ISSN: 1983 7402 ITA, 28 a 29 SET 2021

Analysis and Comparison of the Combustion Performance of Paraffin Hybrid Rocket Solid Fuel Formulations by RMD Simulations

Daniel Abreu Duarte, Jose Atílio Fritz Fidel Rocco, Rene Francisco Boschi Gonçalves e Renan Bispo Salvador
Instituto Tecnológico de Aeronáutica (ITA), São José dos Campos/SP – Brasil

Abstract — There is a continued interest in hybrid propellant research with the aerospace industry. In this study, different formulations of paraffin based propellants were analyzed and compared from the kinetic point of view. For this, computational simulations of these reactions were performed through the ReaxFF interatomic interaction model, through Reactive Molecular Dynamics (RMD) simulations, which allowed the control of the temperature variable during the progress of the reaction. The analysis revealed that the addition of aluminum causes an increase in the activation energy of the reaction, which makes the reaction slower for the temperature control applied, but increases the frequency of collisions between molecules, making the hybrid propellants added with this compound more reactive at higher temperatures.

Keywords — Hybrid propellants, Paraffin, computational simulation.

I. INTRODUCTION

Hybrid propulsion technology for aerospace applications has received increasing attention in recent years due to its important advantages over competitive solutions, capable of generating high and controllable thrust through fuel injection control. Hybrid rocket engines have great potential for various aeronautical and aerospace applications due to their safety, reliability, low cost and high performance. As a result, this propulsion technology is feasible in many innovative missions, including space tourism [1]. In this context, an efficient hybrid propellant must be able to produce specific high thrust per unit of time so that it must have rapid combustion so that the volume of gas expelled in this reaction is sufficient to propel the load.

Hybrid thrusters can be employed in orbital satellite transfer, orbital eccentricity alteration, orbital maneuvers, space vehicle control, interplanetary vehicle propulsion, atmospheric reentry vehicles, orbiting systems, light rocket launch, reusable vehicles for space missions, *and boosters.* Hybrid propulsion has several advantages over solid and liquid propellant systems. The phases of a hybrid propellant are stored separately, reducing the risk of explosion compared to solid rockets, which entails greater reliability, reduced costs and reduces the cost of the system. Since then the development of this technology becomes attractive in aerospace propulsion [1]-[2].

Previously, the low fuel regression rate and the need for complex fuel grain geometries were disadvantages that contributed to large-scale hybrid propellant mission failures. However, over the past twenty years, the use of paraffin as fuel has made hybrid propellant viable in large-scale applications. This was mainly because paraffin wax has a higher regression rate than conventional hybrid fuels, in addition to high efficiency and low added value. In relation to many fuels, paraffin also presents more safety in its handling and is also nontoxic and non-carcinogenic [3]-[5].

Aluminum is added to the fuel for the purpose of increasing the specific impulse and simultaneously reducing the flame temperature [6]-[7]. Another issue that the materials have is in absorbing small radiations in solid phases, and can burn uncontrolled, due to the possibility of detachment of the propellant in which it is heated internally. This can be solved by adding carbon black to the fuel to reduce internal heat absorption due to radiation. Usually a small amount of carbon black is added for thermochemical parameters to suffer minimal effects, such as flame temperature [8]-[9]. The carbon black also improves mechanical characteristics, such as increasing the stiffness of the propellant structure.

The complex physical-chemical processes involved in the combustion of hybrid rocket engines are of great importance for the prediction and control of engine performance. Therefore, many investigations have been carried out a better understanding of these phenomena. However, experimental analyses involving combustion of energy materials are generally difficult due to high reactivity and safety in handling these materials. There is a great effort in elucidating the mechanisms and evaluating intermediate rates and species. For this reason, kinetic modeling plays a crucial role in understanding complex reaction mechanisms [10].

In this study, different formulations of paraffin-based propellants ($C_{24}H_{50}$) and additives of carbon black and aluminum were analyzed and compared from the kinetic point of view. To this end, computational simulations of these reactions were performed through the ReaxFF interatomic interaction model, which allows the control of the temperature variable during the progress of the reaction. Reactive Molecular Dynamics (RMD) simulations can be used in these cases, as it requires low computational cost and provides accurate estima-

tion of the interactions between the species present in the simulation limits. ReaxFF is a force field designed to simulate chemical reactions, in which bonds are broken and formed many times during simulation. This method has been extensively used for combustion of energy materials, thermal decomposition of polymers, fuel cells, catalysts [10].

II. METHODOLOGY

In order to find an ideal formulation for a hybrid propellant based on paraffin (chain hydrocarbons with about 20 carbon atoms) molecular-scale combustion reactions of different fuel compositions were simulated in LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software [11], which defines the trajectory of atoms in the simulation system by integrating the differential equations, as presented in (1) and (2).

$$m_i \frac{d\vec{v}_i}{dt} = \sum_j \vec{F}_2(\vec{r}_i, \vec{r}_j) + \sum_j \sum_k \vec{F}_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) \ldots \quad (1)$$

$$\frac{d\vec{r}_i}{dt} = \vec{v}_i \quad (2)$$

In which $\vec{v}_i$, $\vec{r}_i$ and m_i represents respectively the mass, velocity and position of an atom i of the system and $\vec{F}_n$ the force of interaction between the n atoms in the positions $\vec{r}_i, \vec{r}_j, \vec{r}_k$ and so on.

The resolution of these equations through the ReaxFF model of interatomic interactions [12] provides a complete overview of the description of the temporal evolution of the system, which includes the formation and breaking of chemical bonds. Thus, paraffin was modeled as the hydrocarbon $C_{24}H_{50}$ to analyze the different formulations of propellant, and its oxidation reaction was observed, as described by (3):

$$C_{24}H_{50} + 36.5\ O_2 \rightarrow 24\ CO_2 + 25\ H_2O \quad (3)$$

In addition to the modeling of the system, it was also necessary to establish a kinetic criterion for comparison between the formulations. For this, the kinetic parameters of the Arrhenius equation, expressed in (4) were adopted, such as activation energy and pre-exponential factor, represent, respectively, the energy barrier at the beginning of the chemical reaction and the frequency of collisions between the reactants.

$$k(T) = A \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

In which A, E_a, R and T represents the pre-exponential factor, the activation energy, the universal constant of the gases and the temperature at which the reaction occurs, respectively. Based on these parameters, the increase of A and the reduction of E_a to the reaction corresponds to a higher firing speed, that is, related to the propellant's propulsive capacity.

A. Modeling the Initial Conditions of the Simulation System

For simulation results to be consistent with actual design conditions, the simulation system must resemble a cell of the complete reaction system of a combustion chamber, in which the tested hybrid propellant is burned. Therefore, the paraffin molecules were placed grouped in a cobblestone, the additives dispersed inside it and the oxygen molecules grouped in another block, so that there is superficial contact between paraffin and oxygen gas, as in Fig. 1. For this modeling, the software Packmol [13] and Avogadro [14] were used. After the positional modeling of the simulation system, in the LAMMPS simulation environment the system was minimized in low temperature and energy in order to keep it static in the first moments of the simulation, allowing the initial adjustment of the atoms in their proper positions.

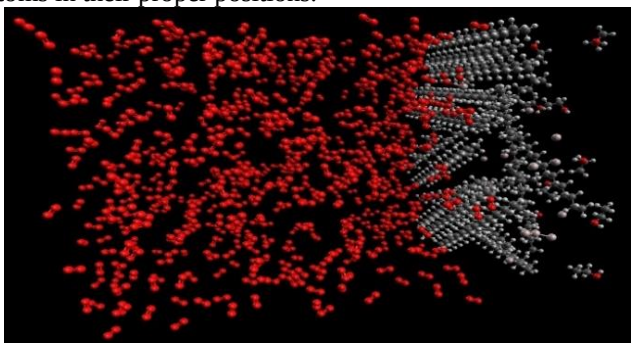

Fig. 1. Initial layout of a simulation system.

The simulations were performed in the simulator under controlled temperature, made by imposing velocities to the atoms of the system during the distance of the linear adjustment within the pre-established temperature range. Thus, applying four different controls for each simulation system, information was obtained about the behavior of the propellant analyzed in different situations. It is important to highlight that the first control applied covers a wide temperature range, to identify the minimum temperature required of the combustion reaction in each system, so that the applied control occurred with the constant temperature higher than the minimum temperature found in the other simulations.

The hybrid propellant sums analyzed are based on paraffin (in this work considered as $C_{24}H_{50}$). The real system is a distribution of different molar masses with a given melting temperature. Therefore, this molecule was chosen because it has the same melting temperature as a given real system. From this base, black smoke (C) and nanoparticles of aluminum (Al) were added in different proportions. The description of each simulation system and the applied controls are presented in Table I.

TABLE I. ANALYZED FORMULATIONS AND APLLIED CONTROLS

Additives	*Control 1*	*Control 2*	*Control 3*	*Control 4*
-	298 K - 5000 K	3000 K	3100 K	3200 K
1% (w/w) C	298 K - 5000 K	3000 K	3200 K	3200 K
10% (w/w) Al	298 K - 5000 K	3000 K	3100 K	3200 K
1% (w/w) C + 5% (w/w) Al	298 K - 5000 K	3000 K	3100 K	3200 K
1% (w/w) C + 10% (w/w) Al	298 K - 5000 K	3000 K	3100 K	3200 K

B. Data Acquisition and Analysis

After processing the simulation in LAMMPS, one of the generated files contains the amounts of each molecule present in the system for each simulation instant. Thus, by controlling the number of oxygen molecules, the constant velocity

of the combustion reaction can be determined by knowing the reaction order. However, the combustion mechanism of a hydrocarbon contains a large number of steps, so that it is not possible to accurately estimate the order of each reagent at the speed of the reaction. Therefore, for the purpose of comparing the formulations, the total reaction was adopted as first order to obtain the reaction velocity constant (k) through the linear regression of the graph $\ln n(O_2) \times t$ described in (5).

$$\ln n(O_2) = \ln\ n_0(O_2) - kt \quad (5)$$

In which t, $n(O_2)$ and $-k$ represent the time elapsed since the beginning of the simulation, the number of oxygen molecules at that instant and the angular coefficient, respectively.

For each formulation, three simulations were performed, with constant and distinct temperatures. Evidently, three distinct velocity constants were generated and, as a result, the activation energy and frequency factor of the reaction were determined by the linear regression of the graph $\ln k \times 1/T$ by (4), since the temperatures for which the constant k was calculated are close and the behavior of Arrhenius [15].

$$\ln k(T) = \ln A + \left(\frac{-E_a}{R}\right) \cdot \left(\frac{1}{T}\right) \quad (6)$$

In which $\ln A$ will be the linear coefficient and $\frac{-E_a}{R}$ the angular coefficient of the regression.

III. RESULTS AND DISCUSSION

The values of kinetic parameters found through linear regression are presented in Table II.

TABLE II. KINETIC DATA FOR THE COMBUSTION REACTION OF EACH PROPELLANT

Additives		*Kinetic Factors*	
Carbon Black	Aluminum	E_a (kJ. mol^{-1})	A ($\times 10^{10}$ s^{-1})
-	-	105.2	160.4
1% (w/w)	-	75.07	46.49
-	10% (w/w)	92.30	25.86
1% (w/w)	5% (w/w)	188.6	110.7
1% (w/w)	10% (w/w)	129.2	122.8

It was observed that the additive formulations of aluminum have higher E_a, and the formulation with 1% (w/w) of carbon black and 5% (w/w) of aluminum with higher E_a and A (Table II). In this formulation it is verified that the frequency factor is about 10 times higher than the other, due to the linearization being calculated on the logarithm of the frequency factor, that is, the margin of error is logarithmic.

Because the system is kept under high temperatures, collisions are more effective and cause external connection breaks. During the simulation, fragments of C_2H_4, C_2H_6 and C_2H_2 are produced. In aluminum simulations, these fragments appear due to the breakage of the Al-C bond, possibly due to the strong collisions of the gas particles or even the other fragments present in the system [10].

With the data from Table II, $\ln k \times 1/T$ curves were generated with the respective linearizations for each of the simulated formulations using Arrhenius plots.

These linearizations show that the greatest deviation occurs in the formulation with 10% (w/w) aluminum, reducing the reliability of the data. This error occurs mainly due to the identification of large groups of molecules as a single by LAMMPS and other problems involving the identification of chemical bonds in the simulation environment.

Another possible analysis is given in the comparison between the decay curves of the number of oxygen molecules in the system, of different formulations with temperature varying linearly in the range of 298 K to 5000 K. In Fig. 2 it is observed that the reactions involving aluminum additive compounds take longer to start, as well as that the reactions occur more slowly under controlled temperature.

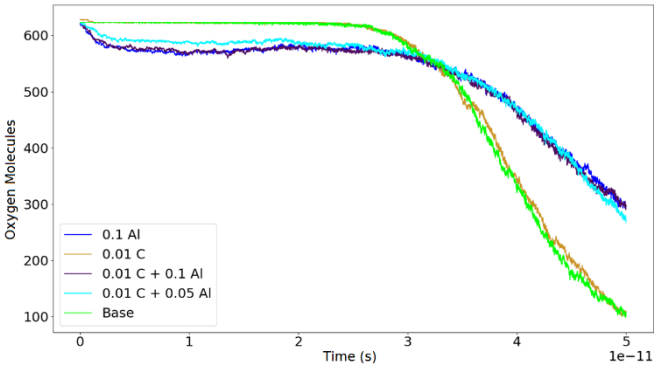

Fig. 2. Temporal decay of the number of oxygen molecules present in each of the simulation systems under control of linear temperature variation.

However, outside the simulation environment, aluminum additive propellants quickly ignite in the absence of temperature control. Given the kinetic model worked, it means that the combustion of these compounds has greater heat release power, keeping the flame at high temperature, so that the frequency factor becomes more influential on the reaction speed than the activation energy. This greater release of heat can be explained by breaking aluminum complexes with other compounds, especially oxygen, which form at the beginning of the reaction and, as it advances, fall apart, releasing energy, as shown in Fig. 2 and Fig. 3.

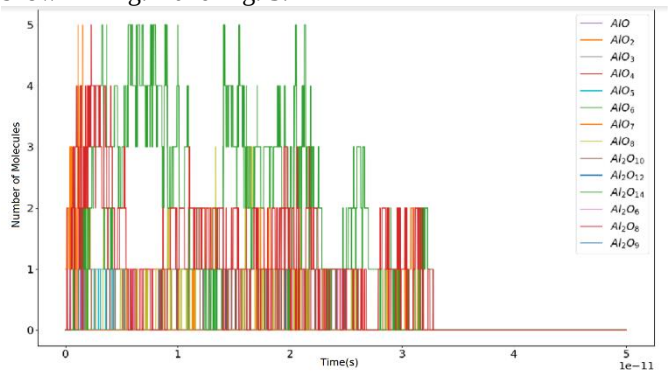

Fig. 3. Formation of Aluminum and Oxygen complexes during the combustion of the formulation with 1% (w/w) C and 5% (w/w) Al.

In addition, the formation of these compounds stabilizes the combustion reaction, making it more uniform and controlled, since it stores part of the flame's energy to later release it.

IV. CONCLUSION

The ReaxFF interatomic interaction model was applied to investigate different formulations in hybrid propulsion

systems based on paraffin fuels. These propellants were enhanced with carbon black and aluminum in the LAMMPS simulation. The values of the kinetic parameters showed that the incorporation of aluminum increases the activation energy of the reaction in combustion, which leads to provide more heat to start the ignition. However, these aluminum-added propellants showed higher frequency of intermolecular collisions during combustion and higher temperatures in which the reaction takes place, due to the formation of aluminum and oxygen complexes that stabilize the reaction and break freeing heat, making the reaction faster. These facts support the addition of aluminum to the propellant to increase its propulsion power. Thus, within the propellant analyzed with aluminum, it was highlighted with the formulation based on paraffin with the addition of aluminum and carbon black, in which it presented the highest frequency factor.

REFERENCES

[1] MAZZETTI, A.; MEROTTO, L.; PINARELLO, G. Paraffin-based hybrid rocket engines applications: A review and a market perspective. Acta Astronautica, v. 126, n. 6, p. 286–297, 2016.

[2] ARNONI, L. V. Experimental research of a hybrid propellant using polyethylene and nitrogen tetroxide. 2014.

[3] LEVERONE, F. et al. Performance sensitivity study on a blowdown nitrous oxide paraffin wax hybrid sounding rocket. Acta Astronautica, v. 160, n. 6, p. 230–239, 2019.

[4] SCHMIERER, C. et al. Low cost small-satellite access to space using hybrid rocket propulsion. Acta Astronautica, v. 159, p. 578–583, 2019.

[5] JOHN, J.; NANDAGOPALAN, P.; BAEK, S. Asian Joint Conference on Propulsion and Power, 2016.

[6] KUBOTA, N. Propellants and Explosives: Thermochemical Aspects of Combustion. 2nd edition. ed. [S.l.]: Wiley-Vch, 2015.

[7] YOUNG, G. et al. Combustion of htpb based solid fuels containing metals and metal hydrides with nitrous oxide. Propellants and explosives, Wiley-VCH Verlag, v. 44, n. 6, p.744–750, 2019

[8] KARABEYOGLU, M.; ALTMAN, D.; CANTWELL, B.JOURNAL OF PROPULSION AND POWER, v. 18, n. 3, p.610–620, 2002.

[9] BERTOLDI, A. E. M. Estudo de instabilidade de combustão em motor foguete a propelente híbrido. 2019.

[10] GONÇALVES, R. F. B.; IHA, K.; ROCCO, J. A. F. Química Nova, v. 41, n. 5, p. 507–511, 2018.

[11] PLIMPTON, S. Fast parallel algorithms for short-range molecular dynamics. Journal of Computational Physics,

v. 117, p. 1–19, 1995.

[12] AKTULGA, H. et al. Parallel reactive molecular dynamics: Numerical methods and algorithmic techniques. Parallel Computing, v. 38, p. 245–259, 2012.

[13] MARTÍNEZ, L. et al. Packmol: A package for building initial configurations for molecular dynamics simulations. Journal of Computational Chemistry, v. 30, p. 2157–2164,2009.

[14] HANWELL, M. et al. Avogadro: An advanced semantic chemical editor, visualization, and analysis platform. Disponível em: https://pubmed.ncbi.nlm.nih.gov/22889332/.

[15] ASHRAF, C. et al. Pyrolysis of binary fuel mixtures at supercritical conditions: A reaxff molecular dynamics study. Fuel, v. 235, p. 194–207, 2019.