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EFFECTS OF O₃ ADDITION ON AMMONIUM PERCHLORATE- BASED SOLID PROPELLANT COMBUSTION

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Abstract. *When a rocket is launched, to overcome the gravitational force that the Earth exerts on the rocket, a major boost is needed, called specific impulse. For this purpose several rocket models and different types of fuels capable of achieving such a result have been developed, as solid, liquid or hybrid fuel - which is nothing more than the joining of the two previous ones. The choice among fuel types is made according to their specificities, for example: the solid fuel presents a high specific impulse, and the liquid one has a lower impulse, but its burning can be controlled.*

Another advantage of solid propellants compared to liquid propellants are their lower cost and ease of production, mostly. Examples of oxidizers used in solid propellants are: Ammonium Perchlorate (AP), Ammonium Nitrate (AN), Ammonium Dintramide (ADN), Cyclotrimethylenetrinitramine (RDX) together with a binder, they compose a solid propellant. In various aerospace projects produced it is observed that one of the most used propellant grains is the AP/HTPB due to the characteristics of the salt, which decomposes generating a high quantity of gaseous oxygen. Usually a solid propellant consists of the oxidizer, binders (connectors and auxiliaries in the production of gases), such as Hydroxyl-Terminated Polybutadiene (HTPB) e Glicidyl Azide Polymer (GAP), and ballistic auxiliaries (commonly metals).

It is also possible to add additives to the fuels, in order to optimize their burning. As an example, ozone (O₃), which is the object in study of this work. The importance of additives that increase propellant fuel efficiency for the advancement of aerospace research is shown at this paper.

Keywords: *Ammonium Perchlorate, Combustion, Rocket, Ozone, Solid Propellant.*

1. INTRODUCTION

The evolution of the areas of knowledge has allowed the scientific community to carry out, on a daily basis, events that were considered impossible some centuries ago. Simple things like driving a car, heating food in the microwave, and communicating with people at a distance getting instant answer through the internet were considered absurd by society living in previous periods. However, ideas and differentiated thoughts have emerged and become actions, changing the lives of all who inhabit this planet. The idea of going to space was one, and despite the numerous difficulties encountered along the way, the goal was achieved. With the arrival of man in outer space, several physical laws, previously theoretical, were proven through the visualization of events.

To leave the earth's crust, leave the atmosphere and reach the vacuum, it takes a transport, the rocket, which must have enough strength, to be freed of the terrestrial gravity, for that, are chosen specific fuels (propellants). In the propellant composition, a large quantity of an oxidizer is used, and a bonding agent is added (binder), which is used to bond the mixture. A metal agent is also commonly added to the propellant that is responsible for stabilizing the firing.

There are different oxidizers for rockets, each with its specifics. Ammonium Perchlorate is the most widely used, otherwise ADN (Ammonium Dintramide) operates similarly and does not emit halogens, yet it is expensive and hard to process, due to the amount of nitrates present in its formulation.

Table 1. Physical and chemical properties, at 1atm, of the monopropellant used.

Ingredients	Density (g/cm ³)	ΔH_f (Kcal/mol)	T _f (K)
Ammonium Perchlorate	1.95	-70.7	1405

Burning a solid propellant requires high pressures and temperatures, because it is necessary that phase changes take place, since the combustion occurs in the gas phase. The fuel, oxidizer and binder are mixed in the solid propellant, the AP decomposes and produces Perchloric Acid (HClO₄) and ammonia (NH₃), The binder labored on the simulation is the HTPB, a polymer, so the combustion final product will have substances such as CO, CO₂, H₂O, HCl e N₂ (Kubota *et al*, 2002).

The purpose of this paper is to add ozone to solid fuel as an attempt to improve the burning process, releasing less polluting gases. The combination of these is what has been looking for in present days, period in which the evolution of inventions in conjunction with the environment.

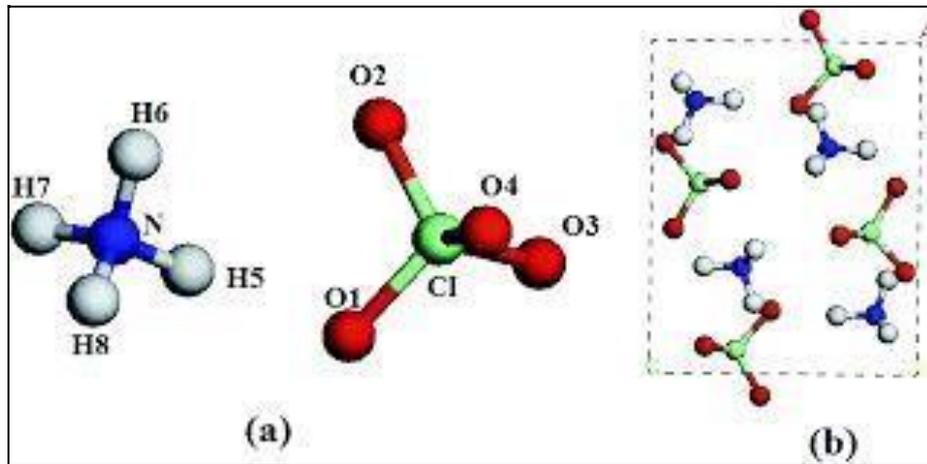


Figure 1. (a) representation of NH₄ and ClO₄ molecules; (b) Ammonium Perchlorate molecules.

2. METHODOLOGY

The combustion analysis of Ammonia Perchlorate was made with the assistance of CHEMKIN-PRO software. It has several reactors for various burning profiles, with the detailed results of the combustion for specific cases. In this paper, the pre-mixed reactor was used, since the AP is part of a solid block of premixed propellant, therefore, the fuel and the oxidizer were aggregated before the beginning of the burning (Kubota *et al*, 2002).

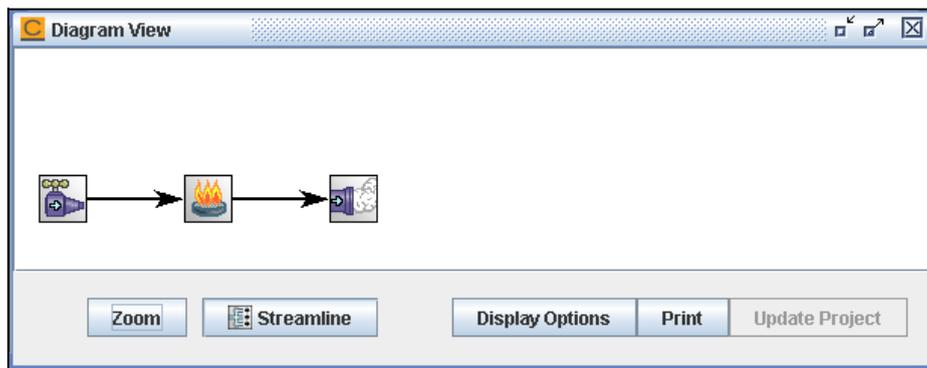


Figure 2. Diagram View of simulation.

Based on experimental data, the molar fractions of the reactants and the physical properties were defined. In order to improve the results, were performed variational studies of some of these properties, such as: temperature, pressure and molar fractions of the reagents. Subsequently a fixed state was determined, and then added the ozone (O₃) as additive in the monopropellant, to analyze and compare the results. The molar fraction of ozone was also varied, between 0.1 and 0.5, to be able to do the best comparison of the possible results. The results obtained were then analyzed in term of the combustion efficiency and the burning sustainability, which today should be approached with

equal importance to any other factor of analysis.

Table 2. Molar fractions of the reagents and products used according to the results obtained by Korobeinichev.

%AP	Reactants		Products										Kinetic Parameters	
	H ₂ TPB	AP	C ₄ H ₆	CO	H ₂ O	HCN	H ₂	CO ₂	ClOH	C ₂ H ₂	NH ₃	HClO ₄	A (1/s)	E (cal/mole)
77.5	1	36	9	5	34	17	23	16	23	6	19	13	1.40x10 ¹¹	1.10x10 ⁴

The initial parameters adopted in the final simulations, which aimed to compare the two burnings, were: temperature equal to 1200K, pressure equal to 60atm and molar fraction of ozone equal to 0.25mol. In the previous simulations, the results configurations, when the amount of ozone was varied, were perceived that there was no big change at the main products.

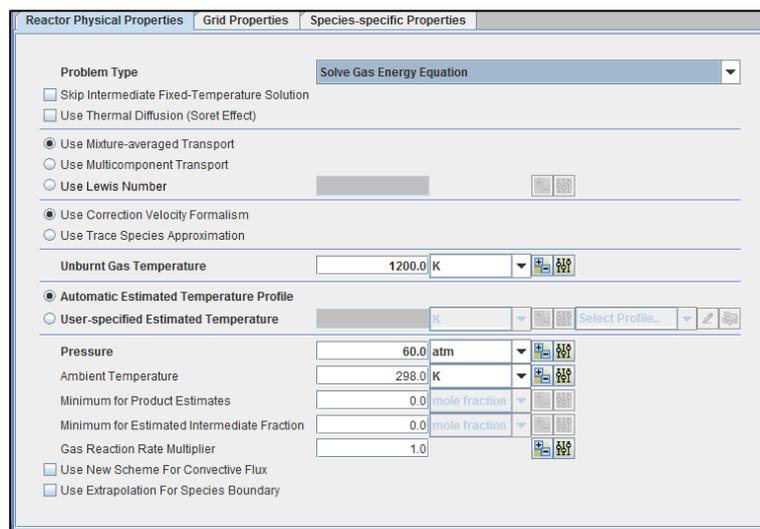


Figure 3. Initial physical parameters of the simulations.

3. RESULTS AND DISCUSSION

With this initial state, the results obtained were analyzed. In these, both the velocity that the gases were expelled and the variation of the molar fractions of the products and main reactants of the burning were observed, in order to estimate the relation efficiency vs environment.

The firsts results obtained were the ones without ozone. As pictured, the gases ejection velocity is higher, ideal to the rocket objective. Carbon dioxide (CO₂), was shown to be at higher levels than carbon monoxide (CO), indicating that most of the combustion was complete. Another important feature of this fuel is the monoxide produced at the start of combustion is consumed again, since it's an intermediate of the reaction, decreasing the total gas released into the atmosphere.

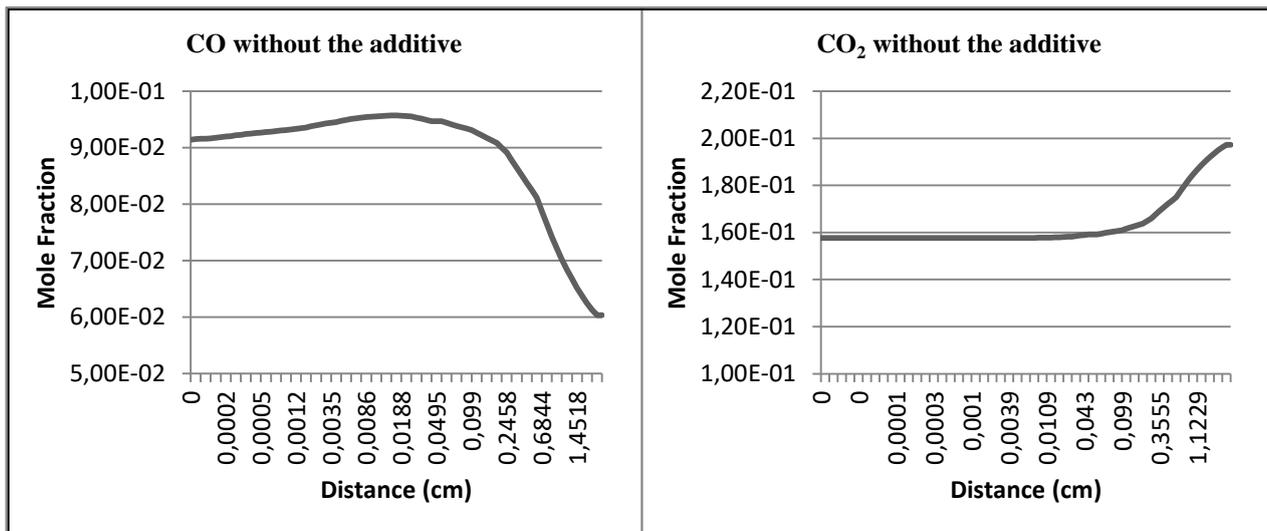


Figure 4. Carbon monoxide and dioxide molar fraction rate in the burn without additive.

When adding the ozone to the process, the results changed significantly. As already predicted, there were changes in product concentrations, since new parameters were added to the process. The increase of oxygen molecules in the process allows an improvement in the fuel burning, but this is not the only factor that interferes in a chemical reaction. The reaction velocity, which is the measure of how quickly the products form and the reagents are consumed (Russel, 1994) is also important for the efficiency of the reaction, since if the reaction time is too short, in other words, high velocity, it will increase the amount of intermediate reactions.

When added the ozone, there was an increase in the production of carbon monoxide, therefore, it is possible to infer that a larger amount of fuel had incomplete burning. As previously stated, this may have occurred for two reasons: either there was a decrease in oxygen molecules or reaction time. Knowing that the additive in this project is ozone, it can be asserted that there was an increase in the quantity of oxygen molecules, thus the CO increase is justified by the increase of the reaction velocity of the combustion.

The addition of O₃ in the propellant, with a proportion of 0.025:36, increases the combustion velocity, because the solid block contains a greater amount of oxygen, which increases the burning power. Its addition also decreases the production of NO_x species, which are the main formers of acid rain. There is also an increase in the concentration of carbon monoxide, however its aggression to the environment is notoriously smaller compared to the nitrogenated species. This behavior is implied due to the decomposition of ozone molecule, i.e. there is a generation of an oxygen radical in a fast process, thus increasing the occurrence of radical reactions, and then creating carbon monoxide from the binder or from the breakage of carbon dioxide, as the oxygen radical has high energy and diffusion velocity. In the fast reaction zone (flame zone), close to the solid surface, the temperature and velocity of ions and radicals is maximum, and then the ozone/ozone decomposition products completely modify the kinetics, enabling several different reactions and processes, then in comparison to the system without the additive.

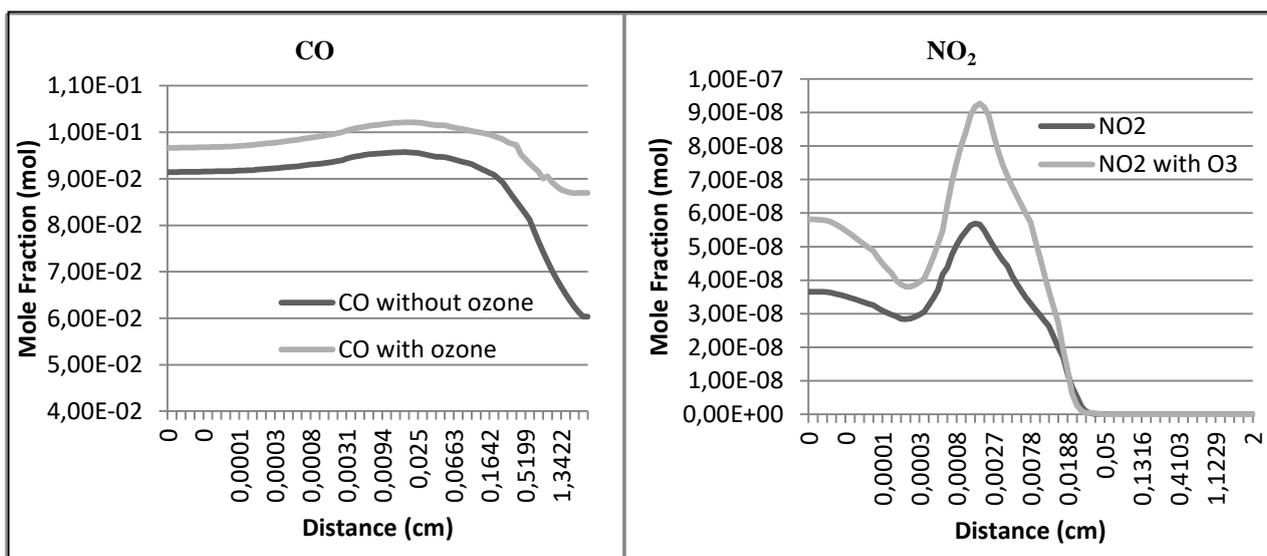


Figure 5. Comparison of CO and NO₂ production with and without ozone.

Each different product is important to ratify the validity of this paper, because their profiles denounce possible failures, such as incomplete combustion and even the non-burning of some component. Furthermore, the increase or decrease in the molar fraction of the substance shown in the graphs helps to detect at which point they are being produced or consumed.

4. CONCLUSIONS

The AP-HTPB monopropellant exhibits high combustion power and is ideal in this area, which requires great forces of impulsion to overcome the terrestrial gravity, besides its formulation does not impose a production with meticulous detail and care.

The increase of CO in the combustion product indicates an increase of the amount of incomplete reactions, however the efficiency is not determined by only one parameter. The quantity of incomplete product depends both on the rate of reaction and the amount of oxidant present in the process, thus if there is an increase in the production of carbon monoxide, with the ozone being an additive, it can be said that the reaction velocity, which grew, was more expressive than the addition of oxygen molecules in the combustion.

After analyzing the results, it was possible to conclude that even with the change in the concentration of carbon monoxide and nitrogenous species, the addition of ozone has some positive results. When comparing the ozone and non-ozone product concentrations, the use of ozone increases the specific impulse, which is directly proportional to the gas ejection velocity.

In future, in more advanced projects, would be interesting to study the fuel combustion phases, since there are innumerable intermediate reactions acting during the process. The control of these would imply an improvement in the burning efficiency, which is directly related to the efficiency of the rocket itself. Beside the addition of metallic substances such as oxides of iron and aluminium, which would increase the overall combustion energy, thus increasing the efficiency of the rocket.

5. REFERENCES

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6. RESPONSIBILITY NOTICE

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