Thermal Gasification of Ammonium Nitrate Based Propellant in an Heated Closed Vessel

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Abstract

Ammonium Nitrate (AN) is the base component of recent family of gas generators and rocket composite propellants. Those propellants have the same plastic binder, hydroxyl terminated polybutadiene (HTPB), of Ammonium Perchlorate (AP) based composite propellants. They have also lower cost and pollutants concentration.

The disadvantages of this kind of AN composite based propellant comes from its low flame temperature and specific impulse. In order to reduce these problems many additives are selected and proposed in the literature. However, there is a lack of information about precise tests, procedures and results. Conventional techniques for propellant studies include generally TGA, DSC and propellant burning rate measurements, at several pressures, in a closed bomb.

An original stainless steel closed heated bomb is presented. It has been designed in order to measure temperature and pressure generated from propellant sample, as a function of time. This experimental apparatus is heated by electrical resistances, insulated with ceramic fibres and foam. AN and AP used particles have average diameters in the range 106-125 μm. Curing agent for HTPB is isophorone disocyanate (IPDI) 7.5% of total binder mass. Experiments have been performed with 200 mg mass samples of pure AN, AN/HTPB-IPDI (80/20 wtpc) and AN/AP/HTPB-IPDI (40/40/20 wtpc). Temperature range of experiments was 373 - 773 K at 2 K/min heating rate. Initial pressure is 0.1 MPa with the closed vessel filled with N2. Final pressure, after gasification, is about 1.4 MPa.

A simplified theoretical model predicts the regression rate of sample, as a function of pressure and temperature inside heated closed vessel. Experimental results obtained in the closed heated bomb are correlated with TGA measurements and theoretical approach. Obtained results and their discussion prove the validity of this original experimental procedures.

INTRODUCTION

Ammonium Nitrate (AN) is the base component of recent family of gas generators and rocket composite propellants. These propellants have the same plastic binder (hydroxyl or carboxyl terminated polybutadiene - HTPB or CTPB) but the filler has been changed from Ammonium Perchlorate (AP) into AN, due to their low cost and low pollutants concentration. AP contains chlorine (Cl) in its composition, which generates
HCl in combustion products. HCl is highly toxic, corrosive and has a strong ambient impact causing acid rain and destruction of ozone layer (Tokui et al., 1990).

The inconvenient of these kind of AN based propellants comes from its low flame temperature and consequently low specific impulse, phase instability (Miedema et al., 1989), and relative low energetic content (Tokui et al., 1990). However low flame temperature and low corrosivity prove to be an advantage for a gas generator. It has been used for ignition in ARIANNE-5 rocket engine (Miedema et al., 1989). In order to reduce these problems many additives are selected and proposed in the literature (vd. Kubota et al., 1991).

Thermal decomposition studies of AN have been carried out in the past: Keenan, (1955), used Differential Thermal Analysis (DTA); Cook and Abbeg, (1956), Feick and Hainer, (1954), and Guiochon, (1967), used Thermogravimetric Analysis (TGA), Brill et al., (1993) used T-jump/Fourier transform infrared (FTIR) Spectroscopy and recently, other authors (Engel et al, 1993; Park et al, 1993), use X-ray diffraction and thermal integrated procedures to analyse phase transition of AN based oxidizers. However, there is a lack of information about precise tests, procedures and correlation between laboratorial and real scale results. Thermal gasification and decomposition of pure AN and their based propellants under pressure (vd. Araujo, 1992) seems also do not allow any precise prediction or evaluation.

Consequently our study has been motivated to design and build an original stainless steel heated closed vessel, to measure temperature and pressure generated from propellant sample. In order to clarify tests and procedures, the propellant must be composed by very well defined chemical products, chosen between the basic components of AN propellant, i.e., AN or AN/AP particles as filler, and Hydroxyl Terminated Polybutadiene (HTPB) with Isophorone Di-isocyanate (IPDI) curing agent as binder. A simple model of gasification allows, as a function of time and temperature, the correlation between measured pressure evolution, inside closed heated bomb, and mass regression rate of sample.

**THEORETICAL APPROACH**

In a closed heated bomb the propellant sample is totally enclosed in a cylindrical confinement of total length $L_O$ and section area $A$, with a internal diameter much less than its length ($\sqrt[3]{4A/\pi}L_O=0$). The top of propellant confinement is connected with a closed chamber of volume $V$, assuming that the initial propellant volume is much less than $V$ ($A.L_O/V \approx 0$). The closed chamber is previously filled with a inert gas ($N_2$) in order to avoid any reaction between propellant gas and inert residual gas. The experiences consist in heating the closed assembled apparatus (sample confinement/chamber) from its initial conditions of pressure $P_0$ and temperature $T_0$, with a constant heating rate ($T=T_0 + aT$), assuming there are no temperature gradients inside sample and closed chamber.

During the heating period, the solid mass of sample $m_s=\rho_s.A. L_O - x$ is reducing from its initial value $m_0=\rho_s.A.L_O$, being $x$ the linear regression variable and $\lambda=x/L_O$ the gasification rate. The gasified mass of sample $m_g=\rho_s.A.x$ can be assumed as a ideal
gas. During gasification process the pressure/temperature ratio, measured inside closed chamber, can be obtained by:

\[
P/T = (N_{N_2^{'}} + \rho_s A x / Mg) R/V\]

(1)

where the total gas number of moles inside chamber is \(N = N_{N_2^{'}} + \rho_s A x / Mg\), \(Mg\) represents the mole mass of gasified sample, \(R\) the universal gas constant and \(N_{N_2^{'}} = P_o V / RT_o\).

Consequently, at any instant of process, it can be considered

\[
P/T = R/V \cdot m_o / Mg \cdot \lambda + P_o / T_o\]

(2)

and

\[
\lambda = \frac{M_g}{\rho_s A L_0} \left( \frac{P V}{R T} - \frac{P_0 V}{R T_0} \right)\]

(3)

The preceding equations, related with the constant heating rate, allows the correlation of measured ratio \(P/T\), as a function of time, to the number of moles of gasified sample, or to the gasification rate \(\lambda\). It allows also the correlation between results obtained in closed heated bomb with TGA measurements, where it is only evaluated the mass loss, as a function of temperature, and not the generated pressure from gasified mass loss.

EXPERIMENTAL COMPOSITIONS, EQUIPMENT, EXPERIMENTS AND DISCUSSION

Experimental compositions

In order to clarify experimental procedures the propellant sample must be composed only by the basic well defined and stable chemical components of an AN based composition. It has been chosen Ammonium Nitrate (AN) (pro analysis - Merck Art. 1188) and Ammonium Perchlorate (AP) (d class = 90 \(\mu m\) - SNPE), as filler components. A stoichiometric mixture of Hydroxyl Terminated Polybutadiene (HTPB) (Poly bd R-45HT, Atochem) cured with 7.5 mass percent of Isophorone Di-isocyanate (IPDI) (Merck, Art. 818586) was the used binder.

Used ammonium nitrate and ammonium perchlorate particles have average diameter (\(d_p\)) in 106 \(\mu m < d_p < 125 \mu m\) granulometric class. Propellant samples has been curing for several days at 48 °C.

Three compositions were selected, as it can be seen in Table 1.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AN</td>
<td>100.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>AN/HTPB-IPDI</td>
<td>80.0</td>
<td>0.0</td>
<td>18.5</td>
<td>1.5</td>
</tr>
<tr>
<td>AN/AP/HTPB-IPDI</td>
<td>40.0</td>
<td>40.0</td>
<td>18.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 1 - Selected propellant compositions.

DSC measurements
In order to verify calorimetric AN properties differential scanning measurements were performed (Perkin Elmer DSC 2). Obtained results (vd. Fig. 1) proves the quality of used AN and they are in a good agreement with general literature. The more important transition can also be observed in the range 550 - 590 K (Feick and Hainer, 1954).

![DSC graph of pure AN](image)

Fig. 1 - Measured DSC of pure AN

TGA Measurements
In order to verify used AN, HTPB-IPDI and AN/HTPB-IPDI mixture properties, thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) was performed (Polymer Laboratories equipment, provided simultaneous with a thermal analyzer (PL-STA 1500) and thermobalance module (TGH 1500) with STA/TGH balance control unit). This thermal analyzer was connected to a personal computer and results (vd. Fig. 2) were analysed with a thermal analysis software system. Pure AN samples were kept in an oven at 48 °C previous to each experiment Linear heating rate of 2 K/min and 30 ml/min N₂ flow were employed in experiments. Sample mass was 200 mg.
<table>
<thead>
<tr>
<th>Composition</th>
<th>( m / m_0 = 0.01 )</th>
<th>( m / m_0 = 0.05 )</th>
<th>( m / m_0 = 0.10 )</th>
<th>( m / m_0 = 0.50 )</th>
<th>( m / m_0 = 0.90 )</th>
<th>( m / m_0 = 0.95 )</th>
<th>Final ( m / m_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>T [K]</td>
<td>480.1</td>
<td>501.7</td>
<td>514.8</td>
<td>544.6</td>
<td>561.3</td>
<td>574.9</td>
<td>590</td>
</tr>
</tbody>
</table>

Table 2 - Measured TGA for AN composition.

For pure AN, initial and final temperatures of TGA measurement test are respectively 423 K and 603 K. 423 K is lower than AN melting point (Federoff, 1960) and 603 K is larger than limiting range of AN decomposition 553-593 K (Brill et al., 1993) and its surface burning temperature (Dode, 1934). HTPB-IPDI confinement of AN particles shows its influence in AN/HTPB-IPDI obtained results (vd. Fig. 2). The possible fast reaction rate of AN/AP/HTPB-IPDI did not allow to test this mixture with TGA equipment.

![TGA graph](image)

Fig. 2 - TGA results of pure AN, HTPB-IPDI and AN/HTPB-IPDI mixture.

**Closed heated bomb - experimental apparatus and results**

An original closed heated bomb was designed and built. This experimental apparatus, shown in Fig. 3, is composed by:

- a stainless steel closed vessel, inserted in a steel cylindrical liner,
- an heating system, insulated with ceramic fibers and foam, connecting to a real time temperature and heating rate controller,
- a pressure and temperature data acquisition system.
The sample, 200 mg in mass, is introduced in a borosilicate test tube, 2.5 mm in inner diameter, 4.0 mm in external diameter and 44 mm in internal length. The internal diameter of this tube has been designed smaller than propellant quenching diameter. Borosilicate is used to ensure no catalytic effect of walls on decomposition of sample.

This tube is introduced in another stainless steel tube, 4.2 mm in internal diameter and 27 mm in length. It is connected to a closed vessel (vd. Fig. 4), of cylindrical shape 32 mm in inner diameter and length and 90 mm in external diameter. All this parts are made of stainless steel. The closed vessel is inserted partially in a steel cylindrical liner 100 mm in external diameter 47 mm in internal diameter and 165 mm in length, that is inside the insulated heating element. This liner is used to have no temperature gradients inside the heating element.

The closed vessel is heated at a low rate of 2° C/minute by a 2100 W heating element insulated with ceramic fibers and foam. The element is supplied by a 1200 W DC power supply (vd. Fig. 3).

The closed vessel is connected to a capacitive absolute pressure transducer (SETRA 205-2), water cooled, of maximum pressure 1.72 MPa (vd. Fig. 4). Gas temperature inside the chamber, chamber wall temperature and environmental temperature are measured by chromel-alumel thermocouples 0.5 mm in diameter, stainless steel gained. Each thermocouple signal is amplified by a thermocouple amplifier IC. Data acquisition is performed by a 8 channel (DI DT2812A) data acquisition board in a PC.
Previously to a new experiment, the closed vessel was pressurised to 1.7 MPa and depressurised to atmospheric pressure for several times, to clean it from the gas of previous experiment. Leakage tests were performed pressuring the closed vessel, with N$_2$, up to 1.72 MPa during 30 minutes. A pressure reduction less than 0.15 % was observed. Data processing includes no correction for gas leakage in closed vessel pressure data.

Initial pressure was 0.1 MPa with the closed vessel filled with N$_2$. Obtained results show (vd. Fig. 5 and Table 3), for AN, an initial temperature of 423 K and a final temperature of 603 K, because melting point and decomposition temperature of AN, and limiting temperature range of AN decomposition are respectively 442.6 K (Guiochon et al, 1960, Federoff, 1960) and 483 K (Federoff, 1960) and 553 - 593 K (Feick and Hainer, 1954). For mixture AN/HTPB-IPDI initial temperature was 423 K and final temperature was 773 K for the same reason as for AN and because HTPB/IPDI decomposition temperature range in 493 - 753 K (Chen adn Brill, 1991). For the last mixture initial temperature was 380 K and final temperature was 773 K, because AP decomposition begins at 380 K (Dode, 1934) and an HTPB/IPDI decomposition for 4-6 mg samples is accomplished about 753 K for 10 K/min heating rate (Chen and Brill, 1991).

<table>
<thead>
<tr>
<th>Composition</th>
<th>$n_g$ [mol]</th>
<th>$n_{g/kgmist}$ [mol/kg]</th>
<th>oxidizer [mol]</th>
<th>prod/oxid [mol/mol]</th>
<th>T (5%) [K]</th>
<th>T (50%) [K]</th>
<th>T(95%) [K]</th>
<th>$P_{\text{max}}$ [MPa]</th>
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</thead>
<tbody>
<tr>
<td>AN</td>
<td>0.00617</td>
<td>32.4</td>
<td>0.00250</td>
<td>2.47</td>
<td>517.0</td>
<td>546.5</td>
<td>550.9</td>
<td>1.32</td>
</tr>
<tr>
<td>AN/HTPB-IPDI</td>
<td>0.00536</td>
<td>26.8</td>
<td>0.00200</td>
<td>2.68</td>
<td>504.4</td>
<td>547.4</td>
<td>613</td>
<td>1.45</td>
</tr>
<tr>
<td>AN/AP/HTPB-IPDI</td>
<td>0.00496</td>
<td>24.8</td>
<td>0.00168</td>
<td>2.95</td>
<td>481.4</td>
<td>576</td>
<td>704</td>
<td>1.37</td>
</tr>
</tbody>
</table>

Table 2. - Results of gasification of compositions with the closed heated bomb.
Fig. 5 - Measure P, as a function of temperature, for a heating rate of 2 K/min in the closed heated bomb.

Presented results in Table 2 and Fig. 6, showing the evolution of gasified mole number $n_g$, as a function a temperature $T$, are calculated from equations (1) to (3). It can be observed $n_g$ has the maximum value for pure AN, and its value for AN/HTPB-IPDI is greater than for AN/AP/HTPB-IPDI mixture. Difference $\Delta T_{95\%-5\%} = T(95\%) - T(5\%)$ has the greatest value for this last composition. $T(95\%)$ has the lowest value for AN/AP/HTPB-IPDI because AP decomposition begins at a lower temperature than any other component.

The shapes of curves of generated number of moles $n_g$, as a function of temperature $T$ (vd. Fig. 6), show some particularities of gasification process for each composition. AN composition has the typical shape of a pure substance. AN/HTPB-IPDI composition curve shows clearly the contribution of two components, situation not observed in the last composition, with no identified gasification steps or phases.

The correlation of obtained results in closed heated bomb, with Coats and Redfern formulation (vd Chen and Brill, 1991), for kinetics evaluation of gasification, shows a activation energy value of 148 kJ/mole for AN in the range 503 - 573 K, with a very good agreement with the value 152.6 kJ/mole proposed by Guiochon, 1960.
Fig. 6 - Mole number of gas generated by gasification, as a function of temperature T.

CONCLUSIONS

An original stainless steel closed heated bomb has been designed in order to measure pressure generated from propellant sample, as a function of time. This experimental apparatus is heated by electrical resistances, insulated with ceramic fibres and foam. AN and AP used particles have average diameters in the range 106-125 μm. Curing agent for HTPB is isophorone diisocyanate (IPDI) 7.5% of binder mass. Experiments have been performed with 200 mg mass samples of pure AN, AN/HTPB-IPDI (80/20 wtpc) and AN/AP/HTPB-IPDI (40/40/20 wtpc). Temperature range of experiments was 373 - 773 K at 2 K/min heating rate. Initial pressure is 0.1 MPa with the closed vessel filled with N₂. Final pressure, after gasification, is about 1.4 MPa.

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Generated number of moles, as a function of temperature T, inside closed heated bomb, show some particularities of gasification process for each composition. AN composition has the typical shape of a pure substance. AN/HTPB-IPDI composition curve shows clearly the contribution of two components, situation not observed in the last composition, with no gasification steps or phases.

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Obtained results and their discussion prove the validity of this original experimental procedures.
REFERENCES


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