

# Comparative Study on Hybrid Rocket Fuels for Space Launch Vehicles Moving in Higher Orbits

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**Abstract.** The current research is focused on understanding the propulsive parameters of hybrid rocket motors. A comparative study is prepared from various research papers. The fuels paraffin wax, hydroxyl-terminated polybutadiene (HTPB) and polymethyl methacrylate (PMMA) with added additives (Al/Mg) were combined with two oxidizers, liquid oxygen (LOX), nitrous oxide (N<sub>2</sub>O). The propulsive parameters examined were the combustion efficiency, combustion or adiabatic flame temperature, characteristics velocity and regression rate. The propellant pair paraffin-N<sub>2</sub>O provided the highest performance for all parameters studied. This study provides an advantageous propellant option for future rocket propulsion based on a comparative investigation.

## 1. Introduction

By selecting one propellant as a liquid, and the other as a solid, an entire concept is created. The resulting rocket motor will have features of both systems, thereby making available a larger number of design options and operational characteristics. Some advantages of this are that throttling is simplified by valving only a single fluid without the necessity of matching hydraulic characteristics (the "fuel injector" being the exposed grain surface automatically adjusts the fuel vaporization to the oxidizer flow rate); secondly, the thrust chamber is automatically insulated with the fuel and needs no cooling and the solid phase is a convenient means of incorporating high energy metallic additives thereby obviating the need for slurries, the energy level of a liquid system is closely matched because the oxidizers are the same (the main reason for the lower Isp of solids is due to the lower energy solid oxidizers), the system is nonexplosive since an intimate mixture of fuel and oxidizer cannot be encountered, and the physical property requirements of the solid fuel are greatly relaxed because of the high binder level and tolerance to cracks and debones in the grain. [18]

Here a comparative study is prepared based on three different propellant combinations [HTPB 40% aluminised and Liquid oxygen(oxidiser), Paraffin mixed with aluminium & magnesium and N<sub>2</sub>O(oxidiser), Poly methyl methacrylate PMMA and Liquid oxygen(oxidiser)]. A few parameters like combustion efficiency, combustion or adiabatic flame temperature, characteristics velocity and regression rate are investigated through different research papers and an advantageous propellant option is provided for future rocket propulsion based on a comparative investigation.

## 2. Literature Review

James C. Thomas (2021) studied the evaluation of HTPB/paraffin fuel for hybrid rockets. Paraffin in HTPB as a regression rate enhancement strategy for HREs was evaluated by the inclusion of molten macro crystalline paraffin wax and solid microcrystalline paraffin particles at mass loadings ranging from 10–75% and 10–60%, respectively. The thermal decomposition behaviour of all fuel specimens was determined by simultaneous Thermogravimetric analysis and Differential thermal analysis experiments. Ballistic experiments were conducted in two separate hybrid rocket experimental apparatuses under gaseous oxygen cross-flow. The plain macro crystalline paraffin fuel exhibited a 300% increase in regression rate in comparison to plain HTPB. First principles modelling of the combustion of plain HTPB, plain paraffin, and mixed-fuel systems are discussed in the paper.[1]

Adam Okninski (2021) carried out a study on hybrid rocket propulsion technology for space transportation. Paraffin is especially popular with LOX and N<sub>2</sub>O as oxidizers. Hybrid stages are expected to allow reusability of the oxidizer feeding system, but not the motor combustion chamber. Therefore, hybrid vehicle commercial operations may be focused on market segments where reusability is not to be implanted in the nearest future - such as micro-launch vehicles. Indeed, most new developments focus on access to space for small LEO payloads.[2]

Yash Pal (2021) has investigated mechanical performance and regression rate improvement techniques. (HTPB), Polymethylmethacrylate (PMMA) regression rate improvement use this approach Physical design modifications, such as swirl oxidizer injection, multi-port fuel grain, metallic additives, and embedding mechanical devices in the fuel grain. The paraffin-based solid fuels were identified as a viable alternative further to improve the performance of the hybrid rocket system.[3]

Ozan Kara (2021) discussed the Ignition Capability of CO<sub>2</sub> in hybrid systems. s the ignition limit of CO<sub>2</sub> by using Paraffin/Metal fuel in a classical hybrid rocket is investigated here. Small-scale experiments provide a maximum ignition

limit of 43% CO<sub>2</sub> by mass in the oxidizer mixture for aluminium powder. Scale-up experiments showed that magnesium has easier ignition capability with CO<sub>2</sub> than aluminium. CO<sub>2</sub> addition slows down the chemical kinetics. Gas phase reactions become impractical at high CO<sub>2</sub> mass fractions, which means that CO<sub>2</sub> reduces the adiabatic flame temperature during combustion. Paraffin/Mg/CO<sub>2</sub>/N<sub>2</sub>O is the most prominent candidate for Mars transportation vehicles.[4]

H. Karakas (2019) tested additives to enhance the performance of hybrid rockets. Aluminium good additive for N<sub>2</sub>O/L systems. It increases the Isp performance and reduces the optimum O/F ratio which in turn reduces the required volume for propellant. Also, it helps to reduce the nozzle erosion rate which is a crucial improvement, especially for upper-stage rocket motors. Lithium aluminium hydride shows similar performance characteristics to aluminium, but its ratio in paraffin wax was only %25 rather than %40 as in the Al cases. This suggests that by increasing the LiAlH<sub>4</sub> mass ratio, performance can be increased beyond Al fuel cases. However, one disadvantage of LiAlH<sub>4</sub> is the material cost. Magnesium addition does not show significant improvement.[5]

Ozan Kara (2019) tested N<sub>2</sub>O/CO<sub>2</sub> Oxidizer Mixtures with Paraffin-based aluminium Fuels. Experiments showed that CO<sub>2</sub> amount by weight percentage in oxidizer formulation should be between 0 and 25% by mass in order to ignite the motor. Average regression rate values of 40% aluminium-based experiments with N<sub>2</sub>O show variable results due to different  $\bar{C}_D$  values. Combustion efficiencies in all experiments are higher than 80% and highest for some 40% of aluminium cases. Therefore, CO<sub>2</sub>-based experiments have around 10% lower efficiency compared to the neat nitrous oxide cases. The overall efficiency is around 77% for carbon-dioxide-included formulations. Characteristic velocity increases as the OF ratio increases towards the optimal O/F for the neat N<sub>2</sub>O based experiments. Adding CO<sub>2</sub> to the mixture reduces the OF ratio (due to increased regression rate) and reduces the overall characteristic velocity.[6]

Yash Pal (2020) evaluated the Heat of Combustion Analysis of Paraffin-Based Fuels as pre-burn Characterization. The heat of combustion and theoretical performance of the paraffin fuel loaded with Al and B additives were analysed using an adiabatic bomb calorimeter. The addition of Al and B additives increased the heat of combustion of paraffin-based fuels. Solid fuel containing the Al additive showed higher heat of combustion compared to the B-loaded fuels. The Chemical Equilibrium Application results showed that the addition of Al is not effective in improving the specific impulse for P/PE/Al formulation. It has shown that the optimum Oxidiser/Fuel shifted to lower values as the metal additive loaded into the fuel. This might be beneficial for specific application areas such as space mission, which demands less oxidizer tank volume for carrying more payloads.[7]

Mariana Conti Tarifa and Loreto Pizzuti (2019) analysed the theoretical performance of hybrid rocket propellants. The specific impulse, characteristic velocity and adiabatic flame temperature over a range of O/F from 1 to 8.5, for a chamber pressure of 10 bar, have been obtained and analysed. The Paraffin/LOX pair presents the highest values for all the propulsive parameters, HTPB/LOX pair shows slightly lower performance parameters value and PMMA/LOX pair presents the lowest values of the performance parameters. Paraffin presents regression rates about three times higher than conventional hybrid fuels.[8]

ArifKarabeyoglu (2014) studied the fuel additive for hybrid rockets. Using performance additives (metals or metal hydrides) to enhance the regression rate of the hybrid or SFRJ fuels is unproductive. Lack of oxidizer and combustion beneath the flame limits the effectiveness of metal combustion. Aluminium is a good additive for energy-deficient oxidizers such as hydrogen peroxide or nitrous oxide. It is not effective in improving the Isp for oxygen systems. The size of the aluminium particles influences the combustion efficiency. Boron does not deliver a significant performance benefit in hybrid rockets. Ammonia borane can also be helpful to improve the system Isp (assuming that the boron can be burned more readily in the motor).[9]

Chikhar S Maharaj (2018) tested the performance characteristics of metal additives in paraffin wax. The hot fire testing aimed to explore the performance gain that can be achieved for a 40% by-mass aluminised fuel gain, if any. The average regression rate of the two pure paraffin wax tests that had a similar burn time was 1.483 mm/s, using LH-001 and LH-007. For the two aluminised tests, LH-006 119 and LH-008, an average regression rate of 1.584 mm/s was calculated. This results in a 6% enhancement that is lower than the reported 25%. The oxidiser mass flow rate was higher than required for the aluminised tests. 40% aluminised fuel grain has a lower stoichiometric O/F ratio than pure paraffin wax, the aluminised tests were oxidiser-rich compared to the pure paraffin wax tests.[10]

N. Gascoin and P.Gillard (2010) studied the preliminary pyrolysis and combustion of hybrid propellants. For HTPB, a sensitivity study has been conducted to ensure the right representation of decomposition phenomena. Twenty-two compounds are considered as final decomposition products to compute their formation during HTPB pyrolysis (CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>8</sub>, C<sub>5</sub>H<sub>8</sub>, C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>8</sub>, C<sub>6</sub>H<sub>10</sub>, C<sub>7</sub>H<sub>8</sub>, C<sub>8</sub>H<sub>12</sub>, C<sub>8</sub>H<sub>14</sub>, C<sub>12</sub>H<sub>14</sub>, C<sub>16</sub>H<sub>26</sub>, H<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>2</sub>O, C<sub>2</sub>H<sub>6</sub>O, solid C). PMMA decomposition has been studied using thermogravimetric experiments. This is a very interesting result because the produced combustible quantity, that is to say, the regression rate is not sufficient to estimate the engine performance. The chemistry is shown to be a relevant phenomenon to be considered in order to estimate the pyrolysis-combustion coupled process.[11]

Lara Cristina SánchezHernández (2017) investigated the characterization and improvement of hybrid chemical rockets. Parametric data like the O/F ratio is considered to determine combustion efficiency. Chamber pressure is rectified by alteration of nozzle throat diameter.[12]

ArifKarabeyoglu (2011) carried out a study on the performance of a hybrid propellant upper-stage motor. The high specific impulse performance of the liquid oxygen/paraffin-based hybrid rockets gives them a competitive advantage for upper stages which are known to be highly sensitive to this performance parameter. Upper stages are typically smaller pressure-fed propulsion systems which make them easier to develop compared to the heavier systems such as boosters used

in medium/heavy launch vehicles. The advanced paraffin-based hybrids can also be applied to larger booster systems in the 250-1,000 klbs thrust range.[13]

Zezhong Wang (2020) studied the combustion performance of hybrid propellant rocket grain. The ignition performance of the novel fuel grain was not affected by the nested helical structure, and the ignition delay time of the novel fuel grain is less than 0.25 s. The regression rate of the novel fuel grain was significantly improved by the nested helical structure. With an oxidizer mass flow rate of 30 g/s, the regression rate of the novel fuel grain increased by 20% compared with that of the paraffin-based fuel grain. According to the fitting equation of the regression rate, further improvements will be obtained as the oxidizer mass flux increase.[14]

Jean-Yves Lestrade (2016) experimented with the Vacuum Specific Impulse of a Hybrid Rocket Engine. The paper presents the experimental results of a hybrid rocket engine fired both at ambient pressure and under low-pressure conditions. The hybrid engine includes a catalyst bed and a vortex injector, and it is fitted with ultrasound sensors to measure the instantaneous fuel regression rate. These tests have enabled the demonstration of the experimentally achievable specific impulse of the hybrid rocket technology under low-pressure conditions and validated the extrapolation of experimental results at ambient pressure to vacuum pressure conditions. The demonstrated combustion efficiency is above 98%, and the specific impulse is experimentally proven to be above 270 s for a conical nozzle with an expansion ratio of 50.[15]

Nicolas Bellomo (2014) investigated the effect of diaphragms on efficiency. An engine was tested with nitrous oxide and paraffin wax as propellants. The presence of recirculation zones produces a considerable increase in the heat flux slightly above the diaphragm position and this, in turn, increases the regression rate. CFD simulations for the numerical investigation of the effect of mixers in hybrid rockets. The efficiency is overestimated by less than 5.5%. [16]

Dario Pastrone (2012) reviewed the low fuel regression rate in hybrid rocket engines. The regression rate of conventional binders such as HTPB is typically an order of magnitude lower than solid propellants and hence a large fuel surface is needed to produce the required thrust level. HREs have a lower overall combustion efficiency than LREs and SRMs. A mixer between the grain aft end and the nozzle inlet can enhance mixing, but the dry weight of the system is larger.[17]

### 3. Parameters Considered for Hybrid Propellants

Various studies on the propellant characteristics of different hybrid propellants for hybrid propulsion systems have been discussed. Comparison is done between various hybrid propellants combinations [HTPB 40% aluminised and Liquid oxygen(oxidiser), Paraffin mixed with aluminium & magnesium and N2O(oxidiser), Poly methyl methacrylate PMMA and Liquid oxygen(oxidiser)].

TABLE 1. Thermodynamics value of Fuels selected

Fuel	Formula	Enthalpy of formation (kJ/mol)	Temperature (K)
Paraffin	C20H42	-594.572	298
HTPB	C3.8462H5.8077O0.0385	23.99	298
PMMA	(C5H8O2) <sub>n</sub>	-348.7	298

**Combustion stability and instability:**Combustion instability is observed in HTPB/Al fuel due to unstable burning connected with the periodic accumulation and break off of the molten  $Al_2O_3$  from the grain surface and the ignition of virgin fuel, which is defined as chuffing instability. [19][20]

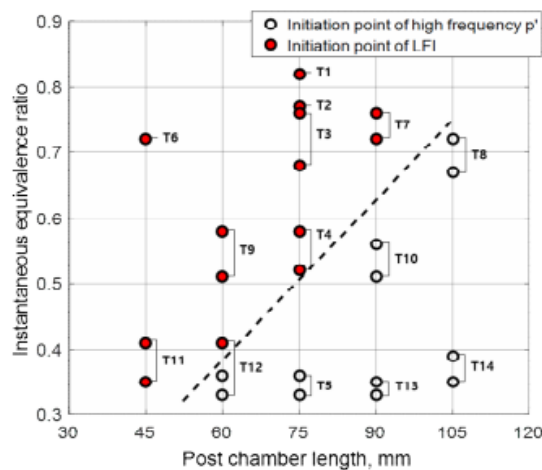


FIGURE 1. Combustion stability map of the initiation behaviour of characteristics of low-frequency instability (LFI) (T= Test number) [21].

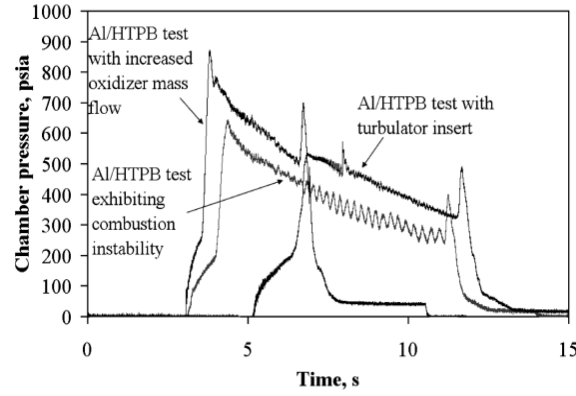


FIGURE 2. Mitigation of Al/HTPB combustion instability [19]

In PMMA (Polymethyl methacrylate) low-frequency instability initiation is strongly related to the variation in equivalence ratio and changes in post-chamber length. The stability map shows the overall behaviour of the initiation of low-frequency instability, and most cases of unstable combustion are found mainly in the left-upper part. This suggests that favourable conditions for the LFI initiation are like a higher equivalence ratio (i.e. in a fuel-lean combustion condition) and a shorter length of post-chamber geometry. [21] The lower density and easy evaporating properties of HTPB are responsible for the earlier appearance of low-frequency instability than in PMMA. Generally, HTPB regressed very quickly than PMMA approaching its critical diameter where instability can be initiated. [22] Paraffin with Al or Mg additives gives a higher exothermic reaction temperature, which resulted in higher combustion enthalpy indicating better combustion. [29] Combustion efficiency ranges between 75% to 83% for paraffin based fuel [30].

**Regression rate:** HTPB/Al & Mg based propellant Mg addition increase the regression rate, the regression rate was consistently approximately 0.2 mm/s greater at each oxidizer flux level tested than that of the 60%HTPB/40%Al fuel, possibly due to increased reactivity of the Al-Mg/HTPB fuel combination [19]. It is clear that the addition of aluminium powder to HTPB produces a positive effect on the regression rate, both with oxygen and nitrous oxide. Aluminized HTPB burned with nitrous oxide, in the range of fluxes and pressures tested, show a regression rate increase, which is not appreciably sensitive to either aluminium particle’s mass fraction or size.

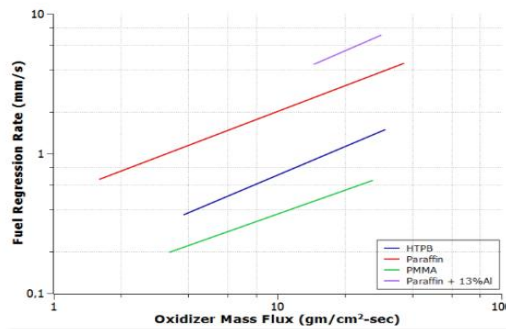


FIGURE 3. Relation between the fuel regression rate and mass flow of oxidant for various fuels used in hybrid rocket engines [25].

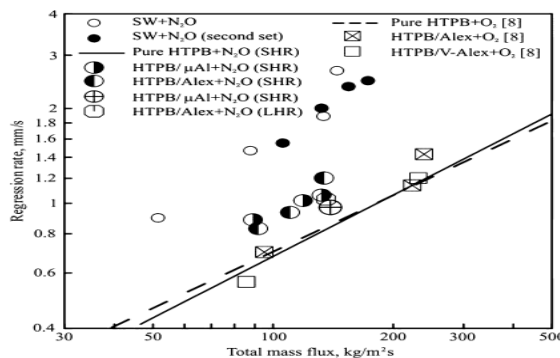


FIGURE 4. Comparison between average regression rates obtained with pure or loaded HTPB fuels and paraffin-based fuels burned with oxygen or nitrous oxide [23].

Moreover, it seems that aluminium improves the regression of HTPB more effectively if burned with nitrous oxide than with oxygen. Regression rates measured with paraffin-wax based fuel and nitrous oxide are the highest amongst all the available combinations of fuel, about an 80% increase compared to aluminized HTPB. [23] PMMA has the lowest regression rate, which implies limited real applications. Fuels composed of hydroxyl-terminated polybutadiene (HTPB) have relatively high regression rates and are the most applicable fuels in the aerospace industry when it comes to hybrid propulsion [33].

**Combustion efficiency:** The Al/HTPB fuel combination's low combustion efficiency resulted from forming aluminium oxide.

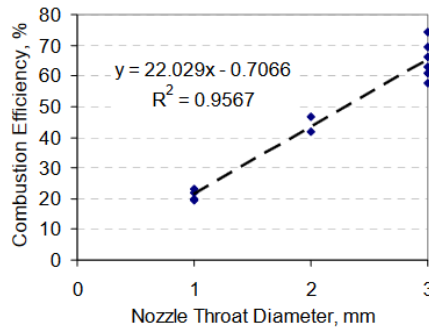


FIGURE 5. Combustion efficiencies as a function of nozzle throat diameter for N2O/PMMA test firings (R-squared value) [26].

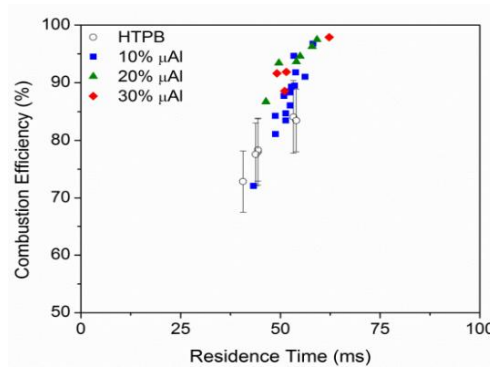


FIGURE 6. Combustion efficiencies as a function of nozzle throat diameter for N2O/PMMA test firings. [19]

(Al<sub>2</sub>O<sub>3</sub>) around the aluminium particles during combustion, inhibiting mass and heat diffusion to the particle's interior.[19] Combustion efficiencies of Paraffin/Aluminium/N<sub>2</sub>O-based experiments are around 70%. Paraffin/Magnesium/CO<sub>2</sub> cases provide better combustion efficiency of 85% most likely due to the easier ignitibility of magnesium.[25] For PMMA fuel the combustion efficiency varies between 19%-88% and PMMA fuel combustion efficiencies scale linearly with nozzle throat diameter. [27]

**Characteristic velocity:** The characteristic velocity efficiency of paraffin grains is considerably lower than that achieved with HTPB-based fuels, in fact, the maximum efficiency obtained through fragment generation is 86%. Lower efficiency is normally expected when burning paraffin grains for the large flow rate of fuel that does not burn in the combustion chamber. [23] The combination of LOX with any fuel provides the highest values of characteristic velocity. The performance of the fuels HTPB and paraffin in combination with LOX are similar with slightly displaced O/F, providing approximately 1800 m/s for an O/F close to 1.8 and 2.2, respectively. On the other hand, the lowest values are presented for HTPB and PMMA when using N<sub>2</sub>O as an oxidizer [25] [32].

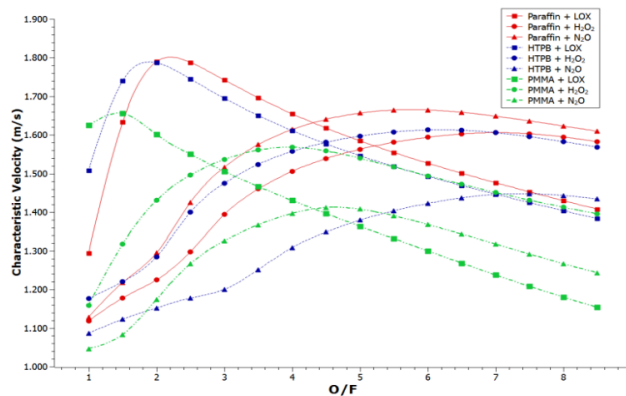
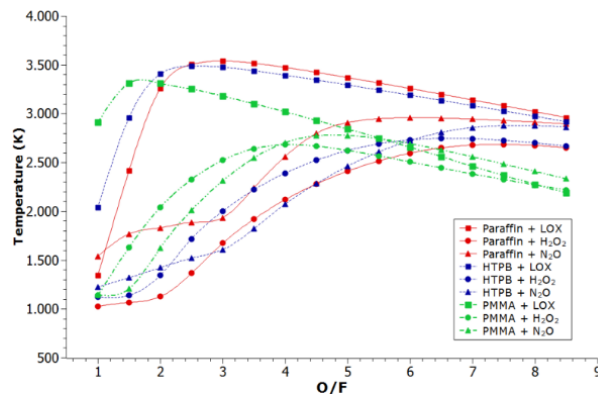


FIGURE 7. The characteristic velocity of the combination of the fuels with different oxidants as a function of O/F.[25]

**Adiabatic flame temperature:** The adiabatic flame temperature in the combustion chamber depends on the oxidant choice. The higher the thermal energy obtained by the combination of the pair, the greater the amount of energy that will be transformed into kinetic energy, which will directly affect the performance parameters [7].



**FIGURE 8.** Adiabatic flame temperature in the chamber considering the combination of the fuels with different oxidants as a function of O/F [25].

The peak temperature occurs when LOX is used as an oxidizer in combination with paraffin, at approximately 3520 K for an O/F ratio of 2.8. Similarly, the combination of LOX and HTPB provides temperature values with the same trend curve, with a peak of 3500K for an O/F of 2.4. For a combination of LOX and PMMA, it is noted that the combustion temperature increases until it reaches an O/F of 1.6. Adiabatic temperatures of paraffin with N<sub>2</sub>O present a quite similar trend for O/F larger than 3 with peak values under 3000K. Taking into account the reactions of PMMA N<sub>2</sub>O, the optimum O/F lies around 8 [25][28][31].

#### 4. Conclusion

The study focuses on the propulsion characteristics of the rocket's hybrid propulsion system. Compared with other systems, hybrid is more efficient and has more advantages. Three fuels, paraffin wax, HTPB and PMMA, reacting with two oxidizers, LOX and N<sub>2</sub>O, are simulated taking into account the equilibrium conditions during the expansion in the nozzle. Here, the most relevant results are summarized:

The HTPB/LOX pair shows a slightly lower performance parameter value. The Paraffin/N<sub>2</sub>O pair represents the highest values for all the thrust parameters considered here. LOX was presented as the best substitute for oxidant in this study. The excellent performance shown by paraffin sparked future research and promising results as paraffin exhibits approximately three times higher regression rates than conventional hybrid fuels.

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