AIAA Propulsion and Energy Forum
July 9-11, 2018, Cincinnati, Ohio
2018 Joint Propulsion Conference

10.2514/6.2018-4962

Simulation of ADN pyrolysis and combustion performance in solid propellant formulation

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I. Introduction

During the past decades, propulsive systems have gone through significant modifications and enhancements, aiming higher efficiencies, lower pollutant emissions and lower fuel consumption. The problem resides in the technical limits of these modifications, i.e. physical changes in the system (e.g. dimensions, design, composite materials etc.) shall not impact so much without modifying the reactant mixture (fuel/oxidizer) in parallel. On the other hand, application of other fuel species may increase the power yield of the engine, but generate even worse pollutant emissions (such as halogenated species). In the hypothesis of using new fuels or formulations, the emissions generated must be severely controlled.

Despite all of the precautions taken according to the Kyoto Protocol United Nations Framework Convention on Climate Change, an increase of 27% was observed in CO_2 emissions from 1990 to 2004, and transport related CO_2 emissions increased by 37% (Sopena *et al.*, 2010). Therefore, enhancements of the current combustion processes require immediate attention for new technologies and improvements.

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.

In this research, Ammonium Dinitramide was analyzed using a reactive molecular dynamics model to evaluate its pyrolysis and stability. Also, a behavioral study of its combustion performance in solid propellant formulation was done. ADN was used in substitution of ammonium perchlorate (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.

II. Methodology

The reactive molecular dynamics simulations were performed using the software LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) and the ReaxFF[5] force field. In this force field, the general energy function takes the following formulation:

$$E_{system} = E_{bond} + E_{ov} + E_{under} + E_{val} + E_{pen} + E_{tors} + E_{conj} + E_{vdWaals} + E_{Coulomb}$$

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Which:

- E_{bond} represents the bond energy;
- E_{ov} and E_{under} denotes the over- and under-coordinated atom in the energy contribution, respectively;
- E_{val}, E_{pen}, E_{tors} are the valence angle term, penalty energy and torsion energy, respectively;
- E_{conj}, $E_{vdWaals}$, $E_{Coulomb}$ represent the conjugation effects to molecular energy, nonbonded van der Waals interaction and Coulomb interaction, respectively.

At every MD step, this force field updates the bond orders and provides a pathway for bonds to form and break during the course of the simulation. ReaxFF can reproduce with acuity all relevant quantum mechanical data, as well as provide atomistic descriptions of several complex chemical reactions. In this work, RMD simulations results are also employed for the calculation of the Arrhenius parameters for the global reaction.

The pyrolysis simulation was done using the condensed phase structure of ADN, in three different temperatures (2000 K, 3000 K and 4000 K). Twelve molecules of AND were inserted in a unit cell measuring 15.4 x 9.8 x 25.4 Å, generating a condensed phase structure with approximate density of 1.80 g cm^{-3} (experimental density: 1.81 g cm^{-3}). The system was minimized using low temperature (5K) molecular dynamics with constant number of atoms (N), constant volume (V) and control of the potential energy (E), denoted as NVE. After minimization, for the production phase, the NVT ensemble was used. As reactive molecular dynamics involve usually fast reactions, a timestep of 0.1 femtoseconds (fs) was used. The total simulation time was 50 ps for each of the selected temperatures. The temperatures were controlled by the Berendsen thermostat, with temperature damping constant of 100 fs. For the kinetic analysis, the water content was considered for calculating the average velocity, according to the linear fitting of the number of molecules against the simulation time.

The combustion simulations were done using Chemkin 4.1 software, by Sandia Labs. 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 1). A combustion modeling 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.

Table 1. 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	$1.40x10^{11}$	$1.10x10^{4}$

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). Therefore, a variational study of ADN combustion was done and compared to the literature data.

The final stage of the combustion analysis was the addition of different quantities of ADN in substitution to the AP in the solid propellant formulation (dispersed with HTPB). 5, 10 and 25% of ADN were used for comparison purposes.

III. Results and Discussion

Reactive Molecular Dynamics Simulations

The unit cell used for the RMD simulations, before minimization and equilibrium, is shown in Fig. 1.

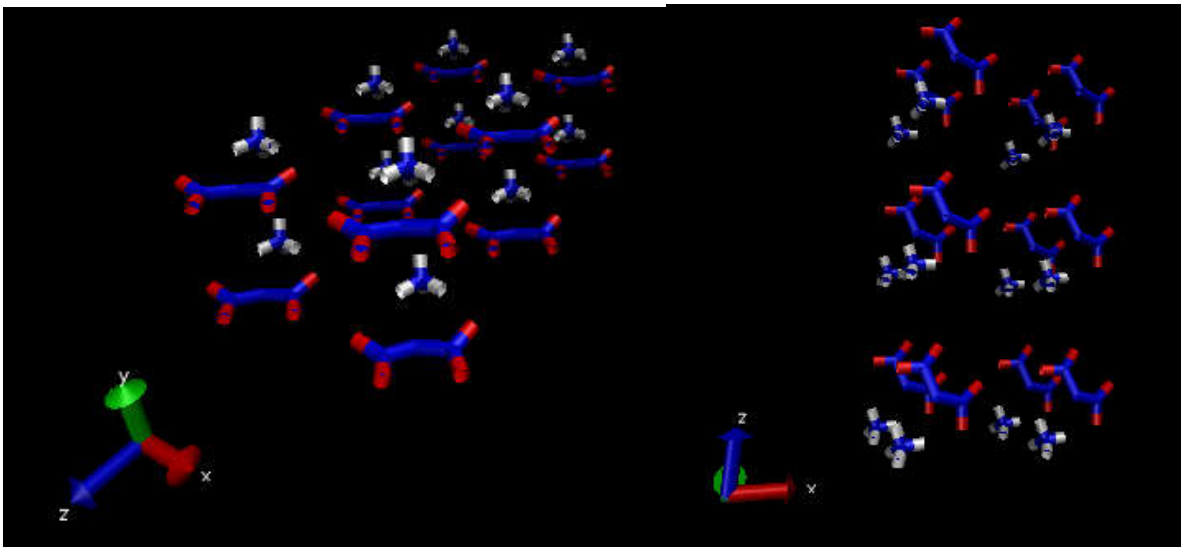

Figure 1 – ADN unit cell input

Fig. 2 below presents the unit cell of ADN after 50 ps, considering an evolution from 0 to 2000 K, at a constant rate of 100 K/ps. As observed, the molecules have decomposed and there is a large quantity of NO, H_2O, O_2, N_2 and OH species.

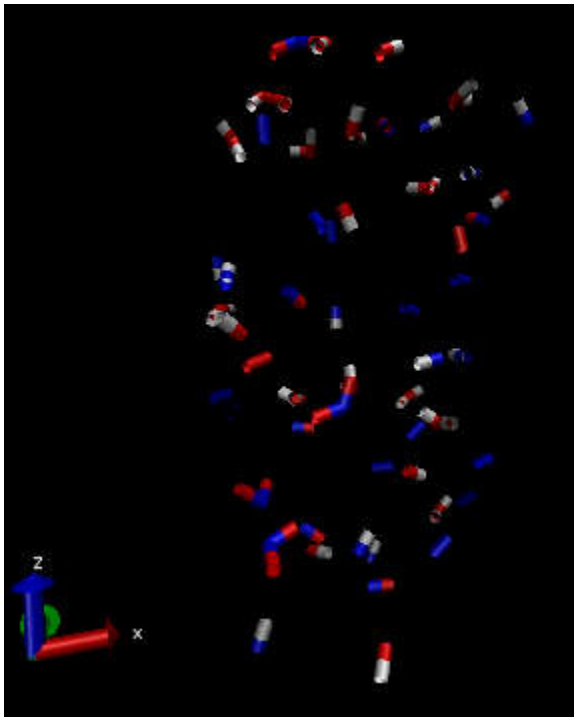

Figure 2 – Cell structure after 50 ps at a constant rate of 100K/ps, up to 2000 K

Considering the analysis of the system's energy, the decomposition of ADN species released an energy amount of approximately 310 kcal/mol after 50 ps. This quantity of energy released is in accordance to an energetic material, considering the approximation of a combustion enthalpy.

The temperature in all of the RMD simulations was increased from 0 K to the target temperature in a constant rate. However, around 500 K, there is the occurrence of the first decomposition reaction of ADN, involving a hydrogen abstraction and consequent generation of ammonia and dinitramic acid, according to the reaction below.

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

This first step of the overall decomposition process is exothermic, so there is a significant influence over the temperature. Fig. 3 below presents the temperature variation during each simulation.

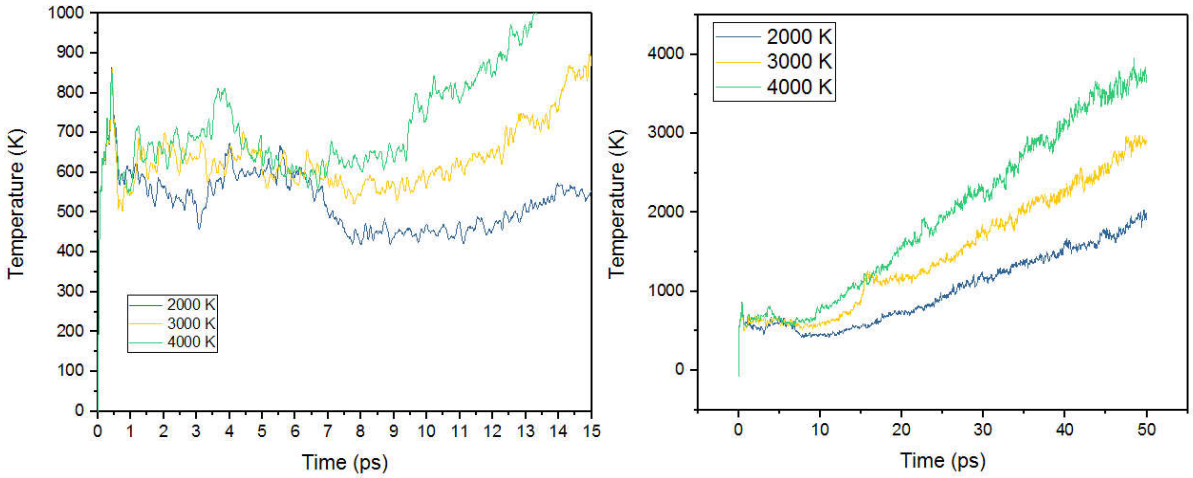

Figure 3. Temperature variation of the system in the whole simulation and in the first 15 ps, respectively.

The effect of the decomposition is observed in the beginning of the simulation, as the temperature rapidly rises and stabilizes during approximately 15 ps. During this time, the temperature is controlled by the occurrence of the mentioned elementary reaction. After all ADN molecules degraded, the temperature of the system begins to rise again at a constant rate.

ADN's decomposition pathways has been extensively studied over the past few years. After the initial decomposition to NH_3 and $HN(NO_2)_2$, this last species decomposes into NO_2^- and N_2O_2, Experimental results (Ermolin and Formin, 2016) indicate that the global decomposition reaction of ADN molecule is:

$$12\ ADN \rightarrow 3\ NH_3 + 10\ N_2O + 6\ NO_2 + 15\ H_2O + 2\ NO + 6\ N_2 + 1\ HNO_3 + 2\ NH_4NO_3$$

It is well known, however, that the global reaction is completely modified when certain variables (like pressure or temperature) are modified. Table 2 presents the products generated in each simulation, compared to the literature data. An increase on the temperature of the system generates higher content of water molecules, as well as nitrogen gas and NO_2, which shows a clear increase in the kinetics of the system, leading to a more complete combustion (lower intermediates content). The simulation held to 2000 K is the one which generated the most similar results when compared to the literature; the divergences are due to the higher temperature than the ones used experimentally. As an example, the ammonium nitrate present as a product in the literature is previously decomposed during the simulation, thus oxidating the nitrogen and generating more water molecules. Based on the results, higher oxidation states are preferred, as the molecules present in higher temperatures tend to be the most stable ones.

Perhaps the employment of ADN in solid propellants, as a substitute to ammonium perchlorate, can occur until certain temperature levels, or the oxygen shall be mostly consumed by the oxidizer itself, without being able to react with the binder or the other ingredients present in the formulation.

Table 2. Experimental / simulation comparison of ADN thermal decomposition products (molar units)

	ADN	→	NH_3	N_2O	NO_2	H_2O	NO	N_2	HNO_3	NH_4NO_3	HNO	N_2O_2	HN_2O_4	H_2N_2O	HNO_2	OH
Ermolin and Fomin, 2016	12	→	3	10	6	15	2	6	1	2	-	-	-	-	-	-
Present work – 2000K	12	→	2	2	5	16	2	10	2	-	1	2	1	3	-	-
Present work – 3000K	12	→	-	1	5	21	5	15	2	-	3	-	-	-	1	-
Present work – 4000K	12	→	-	-	6	20	4	17	-	-	-	-	-	-	4	4

In Figs. 4-6 are presented most of the decomposition process of ADN molecules over time. As ADN decomposes very fast into ammonia and dinitramic acid, ADN molecule was kept off the plots. Clearly, the velocity of species formation is increasing in accordance to the temperature, until the system reaches an approximate steady state (in the simulations, close to 50 ps).

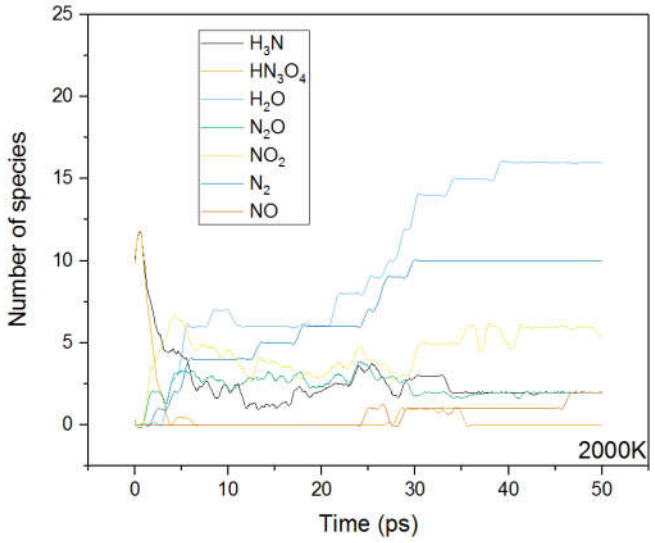

Figure 4. Main species of ADN decomposition (2000 K)

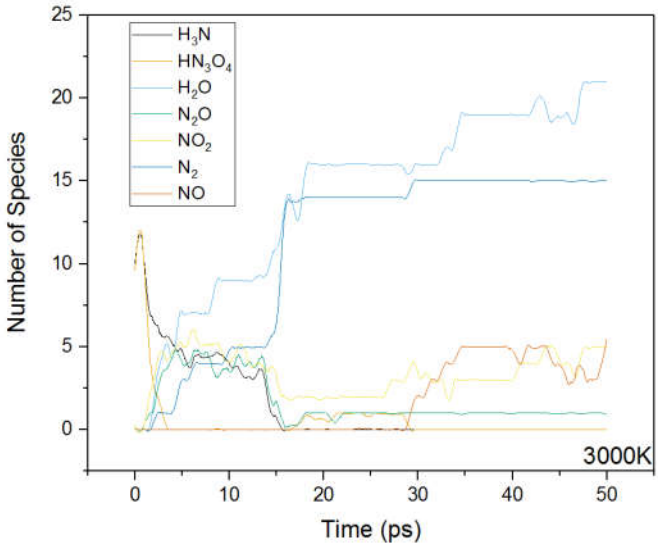

Figure 5. Main species of ADN decomposition (3000 K)

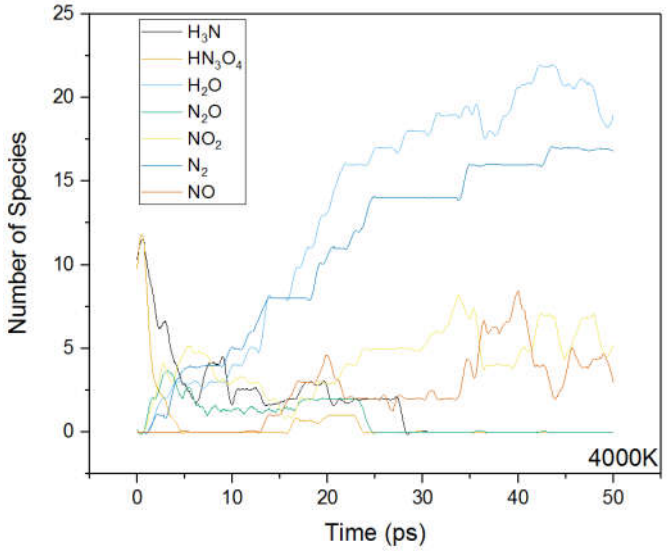

Figure 6. Main species of ADN decomposition (4000 K)

As an hypothesis, one could approach the formation of water molecules as being a first-order reaction, and create a trendline to calculate the average velocity of main products formation over the three simulations.

A liner fit over the data provides values of 0.33, 0.35 and 0.47 molecules per picosecond for the temperatures of 2000, 3000 and 4000 K, respectively. Therefore, as previously stated, higher temperatures lead to higher chemical velocities, in complete accordance to the concepts of kinetics and thermodynamics.

Figure 7 presents the linear fit and data for water formation.

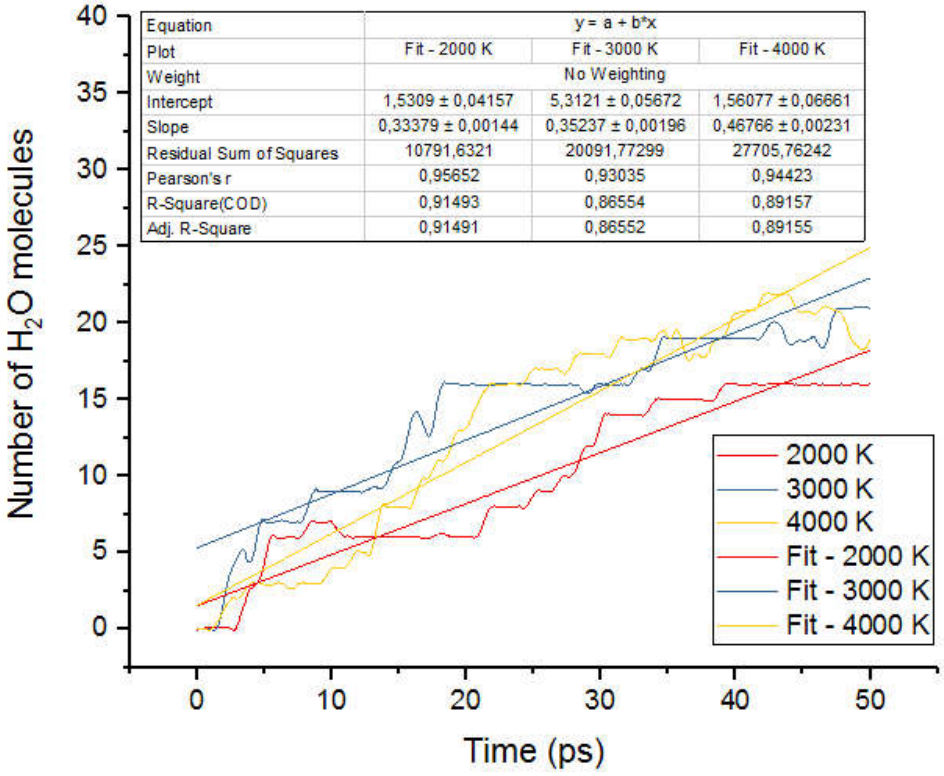

Figure 7. Water molecules formation over time at different temperatures and their respective trendlines.

Combustion modeling

A combustion modeling 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. 8).

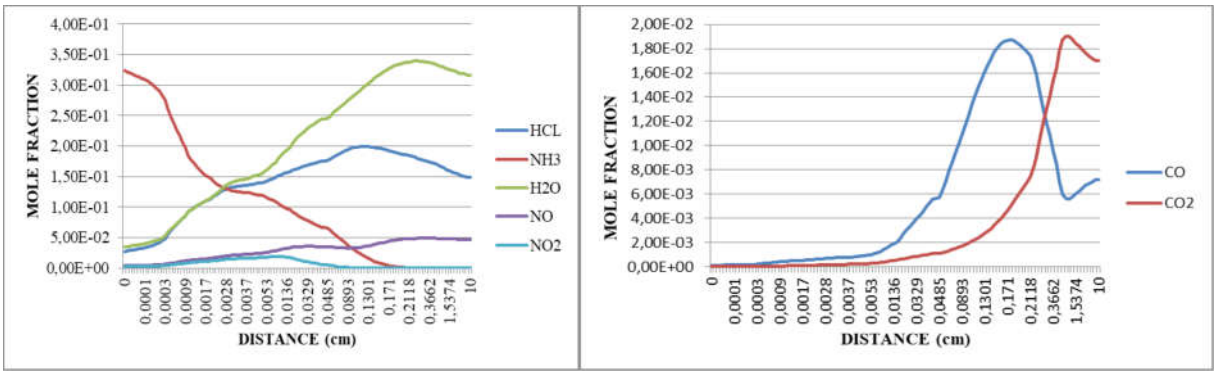

Figure 8. AP/HTPB combustion simulation at 1200 K and 10^5 Pa

As observed, the combustion of AP/HTPB in the conditions shown (1200 K and 1 atm) showed an interesting efficiency, as the NH3 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.

When analyzing the chemical kinetics of the ADN combustion in order to compare with the experimental process, a behavior similar to the experimental data (Fig. 9) 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. 10). 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.

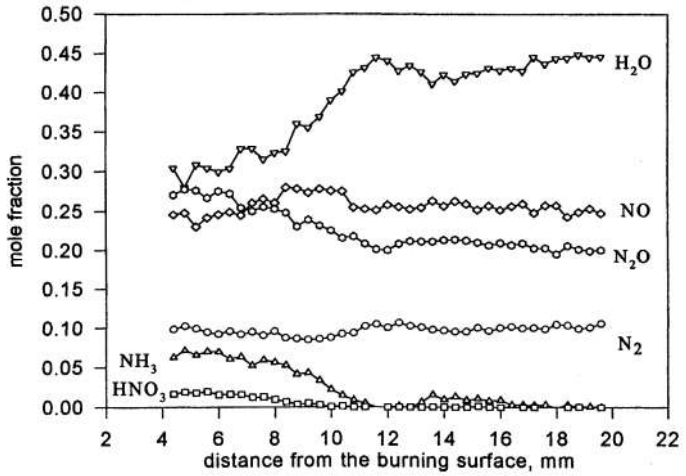

Figure 9. Species mole fraction profiles and element balances in ADN flame at 60.8E5 Pa by Korobeinichev, 1998 (u = 20.3 mm s^{-1}).

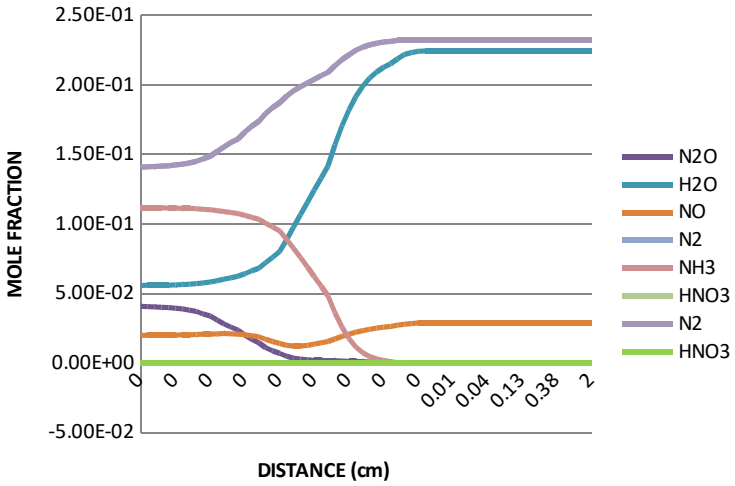

Figure 10. Molar fraction of main ADN combustion products at 6atm, 1800K and inlet of 3,85g $cm^{-2}s^{-1}$.

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 ADN, not in total agreement with the real process. However, when analyzing the percentage data of the molar variations of the species, 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.

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:

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

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

$$NH_4NO_3 \rightarrow NH_3 + HNO_3 \qquad (3)$$

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

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.

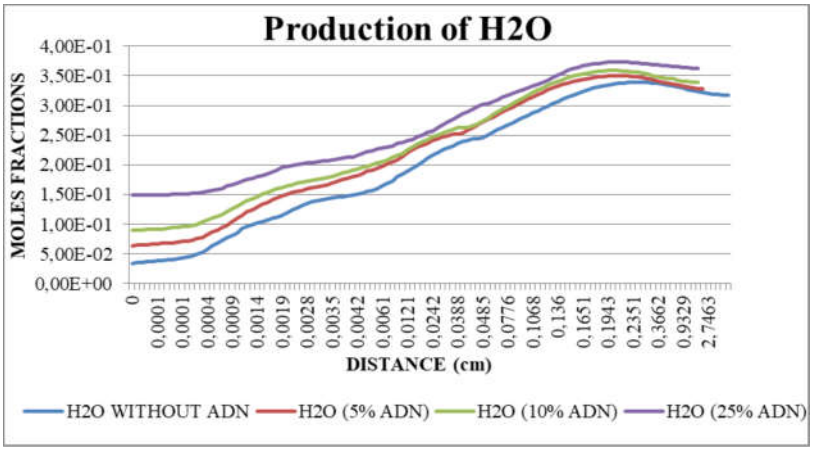

Figure 11. Fraction of H_2O production in the presence and absence of ADN.

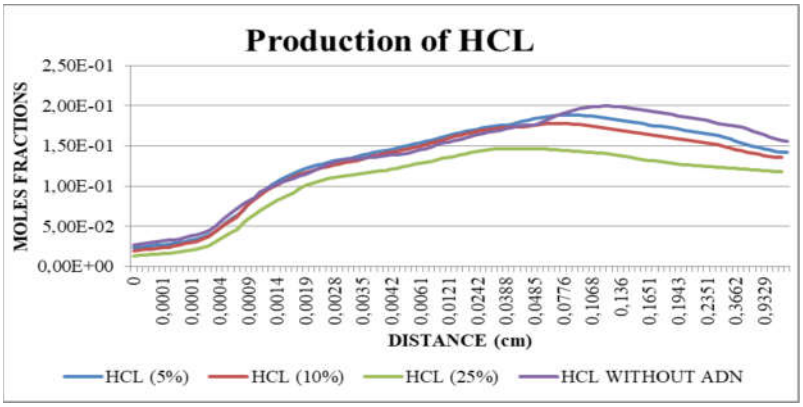

Figure 12. Fraction of HCl production in the presence and absence of ADN.

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 3.

Table 3. 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.

IV. Conclusion

.Reactive molecular dynamics simulations of ammonium dinitramide thermal decomposition under different heating rates and temperature targets were successful. Based on the results, higher temperatures lead to higher ADN self oxidation, which could be an issue in a solid propellant formulation if the combustion temperature is not properly

controlled. The mechanism developed in the simulations follows the one elucidated experimentally, therefore increasing the reliability of the results. A simple kinetic analysis was carried out based on the water molecules generation; when fitting the results, it is clear that the velocity of H_2O formation is also increased with the temperature, as expected from the known laws of thermodynamics and kinetics.

Regarding the combustion, this 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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