Ammonium Dinitramide (ADN)-Hydroxyl Terminated Polybutadiene (HTPB) Simulated Combustion

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***Abstract* — The combustion simulation of ammonium dinitramide (ADN) with hydroxyl terminated polybutadiene (HTPB) binder was carried out with the software Chemkin 4.1, using the "Transient or steady-state perfectly stirred reactor" (PSR) reactor model. The proposed combustion mechanism is composed by 164 different elementary reactions and their respective Arrhenius kinetic parameters, obtained from literature. In this work, the ambient pressure was varied, in order to verify its influence in the system. During the combustion process the data obtained for the system behavior, regarding mainly the mole fractions of the chemical species present in AND/HTPB mechanism were compiled and analysed.**

***Keywords* — Ammonium Dinitramide, Hydroxyl Terminated Polybutadiene binder, Chemkin..**

I. INTRODUTION

The first solid propulsion rocket motors date from the XIII century and are assigned to the Chinese [1]. The rocket red glare from Spangled Banner of Francis Scott Key was initially used in 1812 in a war involving United States of America and England. Significant advances in solid propellants technology occurred during the World War II and continue until today. Nowadays solid propellants are used in satellite launcher vehicles, boosters and sustainers motors in military artifacts propulsion and alteration and correction engines of geo-stationary satellites orbits, among others.

Solid rocket-motors are traditionally identified as solid engines. The solid propellant rocket-motor is a container filled with solid propellant grain which, when entering in permanent flow, expels hot gases from the nozzle, generating enough thrust to the system displacement. The solid propellant grain must burn in a pre-determined project speed (burning rate) to maintain the projected pressure in the combustion chamber and must have enough structural rigidity (mechanical properties) to support the mechanical efforts, during the ignition stages and the burning period. Solid propellants combine next to stoichiometric quantities both in fuel and oxidizing chemical species, in a solid block named solid propellant grain.

These materials are classified as simple based, double based, composite or double based composite propellants [2]. Simple based propellants are active energetic materials considered separately like nitrocellulose or nitroglycerin. They're unstable materials and rarely employed in modern solid engines. Double based propellants are the result of a homogenous mixture of two active ingredients, typically the nitrocellulose and a nitrated plasticizer (energetic), like the nitroglycerin, which dissolves and hardens inside of the uniform solid (grain). Composite propellants have a heterogeneous mixture of a fuel species and an oxidizer one like distinct compounds suspended in a polymeric binder, which provides support to the combustion process in ballistic and mechanical behavior terms.

Modern solid rocket-motors are mostly charged by composite propellants. The mass distribution of its constituents are 20-40% of metallic fuel to increases its specific impulse, usually aluminum, 50-70% of oxidizer (like ADN) and 10-20% of binder matrix, main source of carbon, that acts as fuel. Eventually, 0-5% of plasticizer can be added to improve the flexibility and to help during the propellant processing when it is still in the liquid phase [2].

Examples of typical constituents of solid propellants are presented in Table I. It is possible to make the synthesis of many solid propellant formulations from the combination of these compounds.

The polymeric matrix, named binder, plays the role of binder of all the raw materials that compose the composite solid propellant grain. Molded in the rocket motor case, it goes through a curing process where develops the mechanical and ballistic properties needed to the projected performance of the motor, rocket-motor, in the handling, transport, flight and storage phases [3].

The metallic additives have the function of stabilizing the burning process against instabilities and increase the involved energy during the solid grain combustion.

As the combustion of the solid rocket-motor propellant expels a large quantity of gas residue, the concern about the environment has been growing significantly nowadays, with the current sustainability wave, so the pursuit to find an energetic material environmentally friendly is getting place. Ammonium Dinitramide ($NH4^+[N(NO_2)_2]^-$) is a powerful oxidizer salt that is relatively new and is environmentally harmless, because it doesn't release halogenated products, which is very important when it is used in satellite launch vehicles, where there are devices that are sensitive to chloridric acid (generated in large quantities when using Ammonium Perchlorate, the most common oxidizer) and it can be used in underwater explosives. This salt is soluble in water facilitating its extraction from any system. The oxidizer

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decomposition has been extensively studied, for it represents a major chemical energy which undergoes to an increase of specific impulse (Isp), or thrust, of solid propellant rocket-motors and has residueless combustion. These are the reasons why ADN has a great potential to replace the current oxidizer Ammonium Perchlorate (AP).

ADN is used in solid propellant formulations for its application in aerospace and defense materials industries. It is obtained by nitration of potassium and ammonium sulfamate [4], but there are other synthetic routes as well [5].

Error! Reference source not found.II shows some ADN's chemical and physical properties. [6]

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TABLE I EXAMPLES OF TYPICAL CONSTITUENTS OF SOLID PROPELLANT FORMULATIONS

Metallic/ Non-metallic Fuels	Oxidizers	Binders	Curing Agents	Plasticizers
Al	Ammonium Perchlorate (NH_4ClO_4)	Carboxyl Terminated Polybutadiene (CTPB)	Isocyanates	DOA/ DBT
Be	Lithium Perchlorate ($LiClO_4$)	Epoxydes	Amines/ Amides	Triethylen eglicol dinitrate
Mg	Potassium Perchlorate ($KClO_4$)	Hydroxyl terminated polybutadiene (HTPB)		Trimethyl ethane trinitrate
Na	Ammonium Nitrate (NH_4NO_3)	Nitrocellulose		
Hydrocarbons	Potassium Nitrate (KNO_3)	Polybutadiene acrylic acid (PBAC)		
Polymers	Sodium Nitrate ($NaNO_3$)	Polybutadiene acrylonitrile (PBAN)		
Plastics	Cyclotetramethylene tetranitramine-HMX	Asphalt		
Rubbers	Cyclotetramethylene trinitramine-RDX	PVC		

TABLE II ADN'S CHEMICAL/PHYSICAL PROPERTIES.

Chemical/ Physical Property	Value
Melting point	92-94 °C
Sensitive to light	Yes
Higroscopyc	Yes
Water solubility	Very high
Impact sensitivity	Moderate
Friction sensitivity	low
Thermal decomposition (onset)	160 °C (20 °C/min)
Particle dimensions	Long needles
Incompatibilities	Isocyanates

The thermal decomposition mechanism of this kind of material has not been totally elucidated yet, because of its elevated physical-chemical complexity. However, several studies have been published [7].

During the decomposition process of ADN crystals, is possible to observe the formation of nitric acid, ammonia, nitrous oxide, nitric oxide and water. Where at 55 and 100 °C, ADN decomposes slowly to nitrous oxide and ammonium nitrate (AN), then AN is produced by the recombination of ammonia and nitric acid.[8]

According to Beckstead and Puduppakkam [9], the combustion of a monopropellant can be divided in three regions (condensed, liquid-gas two-phase region and gas region). The two-phase region consists of liquid and gaseous species resulting from the melting and/or decomposition of the solid phase. The precise division between the two-phase and gas-phase region (i.e. the 'burning surface') is not well defined due to chemical reactions, bubbles, and condensed material being convected away from the surface. In the gas phase region of a monopropellant, the flame is essentially premixed. The species emanating from the surface react with each other and/or decompose to form other species. A wide variety of reactions involving many species occur in the gas flame until equilibrium is reached in the final flame zone.

Due to the difficulty in obtaining and performing experiments with these materials in real combustion conditions, it is common to employ computational modeling techniques to estimate the burning behavior of solid propellants.

A widely used software for the study of the flame formed during energetic materials combustion is Chemkin. This software considers the equations of mass and energy conservation, chemical species involved and linear momentum and enables the analysis through temperature and chemical species molar fractions variation in function of time, volume pressure and temperature.

The present work treats the combustion study of ammonium dinitramide formulated in a solid composite propellant grain using HTPB as binder focusing the dependence of the molar fraction with pressures variation.

II. EXPERIMENTAL PART

The elementary reactions that compose the burning mechanism of ammonium dinitramide are listed on **Error! Reference source not found.**. This mechanism was proposed by Korobeinichev [10] and Gross' work [11] according to data obtained from the literature. Some reactions had to be taken off to adapt to the model[12].

TABLE III DECOMPOSITION REACTIONS OF AMMONIUM DINITRAMIDE, WHERE A IS IN MOL, CM, S E K, B IS DIMENSIONLESS AND E_A IN KJ/MOL.

Reação	A	b	E_a
$H_2+M=H+H+M$	4.57E19	-1.40	34.72
$O+H_2O=OH+OH$	2.97E6	2.0	56.01
$O+H_2=H+OH$	5.06E4	2.67	26.29
$O+O+M=O_2+M$	6.17E15	-0.50	0.00
$H+O_2=O+OH$	1.94E14	0.00	68.72
$H+O_2=HO_2$	4.52E13	0.00	0.00
$H+O+M=OH+M$	4.72E18	-1.00	0.00
$OH+H_2=H_2O+H$	2.16E8	1.51	14.34
$OH+H+M=H_2O+M$	2.21E22	-2.00	0.00
$HO_2+O=O_2+OH$	1.75E13	0.00	-1.66
$HO_2+H=H_2+O_2$	6.62E13	0.00	8.90
$HO_2+H=OH+OH$	1.69E14	0.00	3.65
$HO_2+OH=H_2O+O_2$	1.90E16	-1.00	0.00
$HO_2+HO_2=H_2O_2+O_2$	4.20E14	0.00	50.08

TABLE III – Cotinuation

Reação	A	b	E_a
$H_2O_2=OH+OH$	2.95E14	0.00	202.56
$H_2O_2+O=OH+HO_2$	9.64E6	2.00	16.59
$H_2O_2+H=H_2O+OH$	1.00E13	0.00	15.01
$H_2O_2+H=HO_2+H_2$	4.82E13	0.00	33.23
$H_2O_2+OH=H_2O+HO_2$	1.00E12	0.00	0.00
$N+H_2=H+NH$	1.60E14	0.00	105.09
$CH_2+CH_4<=>2CH_3$	2.46E0	2	8270
$N+O_2=NO+O$	6.40E09	1.00	26.25
$N+OH=NO+H$	3.80E13	0.00	0.00
$N+HO_2=NH+O_2$	1.00E13	0.00	8.36
$N+HO_2=NO+OH$	1.00E13	0.00	8.36
$N+NO=N_2+O$	3.27E12	0.30	0.00
$N+NO_2=NO+NO$	4.00E12	0.00	0.00
$N+NO_2=N_2O+O$	5.00E12	0.00	0.00
$N+NO_2=N_2+O_2$	1.00E12	0.00	0.00
$N+HNO=NH+NO$	1.00E13	0.00	8.36
$N+HNO=N_2O+H$	5.00E10	0.50	12.54
$N+N_2O=N_2+NO$	1.00E13	0.00	83.06
$NO+M=N+O+M$	9.64E14	0.00	620.31
$NO+H=HNO$	1.52E15	-0.41	0.00
$NO+OH=HONO$	1.99E12	-0.05	-3.01
$HO_2+NO=NO_2+OH$	2.11E12	0.00	-2.00
$NO_2=NO+O$	7.60E18	-1.27	306.35
$NO_2+O=O_2+NO$	3.91E12	0.00	-0.99
$NO_2+O=NO_3$	1.33E13	0.00	0.00
$NO_2+H=NO+OH$	1.32E14	0.00	1.51
$NO_2+OH=HNO_3$	2.41E13	0.00	0.00
$NO_2+NO_2=NO_3+NO$	9.64E9	0.73	87.45
$NO_2+NO_2=2NO+O_2$	1.63E12	0.00	109.18
$NH+M=N+H+M$	2.65E14	0.00	315.63
$NH+O_2=HNO+O$	3.89E13	0.00	74.78
$NH+O_2=NO+OH$	7.60E10	0.00	6.40
$NH+O=NO+H$	5.50E13	0.00	0.00
$NH+O=N+OH$	3.72E13	0.00	0.00
$NH+OH=HNO+H$	2.00E13	0.00	0.00
$NH+OH=N+H_2O$	5.00E11	0.50	8.36
$NH+N=N_2+H$	3.00E13	0.00	0.00
$NH+NO=N_2O+H$	2.94E14	-0.40	0.00
$NH+NO=N_2+OH$	2.16E13	-0.23	0.00
$NH+NO_2=NO+HNO$	1.00E11	0.50	1 6.72
$NH+NO_2=N_2O+OH$	1.00E13	0.00	0.00
$NH+NH=N_2+H+H$	5.10E13	0.00	0.00
$NH_2+O_2=HNO+OH$	1.78E12	0.00	62.28
$NH_2+O=HNO+H$	6.63E14	-0.50	0.00
$NH_2+O=NH+OH$	6.75E12	0.00	0.00
$NH_2+H=NH+H_2$	6.92E13	0.00	15.26
$NH_2+OH=NH+H_2O$	4.00E6	2.00	4.18
$NH_2+N=N_2+2H$	7.20E13	0.00	0.00
$NH_2+NO=NNH+OH$	9.19E22	-3.00	40.09
$NH_2+NO=N_2+H_2O$	3.40E14	-1.00	-10.88
$NH_2+NO=N_2O+H_2$	5.00E13	0.00	103.00
$NH_2+NO=HNO+NH$	1.00E13	0.00	167.20
$NH_2+NO_2=N_2O+H_2O$	3.28E18	-2.20	0.00
$NH_3+M=NH_2+H+M$	2.20E16	0.00	390.70
$NH_3+O=NH_2+OH$	9.40E6	1.94	27.00
$NH_3+H=NH_2+H_2$	6.40E5	2.39	42.51
$NH_3+OH=NH_2+H_2O$	2.04E6	2.04	2.37
$NH_3+HO_2=NH_2+H_2O_2$	3.00E11	0.00	91.96
$NH_2+HO_2=NH_3+O_2$	1.00E13	0.00	0.00
$NH_2+NH_2=NH_3+NH$	5.00E13	0.00	41.80
$NNH+M=N_2+H+M$	1.00E14	0.00	12.54
$NNH+O=N_2O+H$	1.00E14	0.00	0.00
$NNH+H=N_2+H_2$	1.00E14	0.00	0.00
$NNH+OH=N_2+H_2O$	5.00E13	0.00	0.00
$NNH+NO=N_2+HNO$	5.00E13	0.00	0.00
$NNH+NH=N_2+NH_2$	5.00E13	0.00	0.00
$NNH+NH_2=N_2+NH_3$	5.00E13	0.00	0.00
$HNO+O_2=NO+HO_2$	1.00E13	0.00	104.50
$HNO+O=OH+NO$	1.81E13	0.00	0.00
$HNO+H=H_2+NO$	1.81E13	0.00	4.15
$HNO+OH=H_2O+NO$	1.00E13	0.00	4.15
$HNO+NO=N_2O+OH$	2.00E12	0.00	108.68
$HNO+NO_2=HONO+NO$	6.02E11	0.00	8.31
$HNO+NH_2=NO+NH_3$	2.00E13	0.00	4.18
$HNO+HNO=H_2O+N_2O$	8.51E8	0.00	12.87
$HONO+O=OH+NO_2$	1.20E13	0.00	24.92
$HONO+H=H_2+NO_2$	1.20E13	0.00	30.73

Reação	A	b	E_a
$HONO+OH=H_2O+NO_2$	1.26E10	1.00	0.56
$N_2O+M=N_2+O+M$	1.30E11	0.00	249.17
$N_2O+O=O_2+N_2$	1.00E14	0.00	117.04
$C_2H_4+O_2=2CO+2H_2$	1.80E14	0	35500
$2H+CO_2<=>H_2+CO_2$	5.50E20	-2	0
$N_2O+O=2NO$	1.00E14	0.00	117.04
$N_2O+H=N_2+OH$	2.53E10	0.00	19.02
$N_2O+OH=HO_2+N_2$	2.00E12	0.00	167.20
$N_2O+NO=NO_2+N_2$	1.00E14	0.00	209.00
$HNO_3+OH=NO_3+H_2O$	1.03E10	0.00	-5.18
$NO_2+HO_2=HONO+O_2$	4.64E11	0.00	2.00
$NH_3+NO_2=NH_2+HONO$	2.54E11	0.00	104.79
$NO+NO=N_2+O_2$	1.30E14	0.00	316.13
$NH_3+O=H_2+HNO$	1.10E10	0.00	2.09
$NH_2+NO=N_2+OH+H$	1.08E11	0.00	-5.43
$NH+H_2O=HNO+H_2$	1.00E11	0.50	12.54
$NH+NO=NNH+O$	3.00E13	0.00	71.06
$NO+N_2H_2=HNO+NNH$	5.00E12	0.00	41.80
$NH_2+NO_2=H_2NO+NO$	6.56E16	-1.50	1.12
$H_2NO+H=HNO+H_2$	3.00E7	2.00	8.36
$H_2NO+H=NH_2+OH$	5.00E13	0.00	0.00
$H_2NO+M=H_2+NO+M$	7.83E27	-4.30	252.10
$H_2NO+M=HNO+H+M$	1.69E32	-5.00	260.46
$H_2NO+M=H_2NO+M$	4.46E30	-3.80	237.80
$H_2NO+NO=HNO+HNO$	2.00E7	2.00	54.34
$H_2NO+NO_2=HONO+HNO$	6.00E11	0.00	8.36
$H_2NO+O=HNO+OH$	3.00E7	2.00	8.36
$H_2NO+O=NH_2+O_2$	4.00E13	0.00	0.00
$H_2NO+OH=HNO+H_2O$	2.00E7	2.00	4.18
$N_2H_2+OH=H_2O+N_2+H$	2.50E12	0.00	0.00
$HO_2+H=O+H_2O$	3.00E13	0.00	7.19
$HONO+H=HNO+OH$	5.64E10	0.90	20.77
$HONO+H=NO+H_2O$	8.13E6	1.90	16.08
$HONO+HONO=NO+NO_2+H_2O$	9.69E10	0.00	59.06
$HONO+NH=NH_2+NO_2$	1.00E13	0.00	0.00
$N_2H_2+H=NNH+H_2$	5.00E13	0.00	4.18
$N_2H_2+M=NNH+H+M$	5.00E16	0.00	209.00
$N_2H_2+NH=NNH+NH_2$	1.00E13	0.00	4.18
$N_2H_2+NH_2=NNH+NH_3$	1.00E13	0.00	4.18
$N_2H_2+OH=NNH+H_2O$	1.00E13	0.00	4.18
$N_2H_2+NO=N_2O+NH_2$	3.00E12	0.00	0.00
$N_2H_2+O=NH_2+NO$	1.00E13	0.00	4.18
$N_2H_2+O=NNH+OH$	2.00E13	0.00	4.18
$N_2H_3+H=NH_2+NH_2$	1.60E12	0.00	0.00
$N_2H_3+M=N_2H_2+H+M$	3.50E16	0.00	192.28
$N_2H_3+NH=N_2H_2+NH_2$	2.00E13	0.00	0.00
$N_2H_3+O=N_2H_2+OH$	5.00E12	0.00	20.90
$N_2H_3+O=NH_2+HNO$	1.00E13	0.00	0.00
$N_2H_3+OH=N_2H_2+H_2O$	1.00E13	0.00	4.18
$N_2H_3+OH=NH_3+HNO$	1.00E12	0.00	62.70
$N_2H_4+H=N_2H_3+H_2$	1.30E13	0.00	10.45
$N_2H_4+NH_2=N_2H_3+NH_3$	3.90E12	0.00	6.27
$N_2H_4+O=N_2H_2+H_2O$	8.50E13	0.00	5.02
$N_2H_4+OH=N_2H_3+H_2O$	4.00E13	0.00	0.00
$NH_2+HO_2=H_2NO+OH$	2.50E13	0.00	0.00
$NH_2+NH=N_2H_2+H$	5.00E13	0.00	0.00
$NH_2+NH_2=N_2H_2+H_2$	8.50E11	0.00	0.00
$NH_3+HNO_3=H_2NO+H_2O+NO$	2.32E1	3.50	187.81
$NNH=N_2+H$	1.00E6	0.00	0.00
$NO_3+H=NO_2+OH$	6.00E13	0.00	0.00
$NO_3+HO_2=NO_2+O_2+OH$	1.50E12	0.00	0.00
$NO_3+NO_2=NO+NO_2+O_2$	4.90E10	0.00	12.29
$NO_3+O=NO_2+O_2$	1.00E13	0.00	0.00
$NO_3+OH=NO_2+HO_2$	1.00E13	0.00	0.00
$CH_4+H=CH_3+H_2$	6.60E08	1.6	10840
$CH_4+OH=CH_3+H_2O$	1.00E08	1.6	3120
$CH_3+H+M=CH_4+M$	1.27E16	-0.6	383
$CO+OH=CO_2+H$	4.76E07	1.2	70
$CH_2+H_2=CH_3+H$	5.00E05	2	7230
$CH_2+H+M=CH_3+M$	2.50E16	-0.8	0
$CH_4+O=CH_3+OH$	1.02E09	1.5	600
$OH+CH_3=CH_2+H_2O$	5.60E07	1.6	5420
$HO_2+CH_3<=>O_2+CH_4$	1.00E12	0	0

$k = A\,T^b \exp(-E/RT)$. Units: A (mol-cm-s-K), E (J/mol).

As previously mentioned, a Transient or steady-state perfectly stirred reactor was used in the simulation. This model considers a perfectly stirred gas phase while in combustion.

For the experiments, the system pressure of the combustion chamber was varied from 1 to 12 atmospheres, in order to study its influence in the products and oxidizer molar fraction; the combustion was simulated in an atmosphere composed by the initial products of ADN formulated with hydroxyl terminated polybutadiene (HTPB) binder decomposition, with composition and concentration obtained from the literature [13]. The initial concentration of the species inside the chamber was set according to an ADN/HTPB rate of 1:1.

III. RESULTS AND DISCUSSION

In ammonium dinitramide combustion simulation process at pressure of 1 atm (**Error! Reference source not found.**), it can be noticed that the curves starts to stabilize after 0.010 s. This profile is characteristic of a transient state, presenting in detail the ignition variance, until the system reaches the steady state.

As observed, NH_3 (one of two main species of ADN initial decomposition) is completely and instantly consumed in the beginning of the process, then appearing again, because it is a product of recombination of intermediated reactions. This fact indicates that this specie is most likely the principal for the combustion ignition, and also consumed in the first steps of the mechanism. Fig. 2 and 3 shows that carbon monoxide and carbon dioxide, respectively, (from HTPB decomposition) are generated during the process, CO generation is initially fast and later suffers a decay, as there's also formation of CO_2 from CO. Regarding the other species there is a sudden decay on the mole fractions of water and nitrogen (Fig. 3), followed by increase in the water molar fraction with stabilization and slight continuous decay of nitrogen. The N_2 (obtained from air) usually does not participates in combustion reactions, but as may be seen, there's consumption oh this species, because of the high temperature developed in the combustion chamber (~1800K).

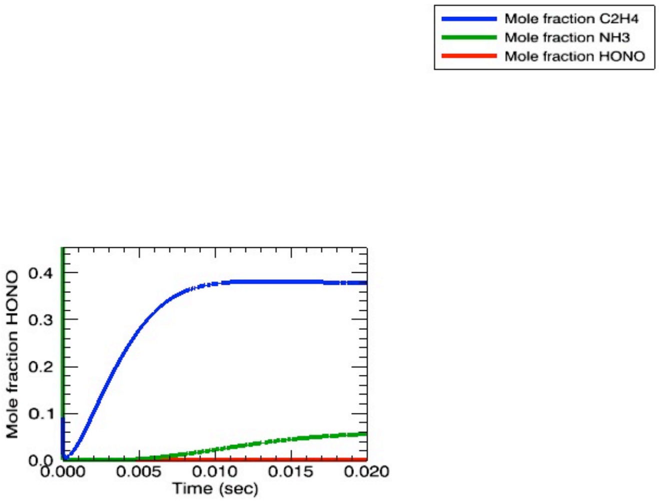

Fig. 1. ADN/HTPB decomposition under pressure of 1 atmosphere.

As the pressure on the combustion chamber rises, significant differences on the combustion process of ADN/HTPB were noticed. **Error! Reference source not found.**4 shows the combustion simulation of the material at pressure of 5 atm.

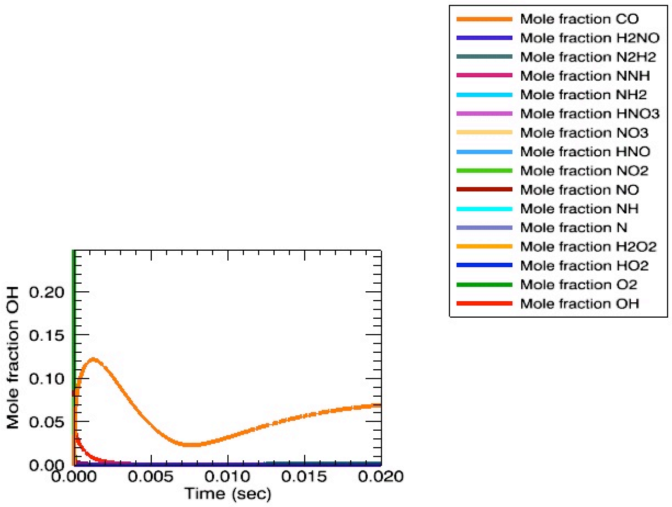

Fig. 2. ADN/HTPB intermediated products under pressure of 1 atmosphere.

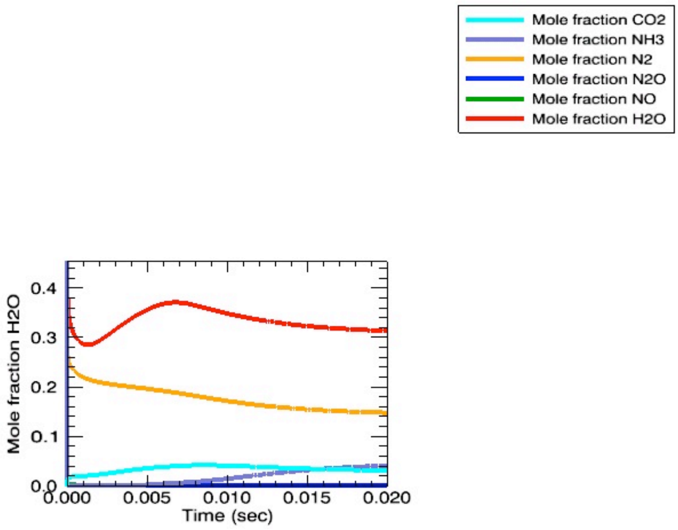

Fig. 3. ADN/HTPB products under pressure of 1 atmosphere.

The curves present again slight stabilization after 0.010 s. As the pressure increases, the speed of the elementary reactions presented in ADN decomposition mechanism rises, where there is an increase and posterior a decay of the molar fraction, for CO (Fig. 4) and decay and posterior increase of the molar fraction, for water (Fig 5). As it shows, the decomposition of ADN does not suffer with the pressure variation (Fig. 6).

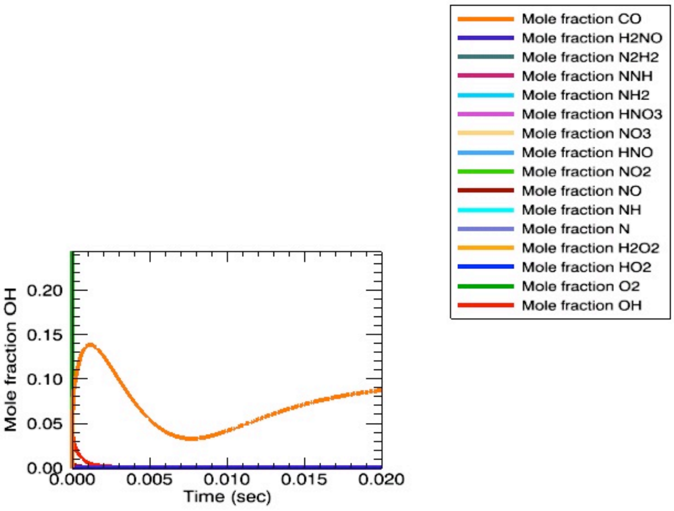

Fig. 4. ADN/HTPB intermediated products under pressure of 5 atmospheres.

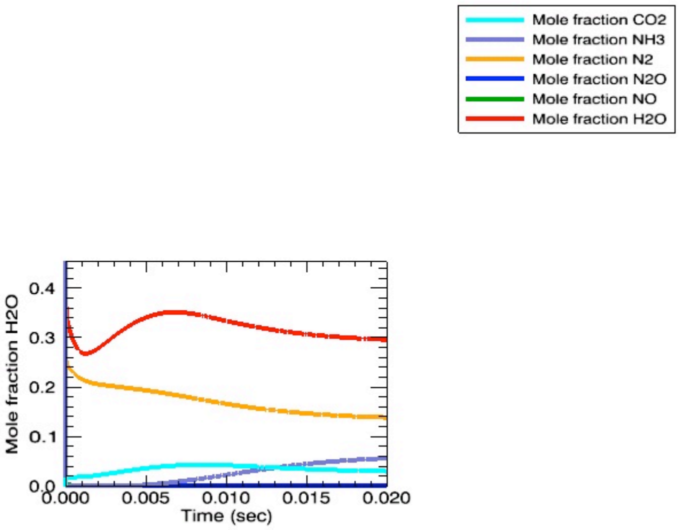

Fig. 5. ADN/HTPB products under pressure of 5 atmospheres.

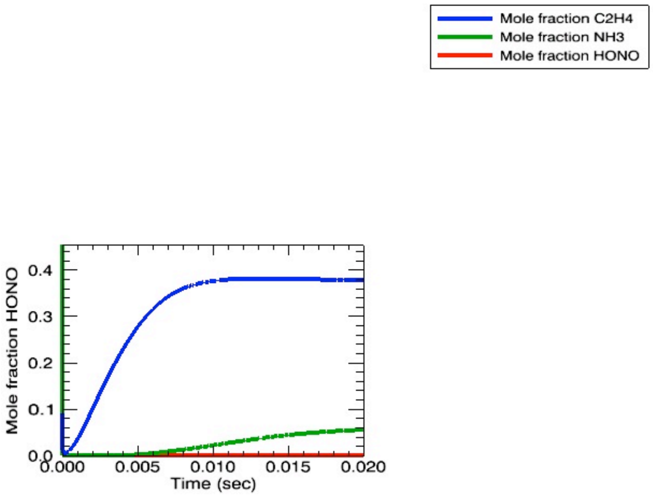

Fig. 6. ADN/HTPB decomposition under pressure of 5 atmospheres.

As expected C_2H_4's molar fraction increases, because it is the HTPB's initial product, in the beginning of the combustion this specie is consumed by the oxygen produced by ammonium dinitramide's decomposition, but as the ratio of ADN/HTPB is 1:1, there is not enough oxygen to consume all the present binder. The mass balance of the species is maintained from the beginning to the end of the simulation.

While observing the variation on the curves, comparing Figs. 1-3 and 4-6, it is noticed an increase on the formation/consumption rates of the species, as the slopes are slightly higher in 5 atm. This behavior indicates an increase of chemical speed generated by the higher pressure.

The "elbows" appear due to the increase of the occurrence of intermediate reactions in the flame zone. This phenomenon generates a great variation of intermediates mole fractions, which modify the concentration of the main species (especially in the flame zone), so the different slope is observed.

Between 10 (Fig. 7) and 12 atmospheres (Fig. 8), there is only a minimum variation on the CO curves after 0.005 s. After a certain point, the pressure no longer interferes in the behavior.

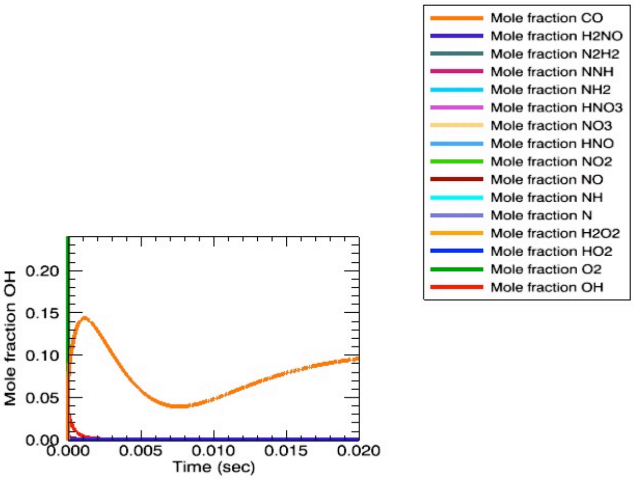

Fig. 7. ADN/HTPB intermediated products under pressure of 10 atmospheres.

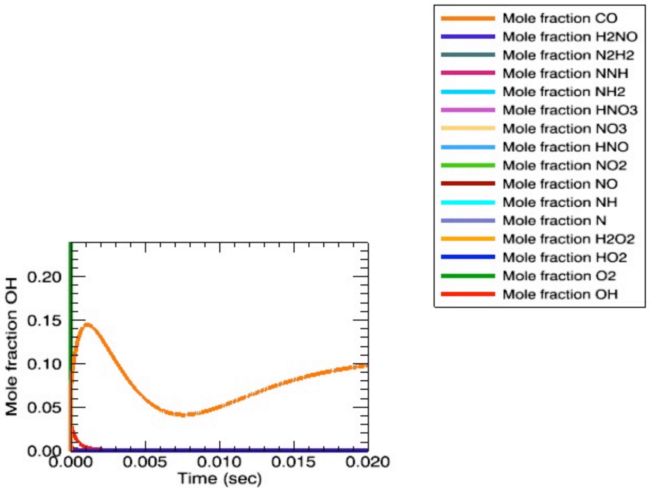

Fig. 8. ADN/HTPB intermediated products under pressure of 12 atmospheres.

This gain in chemical speed is converted in gain in thrust and specific impulse rocket-motors. Therefore, this kind of simulation is interesting to know the behavior of one or more materials, internally to a rocket motor combustion chamber, to develop the optimum propellant formulation, i.e., the one that generates higher thrust, specific impulse and generates fewer residues.

The combustion process of ADN/HTPB has presented a behavior of no significant variation with pressure. This behavior should be attributed to the homogeneous dispersion of ADN inside the binder, in the solid phase. Also, it is assumed that all of the liquid ADN and HTPB present on the condensed phase decompose to form gaseous species; evaporation not included. At low pressures, the propellant is more likely to have a premixed flame during combustion, with the oxidizer and binder decomposition products (from the condensed phase) mixing completely before the gas phase reactions occur [14]. As the pressure increases, the diffusion of the fuel products into the reacting stream above the oxidizer is disrupted and the gas phase flame becomes increasingly diffusion limited. Independent of the pressure in the chamber, the packing and the molecular distribution of the material will not suffer alteration and will not lead to pressure variations in its behavior, proving the limitations of the model.

In this simulation, the oxygen molar fraction suffers an instant decrease, meaning total consumption of it. According to the reactions with HTPB decomposition products the formation of carbon dioxide is maintained relatively constant with the increase of pressure, as its oxidation doesn't vary with the pressure. In this simulation, the molar fractions of CO2 is not null initially, because given the system temperature, HTPB suffers an initial decomposition that should not be discarded, generating carbon oxide.

IV. CONCLUSION

The ammonium dinitramide decomposition process was simulated in different situations using the computational package Chemkin, PSR module. With the reactions involved in the proposed mechanisms, the variation of ADN combustion behavior was observed as the pressure of the combustion chamber of a solid propellant rocket-motor was varied. Based on the results, the profiles of the molar fraction with time originated from the ADN/HTPB combustion were modeled, presenting the different molar fraction variation of the chemical species, generated by the materials decomposition. This study showed that ADN/HTPB's products are less harmful to environment when compared to halogenated oxidizers, because the major products are water, ammonia and carbon dioxide. This study contributes to the better understanding of the decomposition process, i.e. how the species involved behaves during the combustion and with variations of different parameters. The procedure adopted may be of use with new formulations of propellants, avoiding costly and long tests.

REFERENCES

[1] MARK, H. Encyclopedia of Space Science and Technology; v. 2, Wiley interscience, 2003, 531.

[2] PISACANE, V.L. Fundamentals of Space Systems, 2th ed., Oxford University Press, 2005, 206.

[3] MONTEIRO, R.R.; IHA, K.; ROCCO, J.A.F.F.; *Vulnerabilidade de motor-foguete a propelente sólido em relação ao impacto balístico (Arma de Fogo)*- IX SIGE, 2007.

[4] HOSSEIN, N. G., RAMIN, M., MOHAMMAD, F., PARVIZ, K., Synthesis of Ammonium Dinitramide by Nitration of Potassium and Ammonium Sulfamate. The Effect of Sulfamate Conterion on ADN Purity, Iran. J. Chem. Chem. Eng. Vol. 27, No.1, 2008.

[5] VENKATACHALAM, S., SANTHOSH, G., NINAN, K. N., An Overview on the Synthetic Routes and Properties of Ammonium Dinitramide (ADN) and other Dinitramide Salts, Propellants and Special Chemicals Group, Vikram Sarabhai Space Centre, Trivandrum 695 022 (India), Propellants, Explosives, Pyrotechnics 29 (2004), No. 3.

[6] CANNIZZO, L. F., HIGHSMITH, T. K., WARDLE, R. B., CAMPBELL, C. J., et al, Utilization of Ammonium Dinitramide (ADN) in Propellant Formulations, Report Documentation Page, Form Approved OMB No. 0704-0188.

[7] KOROBEINICHEV, O. P., et al, Modeling the Chemical Reactions of Ammonium Dinitramide (ADN) in a Flame, Combustion and Flame 126:1516-1523(2001).

[8] MISHRA, I. B., RUSSEL, T. P., Thermal Stability of ammonium dinitramide, Thermochimica Acta 384 (2002) 47-56.

[9] BECKSTEAD, M. W.; PUDUPPAKKAM, K. V., Modeling and Simulation of Combustion of Solid Propellant Ingredients Using Detailed Chemical Kinetics, 40th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, 2004.

[10] KOROBEINICHEV, O. P., et al, Modeling the Chemical Reactions of Ammonium Dinitramide (ADN) in a Flame, Combustion and Flame 126:1516-1523(2001).

[11] GROSS, M.L.; Two-dimensional modeling of AP/HTPB utilizing a vorticity formulation and one-dimensional modeling of AP and ADN, 2007.

[12] GONÇALVES, R. F. B., ROCCO, J. A. F. F., IHA, K. e MACHADO, F. B. C., Modelagem Da Combustão Da Dinitramida De Amônio Por Simulação Computacional, Quim. Nova, Vol. 32, No. 7, 1698-1703, 2009.

[13] KOROBEINICHEV, O. P., et al, Flame Structure of ADN/HTPB Composite Propellants, COMBUSTION AND FLAME 127:2059–2065 (2001).

[14] Gonçalves, R. F. B., IHA, K., MACHADO, F. B. C., ROCCO, J. A. F. F.,Ammonium'Perchlorate'and'Ammonium'Perchlorate1Hydroxyl'Terminated'Polybutadiene'Simulated'Combustion, J. Aerosp. Technol. Manag., São José dos Campos, Vol. 4, No1, pp. 33-39, Jan-Mar, 2012.