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Ammonium Perchlorate and Ammonium Perchlorate-Hydroxyl Terminated Polybutadiene Simulated Combustion

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Abstract: The combustion simulation of ammonium perchlorate was carried out with the software Chemkin, in two steps: the burning behavior of pure ammonium perchlorate and the one of formulated ammonium perchlorate with hydroxyl terminated polybutadiene binder. In both cases, the room pressure varied in order to verify its influence in the system. The burning environment conditions were diverse. During the combustion process, the data obtained from the kinetic chemistry simulation software were compiled. The flame structure can be described by the molar fraction of the burning products and the temperature evolution from the surface of the material.

Keywords: Ammonium Perchlorate, Ammonium Perchlorate, Hydroxyl Terminated Polybutadiene, Hydroxyl Terminated Polybutadiene Binder, Chemkin.

INTRODUCTION

The first solid propulsion rocket motors date from 13th century and they are assigned to the Chinese (Mark, 2003). The rocket red glare from Spangled Banner of Francis Scott Key was initially used in 1812 in a war involving the 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 sustainer motors in military artifacts propulsion, alteration, and correction engines of geo-stationary satellites orbits, among others.

Solid rockets 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 it 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 in

oxidizing chemical species, in a solid block called solid propellant grain.

These materials are classified as simple-based, double-based, composite or double-based composite propellants (Pisacane, 2005). Simple-based propellants are active energetic materials separately considered, such as nitrocellulose or nitroglycerin. They are 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 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 their constituents is from 20 to 40% of metallic fuel to increase specific impulse of the propellant, usually aluminum, from 50 to 70% of oxidizer (like ammonium perchlorate – AP) and from 10 to 20% of the binder matrix, main source of carbon, which acts as fuel. Eventually, from 0 to 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 (Pisacane, 2005).

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Examples of typical constituents of solid propellants are presented in Table 1. 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 passes through a curing process where mechanical and ballistic properties are developed, which are needed to the projected performance of the motor, rocket-motor, in the handling, transport, flight, and storage phases (Monteiro *et al.*, 2007).

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

AP (NH_4ClO_4) is a powerful salt oxidizer largely used in solid-propellant formulations for application in airspace and for defense of materials industries. It is obtained by the reaction between ammonia and perchloric acid, or by double decomposition between an ammonium salt and sodium perchlorate, and it is crystallized with romboedric structure in room temperature and pressure, with relative density of 1.95 (Beckstead *et al.*, 2007).

Similarly to most ammonium salts, AP thermal decomposition occurs before its fusion. When submitted to a low-heating rate, it decomposes by releasing gases chlorine, nitrogen and oxygen and water in the vapor state; while with a high-heating rate stimulus, there are instant reactions with high energy release. 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 (Korobeinichev *et al.*, 1990; Boggs, 1970; Beckstead and Puduppakkam, 2004; Jeppson *et al.*, 1997).

During the combustion process of AP crystals at high pressures, it is possible to observe the formation of a tiny layer of AP in the liquid phase at the grain surface (Boggs, 1970), followed by a region where gaseous AP is presented.

According to Beckstead and Puduppakkam (2004), the combustion of a monopropellant can be divided into three regions (condensed, liquid-gas two-phase, and gas). 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, occurs in the gas flame until equilibrium is reached in the final flame zone. A schematic profile of the temperatures developed from the grain surface during the combustion is presented in Fig. 1.

This consideration is based on a reactor model, which can be found in the computational package named Chemkin Chemical Kinetics, developed by Sandia Laboratories.

Table 1. Examples of typical constituents of solid propellant formulations.

| Metallic/ non-metallic fuels | Oxidizers | Binders | Curing Agents | Plasticizers |
|---------------------------------|--|--|---------------|-----------------------------|
| Aluminum | Ammonium Perchlorate (NH_4ClO_4) | Carboxyl Terminated Polybutadiene (CTPB) | Isocyanates | DOA/DBT |
| Beryllium | Lithium Perchlorate (LiClO_4) | Epoxydes | Amines/Amides | Triethyleneglicol dinitrate |
| Magnesium | Potassium Perchlorate (KClO_4) | Hydroxyl terminated polybutadiene (HTPB) | | Trimethylethane trinitrate |
| Sodium | Ammonium Nitrate (NH_4NO_3) | Nitrocellulose | | |
| Hydrocarbons | Potassium Nitrate (KNO_3) | Polybutadiene acrylic acid(PBAC) | | |
| Polymers | Sodium Nitrate (NaNO_3) | Polybutadiene acrylonitrile (PBAN) | | |
| Plastics | Cyclotetramethylenetetranitramine-HMX | Asphalt | | |
| Rubbers | Cyclotetramethylenetrinitramine-RDX | PVC | | |

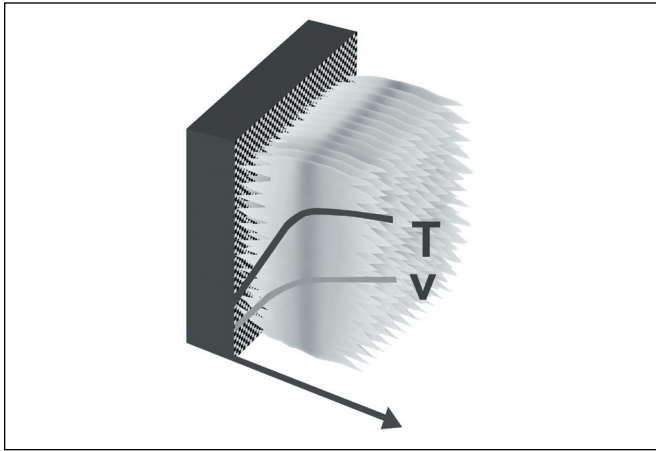


Figure 1. Scheme of the ammonium perchlorate crystal combustion process with evolution of the temperatures from the material surface.

Due to the difficulty of 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 it enables the analysis through temperature and chemical species molar fractions variation in function of the distance from the material surface, among others.

The present paper treats the combustion study of pure AP and formulated in a solid composite propellant grain, focusing in the structure of the flame formed in this process.

EXPERIMENTAL PART

The elementary reactions that compose the burning mechanism of AP are listed on Table 2. This mechanism was proposed by Gross (2007), according to data obtained from the literature.

In the used simulation module, it is necessary the insertion of a temperature profile. This profile lists the developed temperature in the material burning in function of the distance from the solid surface. The data can be observed in Fig. 2. The present profile was obtained from the software's database, and it is a good approach to the solid fuel used in the study. As this profile was developed for 1 atm, temperatures from 2,000 to 3,200K are expected for the simulations.

Table 2. Decomposition reactions of ammonium perchlorate^a.

| Reaction | A | b | Ea |
|--|----------|------|---------|
| $\text{HClO}_4 = \text{ClO}_3 + \text{OH}$ | 1,00E+14 | 0.0 | 39100.0 |
| $\text{HClO}_4 + \text{HNO} = \text{ClO}_3 + \text{H}_2\text{O} + \text{NO}$ | 1,50E+13 | 0.0 | 6000.0 |
| $\text{ClO}_3 = \text{ClO} + \text{O}_2$ | 1,70E+13 | 0.5 | 0.0 |
| $\text{Cl}_2 + \text{O}_2 + \text{M} = \text{ClO}_2 + \text{Cl} + \text{M}$ | 6,00E+08 | 0.0 | 11200.0 |
| $\text{ClO} + \text{NO} = \text{Cl} + \text{NO}_2$ | 6,78E+12 | 0.0 | 311.0 |
| $\text{ClO} + \text{ClOH} = \text{Cl}_2 + \text{HO}_2$ | 1,00E+11 | 0.0 | 10000.0 |
| $\text{ClOH} + \text{OH} = \text{ClO} + \text{H}_2\text{O}$ | 1,80E+13 | 0.0 | 0.0 |
| $\text{HCl} + \text{OH} = \text{Cl} + \text{H}_2\text{O}$ | 5,00E+11 | 0.0 | 750.0 |
| $\text{Cl}_2 + \text{H} = \text{HCl} + \text{Cl}$ | 8,40E+13 | 0.0 | 1150.0 |
| $\text{ClO} + \text{NH}_3 = \text{ClOH} + \text{NH}_2$ | 6,00E+11 | 0.5 | 6400.0 |
| $\text{NH}_3 + \text{Cl} = \text{NH}_2 + \text{HCl}$ | 4,50E+11 | 0.5 | 100.0 |
| $\text{NH}_3 + \text{OH} = \text{NH}_2 + \text{H}_2\text{O}$ | 5,00E+07 | 1.6 | 955.0 |
| $\text{NH}_2 + \text{O}_2 = \text{HNO} + \text{OH}$ | 3,00E+09 | 0.0 | 0.0 |
| $\text{NH}_2 + \text{NO} = \text{H}_2\text{O} + \text{N}_2$ | 6,20E+15 | -1.3 | 0.0 |
| $\text{HNO} + \text{OH} = \text{NO} + \text{H}_2\text{O}$ | 1,30E+07 | 1.9 | -950.0 |
| $\text{HNO} + \text{O}_2 = \text{NO}_2 + \text{OH}$ | 1,50E+13 | 0.0 | 10000.0 |
| $\text{HNO} + \text{H} = \text{H}_2 + \text{NO}$ | 4,50E+11 | 0.7 | 660.0 |
| $\text{NO} + \text{H} + \text{M} = \text{HNO} + \text{M}$ | 8,90E+19 | -1.3 | 740.0 |
| $\text{HO}_2 + \text{N}_2 = \text{HNO} + \text{NO}$ | 2,70E+10 | 0.5 | 41800.0 |
| $\text{NO} + \text{HO}_2 = \text{NO}_2 + \text{OH}$ | 2,11E+12 | 0.0 | 480.0 |
| $\text{H} + \text{NO}_2 = \text{NO} + \text{OH}$ | 3,47E+14 | 0.0 | 1480.0 |
| $\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{H}$ | 2,16E+08 | 1.5 | 3430.0 |

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

^a kinetic data composed from Korobeinichev *et al.* (1990).

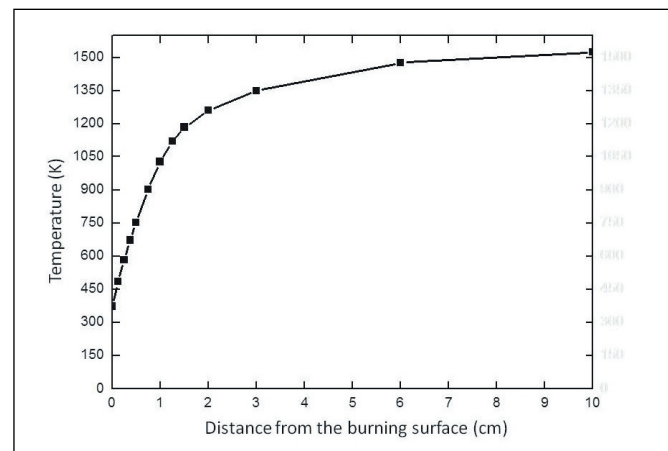


Figure 2. Temperature profile used in the simulations.

For the experiments, the system pressure of the combustion chamber varied, in order to study its influence in the flame structure; it was simulated the combustion in atmosphere composed by the initial products of AP decomposition (pure), with composition and

concentration obtained from literature (Beckstead and Puduppakkam, 2004).

A study of AP formulated with hydroxyl terminated polybutadiene (HTPB) binder was also carried out, whose mechanism can be observed in Table 3. This mechanism was based on Gross' work (Korobeinichev *et al.*, 1990), according to data obtained from the literature. The initial concentration of the species inside the chamber was set according to an AP-HTPB rate of 30/70.

Table 3. Decomposition reactions of ammonium perchlorate^a.

| Reaction | A | b | Ea |
|---|----------|------|-------|
| $\text{Cl}_2 + \text{O}_2 + \text{M} = \text{ClO}_2 + \text{Cl} + \text{M}$ | 6,00E+08 | 0 | 11200 |
| $\text{ClO} + \text{NO} = \text{Cl} + \text{NO}_2$ | 6,78E+12 | 0 | 311 |
| $\text{HCl} + \text{OH} = \text{Cl} + \text{H}_2\text{O}$ | 5,00E+11 | 0 | 750 |
| $\text{Cl}_2 + \text{H} = \text{HCl} + \text{Cl}$ | 8,40E+13 | 0 | 1150 |
| $\text{NH}_3 + \text{Cl} = \text{NH}_2 + \text{HCl}$ | 4,50E+11 | 0.5 | 100 |
| $\text{NH}_3 + \text{OH} = \text{NH}_2 + \text{H}_2\text{O}$ | 5,00E+07 | 1.6 | 955 |
| $\text{NH}_2 + \text{O}_2 = \text{HNO} + \text{OH}$ | 3,00E+09 | 0 | 0 |
| $\text{NH}_2 + \text{NO} = \text{H}_2\text{O} + \text{N}_2$ | 6,20E+15 | -1.3 | 0 |
| $\text{HNO} + \text{OH} = \text{NO} + \text{H}_2\text{O}$ | 1,30E+07 | 1.9 | -950 |
| $\text{HNO} + \text{O}_2 = \text{NO}_2 + \text{OH}$ | 1,50E+13 | 0 | 10000 |
| $\text{HNO} + \text{H} = \text{H}_2 + \text{NO}$ | 4,50E+11 | 0.7 | 660 |
| $\text{NO} + \text{H} + \text{M} = \text{HNO} + \text{M}$ | 8,90E+19 | -1.3 | 740 |
| $\text{HO}_2 + \text{N}_2 = \text{HNO} + \text{NO}$ | 2,70E+10 | 0.5 | 41800 |
| $\text{NO} + \text{HO}_2 = \text{NO}_2 + \text{OH}$ | 2,11E+12 | 0 | 480 |
| $\text{H} + \text{NO}_2 = \text{NO} + \text{OH}$ | 3,47E+14 | 0 | 1480 |
| $\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{H}$ | 2,16E+08 | 1.5 | 3430 |
| $\text{CH}_4 + \text{Cl} = \text{CH}_3 + \text{HCl}$ | 2,50E+13 | 0 | 3830 |
| $\text{CH}_4 + \text{H} = \text{CH}_3 + \text{H}_2$ | 6,60E+08 | 1.6 | 10840 |
| $\text{CH}_4 + \text{OH} = \text{CH}_3 + \text{H}_2\text{O}$ | 1,00E+08 | 1.6 | 3120 |
| $\text{CH}_3 + \text{H} + \text{M} = \text{CH}_4 + \text{M}$ | 1,27E+16 | -0.6 | 383 |
| $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ | 4,76E+07 | 1.2 | 70 |
| $\text{CO} + \text{ClO} = \text{CO}_2 + \text{Cl}$ | 3,00E+12 | 0 | 1000 |
| $\text{CO} + \text{ClO}_2 = \text{CO}_2 + \text{ClO}$ | 1,00E+10 | 0 | 0 |
| $\text{H} + \text{O}_2 = \text{O} + \text{OH}$ | 8,30E+13 | 0 | 14413 |
| $\text{CH}_2 + \text{H}_2 = \text{CH}_3 + \text{H}$ | 5,00E+05 | 2 | 7230 |
| $\text{CH}_2 + \text{H} + \text{M} = \text{CH}_3 + \text{M}$ | 2,50E+16 | -0.8 | 0 |
| $\text{CH}_4 + \text{O} = \text{CH}_3 + \text{OH}$ | 1,02E+09 | 1.5 | 600 |
| $\text{OH} + \text{CH}_3 = \text{CH}_2 + \text{H}_2\text{O}$ | 5,60E+07 | 1.6 | 5420 |
| $\text{C}_2\text{H}_4 + \text{O}_2 = 2\text{CO} + 2\text{H}_2$ | 1,80E+14 | 0 | 35500 |
| $\text{NH}_2 + \text{NO}_2 = 2\text{HNO}$ | 1,40E+12 | 0 | 0 |
| $\text{NH}_2 + \text{ClO} = \text{HNO} + \text{HCl}$ | 2,50E+12 | 0 | 0 |
| $\text{O}_2 + \text{HNO} = \text{NO} + \text{HO}_2$ | 1,00E+13 | 0 | 13000 |
| $\text{H} + \text{Cl} + \text{M} = \text{HCl} + \text{M}$ | 5,30E+21 | -2 | -2000 |
| $\text{Cl} + \text{Cl} + \text{M} = \text{Cl}_2 + \text{M}$ | 3,34E+14 | 0 | -1800 |

| Reaction | A | b | Ea |
|---|----------|------|-------|
| $\text{Cl} + \text{HO}_2 = \text{ClO} + \text{OH}$ | 2,47E+13 | 0 | 894 |
| $\text{ClO} + \text{O} = \text{Cl} + \text{O}_2$ | 6,60E+13 | 0 | 440 |
| $\text{H} + \text{HCl} = \text{Cl} + \text{H}_2$ | 7,94E+12 | 0 | 3400 |
| $\text{HCl} + \text{O} = \text{Cl} + \text{OH}$ | 2,30E+11 | 0.6 | 900 |
| $\text{Cl}_2 + \text{O} = \text{Cl} + \text{ClO}$ | 2,51E+12 | 0 | 2720 |
| $\text{N}_2\text{O} + \text{M} = \text{N}_2 + \text{O} + \text{M}$ | 6,20E+14 | 0 | 56100 |
| $\text{N}_2\text{O} + \text{OH} = \text{N}_2 + \text{HO}_2$ | 2,00E+12 | 0 | 21060 |
| $\text{N}_2\text{O} + \text{O} = \text{NO} + \text{NO}$ | 2,90E+13 | 0 | 23150 |
| $\text{N}_2\text{O} + \text{O} = \text{N}_2 + \text{O}_2$ | 1,40E+12 | 0 | 10810 |
| $\text{N}_2\text{O} + \text{H} = \text{N}_2 + \text{OH}$ | 4,40E+14 | 0 | 18880 |
| $2\text{H} + \text{M} \rightleftharpoons \text{H}_2 + \text{M}$ | 1,00E+18 | -1 | 0 |
| $2\text{H} + \text{H}_2 \rightleftharpoons 2\text{H}_2$ | 9,00E+16 | -0.6 | 0 |
| $2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{H}_2\text{O}$ | 6,00E+19 | -1.3 | 0 |
| $2\text{H} + \text{CO}_2 \rightleftharpoons \text{H}_2 + \text{CO}_2$ | 5,50E+20 | -2 | 0 |
| $\text{ClO}_2 + \text{NO} = \text{ClO} + \text{NO}_2$ | 1,00E+11 | 0 | 0 |
| $\text{Cl} + \text{ClO}_2 = \text{ClO} + \text{ClO}$ | 5,00E+13 | 0 | 6000 |
| $\text{ClO} + \text{ClO} = \text{Cl}_2 + \text{O}_2$ | 1,00E+11 | 0 | 0 |
| $\text{Cl} + \text{HO}_2 = \text{HCl} + \text{O}_2$ | 1,80E+13 | 0 | 0 |
| $\text{Cl} + \text{O}_2 + \text{M} = \text{ClO}_2 + \text{M}$ | 8,00E+06 | 0 | 5200 |
| $\text{NO}_2 + \text{O} = \text{NO} + \text{O}_2$ | 1,00E+13 | 0 | 600 |
| $\text{HNO} + \text{HNO} = \text{H}_2\text{O} + \text{N}_2\text{O}$ | 3,95E+12 | 0 | 5000 |
| $\text{NO}_2 + \text{NO}_2 = \text{NO} + \text{NO} + \text{O}_2$ | 1,00E+14 | 0 | 25000 |
| $\text{Cl} + \text{N}_2\text{O} = \text{ClO} + \text{N}_2$ | 1,20E+14 | 0 | 33500 |
| $\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$ | 6,00E+08 | 1.3 | 0 |
| $\text{NH}_2 + \text{NO}_2 = \text{H}_2\text{O} + \text{N}_2\text{O}$ | 4,50E+11 | 0 | 0 |
| $\text{HNO} + \text{NH}_2 = \text{NH}_3 + \text{NO}$ | 5,00E+11 | 0.5 | 1000 |
| $\text{ClO} + \text{HNO} = \text{HCl} + \text{NO}_2$ | 3,00E+12 | 0 | 0 |
| $\text{HCl} + \text{HO}_2 = \text{ClO} + \text{H}_2\text{O}$ | 3,00E+12 | 0 | 0 |
| $\text{NH}_2 + \text{NO} = \text{H} + \text{N}_2 + \text{OH}$ | 6,30E+19 | -2.5 | 1900 |
| $\text{NH}_2 + \text{OH} = \text{H}_2\text{O} + \text{NH}$ | 4,00E+06 | 2 | 1000 |
| $\text{NH}_2 + \text{NH}_2 = \text{NH} + \text{NH}_3$ | 5,00E+13 | 0 | 10000 |
| $\text{NH} + \text{NO} = \text{N}_2 + \text{OH}$ | 1,00E+13 | 0 | 0 |
| $\text{NH} + \text{NO} = \text{H} + \text{N}_2 + \text{O}$ | 2,30E+13 | 0 | 0 |
| $\text{Cl} + \text{NH}_2 = \text{HCl} + \text{NH}$ | 5,00E+10 | 0.5 | 0 |
| $\text{ClO}_2 + \text{NH} = \text{ClO} + \text{HNO}$ | 1,00E+14 | 0 | 0 |
| $\text{N} + \text{NO}_2 = \text{NO} + \text{NO}$ | 1,00E+14 | 0 | 0 |
| $\text{N} + \text{N}_2\text{O} = \text{N}_2 + \text{NO}$ | 5,00E+13 | 0 | 0 |
| $\text{NH} + \text{OH} = \text{H}_2\text{O} + \text{N}$ | 5,00E+11 | 0.5 | 2000 |
| $\text{NH} + \text{OH} = \text{H}_2 + \text{NO}$ | 1,60E+12 | 0.6 | 1500 |
| $\text{NH} + \text{NH}_2 = \text{N} + \text{NH}_3$ | 1,00E+13 | 0 | 2000 |
| $\text{HO}_2 + \text{CH}_3 \rightleftharpoons \text{O}_2 + \text{CH}_4$ | 1,00E+12 | 0 | 0 |
| $\text{CH}_2 + \text{CH}_4 \rightleftharpoons 2\text{CH}_3$ | 2,46E+06 | 2 | 8270 |

$k = A T^b \exp(-E/RT)$. Units: A (mol-cm-s-K), E (J/mol); M: any metal surface or metallic additive used only as support or catalyst;

^a kinetic data composed by Korobeinichev *et al.*, (1990).

Similarly, in AP-HTPB simulation, the pressure of the combustion chamber was varied in order to study its influence in the flame structure. The atmosphere of the chamber was composed by the initial products of AP and HTPB binder decomposition.

RESULTS AND DISCUSSION

In AP combustion simulation process at pressure of 1 atm (Fig. 3), it can be noticed that the curves have exponential profiles, according to the equation proposed by Arrhenius, and also the flame must be presented in the region from 2 to 3mm of the burning material surface. There is a significant decay of the molar fractions of water and chlorine, while there is an increase on the mole fractions of chloridric acid, nitrogen, and oxygen. From this result, it was possible to observe that the combustion of AP in a combustion chamber is not complete, due to the reduced permanence time on it; therefore, there is the formation of a great quantity of chloridric acid and there is no complete consume of the oxygen. According to Cai *et al.*, (2008), during the decomposition of AP, the formation of nitrogen is expected.

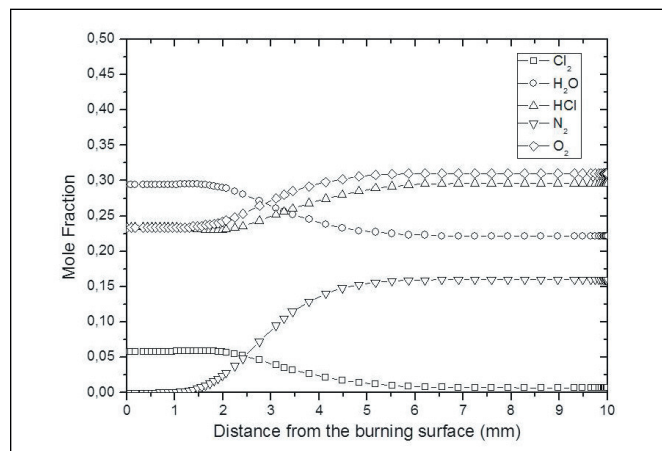


Figure 3. Ammonium perchlorate decomposition under pressure of 1 atmosphere.

The nitrogen usually presents as an inert gas, although in the system temperature ($\sim 1,700\text{K}$), it participates as the mechanism, in reactions with AP decomposition products. However, the decomposition of ammonia in gaseous nitrogen is faster than the reactions of N_2 with other species; therefore, an increase on the molar fraction is observed.

As the pressure on the combustion chamber rises, significant differences on the combustion process of AP were

noticed. Figure 4 shows the combustion simulation of the material at 5 atm pressure.

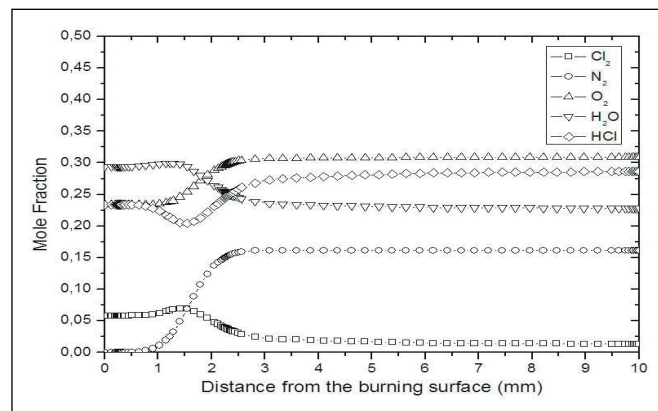


Figure 4. Ammonium perchlorate decomposition under pressure of 5 atmospheres.

The curves are presented with exponential profiles, although there was a displacement of the flame region, now presented at 1 to 2mm from the burning surface. As the pressure increases, the speed of the elementary reactions presented in AP decomposition mechanism rises, therefore, this may be the main cause of the approximation of the flame to the material. It was also observed behavior to the species in the flame region (presence of "elbows"), in which there is decrease and posterior increase of the molar fraction (for HCl) and increase and posterior decrease of the molar fraction (for water and Cl_2). As the AP acts as an oxidizer, the increase of oxygen concentration is expected. The mass balance of the species is maintained from the beginning to the end of the simulation.

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.

Figures 5 and 6 present new AP decomposition simulations for pressures of 30 and 60 atmospheres, respectively.

It is observed that, as the pressure in the combustion chamber increases, there is an approximation of the flame to the surface of the material and an accentuation of the "elbows" presented on the flame region, indicating the influence of the speed increase of elementary reactions in the decomposition process of the material in study. Such gain in chemical speed reactions may be converted in thrust of rocket motor and specific impulse of solid propellant grain. So, this kind of simulation is interesting in order 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 fewer residues.

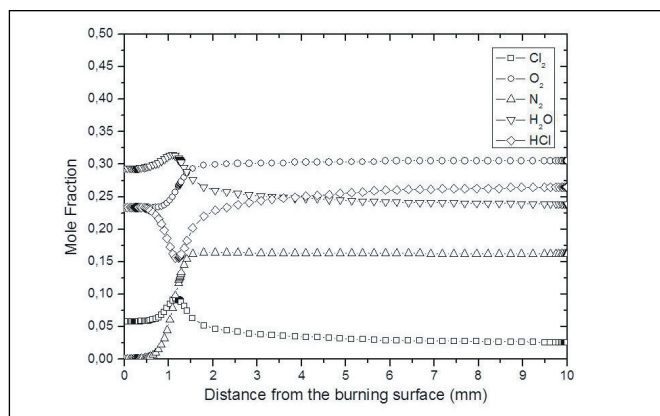


Figure 5. Ammonium perchlorate decomposition under pressure of 30 atmospheres.

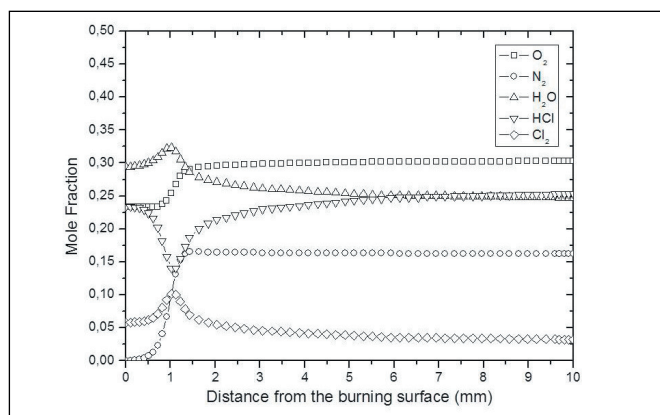


Figure 6. Ammonium perchlorate decomposition under pressure of 60 atmospheres.

Beyond the simulations of pure AP, simulations were carried out with AP formulated with HTPB, to approximate the maximum possible to a real-solid propellant formulation, because HTPB polymer matrix is a binder largely used in formulations. Figure 7 presents AP-HTPB decomposition.

The combustion process of AP-HTPB has been invariable with pressure. This behavior should be attributed to the homogeneous dispersion of AP amidst the binder, in the solid phase, and to the lack of this species in relation to the binder (generating lower concentrations of O_2 than necessary). Also, in the gas phases, it is assumed that all of the liquid AP and HTPB present on the condensed phase decompose to form gaseous species; evaporation is not included. According to Jeppson, Beckstead and Jing (1997), the kinetic model accurately calculates the flame structure up to about 40 to

50atm, in which a separation between the model calculations and experimental data becomes increasingly apparent. At low pressures (1 to 34atm), the propellant is more likely to burn as a premixed flame with the oxidizer and binder decomposition products from the condensed phase, mixing completely before the gas phase reactions occur. 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. Thus, at pressures above 40 to 50atm, the kinetic model, which assumes completely premixed combustion, would be expected to begin to yield calculations in excess of the measured burn rate. Independently of the pressure in the chamber, the packing and the molecular distribution of the material are not going to suffer alteration and are not going to lead to pressure variations in their behavior, proving the limitations of the model.

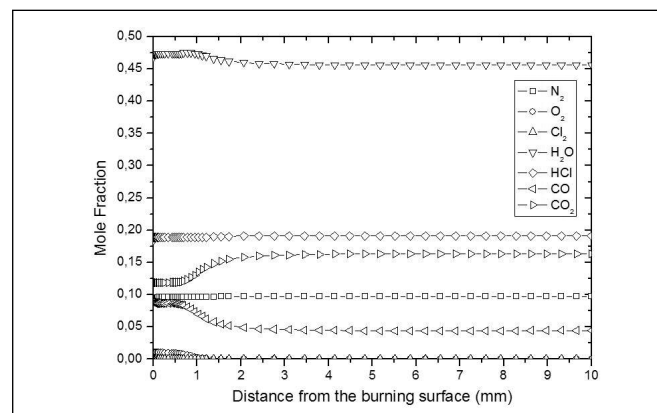


Figure 7. Ammonium perchlorate HTPB binder decomposition.

In this simulation, the oxygen molar fraction suffers a decrease (and cancels), according to the reactions with HTPB decomposition products, for the formation of carbon monoxide and dioxide. Furthermore, it is interesting to highlight that in this case the carbon monoxide molar fraction suffers a decrease, because the restriction of oxidizer species makes the oxygen presented in CO to be also used as oxidizing source, viewing the reactive behavior of this species. In this simulation, the molar fractions of CO and CO_2 are not null initially, given the system temperature, HTPB suffers an initial decomposition that should not be discarded, generating both carbon oxides.

CONCLUSIONS

The AP decomposition process was simulated in different situations using the computational package Chemkin,

Premix module. With the reactions involved in the proposed mechanisms, the variation of the AP 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 flames originated from the AP and AP-HTPB combustion were modeled, presenting the different temperature regions and the molar fraction variation of chemical species, generated by the decomposition of the materials. This study contributes to understand 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.

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