guns. HAN is also considered as an oxidizer for hybrid rockets, because hybrid rockets are entirely different and it produces relatively high specific impulse with high density and is environmentally benign and safe. However, several crucial operational problems must be solved to realize these advantages, including combustion instability, material incompatibility, and reliable ignition at low pressure. Extensive studies have been conducted to characterize HAN's ignition and combustion behavior.

In contrast, hydrogen peroxide (H_2O_2) and HAN exhibit favorable thermochemical properties, produce non-toxic exhaust, and offer attractive density-specific impulses. Although their regression rates and combustion efficiencies are comparable to those achieved with LOX, hydrogen peroxide and HAN have the added advantages of being easy to store and environmentally friendly (Sutton and Biblarz, 2017).

5. FUEL

Mishra (2017) defines fuel as a chemical substance that, when combined with an oxidizer, undergoes a chemical reaction and releases thermal energy. From a chemical perspective, fuel can be described as a substance capable of donating electrons during the reaction with the oxidizer. On the other hand, an oxidizer is a chemical substance that accepts electrons during the chemical reaction with the fuel. In this section four solid materials that can be used as fuels will be discussed.

5.1 Hydroxyl Terminated Polybutadiene (HTPB)

Tadini *et al.* (2017) explains that HTPB is a type of elastomeric material widely utilized as hybrid rocket fuel. Its prevalence in hybrid rocket applications, as opposed to other polymers or elastomers, can be attributed to its convenience. HTPB is readily accessible and well-known to researchers in the field, particularly those with a background in solid rocketry. Actually, HTPB is one of the fastest-burning polymeric fuels employed in hybrid rocket systems.

HTPB provides several benefits such as cost-effectiveness, absence of self-deflagration risks under all known conditions and the straightforward processing. A commonly employed propellant combination for notable hybrid booster applications is the coupling LOX with HTPB (Sutton and Biblarz, 2017). Thermochemical analyses suggest that HTPB binder can profitably be used as a solid fuel in hybrid rockets, granting higher specific impulse concerning to solid propulsion. However, the realization of expected performance enhancement requires knowledge of all interleaving phenomena during the combustion; thus, a complete characterization is required, DeLuca *et al.* (2013).

5.2 Paraffin (C_nH_{2n+2})

Piscitelli *et al.* (2018) compared to the classical HTPB system, paraffin waxes offer several other advantages, i.e., non-toxic, non-hazardous, shippable as freight cargo, low cost and reusable (recycling possibilities). In addition, it possess the same energy per unit mass as kerosene, but their density is 16% greater, with no scrap possibility and a long shelf life. Finally, since this fuel is non explosive, grains can be fabricated on site and thus can save both manufacturing and launch operation costs. Despite the aforementioned advantages, which encourage the placement of HTPB, paraffin waxes have two disadvantages: poor mechanical properties and a complex manufacturing process.

Mazzetti *et al.* (2016) emphasizes that paraffin based fuels offer significant benefits to overcome the aforementioned limits. They allow conjugating high thrust performance with a simple, single circular central port and thrust tailorability by port variable geometry to achieve the desired mission profile. In addition, paraffin-based hybrid fuels are intrinsically safe (zero-TNT equivalence) in all phases, including storage, transport and handling. This characteristic is a definite advantage for using such systems in tactical operations scenarios.

Given its extensive use in hybrid rocket propulsion and the operational similarities shared with solid fuel ramjet (SFRJ) systems, such as the presence of a gaseous oxidizer and a solid fuel in the combustion chamber, paraffin-based fuels present an intriguing potential for application in air-breathing engines. However, there is a lack of published research on the utilization of paraffin in this specific type of engine. A laboratory investigation into the performance of paraffin fuel in a supersonic ramjet propulsion system was conducted in University of Brasilia (UnB), Azevedo *et al.* (2019).

5.3 Acrylonitrile Butadiene Styrene (ABS)

According to Whitmore *et al.* (2013), ABS (acrylonitrile-butadiene-styrene) is a thermoplastic material widely used in FDM (Fused Deposition Modeling) manufacturing. It is a cost-effective and recyclable option that has a relatively low melting point of 250°C. This characteristic enables precise control over the melting process and allows for reshaping and recycling of ABS multiple times without significant degradation of its properties. ABS possesses several mechanical properties that make it appealing as a potential fuel for hybrid rockets. With modern additive manufacturing and rapid-prototyping techniques, ABS can be shaped into various forms, facilitating the incorporation of complex flow paths with high surface areas within the fuel grain. These internal flow paths can open up during combustion, enabling the design of hybrid rocket motors with significantly shorter aspect ratios compared to traditional motor-casting technologies.

Whitmore (2018) in his research identify ABS as non-crystalline material with an amorphous structure, which means it does not have a distinct melting point but instead transitions into a highly softened and semi-fluid state before vaporization. Typically, ABS plastics exhibit a glass transition temperature of 105°C, and this semi-fluid state remains within a wide temperature range. Due to this unique melting behavior, ABS is widely utilized in FDM printers. Interestingly, ABS showcases specific impulse (Isp) and characteristic velocity (c^*) values that are remarkably similar to HTPB. The mechanical properties of ABS contribute to its attractiveness as a hybrid rocket fuel.

ABS has several mechanical properties that make it very attractive as a hybrid rocket fuel. Due to its significantly elevated heat of gasification and thermal capacitance, minimal heat transfer occurs, enabling the outer motor casing to remain cool throughout the combustion process. This inherent self-cooling attribute of ABS presents a substantial advantage, particularly in the context of space applications where effective thermal management poses a significant challenge. Furthermore, ABS boasts an impressive structural modulus of 2.3 GPa and a tensile yield strength of 40 MPa. With the progress in the rapid prototyping of ABS, intricate grain geometries can be produced at a low cost and within a reasonable timeframe (McCulley, 2013). Recent research (Urrego *et al.*, 2021), which focused on examining how varying helical geometries in the burning ports of ABS fuel grains impact the combustion performance of hybrid rocket motors, has concluded that the utilization of commercially available ABS currently provides a viable alternative for the development of small to medium-sized hybrid rocket engines, especially in countries facing challenges in obtaining high-performance rocket propellants. ABS can also be blended with paraffin for superior performance and combustion efficiency, as stated by Bresler and Natan (2019).

5.4 Polyethylene (PE)

Heister *et al.* (1998) identified that in contrast to HTPB, PE is a thermoplastic commonly produced via extrusion from a die in a continuous process. Hence, this approach could produce PE grains by simply cooling the extruded product and cutting it to the desired length. Thermoplastics also eliminate waste since the product can be remelted if a part is made incorrectly. In addition, PE has a lower cost than HTPB and is much easier to machine even though the thermochemical combustion performance of the two materials is virtually identical. For these reasons, this material represents an attractive alternative for many missions.

Tadini *et al.* (2017) explained that during the years, the attention of research studies was mainly focused on carbon-based polymers and paraffin wax materials, depending on their costs, mechanical properties and combustion performances. In the polymers group, typical fuels are polyethylene (PE), polymethyl methacrylate (PMMA), and polybutadiene (PB), with hydroxyl or carboxyl ions as chain terminators. These materials are quite cheaper than typically employed liquid propellants. Moreover, cracks and voids in solid fuel are not critical as in solid propellants, thus reducing the need for industrial-level high-quality control and assurance in terms of both manufacture and final product inspection. This aspect also contributes to reducing costs (Humble *et al.*, 1995).

5.5 Blended fuels

Direct application of pure paraffin in hybrid rocket engines and solid fuel ramjets may cause failure of the motor due to the low structural quality of the grain. A good deal of research is being conducted to improve the quality of the grain when mixed with more traditional polymeric fuel. Some possible polymers that can be blended with paraffin are PE, HTPB and ABS. However, it penalizes the solid fuel regression rate, as investigated and discussed in Kim *et al.* (2015), Tang *et al.* (2017), Bresler and Natan (2019), Thomas *et al.* (2021) and Cruz *et al.* (2023).

6. BURNING PERFORMANCE

Mishra (2017) observed that various types of chemical propellants based on physical entities possess desirable characteristics for achieving high-level performance. Each propellant must exhibit superior energetic properties to obtain a higher heat release rate, a elevated combustion temperature, characteristic velocity, and specific impulse. Additionally, ballistic properties including low density, high ignitability, reproducible performance, and minimal combustion instability are desirable. Among the fuel options available for hybrid motors, HTPB, in combination with LOX, H_2O_2 , and N_2O , stands out. The use of N_2O in particular offers advantages as it is self-pressurizing, eliminating the need for a pumping system during flight, which in turn simplifies the motor and reduces weight. Moreover, N_2O is cost-effective, highly safe, non-toxic, and can be stored at ambient temperature, Rezaei *et al.* (2018).

Burning parameters like fuel density, regression rate and specific impulse for some hybrid propellants are show in Table 4 for later comparison.

7. ECONOMIC VIABILITY

As stated by Whitmore *et al.* (2013), over the past 50 years, significant advancements have been made in conventional launch systems, resulting in highly capable vehicles. However, operating these vehicles has become increasingly

Oxidizer	Fuel	Fuel density (kg.m^{-3})	Regression rate	Isp (s)	Reference
LOX	Paraffin	910	High	340	Mazzetti <i>et al.</i> (2016)
LOX	HTPB	920	Medium	360	Tadini <i>et al.</i> (2017), Paquot (2021), Kumar <i>et al.</i> (2011)
LOX	PE	941	Medium	300	Mazzetti <i>et al.</i> (2016)
N_2O	Paraffin	910	High	310	Mazzetti <i>et al.</i> (2016)
N_2O	HTPB	920	Low	250	Mazzetti <i>et al.</i> (2016)
N_2O	ABS	975	Low	272	Whitmore <i>et al.</i> (2013)
H_2O_2 90%	ABS	975	Medium	302	Whitmore <i>et al.</i> (2018)
H_2O_2 98%	Paraffin	910	High	320	Mazzetti <i>et al.</i> (2016), Srivastava <i>et al.</i> (2019)
H_2O_2 98%	PE	941	Low	228	Mishra (2017), Kumar <i>et al.</i> (2011)
H_2O_2 98%	HTPB	920	Medium	320	Surmacz <i>et al.</i> (2009)
HAN 95%	HTPB	920	Low	260	Paquot (2021)
HAN 95%	Paraffin	910	Low	302	Paquot (2021)

Table 4. Burning proprieties from different pairs of oxidizer and fuel.

expensive due to various factors. These factors include the complexity of manufacturing and operations, compliance with safety and environmental regulations regarding hazardous materials, and the need for a substantial workforce to prepare for flight. Given the demanding requirements for high launch performance, such as specific impulse (Isp) and thrust-to-weight ratio, conventional rocket stages that utilize highly energetic, explosive, or toxic propellants are expected to remain the preferred choice for large military payloads and human spaceflight. While hybrid systems generally exhibit lower specific impulse compared to conventional liquid and solid rockets of equivalent thrust, their key advantage lies in the inherent safety provided by the fact that the propellant components remain inert until ignited within the motor chamber. This inherent safety significantly reduces costs associated with ground handling and transportation, making hybrid rockets safer and more cost-effective to transport, load, store, and operate. Consequently, the utilization of hybrid motors can potentially lead to an overall reduction in system operating costs.

Liquid oxygen is widely employed as the primary oxidizer in present-day hybrid rocket engines due to its advantageous attributes such as high specific impulse, availability, and established usage. However, the cryogenic properties of liquid oxygen (LOX) pose challenges for the plumbing and feed systems of the hybrid rocket engines, making it unsuitable for long-term in-space missions. While LOX offers exceptional performance, it may not be suitable for certain military and space applications that prioritize storability and simplicity (Paquot, 2021).

For Mazzetti *et al.* (2016), the advancement of hybrid rocket engine technology for widespread access to space highlights the significant role of paraffin. Paraffin offers the advantage of providing low-cost, high-performance fuels with minimal environmental impact. Particularly noteworthy is the ability to obtain paraffin through recycling industrial waste, which contributes to pollution reduction and cost savings. Additionally, the combustion mechanism of paraffin enables higher fuel regression rates compared to standard polymeric fuels, resulting in enhanced engine performance. Given these factors, paraffin plays a crucial role in the manufacturing of innovative hybrid rocket engine fuels.

8. ENVIRONMENTAL IMPACTS AND RISKS

The utilization of energetic materials may cause significant environmental contamination in certain regions. Previous approaches to creating eco-friendly propellants mainly involved substituting toxic materials with more environmentally friendly alternatives. However, it is important to note that there is no rocket propellant that can be considered entirely free of environmental impact, Tadini *et al.* (2017).

The primary source of hazard in chemical rocket propulsion lies in the process of combining the oxidizer and fuel within the rocket combustion chamber to release energy. In the case of liquid bipropellant rockets, an uncontrolled mixing of these chemicals can occur in the event of a pump leak or tank rupture, leading to a significant explosion. On the other hand, solid propellant rockets the presence of cracks or imperfections in the propellant can result in uncontrolled combustion and eventual explosion (Cantwell *et al.*, 2010).

Sutton and Biblarz (2017) emphasizes that the corrosion resulting from expelled gaseous reaction products is particularly critical in applications where these reaction products have the potential to damage launch or ground test structures, vehicle components, or impact nearby communities and housing in the vicinity of a test facility or launch site. Certain propellants, such as hydrogen peroxide or nitromethane, can become unstable in their storage tanks and may even provoke detonation under specific conditions, which depend on local impurities, temperatures, and the magnitude of shocks. Additionally, the unintentional mixing of liquid oxidizers (e.g., liquid oxygen) and fuels can lead to detonation in certain cases.

Paquot (2021) states that HAN-based monopropellants have emerged as highly promising alternatives to environmentally unfriendly propellants like hydrazine for rocket engines. HAN also exhibits excellent oxidizing capabilities for hybrid rocket engines. Ensuring thermal stability and consistent decomposition behavior is crucial when utilizing HAN in space thrusters. However, impurities originating from production or by-products have the potential to alter the reaction mechanism of HAN decomposition and trigger an auto-catalytic reaction in extreme cases. Nevertheless, the occurrence of catalytic ignition is generally avoided in hybrid rocket engines using HAN.

It is widely recognized that nitrous oxide (N_2O), as a greenhouse gas originating from human activities, possesses a significantly higher heat-trapping potential compared to carbon dioxide, estimated to be around 300 times greater. However, the use of N_2O in rocket propulsion applications is relatively minimal in comparison to other industries, resulting in a minimal contribution to global warming. One area of concern is the potential danger associated with the decomposition of N_2O vapor in the oxidizer tank. Due to the substantial amounts of N_2O present in the tank's ullage, a decomposition event could potentially lead to a significant explosion (Paquot, 2021).

9. DISCUSSION

This paper reviewed four oxidizers and four fuels for possible combinations to use as propellant in HRP. Analyzing the data for efficiency burning parameters obtained from Table 4 and knowing from literature that lower fuel density, high regression rate and high specific impulse are desired in hybrid propellants, the three best performance propellants are LOX/Paraffin, N_2O /Paraffin and H_2O_2 98%/Paraffin. Blended fuels will not be considered in this analysis because of the large variety of possible compositions and the lack of precise experimental data in the literature.

Paraffin is the most promising material for solid fuel because of advantages like non toxic, safety, low price and high regression rate. However, considering the poor mechanical proprieties of paraffin and the complex manufacturing process, some researchers eg.(Thomas *et al.*, 2021) pursue enhancing paraffin properties by mixing paraffin and HTPB in a heterogeneous fuel system to obtain the good mechanical properties of HTPB and the high regression rates of paraffin.

Considering handling factors, LOX is not storable (cryogenic), which raises the cost of transportation and stockage. For high concentrations in long-term exposure, N_2O can cause neurotoxic effects for humans, so it's necessary to take additional handling protections. The higher H_2O_2 concentration, the higher performance as oxidizer in HRP, but also increases the difficulty to obtain and storage.

Regarding all arguments mentioned in this section, the propellant N_2O /Paraffin was chosen the most promising for HRP. Despite the specific impulse for the pair H_2O_2 /Paraffin is slightly better, high concentration H_2O_2 (98%+) is harder to produce and manage and also hazardous to human skin. Launching rockets using N_2O compared to H_2O_2 might be cheaper since N_2O is a self-pressured liquid and eliminate addition pressurization system in rocket engine. Besides that, N_2O is an easily accessible chemical commonly used in several other industries.

10. CONCLUSION

This paper has presented a systematic review using the InOrdinatio methodology to select the best-ranked articles, authors and references in the research theme to achieve the best combination of oxidizer and fuel for hybrid rocket propellant. The analysis approaches the oxidizers and fuels chemical and mechanical properties that enable the application in HRP. Some propellant combinations were shown and evaluated regarding of burning performance, economic viability and environmental impacts and risks. Finally, the pair N_2O /Paraffin was chosen as the most promising propellant made of homogeneous materials for HRP in Brazilian scenario.

HTPB, PE and ABS are examples of fuels with good mechanical proprieties, but a low regression rate when burned, which result in low specif impulse. Blending these fuels with paraffin can be a possible solution to enhance the regression rate and combustion efficiency.

Indeed, fewer researches that approach HAN as an oxidizer in HRP compared to others oxidizers can be found in literature. It's commonly used as a monopropellant in liquid propellant rocket engines because it decomposes easily. However, recently it has been considered to be used as oxidizer HRP since it produces high specific impulse and is environmental friendly. HAN is a good candidate in the future as a strong oxidizer in HRP due to its thermal stability and reproducible decomposition behavior.

11. REFERENCES

- Amrousse, R., Katsumi, T., Azuma, N. and Hori, K., 2017. "Hydroxylammonium nitrate (han)-based green propellant as alternative energy resource for potential hydrazine substitution: From lab scale to pilot plant scale-up". *Combustion and Flame*, Vol. 176.
- Azevedo, V.A., Alves, I., Shynkarenko, O. and Veras, C.A.G., 2019. "Experimental investigation of high regression rate paraffin for solid fuel ramjet propulsion". In *AIAA Propulsion and Energy 2019 Forum*.
- Bertoldi, A.E.d.M., Bouziane, M., Lee, J., Veras, C.A.G., Hendrick, P. and Simone, D., 2019. "Theoretical and experi-

- mental study of combustion instability in hybrid rocket motors”.
- Bertoldi, A.E.D.M., Veras, C.A.G., Shynkarenko, O., Andrianov, A., Lee, J. and Simone, D., 2022. “Overview of the past and current research on hybrid rocket propulsion at the university of Brasília”.
- Bouziane, M., Bertoldi, A., Milova, P., Hendrick, P. and Lefebvre, M., 2019. “Performance comparison of oxidizer injectors in a 1-kN paraffin-fueled hybrid rocket motor”. *Aerospace Science and Technology*, Vol. 89.
- Bresler, J. and Natan, B., 2019. “Experimental investigation of abs-paraffin 3D printed hybrid rocket fuels”. In *AIAA Propulsion and Energy 2019 Forum*. p. 4094.
- Cantwell, B., Karabeyoglu, A. and Altman, D., 2010. “Recent advances in hybrid propulsion”. *International Journal of Energetic Materials and Chemical Propulsion*, Vol. 9, No. 4.
- Cruz, R., Veras, C. and Shynkarenko, O., 2023. “Paraffin-based ramjet missile preliminary design”. *Advances in Aircraft and Spacecraft Science*, 10 (4), 317-334, <https://10.12989/aas.2023.10.4.317>.
- Da Cás, P.L.K., Vilanova, C.Q., Barcelos Jr, M.N.D. and Veras, C.A.G., 2012. “An optimized hybrid rocket motor for the sara platform reentry system”. *Journal of Aerospace Technology and Management*, Vol. 4, No. 3.
- DeLuca, L.T., Galfetti, L., Maggi, F., Colombo, G., Merotto, L., Boiocchi, M., Paravan, C., Reina, A., Tadini, P. and Fanton, L., 2013. “Characterization of htpb-based solid fuel formulations: Performance, mechanical properties, and pollution”. *ACTA ASTRONAUTICA*, Vol. 92, No. 2, SI. ISSN 0094-5765. doi:10.1016/j.actaastro.2012.05.002.
- Heister, S., Wernimont, E. and Rusek, J., 1998. “High test peroxide hybrid rocket research”. In *Hydrogen Peroxide Propulsion Workshop, Surrey, England*.
- Humble, R.W., Gary, H.N. and Larson, W.J., 1995. “Space propulsion analysis and design”.
- Kim, S., Moon, H., Kim, J. and Cho, J., 2015. “Evaluation of paraffin–polyethylene blends as novel solid fuel for hybrid rockets”. *Journal of Propulsion and Power*, Vol. 31, No. 6, pp. 1750–1760.
- Kumar, S., Panda, A.K. and Singh, R.K., 2011. “A review on tertiary recycling of high-density polyethylene to fuel”. *Resources, Conservation and Recycling*, Vol. 55, No. 11.
- Lee, T.S. and Tsai, H.L., 2009. “Fuel regression rate in a paraffin-htpb nitrous oxide hybrid rocket”. *Fuel*, Vol. 24.
- Marothiya, G., Ramakrishna, P.A., Saravanan, N. and Kumar Solasa, P., 2021. “Development of h₂o₂ based mixed hybrid rocket”. *PROPELLANTS EXPLOSIVES PYROTECHNICS*, Vol. 46, No. 11. ISSN 0721-3115. doi: 10.1002/prop.202100061.
- Mazzetti, A., Merotto, L. and Pinarello, G., 2016. “Paraffin-based hybrid rocket engines applications: A review and a market perspective”. *ACTA ASTRONAUTICA*, Vol. 126, No. SI. ISSN 0094-5765. doi:10.1016/j.actaastro.2016.04.036.
- McCulley, J.M., 2013. *Design and testing of digitally manufactured paraffin acrylonitrile-butadiene-styrene hybrid rocket motors*. Utah State University.
- Mishra, D., 2017. *Fundamentals of Rocket Propulsion*. CRC Press.
- Okninski, A., Surmacz, P., Bartkowiak, B., Mayer, T., Sobczak, K., Pakosz, M., Kaniewski, D., Matyszewski, J., Rarata, G. and Wolanski, P., 2021. “Development of green storable hybrid rocket propulsion technology using 98% hydrogen peroxide as oxidizer”. *AEROSPACE*, Vol. 8, No. 9. doi:10.3390/aerospace8090234.
- Paquot, Q.S., 2021. “Storable green oxidizers for hybrid rocket propulsion”.
- Piscitelli, F., Saccone, G., Gianvito, A., Cosentino, G. and Mazzola, L., 2018. “Characterization and manufacturing of a paraffin wax as fuel for hybrid rockets”. *PROPULSION AND POWER RESEARCH*, Vol. 7, No. 3. ISSN 2212-540X. doi:10.1016/j.jprr.2018.07.007.
- Rezaei, H., Soltani, M.R. and Mohammadi, A.R., 2018. “Experimental study of fuel regression rate in an htpb/n₂o hybrid rocket motor”. *SCIENTIA IRANICA*, Vol. 25, No. 1. ISSN 1026-3098. doi:10.24200/sci.2017.4317.
- Santos, L., Almeida, L., Fraga, A. and Veras, C., 2006. “Experimental investigation of a paraffin based hybrid rocket”. *Revista de Engenharia Térmica*, Vol. 5, No. 1.
- Santos, L., Contalfer, R., Bertoldi, A.E.M., Medeiros, E.G., Sousa, L.C.P.C., Borges, A. and Veras, C.A., 2005. “Regression rate studies of a paraffin-based hybrid rocket”. *18th International Congress of Mechanical Engineering*.
- Shynkarenko, O., Azevedo, V., Veras, C. and Alves, I., 2019. “Experimental investigation of hydrocarbon based fuels in solid fuel ramjet propulsion”. In *70th International Astronautical Congress (IAC 2019), Washington, USA*.
- Srivastava, S., Ingenito, A., Andriani, R. et al., 2019. “Numerical and experimental study of a 230 N paraffin/n₂o hybrid rocket”. In *EUCASS 2019-8th European Conference for Aeronautics and Space Sciences*.
- Surmacz, Rarata, P. and Grzegorz, 2009. “Hybrid rocket propulsion development and application”. *Institute of Aviation, Al. Krakowska*, Vol. 110, No. 114.
- Sutton, G.P. and Biblarz, O., 2017. *Rocket Propulsion Elements*. John Wiley & Sons.
- Tadini, P., Tancredi, U., Grassi, M., Pardini, C., Anselmo, L., Shimada, T. and DeLuca, L.T., 2017. “Comparison of chemical propulsion solutions for large space debris active removal”. In L. DeLuca, T. Shimada, V. Sinditskii and M. Calabro, eds., *CHEMICAL ROCKET PROPULSION: A COMPREHENSIVE SURVEY OF ENERGETIC MATERIALS*. Springer Aerospace Technology. ISBN 978-3-319-27748-6; 978-3-319-27746-2. ISSN 1869-1730. doi:10.1007/978-3-319-27748-6_41. 12th International Workshop on Combustion and Propulsion - New Energetic Materials for Space Exploration, Politecnico Milano, Campus Bovisa, Milan, ITALY, JUN 09-10, 2014.

- Tang, Y., Chen, S., Zhang, W., Shen, R., DeLuca, L.T. and Ye, Y., 2017. “Mechanical modifications of paraffin-based fuels and the effects on combustion performance”. *Propellants, Explosives, Pyrotechnics*, Vol. 42, No. 11, pp. 1268–1277.
- Thomas, J.C., Paravan, C., Stahl, J.M., Tykol, A.J., Rodriguez, F.A., Galfetti, L. and Petersen, E.L., 2021. “Experimental evaluation of htpb/paraffin fuel blends for hybrid rocket applications”. *COMBUSTION AND FLAME*, Vol. 229. ISSN 0010-2180. doi:10.1016/j.combustflame.2021.02.032.
- Urrego, J.A., Rojas, F.A. and Muñoz, J.R., 2021. “Variability analysis of abs solid fuel manufactured by fused deposition modeling for hybrid rocket motors”. *Journal of Mechanical Engineering and Sciences*, Vol. 15, No. 2.
- Viegas, F. and Salemi, L., 2000. “Design and construction of a test bench for hybrid rocket static firings and its hybrid engine”. *Mechanical Engineering Department, University of Brasilia*.
- Wernimont, E., Ventura, M., Garboden, G. and Mullens, P., 1999. “Past and present uses of rocket grade hydrogen peroxide”. *General Kinetics, LLC Aliso Viejo, CA*, Vol. 92656.
- Whitmore, S.A., 2018. “Three-dimensional printing of “green” fuels for low-cost small spacecraft propulsion systems”. *JOURNAL OF SPACECRAFT AND ROCKETS*, Vol. 55, No. 1. ISSN 0022-4650. doi:10.2514/1.A33782.
- Whitmore, S.A., Armstrong, I.W., Heiner, M.C. and Martinez, C.J., 2018. “High-performing hydrogen peroxide hybrid rocket with 3-d printed and extruded abs fuel”. In *2018 Joint Propulsion Conference*. p. 4443.
- Whitmore, S.A., Peterson, Z.W. and Eilers, S.D., 2013. “Comparing hydroxyl terminated polybutadiene and acrylonitrile butadiene styrene as hybrid rocket fuels”. *Journal of Propulsion and Power*, Vol. 29, No. 3.

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