Thermal Decomposition, Ignition and Kinetic Evaluation of Magnesium and Aluminium Fuelled Pyrotechnic Compositions

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Abstract: This paper describes the thermal, kinetic and ignition behaviour of three pyrotechnic mixtures comprising Al + Ba(NO₃)₂, Mg + NH₄ClO₄, and Mg + KMnO₄. Aluminium (Al) and magnesium (Mg) are metal fuels whereas barium nitrate, potassium permanganate and ammonium perchlorate are oxidants. The main objective of the paper is to assess the safety and relative reactivity of these pyrotechnic combinations. The experimental results indicate that aluminium powder reacts exothermically with the decomposition products of barium nitrate near 601 °C. A similar kind of exothermic reaction takes place between magnesium powder and ammonium perchlorate at 338 °C. Heat flow data obtained from multiple heating rate experiments were used to calculate the kinetic parameters, such as activation energy, reaction rate constant and frequency factor, using the Kissinger method. Critical ignition temperatures of all three compositions have been estimated in order to evaluate their thermal stability. The results show that all of these compositions are thermally stable and their relative reactivity decreases in the following order: Mg + NH₄ClO₄ > Mg + KMnO₄ > Al + Ba(NO₃)₂

Keywords: aluminium, magnesium, pyrotechnic mixtures, kinetic data, critical ignition temperature

1 Introduction

Pyrotechnic compositions are generally made up of some kind of fuel and one or more oxidizers. The nature of both the fuel and the oxidizer has an effect on the
ignition behaviour and the reliability of pyrotechnic compositions [1-3]. These compositions are used for both military and civilian applications, to produce special effects such as heat, light or coloration [4, 5]. The reaction between the fuel and the oxidizer present in the pyrotechnic composition can be classed as a redox reaction. These reactions can be very effectively investigated by using thermal analysis techniques, such as differential thermal analysis (DTA) and thermogravimetry (TG). Different types of energetic materials, including pyrotechnic mixtures, are frequently investigated by using thermal analysis [6-10].

The choice of oxidizer plays an important role in the performance of a pyrotechnic mixture. The ignition behaviour of pyrotechnics depends on different factors, such as oxygen balance, thermal stability and the decomposition temperature of the oxidizer. Three different oxidizers have been used in the present work to investigate the effect of the aluminium and magnesium fuels. These oxidizers were barium nitrate, potassium permanganate and ammonium perchlorate. All of these oxidizers are frequently used in different kinds of pyrotechnics [11-14]. Aluminium and magnesium are perhaps the most widely used metallic fuels in pyrotechnic compositions, and produce a very high light output. Such compositions are used to make different type of flares, as well as tracer applications [15-16].

The aim of the present work was to carry out an experimental study of the three different pyrotechnic compositions and their ingredients to elucidate the reaction processes and to assess the safety and reactivity of these mixtures. Thermal and kinetic analysis of Mg + KMnO4 has been reported earlier as well [15], but the critical ignition temperature has not been reported. The thermo kinetic behaviour and the critical ignition temperatures of the mixtures comprising Al + Ba(NO3)2 and Mg + NH4ClO4 are reported in detail in the present work.

2 Materials and Methods

Analytical grade magnesium powder, aluminium powder, potassium permanganate and barium nitrate were purchased from Scharlau (Spain) and ammonium perchlorate was purchased from National Development Complex. The average particle size of the aluminium powder was 20 µm whereas the average particle size of the magnesium powder was 24 µm. The particle size analysis of both aluminium and magnesium was carried out and the particle size distribution of aluminium is shown in Figure 1. All three oxidizers were sieved through a 300 mesh sieve before mixing with the fuel. The fuels and the oxidizers
were mixed in their respective stoichiometric mass ratios. A thermo analytical instrument by Shimadzu was used for the thermal analysis. TG/DTA curves of all of the ingredients and the mixtures were obtained using a sample mass of 3 mg. A heating rate of 10 °C·min⁻¹ was used for the individual components, i.e., fuels and oxidizers. The pyrotechnic mixtures were investigated at four different heating rates, i.e., 10 °C·min⁻¹, 20 °C·min⁻¹, 30 °C·min⁻¹ and 40 °C·min⁻¹, so that the kinetic parameters of the mixtures could be calculated. The nitrogen flow rate was maintained at 50 mL·min⁻¹. An air atmosphere was used for the analysis of the fuels, whereas nitrogen gas was used for the analysis of the oxidizers.

**Figure 1.** Particle size distribution of aluminium powder (D_{avg} = 20 µm).

### 3 Results and Discussion

#### 3.1 Thermal analysis of the pyrotechnic ingredients

The TG curve of the pure magnesium powder is shown in Figure 2. This shows that the sample mass increases significantly in the temperature range 400 to 900 °C, due to oxidation of the magnesium. The TG curve initially shows a slight mass loss in the temperature range 200 to 350 °C due to decomposition of magnesium hydroxide and evaporation of residual water. The mass gain is quite slow in the temperature range 350 to 550 °C. The main oxidation reaction takes place near 600 °C, due to ignition of the magnesium fuel and results in a large mass gain. The mass gain becomes slower after 650 °C and oxidation becomes complete near 900 °C. The total mass gain of the magnesium powder
was approximately 67%, which is very close to the theoretical value, showing that all of the magnesium has become oxidized to MgO as indicated in the following equation:

\[
\text{Mg} + \frac{1}{2} \text{O}_2 \rightarrow \text{MgO}
\]  

Figure 2. TG curve of magnesium powder showing the mass gain due to oxidation.

Figure 3. XRD plot of the residue obtained after oxidation of magnesium powder showing typical MgO peaks.
XRD analysis of the residue was also carried out to identify the end product of oxidation. The XRD plot shown in Figure 3 shows five distinct diffraction peaks. Analysis of these data shows that these are the characteristic peaks of MgO. The XRD result also confirms complete oxidation of the magnesium.

TG analysis of the aluminium powder shows a two-step mass gain in the presence of air. The first oxidation stage takes place in the temperature range 400 °C to 700 °C and results in a mass gain of about 20%. The mass gain is slow until 800 °C and thereafter there is a rapid increase in the mass of the sample, showing a further ~50% mass gain up to 1000 °C. Complete oxidation of the sample results in the production of aluminium oxide:

\[ 2 \text{Al} + \frac{3}{2}\text{O}_2 \rightarrow \text{Al}_2\text{O}_3 \]  

Figure 4. TG/DTA curves of barium nitrate showing the heat flow and mass loss.

The TG/DTA curve of pure barium nitrate is shown in Figure 4. This shows that barium nitrate melts near 592 °C, appearing as an endothermic peak. Decomposition of barium nitrate takes place in a series of overlapping endothermic peaks. The TG curve shows that the decompositions of barium nitrate are associated with a 40% mass loss in the temperature range 580 to 700 °C. It decomposes close to 690 °C, releasing oxygen. The decomposition reaction of barium nitrate has been reported previously in the literature [4, 17].

\[ \text{Ba(NO}_3\text{)}_2 \rightarrow \text{BaO} + 2 \text{NO} + \frac{3}{2}\text{O}_2 \]
The heat flow curve of ammonium perchlorate shows three main peaks (not illustrated). The first endothermic peak appears at 241 °C and corresponds to a solid phase transformation of ammonium perchlorate [18]. The next peak is exothermic in nature and appears at 310.7 °C (Table 1). This peak represents the low temperature decomposition of ammonium perchlorate. The final exothermic peak near 384.1 °C depicts the high temperature decomposition of ammonium perchlorate. The decomposition of ammonium perchlorate yields the following products [2]:

\[ 2 \text{NH}_4\text{ClO}_4 \rightarrow \text{N}_2 + 3 \text{H}_2\text{O} + 2 \text{HCl} + 2.5 \text{O}_2 \]  

(4)

The DTA curve of potassium permanganate shows two distinct peaks. The first peak is exothermic in nature and appears at 284 °C (Table 1). This peak represents the decomposition of potassium permanganate. The second peak near 511 °C is endothermic in nature and represents the high temperature decomposition stage of potassium permanganate.

Table 1. Summary of experimental thermal data

<table>
<thead>
<tr>
<th>No.</th>
<th>Composition</th>
<th>Mass ratio [%]</th>
<th>Fusion temp. °C</th>
<th>Decomposition temp. °C</th>
<th>T* °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ba(NO₃)₂</td>
<td>100</td>
<td>592</td>
<td>690</td>
<td>580-700</td>
</tr>
<tr>
<td>2</td>
<td>NH₄ClO₄</td>
<td>100</td>
<td>------</td>
<td>310</td>
<td>280-410</td>
</tr>
<tr>
<td>3</td>
<td>KMnO₄</td>
<td>100</td>
<td>------</td>
<td>284</td>
<td>240-290</td>
</tr>
<tr>
<td>4</td>
<td>Al + Ba(NO₃)₂</td>
<td>17/83</td>
<td>569</td>
<td>601</td>
<td>550-620</td>
</tr>
<tr>
<td>5</td>
<td>Mg + NH₄ClO₄</td>
<td>34/66</td>
<td>------</td>
<td>338</td>
<td>330-380</td>
</tr>
<tr>
<td>6</td>
<td>Mg + KMnO₄</td>
<td>18/82</td>
<td>------</td>
<td>292</td>
<td>260-320</td>
</tr>
</tbody>
</table>

# The temperatures have been stated at maximum/minimum heat flux. All of these are the actual experimental results, some of which have not been represented in the figures.
T* The temperature range during which there is a change in the mass of the sample (increase or decrease).

3.2 Thermal analysis of the pyrotechnic compositions

The heat flow curve of the Al + Ba(NO₃)₂ pyrotechnic composition indicates that the mixture melts close to 569 °C (Figure 5). Just after melting, the mixture decomposes exothermically at 601 °C and ignition of the fuel and the oxidizer takes place. The TG curve remains stable until melting of the mixture and then shows a mass loss of almost 20%. Such a behaviour of the TG curve means that the mixture is highly stable until its melting temperature. The oxidation reaction between fuel and oxidant is shown below:
2 Al + Ba(NO$_3$)$_2$ \rightarrow$BaO + 2 NO + Al$_2$O$_3$ \hfill (5)

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5.png}
\caption{TG/DTA curves of the Al + Ba(NO$_3$)$_2$ pyrotechnic composition showing the mass loss and heat flow.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure6.png}
\caption{TG/DTA curves of the Mg + NH$_4$ClO$_4$ pyrotechnic composition showing the mass loss and heat flow.}
\end{figure}

The heat flow curve of the Mg + NH$_4$ClO$_4$ pyrotechnic mixture shows an endothermic peak at 254 °C (Figure 6). This peak is due to the phase change in ammonium perchlorate and appears at a slightly higher temperature than for pure ammonium perchlorate. There is a sharp exothermic peak at 338 °C which
represents the decomposition of the mixture. The decomposition is associated with nearly 17% mass loss in the temperature range 330 to 380 °C. The oxidation reaction between the fuel and oxidizer is represented below:

\[
5 \text{Mg} + 2 \text{NH}_4\text{ClO}_4 \rightarrow 5 \text{MgO} + 3 \text{H}_2\text{O} + 2 \text{HCl} + \text{N}_2
\] (6)

**Figure 7.** TG/DTA curves of the Mg + KMnO\(_4\) pyrotechnic composition showing the mass loss and heat flow.

**Figure 8.** Effect of heating rate on the thermal decomposition of the \(\text{Al} + \text{Ba(NO}_3\text{)}_2\) pyrotechnic composition.
The heat flow curve of Mg + KMnO₄ is shown in Figure 7. A single exothermic peak can be seen near 292 °C. This peak represents the decomposition of the pyrotechnic mixture. The mixture in this case does not show any phase transformations or melting before decomposition. The reaction between the two has been reported as follows [15]:

\[
\text{Mg} + 2 \text{KMnO}_4 \rightarrow \text{MgO} + \text{K}_2\text{O} + 2 \text{MnO}_2 + \text{O}_2
\] (7)

Potassium permanganate decomposes to release oxygen and oxidizes the metal fuel to form MgO. The TG curve shows approximately 11% mass loss in the temperature range 260 to 320 °C.

<table>
<thead>
<tr>
<th>No.</th>
<th>Composition</th>
<th>Heating rate [°C·min⁻¹]</th>
<th>Peak temp. [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al + Ba(NO₃)₂</td>
<td>10</td>
<td>600.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>624.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>641.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>655.7</td>
</tr>
<tr>
<td>2</td>
<td>Mg + NH₄ClO₄</td>
<td>10</td>
<td>338.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>346.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>352.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>358.1</td>
</tr>
<tr>
<td>3</td>
<td>Mg + KMnO₄</td>
<td>10</td>
<td>292.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>302.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>310.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>319.5</td>
</tr>
</tbody>
</table>

3.3 Variation in peak temperatures at multiple heating rates

DTA experiments were carried out according to the guidelines given by the International Committee of Thermal Analysis and Calorimetry (ICTAC) [19]. The heating rates were 10 °C·min⁻¹, 20 °C·min⁻¹, 30 °C·min⁻¹ and 40 °C·min⁻¹ (Table 2). The effect of the heating rate increases was similar for all three pyrotechnic mixtures and the decomposition peaks shifted to higher temperatures with increases in the heating rate. The effect of the heating rate increases on the composition containing Al/Ba(NO₃)₂ is shown in Figure 8. Ideally speaking, the heating rate should not have an effect on the melting peak of the mixture; however, as Figure 8 shows, the melting peak also shifts to higher temperatures with increasing heating rate. This could be due to non-uniform heating of the sample at the higher heating rates caused by the thermal lag phenomenon. Similar
trends of increases in the melting peak temperatures of pyrotechnic mixtures have also been reported by other researchers [4, 11].

3.4 Description of the kinetic method

The kinetic parameters of the pyrotechnic compositions were determined using the Kissinger method [20]. Kissinger has proposed several ways of calculating the kinetic parameters from the heat flow data.

\[
\ln \left( \frac{\beta}{T_p^2} \right) = \ln \left( \frac{A}{RT} \right) - \frac{E}{R} \times \frac{1}{T_p} \quad \text{for } n = 1
\]  

(8)

where: \( T_p \) is the temperature of the decomposition peak, \( \beta \) is the heating rate, \( A \) is the pre-exponential factor, \( R \) is the gas constant, \( T \) is the temperature of the sample, \( n \) is the order of the reaction and \( E \) is the activation energy in kJ·mol\(^{-1}\). When the order of reaction is other than one, the parameters are calculated by [21, 22]:

\[
\ln \left( \frac{\beta}{T_p^2} \right) = \ln \left( \frac{c_0^{n-1} \times A \times R}{E} \right) - \frac{E}{R} \times \frac{1}{T_p}
\]  

(9)

The slope of the graph based on the above mentioned relationships is used to calculate the value of the activation energy \( E \). When the activation energy is known, the Arrhenius parameter ‘\( A \)’ can be calculated using the following equation (10) [23, 24]:

\[
A = \left[ \beta E \exp \left( \frac{E}{RT_p} \right) \right] / R T_p^2
\]  

(10)

The kinetic and thermodynamic parameters of the mixtures are presented in Table 3.

<table>
<thead>
<tr>
<th>Composition</th>
<th>E [kJ·mol(^{-1})]</th>
<th>Frequency factor A [s(^{-1})]</th>
<th>Reaction constant k [s(^{-1})]</th>
<th>( \Delta H^# ) [kJ·mol(^{-1})]</th>
<th>( *T_b ) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al + Ba(NO(_3))(_2)</td>
<td>155.9 ± 4%</td>
<td>8.58×10(^6)</td>
<td>0.0040</td>
<td>148.6</td>
<td>599.2</td>
</tr>
<tr>
<td>Mg + NH(_4)ClO(_4)</td>
<td>214.3 ± 7%</td>
<td>2.38×10(^{16})</td>
<td>0.0115</td>
<td>209.2</td>
<td>338.4</td>
</tr>
<tr>
<td>Mg + KMnO(_4)</td>
<td>134.6 ± 10%</td>
<td>2.28×10(^{10})</td>
<td>0.0084</td>
<td>129.9</td>
<td>289.3</td>
</tr>
</tbody>
</table>

\(^*\)\( T_b \) is the critical ignition temperature.
3.5 Determination of the critical ignition temperature

The critical ignition temperature is the minimum temperature up to which energetic materials can be heated without risk of a runaway reaction [25, 26]. It is often estimated by using the thermo kinetic parameters obtained from heat flow data and employing the equations (11) and (12). This has been commonly used for some time in order to estimate critical ignition temperatures [27, 28].

\[
T_b = \frac{E - \sqrt{E^2 - 4RT_0}}{2R}
\]  

(11)

\[
T = T_0 + b\beta_i + c\beta_i^2, \quad i = 1 - 4
\]

(12)

where \(T_b\) is the critical ignition temperature, \(E\) is the activation energy, \(R\) is the gas constant, is the onset temperature corresponding to \(\beta \to 0\). The values of \(T_0\) obtained by using equation (12) were 585.2 °C, 332.3 °C and 284.2 °C respectively, for the mixtures Al/Ba(NO\(_3\))\(_2\), Mg/NH\(_4\)ClO\(_4\) and Mg/KMnO\(_4\). The critical ignition temperatures calculated using the above values of \(T_0\) were 599.2 °C, 338.4 °C and 289.3 °C respectively, for the same mixtures (Table 3).

3.6 Comparative analysis of the kinetic data and ignition temperatures

The data presented in Table 3 show that the pyrotechnic mixture containing Mg and KMnO\(_4\) has the lowest activation energy. The critical ignition temperature of this composition is 289.3 °C, which is the lowest of the three compositions, indicating that it is the least stable composition. However, even this value of the critical ignition temperature is rather higher than that normally encountered in storage and operational temperatures, and therefore it is considered to be thermally stable. The values of the activation energy and the enthalpy of activation in our work were 134.6 kJ·mol\(^{-1}\) and 129.9 kJ·mol\(^{-1}\) respectively, very close to the values of 135 kJ·mol\(^{-1}\) and 130 kJ·mol\(^{-1}\) reported by Pourmortazavi et al. [15]. However, the critical ignition temperature in our case was 289.3 °C. This was not reported in the earlier work.

The data presented in Table 3 show that the values of the reaction rate constant and the critical ignition temperatures for compositions containing Mg/NH\(_4\)ClO\(_4\) were 0.0115 s\(^{-1}\) and 338.4 °C, respectively. These values are higher than the respective values for the mixture containing Mg/KMnO\(_4\), showing that the former is more reactive as well as being more stable than the later.

The composition containing Al + Ba(NO\(_3\))\(_2\) has the highest value of the critical ignition temperature i.e. 599.2 °C, and can be regarded as the most stable
composition of the three. The rate constant for this composition is the lowest and therefore it is the least reactive. The results indicate that the relative reactivity of the pyrotechnic mixtures follows the order: \( \text{Mg} + \text{NH}_4\text{ClO}_4 > \text{Mg} + \text{KMnO}_4 > \text{Al} + \text{Ba(NO}_3\text{)}_2 \).

4 Conclusions

Thermal and kinetic evaluation of three pyrotechnic compositions, containing either aluminium or magnesium as the fuel, has been carried out to elucidate the decomposition processes and to evaluate their stability and reactivity. The experimental results show that the pyrotechnic composition containing Al/ Ba(NO\(_3\))\(_2\) is the least reactive and the most stable, whereas the composition containing Mg/NH\(_4\)ClO\(_4\) is the most reactive and moderately stable. An increase in the heating rate causes a corresponding increase in the decomposition temperature of the mixture in each case. The critical ignition temperatures were calculated to determine the stability of these mixtures. The conclusions of the above were that all three compositions are thermally stable and the relative reactivity of these pyrotechnic mixtures decreases in the following order: \( \text{Mg} + \text{NH}_4\text{ClO}_4 > \text{Mg} + \text{KMnO}_4 > \text{Al} + \text{Ba(NO}_3\text{)}_2 \).

5 References


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