Chemical and Physical characterization of Gunpowder

Vermelho, L. C. R.

Department of Mechanical Engineering,
Instituto Superior Técnico,
Av. Rovisco Pais, 1049-001, Lisbon, Portugal, 2012

Abstract

This work aims the chemical and physical characterization of gunpowder. This characterization was performed for some types of gunpowder. Physical characterization included, mainly, the morphological characterization of the samples such as multi-perforated, tubular, tubular (rocket), cylindrical, spherical, lamellar, black gunpowder, and gunpowder on tape. The technique used was the observation through a stereoscope magnifying glass. After combustion, it was used the scanning electron microscope. The chemical characterization was based on the chemical analysis, and also, on the study of combustion, at atmospheric conditions. In chemical analysis, the samples of multi-perforated gunpowder, tubular rocket gunpowder, tubular gunpowder and gunpowder on tape were studied with energy-dispersion X-ray fluorescence spectrometry and flame atomic absorption spectrometry. In the combustion, we studied the burning rate and the propagation velocity of flame, in samples of multi-perforated powder and gunpowder on tape, through techniques of measurement of mass and flame visualization. In the discussion of results, it was established that most types of studied gunpowder belongs to the group of double base propellants. Despite the variability among samples, it was found that the main common element is lead. In the study of combustion, the burning rate presents a roughly linear evolution, in all samples. It was also presented a propagation velocity of flame, which is characteristic for the two types of studied gunpowder.

Key words: Gunpowder; Spectrometry; Burning rate; Propagation velocity of flame.

1. Introduction

Currently, the military forces have a significant number of unused ammunition, whose storage has consequences on their quality when used for military purposes. The ammunition is constituted by a casing and a propelling charge. The casing usually consists of metal and inside contains a propellant which is gunpowder. Due to the deterioration of ammunition, the military forces use its dismantlement in order to harness all available metal. Later, this metal is sold to civil companies, in particular, licensed operators, in order to be used for another future use. At this moment, the only availed recourse is the casing, and the propellant, which is responsible for the propulsion of the projectile, is simply burned in a combustion chamber and it isn’t used for other type of operation. Since the energy released by gunpowder has a great energy power (it is an energetic material), we considered the possibility of reusing this end-of-life material.

The objective of this work is to study the physical and chemical characteristics of gunpowder, including some types of gunpowder. The aim is to contribute to a better understand of the
characteristics of this type of material, so that we can give a final destination that has a higher added value than it currently is given. The proposal is to employ this type of material in other areas, and not only in the military forces, particularly in the arms. We also aim to broaden the topic in study as a contribution to a policy of waste management in Portugal.

2. The Gunpowder

Gunpowder is an energetic material that belongs to the group of propellants [1]. The gunpowder can be defined as a solid propellant, commonly used in military weapons. [2] These propellants produce large volumes of flue gases, at high temperature, making it very suitable for the function of propellant agent, explosive and pyrotechnic rubbers and fires [3]. The energetic materials are divided into three major groups: the group of propellants, explosives and pyrotechnics [1].

![Energetic Material (PEF)](image1)

Figure 1 - Flowchart of energetic materials [1].

These propellants are called smokeless powder, and their main component is nitrocellulose. The smokeless powder is classified in single-base propellants, double-base propellants and triple-base propellants. In single-base propellants it is the only energetic material in the composition, while in double-base powders, nitroglycerin is also present. In triple-base powders, we can find other explosive components, such as nitroguanidine (the most frequent) [4].

According to the type of weapon, it is crucial to have a control of the burning rate, so that it can have maximum efficiency thereof. Therefore, the powder presents several forms and dimensions.

![Legend:](image2)

Legend:
a - Multi-perforated
b - Tubular split
c - Tape
d - Cylindric
e - Rope
f - Disc
g - Lamellar
h - Gunpowder
i - Spherical
j - Tubular

Figure 2 - Examples of shape of powder [4].
3. Experimental techniques

In the accomplishment of the experimental work we used samples from several types of gunpowder, which are shown in Table 1.

Table 1 - Description of the studied samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>POL-MULTPERF</td>
<td>Multi-perforated</td>
</tr>
<tr>
<td>CINZ-MULTPERF</td>
<td>Ashes of multi-perforated</td>
</tr>
<tr>
<td>POL-TUB-1</td>
<td>Green Tubular</td>
</tr>
<tr>
<td>POL-TUB-2</td>
<td>Tubular</td>
</tr>
<tr>
<td>POL-NEG</td>
<td>Black gunpowder</td>
</tr>
<tr>
<td>FITA</td>
<td>Tape</td>
</tr>
<tr>
<td>CIL</td>
<td>Cylindrical</td>
</tr>
<tr>
<td>ESF</td>
<td>Spherical</td>
</tr>
<tr>
<td>LAM</td>
<td>Lamellar</td>
</tr>
</tbody>
</table>

Initially, the material in study was morphologically and chemically characterized. The morphological characterization was performed using a stereoscope, in initial samples, and also through a scanning electron microscopy (SEM), in samples after firing. We used the energy dispersive spectrometer (EDS) to identify the chemical elements present in the sample. The chemical characterization was performed by energy-dispersion X-ray fluorescence spectrometry (EDXRF), to obtain a qualitative result. The quantitative results were obtained through a flame atomic absorption spectrometry (AAS). After that, we also characterized the combustion of gunpowder, in conditions of atmospheric temperature and pressure, specifically, its burn rate, using a scale that indicate the weight loss in real time, and its propagation velocity through visualization techniques.

The experimental procedure performed in this work is schematized in Figure 3.

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Figure 3 - Flowchart of the experimental process.
4. Discussion

4.1. Morphological characterization

As regards the color, it was found that all samples except the TUB-POL-1, have a dark color such as carbon black and a shiny aspect. The sample POL-TUB-1 has a green color. About texture, it appears that most samples have a rough surface. The CIL and POL-TUB-1 samples, unlike the others, present a smooth texture across its entire surface. The sample POL NEG presents a blend of textures: smooth and slightly rough.

Figure 4 - Macrographs of gunpowder samples.
4.2. Elementary Chemical characterization

The Figure 4 presents the spectra obtained by EDXRF.

![Spectrum of the multi-perforated powder](image1)

![Spectrum of the Green Tubular](image2)

Figure 5 - Spectra obtained by EDXRF.

In the spectrum of the multi-perforated powder, it was identified the following elements: iron, copper, calcium and argon. The last one is characteristic of atmosphere air. After burn, the analysis allowed to identify the same metals: iron, copper and calcium. Comparing the two spectra, we can state that the elements identified in the ash are present in higher concentration than in the initial sample. It was also identified, chromium (Cr) and zinc (Zn).

In the spectrum of the Green Tubular, we find well defined peaks of lead and chromium (Pb and Cr). We also observe some vestigial elements such as argon and potassium.

In order to quantify the concentration of elements detected in the samples, in particular, iron, lead, chromium and copper, we proceeded to analysis by atomic absorption spectrometry.

The chemical composition of the samples is shown in Table 2.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Content of elements (ppm)</th>
<th>Pb</th>
<th>Fe</th>
<th>Cu</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>POL-TUB-1</td>
<td></td>
<td>5415</td>
<td>85</td>
<td>38</td>
<td>&lt; ld</td>
</tr>
<tr>
<td>FITA</td>
<td></td>
<td>1676</td>
<td>97</td>
<td>12</td>
<td>&lt; ld</td>
</tr>
<tr>
<td>POL-TUB-2</td>
<td></td>
<td>22</td>
<td>45</td>
<td>5.0</td>
<td>&lt; ld</td>
</tr>
<tr>
<td>POL-MULTPERF</td>
<td></td>
<td>24</td>
<td>60</td>
<td>6.9</td>
<td>&lt; ld</td>
</tr>
</tbody>
</table>

< ld: below the limit of detection, for analytical methodology used it is estimated at about 40 ppm Cr.
The samples TUB-POL-1 and FITA have the highest lead values. According to the values presented in the samples POL-TUB-2 and POL-MULTPERF, they are probably the same type of material, but present different geometric shapes.

4.3. Density

At this stage, we determined the density of the multi-perforated and tape powder, from the relation mass and volume.

<table>
<thead>
<tr>
<th>Multi-perforated powder</th>
<th>Powder on tape</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Multi-perforated powder" /></td>
<td><img src="image" alt=" Powder on tape" /></td>
</tr>
</tbody>
</table>

**Figure 6 - Powders uses.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MULTPERF</td>
<td>1950</td>
</tr>
<tr>
<td>FITA</td>
<td>1650</td>
</tr>
</tbody>
</table>

Table 3 - Densities typical of powders, multi-perforated and tape.

4.4. Characterization of the Combustion

In order to characterize the gunpowder combustion, we perform the burning of the multi-perforated powder and tape. The samples are represented in Figure 7.

**Figure 7 - Description of powder samples for various tests.**

4.4.1. Burn Rate

The burn rate is defined as the weight variation in a certain period of time. The Figure 8 shows the mass variation over time for several samples.
Based on the graphic, we calculated the burn rate from the slope of the samples straight lines, in zone 2, since this zone represents 80% to 90% of the entire burn process. The visualization of this process allows establishing a burn model.

4.4.2 Burn model

Analyzing this behavior, we observe that the dimension that is varying is the propellant length ($l_0$), as shown in Figure 9.

Therefore, the volume in a certain instant,

$$ V(t) = \frac{\pi \cdot D_0^2}{4} \cdot l(t) $$

How the $l(t)$ parameter is varying, we established the following equation,

$$ l(t) = f(t) \cdot l_0 $$

So,

$$ V(t) = \frac{\pi \cdot D_0^2}{4} \cdot f(t) \cdot l_0 $$

Next,

$$ V(t) = V_0 \cdot f(t) $$
Multiplying the density in both members,

\[ \rho \cdot V(t) = \rho \cdot V_0 \cdot f(t) \quad eq. 5 \]

It is verified that \( f(t) \) is the remaining mass fraction, in other words, \( f(t) \) is the ratio between the mass in a certain instant and the initial mass.

\[ f(t) = \frac{m(t)}{m_0} \quad eq. 6 \]

From this ratio, we can establish the burn rate for each sample, and determine the flame propagation velocity.

**4.4.3. Flame propagation velocity**

The flame propagation velocity was determined through three different ways. In the first way we determined the velocity based on the visualization of flame displacement, named experimental velocity, \( S_e \). In second way, we determined the velocity from the presented model above, named apparent velocity, \( S_a \). Finally, the real velocity, \( S_R \), was determined based on the model and on the way the sample is consumed in the burning process.

**Apparent propagation velocity of flame \( S_i \)**

Assuming that the burning area always remains constant in entire firing process (dashed zone), and based on burn model, we can define \( S_i \).

Deriving the equation 2 in order of time,

\[ \frac{dl(t)}{dt} = \frac{df(t)}{dt} \cdot l_0 \quad eq. 7 \]

So,

\[ S_i = \frac{dm}{dt} \cdot \frac{l_0}{m_0} \quad eq. 8 \]

In which \( l_0 \) is the initial propellant length, \( m_0 \) is the initial mass and \( \frac{dm}{dt} \) is the burn rate of propellant, which is the result of experimental data.
Real propagation velocity of flame $S_R$

The figure 11 shows how the samples are being consumed.

![Figure 11 - The different surfaces and burning respective velocity $S_R$](image)

Based on the Figure 12 and on the burn model, we can define the velocity $S_R$. $S_R$ tells us how fast the propellant is, in reality, being consumed.

![Figure 12 - Example velocity $S_R$ a cylindrical pellet.](image)

Defining,

$$\frac{dm}{dt} = \rho \cdot A_{tr} \cdot u \quad \text{eq. 9}$$
So,

\[ S_R = \frac{\frac{dm}{dt}}{\rho \cdot A_{tr}} \]  

\[ \text{eq. 10} \]

Considering that \( A_{tr} \) is the burning surface (yellow in Figure 11), \( \rho \) is the propellant density and \( \frac{dm}{dt} \) is the propellant burn rate.

### 4.4.4. Combustion results

Table 4 - Results obtained from the combustion of gunpowder.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass (g)</th>
<th>Burning rate (g/s)</th>
<th>( S_e ) (mm/s)</th>
<th>( S_i ) (mm/s)</th>
<th>( S_R ) (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>0.100</td>
<td>0.0335</td>
<td>-</td>
<td>2.68</td>
<td>1.24</td>
</tr>
<tr>
<td>P1</td>
<td>0.100</td>
<td>0.0286</td>
<td>-</td>
<td>2.29</td>
<td>1.19</td>
</tr>
<tr>
<td>D2</td>
<td>0.214</td>
<td>0.0571</td>
<td>-</td>
<td>2.13</td>
<td>1.06</td>
</tr>
<tr>
<td>P2</td>
<td>0.214</td>
<td>0.0529</td>
<td>-</td>
<td>1.98</td>
<td>1.25</td>
</tr>
<tr>
<td>D4</td>
<td>0.435</td>
<td>0.1007</td>
<td>-</td>
<td>2.78</td>
<td>1.03</td>
</tr>
<tr>
<td>P4</td>
<td>0.435</td>
<td>0.0942</td>
<td>-</td>
<td>1.81</td>
<td>1.10</td>
</tr>
<tr>
<td>DT</td>
<td>3.715</td>
<td>0.2450</td>
<td>6.83</td>
<td>6.73</td>
<td>0.91</td>
</tr>
<tr>
<td>F</td>
<td>3.230</td>
<td>0.024</td>
<td>8.29</td>
<td>7.58</td>
<td>5.93</td>
</tr>
</tbody>
</table>

Comparing \( S_e \) and \( S_i \) velocities, we can say that they are approximately equal, which allows to validate the model presented in Chapter 4.4.3.

Through the displayed table, we can establish that the typical flame propagation velocity for the two powder types studied is:

Table 5 - Real of flame velocity propagation.

<table>
<thead>
<tr>
<th>Powder</th>
<th>( S_R ) velocity (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multi-perforated</td>
<td>1.1</td>
</tr>
<tr>
<td>Tape</td>
<td>6.0</td>
</tr>
</tbody>
</table>

As regards the burning rate, we can state that it will increase with the sample weight but it tends to a maximum value for a certain mass value. This is because the \( S_R \) velocity is constant, but, the burning area is changed when it is joined the granules.

![Figure 13 - Burn Rate.](image)
4.5. Morphologic characterization after burning

After the burning of the samples POL-MULTPERF, TUB-POL-1 and POL-TUB-2, we proceeded to morphological characterization of the resulting residue from burning. The obtained images for the two samples show a spongy texture with a considerable porosity and relatively compact areas. We also observe rounded holes, corresponding to the gas release, which results from the decomposition of organic matter. As regard the chemical composition, the elements found were chromium, lead, calcium, potassium, silicon, aluminum, sodium, gold and palladium. The presence of gold and palladium is attributed to the fact that the sample has been coated with a thin film containing gold and palladium. The presence of chromium and lead may be attributed to a contamination of the ash from green tubular powder sample, since the tests were performed with the samples very close.

<table>
<thead>
<tr>
<th>a) Micrographs ash multi-perforated</th>
<th>b) Micrographs of gray tubular</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Micrographs" /></td>
<td><img src="image2.png" alt="Micrographs" /></td>
</tr>
<tr>
<td><img src="eds1.png" alt="EDS Analysis" /></td>
<td><img src="eds2.png" alt="EDS Analysis" /></td>
</tr>
</tbody>
</table>

Figure 14 - SEM Micrographs.

This sample presents a spongy texture and a quite apparent porosity, resulting from gas release of the decomposition of organic matter. Its structure is thinner in relation to the previous sample, but we don’t observe zones of binder compact mass, too. It was performed a EDS analysis in zone 2, in order to obtain a chemical composition identical to that obtained in the XRF-DE spectrometer.

| ![Micrographs](image3.png)        | ![Micrographs](image4.png)    |
| ![EDS Analysis](eds3.png)         | ![EDS Analysis](eds4.png)     |

Figure 15 - SEM Micrographs of gray tubular green.
5. Conclusions

In conclusion, the performed tests for the EDXRF and SEM were quite acceptable since they showed the same chemical elements. At the morphological parameter, the samples have mostly a dark and bright color, and we can assert that these samples belong to the double-base propellants group.

Related to the burning, it was found that the burn rate increases proportionally with the sample mass, and it tends to a certain value. We can also characterize the real velocity of propellant consumption. For the multi-perforated powder: $S_R = 1.1 \text{ mm/s}$ and for the tape powder: $S_R = 6.0 \text{ mm/s}$. This difference is due to their chemical composition, since the tape powder has much higher lead values than multi-perforated powder.

6. References


