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EFFECTS OF ADN ADDITION ON COMPOSITE SOLID PROPELLANT FORMULATIONS

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Abstract.

In the last decades, it has been studied new formulations and systems to improve the combustion efficiency of solid propellants, to the reduction of the emission of toxic substances to the environment. Hence, this work has as objective to analyze the influence of Ammonium Dinitramide (ADN), replacing the most common oxidant in solid propellants, Ammonium Perchlorate (AP). Due the absence of halogens, the use of ADN becomes more favorable for environmental issues, and maintains the combustion efficiency in this work. The combustion simulations of the various solid propellant formulations were carried out in Chemkin® software using the Premix reactor model. Based on a set of experimental data obtained in the literature, the best conditions of temperature, pressure, mass flow among others physicals properties were analyzed, by means of variational studies in the range of 10^5 Pa to 60.8E5 Pa and 1000 K to 3000 K, simulating the conditions of a combustion chamber of a rocket motor. Thus, a study of the burning of AP dispersed in HTPB (hydroxyl-terminated polybutadiene) was conducted and compared with the experimental burning of the ADN. The graded addition of ammonium dinitramide over AP was analyzed, verifying the changes caused in the combustion behavior. The results showed significant reduction of halogenated substances, with a slight increase in the combustion intermediates. Therefore, the use of Ammonium Dinitramide as a substitute for Ammonium Perchlorate in solid propellants is possible and relevant, not only improving the combustion process, but also reducing pollutants emission.

Keywords: *Ammonium Dinitramide, Solid Propellant, Rocket-Motor, Ammonium Perchlorate, Combustion.*

1. INTRODUCTION

The study of more efficient, sustainable and lower cost energetic materials is very important to facilitate the use of aerospace systems. In the combustion of solid propellants, the search for formulations that produce large volumes of gases to produce the necessary thrust for the displacement of certain loads is crucial. As experimental researches are costly, alternative methods such as computational simulations are extremely important, as they provide strategic solutions that generate approximations with the real case scenario, as well as a range of results in a short period of time and at low cost, also avoiding possible losses of investments (ACKOFF, 1977).

Propellants are composite materials made up of several components which give them the necessary characteristics for a good performance in the desired application. They are mainly composed by an oxidizer agent and polymers that act as binding agents in the composition, improving their mechanical performance and acting as the main source of carbon. There is also, in some cases, the use of a metallic agent when searching for low smoke production and higher burning stability.

These propellants possess a particular behavioral combustion, which occurs in three different phases: condensed, liquid-gas (where evaporation takes place) and gaseous (Fig. 1). The gas phase sustains a pre-mixed zone, where the combustion reactions occur (the decomposition and formation of products and intermediates takes place).

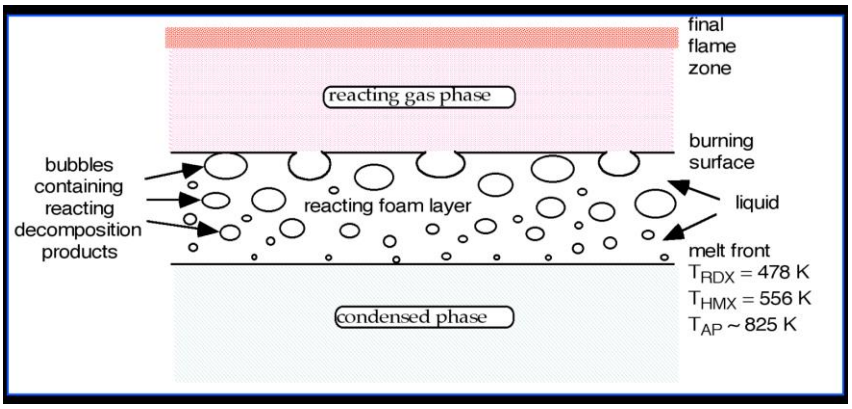

Figure 1 - Burning zones of a solid monopropellant Beckstead (2004).

The computational analysis was possible through the Chemkin® software, which is able to perform complex reaction mechanisms, allowing detailed kinetic results with a range of analyses consisting of flame zone verification, temperature and pressure conditions, molar fractions of the species involved, a solid fuel requires these complex kinetic analyzes in your firing system (Gross, 2007). The program also provides the choice of reactors for several types of simulations. In this work, the *Premix* reactor was used, which consists of a block that simulates a unidimensional premixed flame of a propellant.

In this research, a behavioral study of two main solid propellant formulations was done. First, Ammonium Perchlorate (AP) associated with HTPB (hydroxyl-terminated polybutadiene) as binder – were used due to the advantages and a high Specific Impulse obtained during combustion, although this commonly used formulation is known to produce halogenated emissions.. Ammonium dinitramide (ADN) was used in substitution of AP, as it is an energetic material with high combustion performance and environmentally friendly, but has a high production cost (Jacobs et al, 1969). For the construction of this work and comparison of the results, a set of experimental results from the literature was compiled, among them the work of Korobeinichev (1998 and 2002), which made a broader analysis of the behavior of these fuels. Table 1 summarizes some differences between the different oxidizers analyzed in this work.

Table 1 - Characteristics of AP and ADN monopropellant ingredients

Ingredients	Density (g/cm^3)	ΔH_f (kcal/mol)	T_f (K)
AP (Ammonium Perchlorate)	1.95	-70.7	1405
ADN (Ammonium Dinitramide)	1.72	-35.8	2062

The aim of the present work was to evaluate the replacement of ammonium perchlorate from common propellant formulations with ammonium dinitramide (Wei-qiang Pang et al, 2013), focusing on the kinetic behavior of the chemical species during combustion. Experimental data on the combustion of these materials was found in the literature (Gross, 2007). ADN was added as replacement of AP in the formulation, to analyze whether there would be significant changes in the emissions, without increasing too much the overall cost of the propellant and maintaining or increasing the combustion efficiency and energy released.

2. RESULTS AND DISCUSSIONS

The results will be presented in three stages; the first one will show the Ammonium Perchlorate system chosen, its characteristics and results; in the second will be shown the with Ammonium Dinitramide combustion, as well as its difficulties, characteristics and results. In the last step will be shown the consequences of the association of these oxidizers, analyzing their results and comparing them with those of the AP/HTPB, discussing the advantages obtained.

2.1 Modeling of Ammonium Perchlorate Combustion

Data obtained from Hawkins's experimental studies (Tanner, 2008), which studied the AP / HTPB condensed phase mechanism and determined the molar fractions of reactants and products, were studied for three proportions of the mixture of HTPB and AP, which were: 80% AP, 77.5% AP and 75% AP (Table 2). A combustion modeling (Chemkin® software) was developed for the system composed of 77.5% AP (22.5% HTPB), using temperature variational studies in order to choose the one that presented the best rate , i.e., the one that has the least amount of by-products of the incomplete burning, in a fixed pressure of 1 atm (Fig. 2).

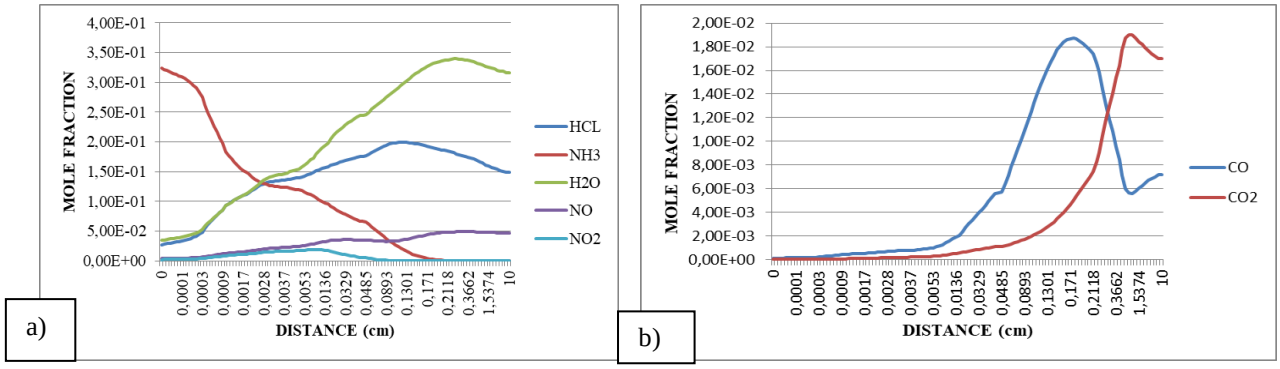

Figure 2. a and b : AP/HTPB simulation in Chemkin at 1200 K and 10^5 Pa

As observed, the combustion of AP/HTPB in the conditions shown (1200K and 1atm) showed an interesting efficiency, as the NH_3 present was totally consumed and the water content increased accordingly. However, there is a high final content of halogens (HCl) and nitrous oxide, which are dangerous components to the environment.

Table 2 –AP/HTPB condensed-phase reaction products for 75, 77.5, and 80% AP, as determined by Hawkins (Tanner, 2008)

%AP	Reactants		Products										Kinetic Parameters	
	HTPB	AP	C_4H_6	CO	H_2O	HCN	H_2	CO_2	ClOH	C_2H_2	NH_3	$HClO_4$	A (1/s)	E (cal/mole)
80	1	41	8	4	35	20	30	22	27	4	21	14	$1.40x10^{11}$	$1.10x10^4$
77.5	1	36	9	5	34	17	23	16	23	6	19	13	$1.40x10^{11}$	$1.10x10^4$
75	1	31	10	10	34	13	15	9	20	7	18	11	$1.40x10^{11}$	$1.10x10^4$

2.2 The Simulation of ADN.

As for ADN, a study of its behavior was made based on the experimental studies made by Korobeinichev (1998a) (2002b) and the most recent one made by Jing (2016) and Piyush Thakre et al.(2014). ADN [$NH_4N(NO_2)_2$] can be used as an oxidant in both solid and liquid fuels, in order to improve fuel performance (Gonçalves et al, 2009). When analyzing the chemical kinetics of the ADN process in Chemkin® software in order to compare with the experimental process, a behavior similar to the experimental data (Fig. 3) is observed, but some divergences occur due to a different injection velocity of the reactants in the simulation, as the simulation analyzes a mass flow rate and not particle velocity as in the experiment. A variational study of several combustion parameters was developed and, with an inlet mass flow of 3.85 g/cm^2.s, temperature of 1800 k and a pressure of 6 atm, a behavior very similar to the one obtained in the literature was found (Fig. 3).The behavior obtained for the chemical species indicate a good reliability of the proposed model and reactor to study the addition of ADN in the AP system.

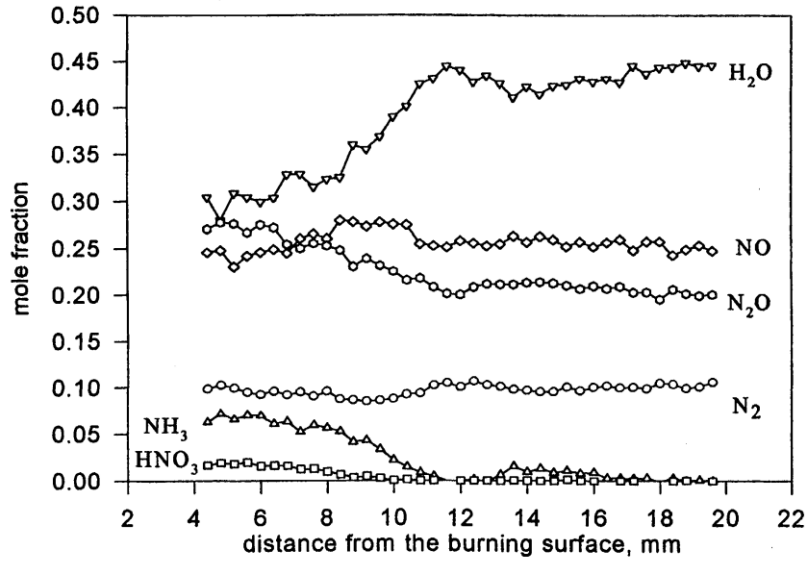

Figure 3 - Species mole fraction profiles and element balances in ADN flame at 60.8E5 Pa by Korobeinichev, 1998 (*u* = 20.3 mm/s).

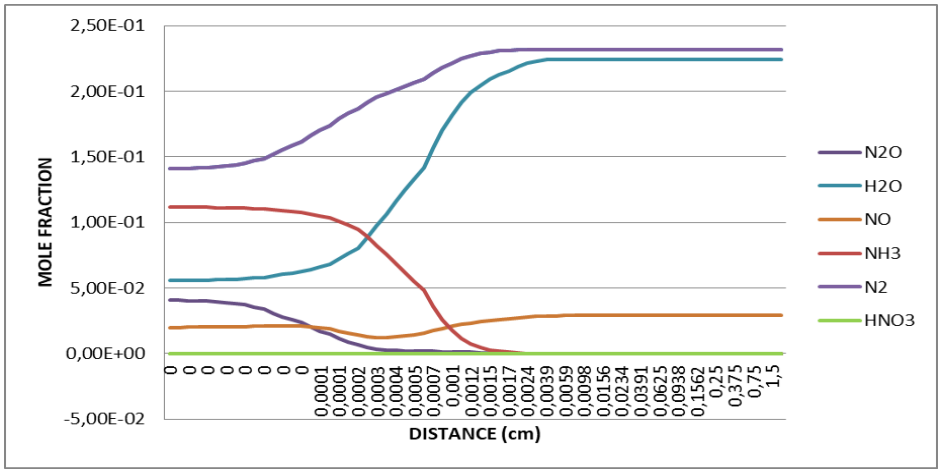

Figure 4 – Molar fraction of main ADN combustion products at 6 atm, 1800 K and inlet of 3,85 g/cm^{2}s.

The difference observed in the molar fractions in comparison of the two graphics, where the experimental data shows moles fractions approximately double of the simulated ones, occurred due to the thermodynamic mechanism of the and,not in total agreement with the real process. However, when analyzing the percentage data of the molar variations of the species, in table 3, it is noticed that the main products like H_2O, N_2O and HNO_3, possess similar values showing a proportionality between the results obtained from the experimental and the simulation. It is also noticed that in elements such as NO and N_2 there were discrepancies which can be explained due to simulation occurring quickly. The fast reactions results in the incomplete combustion of NH_3, which can also be observed in Table 3. In the experimental system, the time was determined in order to obtain the best propellant burning results, thus to a better use of the material, making it smaller the molar fraction obtained from the by-products.

Table 3 – Comparison of experimental and simulated species variation.

Molar Variation of Species	Experimental results	Simulation results
H_2O	1,416E-01	1,69E-01
N_2O	-4,67E-02	-4,08E-02
NO	-2,2791E-02	8,96E-03
NH_3	-6,38E-02	-1,12E-01
N_2	6,7543E-03	9,12E-02
HNO_3	-1,68E-02	-1,06E-07

From these results it was validated the use of these thermodynamic data and proportions of ADN reagents to be used in a new simulation, associating it with the AP, which will be shown next.

2.3 Simulation AP/HTPB+ADN

For this stage of the research, ADN was used as an oxidizer with the objective of optimizing the burning of the Ammonium Perchlorate associated with HTPB, using as the criterion of analysis the molar fractions of the gases produced. When analyzing the interaction of AP with ADN by adding molar fractions of the species that are products of ammonium dinitramide degradation, one of the results showed a significant change in the main products of the system, such as H_2O, where it is possible to notice a raise. It is also analyzed the change of velocity in the two systems and the reduction of points that are obtained from the addition of the ADN.

Stoichiometric equations of ADN decomposition:

$NH_4N(NO_2)_2 \rightarrow NH_3 + HN(NO_2)_2$ (1)

$NH_4N(NO_2)_2 \rightarrow NH_4NO_3 + N_2O$ (2)

$NH_4NO_3 \rightarrow NH_3 + HNO_3$ (3)

$NH_4NO_3 \rightarrow N_2O + 2H_2O$ (4)

Due to the limitations of the ADN thermodynamic mechanism, the addition of the products shown in equations (1), (2), (3) and (4) of ADN degradation were used in the AP burning system . The molar fractions were partially added, performing three simulations, 5%, 10% and 25% ADN addition in relation to the molar proportions of the AP. To successfully and efficiently analyze the effect of ADN on the reactor, the results of H_2O and HCl production were analyzed.

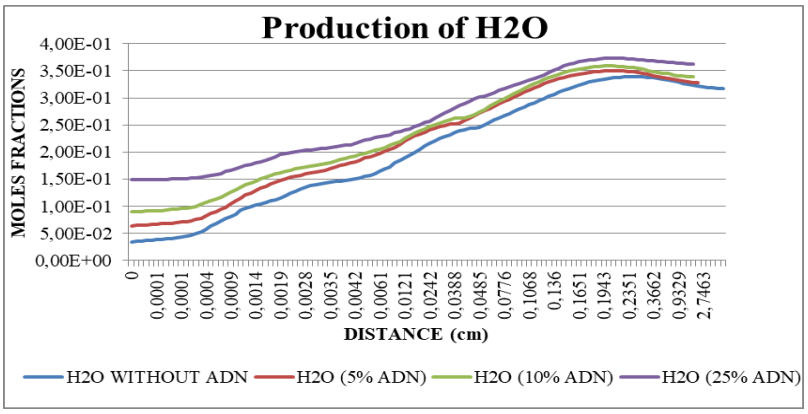

Fig. 5- Fraction of H_2O production in the presence and absence of ADN.

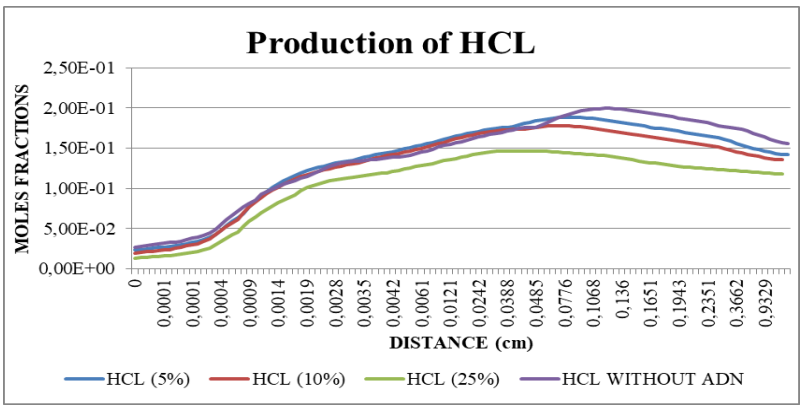

Fig. 6- Fraction of HCl production in the presence and absence of ADN.

When analyzing the different simulations of the systems, a relative increase in H_2O production is noticed, whereas the HCl decreases as ADN is added in the reactor. The initial and final results are better shown in table 4.

Table 4. Molar fractions of H2O and HCl, at the beginning and at the end of the burn.

	H_2O				HCL			
	Without ADN	5%	10%	25%	Without ADN	5%	10%	25%
Initial	0,03446	0,064199	0,089866	0,14887	0,027012	0,022933	0,019657	0,01308
End	0,31683	0,32815	0,33853	0,36244	0,14879	0,14191	0,13543	0,11776

These data clearly show both the relative increase in H_2O production, and it is possible to verify the decrease occurring in the production of the halogenated species (HCl) both at the beginning of the burning process and at the end. The simulation was performed under the same conditions as the AP + HTPB simulations, with a mass fraction flow of 28.6 kg/m^2.

3. CONCLUSION

The work allows to conclude that the even addition of small fractions of the ADN in the small combustion system of the AP will modify the behavior of the burning of the propellant influencing the speed increased considerably from the isolated simulation of the AP to that of 25% of ADN that goes from 55.3 m/s to 64.5 m/s and even with increasing speed the firing rate became more effective with a lower temperature increase for the reactor with ADN reaching a maximum of 2946.2 K while without the ADN reached 3258,4 K both in the 2.18E-3 position, among other factors relevant for use in rocket engines, in order to improve fuel efficiency as well as increase the production of non-harmful gases in relation to the pollutants as verified in the decrease in HCl production. It is also noteworthy the importance of the simulations for the development of more efficient methods for the combustion of solid propellants in order to enable continuous scientific analysis in order to improve the performance of motors, avoiding many expenses, but it is necessary to increase the complexity of the closer to the real one possible, making future experimental ADN research more economically feasible and promising in the results. From this work it is possible to continue the analysis making the reactor system more complex, being able to analyze more effectively the behavior more similar to that of rockets, as to simulate its structure. It is also important to note the need to always diversify sources of fuel to make them not only viable in technological advance but also in sustainability, which should be a pillar for all current scientific developments.

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