Thermodynamic Investigation of Conventional and Alternative Rocket Fuels for Aerospace Propulsion

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Abstract. The magnitude of the exhaust velocity is dependent on molecular and chemical properties of the propellant, and the expansion ratio of the engine. The main requirement for all propellant combinations is to maximize the energy release per kilogram; in other words, the lower the mass for a given energy release, the higher is the ultimate velocity of the vehicle. This also implies that the mass flow rate depends on the density, while the exhaust velocity depends on the energy contained in the hot gas. The main performance parameters can be defined as the thrust coefficient related to the nozzle performance, and the characteristic velocity related to the propellant and combustion performance. The first parameter reaches its optimum when the exhaust pressure is equal to the ambient pressure while the second parameter is defined by the choice of propellant combination. The objective of this work is to investigate, numerically and thermodynamically, different combinations of oxidizers with conventional and alternative fuels, for different rocket propulsion and energy generation systems. Based on the state-of-the-art and the analysis results on the most promising fuel-oxidizer combinations for the future of aerospace propulsion and space transportation, in a technically and environmentally sound manner, conclusions are made.

1. State of the art
The efficiency of a rocket in terms of spacecraft propulsion depends on the achievable exhaust velocity and mass ratio; thrust is mostly important for the first stage of a launcher. All these parameters are defined by the rocket design and propellants combination. These systems consist of solid, liquid or hybrid rocket motors. For more than five decades, Ammonium Perchlorate (AP) based composite propellants have been the main line of development of solid rocket propulsion [1]. Adding metal-particles to propellants help increase the energy density [2]. Among various metal additives, and for some specific cases, Aluminium (Al) seems to be the most promising one due to its high combustion enthalpy, wide availability and low cost [2]. The burning rate of a double base propellant without aluminium was compared with other double base fuels in which aluminium was added by 2% and 4%. It was found that the burning rates and burning heat of the fuels with aluminium additives improved [3]. Moreover, the decomposition and reaction of AP with HTPB produces gases consisting of Carbon Dioxide (CO2), Water vapor (H2O) and Hydrochloric acid (HCl). The added Al particles react with these products to increase the ratio of combustion temperature to gas molecular weight, resulting in higher exhaust velocities [4]. Hydrides can also be added to chemical rocket propellants, as high volumes of Hydrogen (H2) can be released during combustion. Aluminium hydride is expected to perform effectively; however, its industrial application is still unfeasible because of the lack of its
commercial availability [5]. To reduce air pollution during rocket launches, efforts have been done to develop green, or environmentally friendly, propellants with non-toxic combustion products, easier and safer to manufacture and handle than the conventional ones, bringing down the associated transport and storage costs [6]. Several studies on the use of Hydrogen Peroxide/Kerosene (H₂O₂–RP1) as a green propellant combination suited for propulsion applications have been realized [7-12]. Yet, the overall performance can be limited by coking which remains a major problem for current Hydrocarbon cooled rocket engines; but currently and from a different aspect, because of the possibility of harvesting Methane (CH₄) from Mars, the interest of its use for interplanetary missions has increased [13-14]. Another alternative is hybrid systems, as they are known for their simplicity, safety and environmental advantages over conventional ones. However, such systems have not been commercially viable, because they usually use Polymeric fuels with low evaporation rate, and thus low thrust, which limits their use for large launchers. The requirement is to increase the rate at which the fuel evaporates. One approach is to reduce the viscosity in the layer of the melted fuel, by adding a certain amount of Paraffin-wax to the fuel to lower its viscosity [15]. Further studies focused on propellant systems consisting of N₂O/HTPB, N₂O/HDPE and H₂O₂/HDPE [16], bringing also satisfying results. Another approach consists of metals exothermic reaction with air, oxygen, carbon dioxide or even water to generate hydrogen [17-18]. Exploiting metals produced in situ from extra-terrestrial resources as propellants is an alternative which may lower the cost of future space missions by reducing the mass of propellant launched from Earth. Several disadvantages, though, are also inherent in the hybrid metal-oxygen engine concept. A metal fuel grain would act as a high conductivity heat sink, and heat conducted into the fuel could cause more metal to melt than is desired. Nevertheless, some advantages of this concept include the ability to control thrust by controlling the oxygen flow, thus, to throttle, stop, and restart the engine [19].

From the established state of the art, only the most promising alternatives have been selected to be investigated in this work, from a theoretical, thermodynamic and numerical side, by studying the main parameters controlling the rocket design and propellant combination performance; at the same time, providing an overview on the current and future challenges that can encounter the future space exploration and transportation missions. To achieve the current investigation, Python with its package Proptools, as well as the Rocket Propulsion Analysis (RPA) have been used. Proptools helped providing implementation of equations for nozzle flow and rocket structures. It aims to cover most of the commonly used equations in Rocket Propulsion Elements by George Sutton and Oscar Biblarz, and Modern Engineering for Design of Liquid-Propellant Rocket Engines by Dieter Huzel and David Huang. This work is structured as follows: first, the investigated cases are similar to the ones described below in tables 1 and 2; in table 3, concepts of hybrid systems are also presented and examined. Next, results are illustrated and discussed. Finally, conclusions on the most significant results are made.

| Propellant | Ammonium perchlorate 69.6% | Ammonium perchlorate 68% |
|------------|---------------------------|------------------------|
|            | Aluminium powder 16%      | Aluminium powder 18%   |
|            | Polymeric binder 14%      | Polymeric binder 14%   |
|            | Additive iron oxide 0.4%  |                        |

Table 1. Space Shuttle and Ariane 5 solid rocket boosters

| Parameter     | SRB (Space Shuttle) | MPS (Ariane 5) |
|---------------|---------------------|----------------|
| Thrust        | 10.89 MN            | 5.87 MN        |
| Expansion ratio | 11.3             | 10             |
| Exhaust velocity | 2,690 m.s⁻¹       | 2,690 m.s⁻¹   |
| Temperature   | 3,450 K             | 3,600 K        |
| Pressure      | 6.5 MPa             | 6.0 MPa        |
Table 2. Liquid-propellants rocket engines

| Engine   | Raptor  | NK-33   | RD-0120 | RD-701   |
|----------|---------|---------|---------|----------|
| Propellant | LCH$_4$/LOx | RP-1/LOx | LH$_2$/LOx | RP-1&LH$_2$/LOx |
| O/F ratio | 3.8     | 2.7     | 6.0     | 6.0      |
| Nozzle ratio | 40      | 27      | 85.7    | 133.8    |
| Thrust | 2000 kN | 1638 kN | 1517 kN (SL) | 1961 kN (vac.) | 4003 kN |
| Thrust-to-weight ratio | > 170 (goal) | 136.7  | 58      | 111      |
| Chamber pressure | 30 MPa | 14.57 MPa | 21.8 MPa | 29.4     |
| Specific impulse | 330s (SL) | 297s (SL) | 359s (SL) | 330s (SL) | 4003 kN |

SL: Sea Level, Vac.: Vacuum

Table 3. Metal-based hybrid systems

| Engine concept | Hybrid rocket propellant combinations |
|----------------|----------------------------------------|
| Propellant     | Al/LOx | Al/H$_2$O* | Al/H$_2$O*&LOx | B/LOx | B/H$_2$O* |
| O/F ratio      | 1.6    | 1          | 1.47 with:     | 2.5   | 2.5       |
|                |        |            | H$_2$O: 80%    |       |           |
|                |        |            | O$_2$: 20%     |       |           |
| Nozzle ratio   | 15     | 15         | 15             | 15    | 15        |
|                | 33     | 33         | 33             | 33    | 33        |
| Chamber pressure | 10      | 10         | 10             | 10    | 10        |

* Metals mixed with iced water.

2. Analysis results

The specific impulse (Is) has been calculated for the considered propellant combinations as shown in figure 1, 2 and 3. Is is first increased, then lowered, and shifted towards lower mixture ratios (O/F) after adding Al, whether to AP-HPWB or AP-Fe$_3$O$_4$-HPWB; while it is slightly lowered in the case of LO$_2$-H$_2$. This means that solid fuels in particular demonstrate more efficiency for a certain range of Al additives, outside of this range, Is decreases. Propellant mixture, optimum O/F ratio, Is and thrust are significantly influenced by metal addition. The idea behind is that Al addition increases the thrust coefficient ($C_T$) and combustion temperature ($T_c$), but also the molecular weight ($\mathcal{M}$). This is suitable for the first stage, i.e. sea level, where the atmospheric pressure (Pa) is higher, and more thrust is needed to lift off all the payload to upper stages, i.e. higher altitude. Propulsion performance is also considerably influenced by H$_2$ addition to RP1 and O$_2$ addition to burn the H$_2$ generated from Metal-water reaction, as shown in figure 2 and 3 respectively. The reason is that it modifies the bulk density of the considered propellant combination at its current O/F value. Indeed, the mass flow rate depends on density, which is proportional to ($\mathcal{M}/T_c$)$^{1/2}$. Figures 4, 5, 6 and 7 show the variation of $T_c$ and $\mathcal{M}$ with O/F while figures 8, 9, 10 and 11 show the relation between the thermodynamic energy ($E_{th}$), defined by: $RT_c/\mathcal{M}$, the characteristic velocity ($C^*$) and the variation of O/F ratio. $C^*$ varies proportionally with $E_{th}$ with the variation of O/F ratio, the optimums of both are shifted towards the same O/F stoichiometric value. The propellant with high thermodynamic energy is the one for which high $T_c$ and low $\mathcal{M}$ are achieved.
Figure 1. Variation of estimated specific impulse with mixture ratio for solid propellants.

Figure 2. Variation of estimated specific impulse with mixture ratio for liquid propellants.

Figure 3. Variation of estimated specific impulse with mixture ratio for metal-based hybrid systems.
Figure 4. Variation of combustion temperatures and exhaust molecular weight with mixture ratio for solid rocket boosters.

Figure 5. Variation of combustion temperatures and exhaust molecular weight with mixture ratio for liquid propellants.

Figure 6. Variation of combustion temperatures and exhaust molecular weight with mixture ratio for Aluminium-based hybrid system.

Figure 7. Variation of combustion temperatures and exhaust molecular weight with mixture ratio for boron-based hybrid system.
Figure 8. Variation of thermodynamic energy and characteristic velocity with mixture ratio for solid rocket boosters.

Figure 9. Variation of thermodynamic energy and characteristic velocity with mixture ratio for liquid propellants.

Figure 10. Variation of thermodynamic energy and characteristic velocity with mixture ratio for aluminium-based hybrid system.

Figure 11. Variation of thermodynamic energy and characteristic velocity with mixture ratio for boron-based hybrid system.
Finally, the calculated results on the main combustion and performance parameters for the considered conditions in tables 1, 2 and 3 are presented in table 4, as shown below:

**Table 4. Analysis results on combustion and performance parameters**

| Propellants | Parameters | $\gamma$ | $\left(\frac{T_c}{3R}\right)^{1/2}$ | $E_{\text{Thermodynamic}}$ | $\dot{m}/A$ at $A_t$ | $C^*$ | $C_F$ | Mach number |
|-------------|------------|----------|---------------------------------|-----------------|---------------------|------|------|-----------|
| $^1$AP-HPB-Al | -         | -       | KJ.kg$^{-1}$                          | Kg.m$^{-2}$.s$^{-1}$ | m.s$^{-1}$          | -   | -   |            |
| $^1$AP-Fe$_3$O$_5$-HTPB-Al | 1.1826    | 10.74   | 967.81                                      | 3934.58          | 1524.92             | 1.62 | 3.23 |
| $^2$LCH$_4$/ LOx | 1.1968    | 12.59   | 1319.27                                      | 16921.63         | 1772.77             | 1.80 | 4.25 |
| $^2$RP1/ LOx | 1.1908    | 12.01   | 1198.93                                      | 8605.16          | 1693.04             | 1.76 | 3.86 |
| $^2$RP1&LH$_2$/ LOx | 1.1920    | 13.37   | 1485.59                                      | 15605.09         | 1883.93             | 1.92 | 5.00 |
| $^3$LH$_2$/ LOx | 1.2599    | 15.98   | 2123.35                                      | 9872.37          | 2208.13             | 1.82 | 5.27 |
| $^3$Al/ LOx** | 1.5995    | 8.77    | 639.29                                       | 8959.41          | 1116.12             | 1.57$^a$ | 5.50$^a$ |
| $^3$Al/ H$_2$O(s)** | 1.0987    | 9.35    | 727.75                                       | 7362.07          | 1358.23             | 1.72$^a$ | 3.22$^a$ |
| $^3$Al/H$_2$O(s)&LOx** | 1.1038    | 9.52    | 753.31                                       | 7248.61          | 1379.52             | 1.72$^a$ | 3.23$^a$ |
| $^3$B/ LOx | 1.2092    | 10.14   | 854.84                                       | 7033.50          | 1421.74             | 1.67 | 3.60 |
| $^3$B/ H$_2$O(s) | 1.1255    | 9.03    | 677.77                                       | 7696.79          | 1299.24             | 1.71 | 3.30 |

**Two cases of expansion ratio are considered for the estimation of $C_F$ and Mach number: $A_e/A_t = 15$ (a) and $A_e/A_t = 33$ (b)**

3. Conclusion

Flow density depends positively on the molecular weight; but is inversely proportional to temperatures. This is because at higher temperatures, a high pressure is exerted by the gas; thus, the mass flowing is less. For multistage rockets in which the lower stages have the main task to develop high thrust rather than high velocity, propellants with high molecular weight are preferred. Solid propellant boosters are in this class, and the use of aluminium, to generate aluminium oxide in the exhaust, is advantageous. For a same value of the expansion ratio, propellant combinations lead to different Mach number values, that are proportional to $\gamma$. $C_F$ is maximized at the matched expansion condition, where $P_e = P_a$. $C_F$ is thus a measure of the efficiency with which the nozzle extracts energy from the hot stream in the combustion chamber. Therefore, the expansion ratio is selected based on the ambient pressure at which the engine is expected to operate, as previously shown in tables 1 and 2.

On the other hand, methane is keeping sparking interests for space transportation and exploration applications over hydrogen. The reasons are mainly attributed to:
- The benefit of being easily storable than hydrogen and simpler to be operated due to its density.
- The fact that methane does not coke (polymerize) at the operating temperatures of a rocket engine, making it reusable, thus making the implementation of a full-flow stage combustion cycle easier.
- The potential of manufacturing methane in situ from Mars resources.
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