KINETIC STUDY OF THERMAL DECOMPOSITION OF BASE BLEED PROPELLANTS FOLLOWING FRIEDMAN AND OZAWA-FLYNN-WALL METHODS

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ABSTRACT
Explosives, propellants and pyrotechnics are the common classifications given to energetic materials. They can react rapidly with an ignition and releases large amounts of energy with products generated in high velocity. Explosives are very susceptible to initiation and as well as the pyrotechnics. Propellants usually need an ignition system to burn and they have all the oxygen necessary for the combustion. Thermal analysis had been used in energetic materials studies. This work reports the thermoanalytical results for commercial and synthesized base bleed propellants from TG/DTG and DTA curves as well as the kinetic parameters of the decomposition reaction by applying isoconversional methods as Friedman and Ozawa–Flynn–Wall using the Thermokinetics software.

Keywords: Energetic materials, Base bleed propellant, Kinetic study, Thermal analysis

1. INTRODUCTION
Energetic materials are compounds that comprise fuel and oxidizer components materials. They can be bonded chemically in the same molecule or can be physically mixed [1]. Through an initiation, they release large amounts of energy with products generated by the reaction. Explosives, propellants and pyrotechnics are the common classifications given to energetic materials, as can be seen in figure 1. However, in the literature are also found other classifications. According to Rice [2], the differences between explosives, propellants and pyrotechnics are in terms of generated products and burning reaction rate. Akhavan [3] names these materials as chemical explosives and classifies them according to their performances and uses being divided into three classes: primary explosives, secondary explosives and propellants. The pyrotechnic compositions are also classified as chemical explosives. On the other hand, Lee [4] terms the energetic materials as explosives divided into high explosives, propellants and pyrotechnics. Oxley [5] classifies the high explosives into primary and secondary explosives and the propellants and pyrotechnics are called low explosives.

When it comes to propellants, they can have military and non-military purposes. Their applications go from the propulsion of a rocket or missile to the automotive industry including the airbags, in this case just acting like a gas generator.

Propellants can be solid or liquid. The solid ones have good versatility due to security, storage and easy handling. The liquid propellants have more restriction because of their reactivity and special precautions in handling [6].
Solid propellants can be manufactured as grain and then they are named granulated propellant [1]. Depending on the bonds of the compounds they are divided into homogeneous or heterogeneous.

The homogeneous propellants include the simple-base, double-base and triple-base propellants all made from nitrocellulose. Heterogeneous propellants have a polymeric base and crystalline compounds and are known as composite propellants [7]. In this last case, the organic and inorganic compounds are in highest percentages, however, most of formulations contain stabilizers, burning catalysts, additives and plasticizers. One common polymeric base for composite propellants is polyurethane. Polyurethanes present a structure that comprises soft and hard segments. In general, the soft segments are usually oligomers with long methylene, oxy-methylene or other aliphatic sequences, while the hard segments are urethane sequences brought together by reaction of short alkanediol with disiocyanate. The soft and hard domains regulate their physical and mechanical behavior. An example of a chemical structure of polyurethane is displayed in figure 2 [8].

![Figure 2. Probable reaction between the polyl group and the isocyanate.](image)

The polymeric matrix usually is the fuel for the combustion reaction. Nevertheless, solid reducing agents like aluminum can be part of the composition [9].

The application and use of propellants exerts enormous influence in defense and military strategy of a country. One composite propellant that has an important application in the military field is a gas generator propellant called base bleed. However, there are few studies about base bleed propellant thermal decomposition involving kinetic data.

When a gun ammunition is propelled, a total drag is caused by the fluid mechanical reasons and it is the most important performance factor. In the case of a projectile, the total drag can be divided into pressure drag, viscous drag and base drag which has the major contribution for the total drag especially at transonic speed [10]. The base drag reduces the range of the projectile once is a mechanical force acting against the movement of the gun ammunition.

According to Bournot [11], there are two ways of reducing the drag. One is to modify the shape of the projectile using a boat tailed after body in order to reduce the base surface area and the other one is to inject a low velocity fluid behind of the projectile obtaining the base bleed effect. In case of low velocity fluid injection, base bleed propellants are used. Different from rocket propellants, they are not used for propulsion. During the burning of the base bleed propellant, the evolved gases increase the pressure behind the projectile dropping the base drag value. Thus this effect extends the range of the ammunition. Aiming to avoid the extinguishment of the propellant due to the pressure drop in the combustion chamber when the projectile leaves the muzzle, an igniter is also arranged. figure 3 shows a projectile model with a simple base bleed unit.

![Figure 3. Projectile with a base bleed unit.](image)
Since the base of using energetic materials is thermal reaction, thermal analysis study becomes extremely relevant and significant to evaluate base bleed propellants. The kinetic investigation is one of the most important applications of thermal analysis, since the knowledge of the kinetic parameters, and the manufacturing process variables could be better evaluated. Besides this, kinetic data are especially important to understand the material’s decomposition mechanism. So, the study of the kinetics of those materials is very important due to hazard issues as well as its quality and shelf-life [12].

1.1. Kinetic Study

Isoconversional methods

The “Model Free” is a model based on a transformation of a signal like heat flow or mass loss, on conversion degree \((\alpha)\) for each stage of decomposition in which is possible to calculate kinetic parameters including the activation energy and pre exponential factor. It consists on the determination of the conversion degree \((\alpha)\) as a function of reaction time in a constant temperature or when the temperature varies linearly with time. Using thermogravimetric analysis, the decomposed fraction \((\alpha)\) is defined according to eq. (1) [13]:

\[
\alpha = \frac{m_0 - m_f}{m_0 - m_t}
\]  

(1)

Where \(m_0\) is initial mass, \(m_t\) the mass at time \(t\) and \(m_f\) the mass at the end of the reaction and the method is based on the eq. (2) below:

\[
G(\alpha) = \int_a^e_{f(\alpha)} \frac{d\alpha}{\beta f(\alpha)} = \frac{A}{B} \int_a^e \exp \left( -\frac{E}{RT} \right) dT
\]  

(2)

where \(\alpha\) is the conversion degree, \(A\) the pre-exponential factor, \(\beta\) the heating rate, \(T\) the absolute temperature, \(E\) the activation energy, \(R\) the gas universal constant and \(G(\alpha)\) represents the reaction mechanism. In order to determine the kinetic parameters, some approximations were proposed by applying different kinetic models. By using thermokinetic software, the kinetic study was done based on the conversional methods including Friedman and Ozawa-Flynn-Wall. In both methods, the activation energies could be determined by analyzing plots recorded at different heating rates [14].

The Friedman method has the eq. (3) for the calculation of the activation energy \((E)\) and pre-exponential factor \((A)\) by plotting the logarithmic of the conversion rate \((\ln \frac{d\alpha}{dt})\) vs. \(1/T\) [13]:

\[
\ln \left( \frac{d\alpha}{dt} \right) = \ln \left( \beta \frac{d\alpha}{dT} \right) = \ln A + \ln[f(\alpha)] - \frac{E}{RT}
\]  

As in the Friedman method, the Ozawa-Flynn-Wall method can give the activation energy with a specific heating rate \(\beta\) and it can be calculated from the slope of the isoconversional lines as shown in the eq. (4) [15]:

\[
\log \beta + 0.4567 \frac{E}{RT} = \text{constant}
\]  

(4)

The kinetic information calculated using isoconversional methods can provide more reliable insight into the kinetics and mechanism of complex reaction processes since the activation energy \((E)\) is calculated without any prior knowledge of the analytical form of the conversion \(f(\alpha)\) [13].
The objective of this work is to evaluate the kinetic parameters of thermal decomposition through thermal analysis of base bleed propellants, commercial and synthesized samples by applying two models Friedman and Ozawa–Flynn–Wall using a Thermokinetics software.

2. METHODOLOGY

2.1. Materials
Base bleed propellants samples named as A, B (commercial), C and D (synthesized) were studied. All of them had polymeric matrix of polyurethane and ammonium perchlorate as oxidant agent.

2.2. Thermal characterization of propellants
The evaluations by TG/DTG and DTA were carried out on a TA Instruments model SDT Q600 with heating rates of 5, 10, and 20 °C min⁻¹ in a nitrogen atmosphere with a flow rate of 100 mL/min. The sample sizes were about 1.5 mg and the temperature range was from room temperature to 600 °C. The determination of the kinetics parameters was performed by using “Model Free” with Netzsch Thermokinetics software for kinetic modeling.

3. RESULTS AND DISCUSSION
Figure 4 shows the comparison of TG curves for all base bleed propellant samples: A, B, C and D. As for the propellant A, it can be observed that the thermal decomposition had three stages which started at 200 °C. The second stage between 330 to 395 °C referred to polyurethane matrix decomposition [16, 17]. The third and last stage between 430 to 495 °C with a mass loss of 12%, showed a residue of 5% (600 °C) which was the highest amount between all samples. The propellant B presented three stages of decomposition with the first one at the range of 200-280 °C. The second stage was between 280-375 °C with a mass loss of 73% and from 375 until 425 °C there was no mass loss. Then the third stage started at 425 going until 490 °C with a residue of 2% (600 °C). The thermogravimetric curves for propellant C exhibited one stage of decomposition between 100-350 °C with a mass loss of 96% with an inorganic residue of 4% (600 °C). The sample D showed three stages of decomposition at 150-250 °C, 250-390 °C and 430-480 °C respectively with a residue near to zero and it was the least amount of residue of all propellants samples. The sample C presented a less thermal stability in the range of 300-350 °C.

Comparison of DTG curves for all base bleed propellants is shown in figure 5. It can be clearly seen that A and B presented three peaks at 305, 370 and 440 °C for A and 275, 370 and 440 °C for B. As for propellant C it could be observed only one sharp peak at 350 °C which was attributed to the presence of a burning catalyst that accelerated the thermal decomposition. The D sample presented three peaks. The first peak was a slight one at 220 °C and the second one at 370 °C referring to the main decomposition of the polyurethane matrix. The third and the last stage had a peak at 450 °C.
Figure 5. DTG curves for base bleed samples A, B, C and D.

Figure 6 exhibits DTA curves for the base bleed propellants A, B, C and D. There was an endothermic event around 240 °C for all samples which is referred to as a transition between crystalline phases from orthorhombic to cubic of the ammonium perchlorate [18]. Both samples A and B presented two exothermic events referring to oxidation process following decomposition [19] at 310 and 370 °C and at 275 and 360 °C respectively. Concerning to C sample, there was an exothermic event related to the oxidation process and final decomposition at 350 °C. For the propellant D, the DTA curve showed four exothermic events at 285, 330, 370 and 450 °C suggesting that there are more components in its formulation that passed by an oxidation process. Table 1 shows a summary of the thermal analysis of all samples.

Table 1. Summary of thermoanalytical results for base bleed samples from TG/DTG and DTA curves.

<table>
<thead>
<tr>
<th>Propellant Sample</th>
<th>Temperature range per stage of decomposition on TG (°C)</th>
<th>Mass loss(%)</th>
<th>DTG Peak (°C)</th>
<th>DTA Endo Peak (°C)</th>
<th>DTA Exo Peak (°C)</th>
<th>Residue at 600°C(%)</th>
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<tr>
<td>A</td>
<td>200-330</td>
<td>24</td>
<td>305</td>
<td>240</td>
<td>310</td>
<td>5</td>
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<tr>
<td></td>
<td>330-395</td>
<td>59</td>
<td>370</td>
<td></td>
<td>370</td>
<td></td>
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<tr>
<td></td>
<td>425-495</td>
<td>12</td>
<td>440</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>200-280</td>
<td>10</td>
<td>275</td>
<td>240</td>
<td>275</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>280-375</td>
<td>73</td>
<td>370</td>
<td></td>
<td>360</td>
<td></td>
</tr>
<tr>
<td></td>
<td>425-490</td>
<td>15</td>
<td>440</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>100-350</td>
<td>96</td>
<td>350</td>
<td>240</td>
<td>350</td>
<td>4</td>
</tr>
<tr>
<td>D</td>
<td>150-250</td>
<td>5</td>
<td>220</td>
<td>240</td>
<td>285</td>
<td>Non identified</td>
</tr>
<tr>
<td></td>
<td>250-390</td>
<td>87</td>
<td>370</td>
<td></td>
<td>330</td>
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<td></td>
<td>430-480</td>
<td>8</td>
<td>450</td>
<td></td>
<td>370</td>
<td>480</td>
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</table>
3.1. Determination of kinetic parameters by Friedman and Ozawa-Flynn-Wall methods

The Friedman analysis can be seen in figures 7, 8, 9 and 10 for base bleed samples A, B, C and D. Figure 7 exhibits three peaks for sample A at the ranges of 254-333 °C, 302-417 °C and 417-497 °C respectively, showing that the decomposition of propellant A occurs in three different stages confirming what TG/DTG curves showed. As for the sample B, figure 8, the graph exhibited the same number of peaks seen before in the TG/DTG graph as well. The main decomposition had a peak between 292 and 372 °C and the last one at around 407-527 °C.

Figure 9 demonstrates the single decomposition presented by sample C. It had a peak between 215-372 °C and after the fast decomposition reaction many peaks were observed. Concerning to sample D, which graph can be seen in figure 10, three peaks indicates the stages of decomposition, the same number shown by TG/DTG curves.
The Ozawa-Flynn-Wall model for samples A, B, C and D are presented in Figures 11, 12, 13 and 14. Figure 11 and 13 show more inclination in the beginning of the decomposition. Some isoconversional lines indicated the decomposition of more than one component. Figures 12 and 14 also show regular parallels isoconversional lines suggesting a good adjustment of OFW model in all cases.
Figure 11. Isoconversional graphic of Ozawa-Flynn-Wall for base bleed sample A.

Figure 12. Isoconversional graphic of Ozawa-Flynn-Wall for base bleed sample B.

Figure 13. Isoconversional graphic of Ozawa-Flynn-Wall for base bleed sample C.
Figure 14. Isoconversional graphic of Ozawa-Flynn-Wall for base bleed sample D.

Figures 15 and 16 shows the graphs of the activation energies and the pre-exponential factor and their summary is shown in table 2.

The profiles presented in figures 15 and 16 exhibited the dependence between (E) and log (A) versus conversion degree for each sample according to the kinetic model. It showed that sample A decrease both values after 50% of conversion in Friedman analysis while samples B, C and D increase their values.
Figure 15. Graphics of $E$ and log $A$ versus converted fraction ($\alpha$) for base bleed samples A (a), B (b), C (c) and D (d) in Friedman analysis.

Figure 16. Graphics of $E$ and log $A$ versus converted fraction ($\alpha$) for base bleed samples A (a), B (b), C (c) and D (d) in Ozawa-Flynn-Wall analysis.

Table 2. Summary of activation energies and pre-exponential factors results for base bleed samples from Friedman and Ozawa-Flynn-Wall (OFW) model.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>Friedman</th>
<th>Sample A</th>
<th>OFW</th>
<th>Friedman</th>
<th>Sample B</th>
<th>OFW</th>
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<tr>
<td></td>
<td>$E$(KJmol$^{-1}$)</td>
<td>log $A$(s$^{-1}$)</td>
<td>$E$(KJmol$^{-1}$)</td>
<td>log $A$(s$^{-1}$)</td>
<td>$E$(KJmol$^{-1}$)</td>
<td>log $A$(s$^{-1}$)</td>
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<tr>
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<td>6.22</td>
<td>111.21</td>
<td>7.11</td>
<td>210.96</td>
<td>16.84</td>
</tr>
<tr>
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<td>125.23</td>
<td>8.04</td>
<td>109.03</td>
<td>6.85</td>
<td>144.90</td>
<td>10.12</td>
</tr>
<tr>
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<td>156.16</td>
<td>10.62</td>
<td>128.69</td>
<td>8.46</td>
<td>171.86</td>
<td>12.32</td>
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<tr>
<td>0.4</td>
<td>181.04</td>
<td>12.72</td>
<td>143.13</td>
<td>9.65</td>
<td>190.63</td>
<td>13.84</td>
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<td>0.5</td>
<td>198.03</td>
<td>14.09</td>
<td>157.85</td>
<td>10.87</td>
<td>215.97</td>
<td>15.93</td>
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<tr>
<td>0.6</td>
<td>184.34</td>
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<td>168.30</td>
<td>11.72</td>
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<td>16.48</td>
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<table>
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<tr>
<th>$\alpha$</th>
<th>Sample C</th>
<th></th>
<th></th>
<th></th>
<th>Sample D</th>
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<td>0.1</td>
<td>129.57</td>
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<td>2.16</td>
<td>353.78</td>
<td>26.38</td>
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4. CONCLUSION
Regarding to thermal properties and kinetic study, it was made a comparison between commercial and synthesized polymeric base bleed propellant samples in order to verify safety during the use for military application. Since there are few kinetic data about base bleed propellants, the kinetic parameters including activation energy (E) and pre-exponential factor (log A) of all samples were determined by Friedman and Ozawa-Flynn-Wall isoconversional models. Results by thermal analysis showed that sample C presented the less thermal stability while the sample A presented a higher one. All samples exhibited polymorphic transition at 240ºC due to the presence of ammonium perchlorate. The graphic profiles of Friedman and OFW for propellant A were different from B, C and D. The samples A and D presented smaller values of activation energy at 50 and 60% of decomposition while the propellant B showed more thermal stability and highest activation energy for both Friedman (215.97 KJ mol⁻¹) and OFW (179.26 KJ mol⁻¹) analysis.

5. ACKNOWLEDGEMENT
The author C.G.M. thanks the Brazilian Council for Scientific and Technological Development (CNPq) for the financial support.

6. REFERENCES