SLOW PYROLYSIS OF OLIVE STONES IN A ROTARY KILN: CHARACTERIZATION OF SOLID, GAS AND CONDENSABLE PRODUCTS

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EXTENDED ABSTRACT

Olive stone is a lignocellulosic material generated in large amounts by the olive oil industry. The widespread utilization of this residue for energy application encounters technical and economic drawbacks due to the low energy density, high moisture content and poor combustion properties of the raw feedstock, compared to conventional fossil fuels. The aim of this work is to investigate the benefits of using thermal treatment for the conversion of olive stones into higher value products with potential applications in the energy sector. The olive stones, produced at a commercial oil mill, were characterized for their chemical, physical, thermal and fuel properties. The raw feedstock was heated to temperatures between 150 and 900 °C in a laboratory scale rotary furnace under flowing inert atmospheric conditions. Product yields were determined for each experimental condition and the resulting fractions (solid, liquid, gas) were characterized to establish their applications as fuels. Characterization of the solid fractions included elemental and ultimate analysis, heating value (HHV-LHV), hydrophobicity, mass density (apparent and real) and energy density. The condensable fraction (bio-oil) was characterized for its elemental composition, heating value and mass/energy density. The composition of the gases evolved during the pyrolysis process was determined using fast response gas chromatography (micro-GC). The results show that thermal degradation of olive stones in the rotary furnace takes place primarily at temperatures between 300-500 °C. The application of lower or higher temperatures has a less remarkable influence on product yields and characteristics. This thermal treatment had a positive influence in the fuel properties of the solid fraction in terms of: increase in C content and subsequent reduction in O and H content; reduction in volatile matter and moisture content; apparent concentration of ash content; increase in heating values (LHV/HHV); reduction in apparent mass and energy density; reduction in moisture retention capacity.

Keywords: olive stones, biomass, torrefaction, slow pyrolysis, rotary oven

1. INTRODUCTION

Industrialized countries are increasingly concerned about the environmental decline and the economic risks associated with their excessive consumption and dependence on fossil fuels. An alternative receiving increasing attention involves utilizing lignocellulosic biomass as an energy resource for the generation of heat and electricity. This alternative fuels may be obtained directly from purposely grown energy crops or from residues derived from a wide range of industrial, agricultural and municipal activities (IEA, 2010). The olive oil industry is a very remarkable activity, particularly in the Mediterranean area. Olive oil production in the European Union (EU) has averaged 2.2 million tons in the last few years, representing 73 % of world production (EC, 2012). The extraction of this product in oil mills (almazara) generates a solid residue called olive cake (alperujo) that
contains the stones that have been crushed during the milling process. These olive stones, already ground and free from the internal seed, can be readily recovered by filtration of the cake. The utilization of olive stones for domestic and small industrial energy applications is widespread in the local areas around the olive oil mills (Roig et al., 2006; Pattara et al., 2010).

The expansion of this activity encounters technical and economic drawbacks that are associated primarily with the low energy density of the feedstock, which involves high transportation costs and large storage volumes. Besides, despite savings in greenhouse gas emissions, the poor combustion properties of the raw feedstock results in higher levels of other pollutants like volatile organic compounds (VOC), carbon monoxide (CO), nitrogen oxides (NOx) and particulates (shoot and ashes) than conventional fossil fuels (Pattara et al., 2010; Villeneuve et al., 2012). To overcome this problem, biomass feedstocks may be subjected to thermal pre-treatment for their transformation into higher value fuels. Different technologies have been described in the literature, each one intended to maximize the yield and market value of a specific fraction. Slow pyrolysis, carbonization (Strezov et al., 2007; Lehmann and Joseph, 2009) and torrefaction (Chew and Doshi, 2012; van der Stelt et al., 2011) processes are aimed at generating high yields of solid chars that are usually intended for use in the domestic and industrial energy applications. Fast pyrolysis is intended to maximize the generation of condensable products (bio-oil) with potential applications in the energy and chemical sectors (Bridgwater, 2012). Gasification processes are able to generate high yields of gas products (syngas or producer gas), which may be used for their energy value or as a chemical feedstock (Knoef, 2005).

Various papers have been dedicated to investigate different aspects related to the energy valorization of raw olive stones including: direct combustion and co-combustion in laboratory and commercial scale processes (Cliffe and Patumsawad, 2001; Rodríguez et al., 2008; Pattara et al., 2010); kinetics associated with combustion and thermal decomposition of (Jauhiainen et al., 2004); fast pyrolysis and gasification for the generation of bio-oil and combustible gases (Zabaniotou et al., 2000). The conversion of olive stones into high surface area activated carbons has also been investigated (Alaya et al., 2000; Martínez et al., 2006). Slow pyrolysis and carbonization of olive stones in fixed bed reactors has been investigated in a few papers (Della Rocca et al., 1997; Blanco et al., 2002). The aim of this work is to investigate the upgrading of olive stones as a fuel via thermochemical conversion under inert atmospheric conditions using a rotary kiln over a wide range of temperatures (150-900 °C). The yield of solid, liquid and gas products was determined gravimetrically in each case. The original biomass and the fractions resulting from this transformation were characterized for their chemical, physical and fuel properties. The experimental results are discussed to evaluate potential economic, technical and environmental benefits.

2. MATERIALS AND METHODS

2.1. The olive stones and the rotary furnace

The olive stones employed in this work were produced at an industrial oil mill in Jaen (Spain). In this plant, the olive cake obtained from the milling process is filtered mechanically to extract the crushed stones, which are subsequently sundried, packed and commercialized for domestic heat applications. The process was conducted in a rotary kiln set to rotate at 3 rpm and purged with a 200 ml/min of pre-heated nitrogen. The temperature in the reactor vessel, a quartz cylinder of 47 cm length and 15 cm internal diameter, was set using an electric furnace controlled by a PID controller. Each experiment involved loading the reactor with 100 g of raw olive stones and heating at 10
ºC/min to a final temperature (between 150 - 900 ºC), with 15 min of residence time. The purge gas facilitated the exit of the volatile fraction out of the reaction vessel and into a glass flask where condensation of the liquid fraction occurred. The reaction gases were cleaned off any persistent tars by bubbling through a series of 4 glass flasks filled with isopropyl alcohol at -20 ºC, prior to micro-GC analysis. After each experiment, solid and oil yields were determined gravimetrically and gas yields were calculated by difference.

2.2. Characterization methods

The following standard methods were employed to characterize the solid (raw biomass and chars) and condensable fractions: particle size distribution by sieving (EN 15149-2:2006); moisture content by oven drying at 105 ºC (EN 14774-2:2009); ash content by calcination at 550 ºC (EN 14775:2009); calorific value (HHV and LHV) by bomb calorimetry (EN 14918:2009); apparent density (EN 15103:2009); volatile matter at 900 ºC according to EN 15148:2009; elemental analysis (CHNS) (CEN/TS 15104:2005); hydrophobicity was determined by water immersion during 24 hours (Bergman, 2005). Morphology characteristics of the raw and thermally treated stones were investigated by Scanning Electron Microscopy (SEM) using a Philips XL 30 ESEM. The thermal behavior of ground (600-1000 µm) olive stones was investigated by thermogravimetric analysis (TGA) (heating rate 10 ºC/min and purge nitrogen flow 75 ml/min) using a TA Instruments Q500. The chemical composition of the non-condensable gases generated in the rotary furnace were characterized every two minutes using an Agilent 490 micro Gas Chromatograph (micro-GC) fitted with three analytic channels (Molsieve; CP-PoraPLOT Q; Al2O3/KCL) and two carrier gases (Ar, He).

3. RESULTS AND DISCUSSION

3.1. Characterization and thermal properties of the olive stones

The TGA plot in Figure 2 shows three areas of weight loss in the thermal degradation of the olive stones. The first one, at temperatures below 200 ºC, is associated with elimination of free (around 100 ºC) and bound water (at higher temperatures). Weight loss at 200 ºC represented 17.5 wt% of the original biomass. The second area of weight loss, at temperatures between 300 and 500 ºC is associated with the thermal degradation of the biomass polymers (cellulose, hemicellulose and lignin). The derivative plot (DTG) illustrates two distinctive peaks that represent the pyrolysis of hemicellulose ($T_{\text{max}} = 284.9$) and cellulose ($T_{\text{max}} = 353.5$). Thermal decomposition of lignin takes place over a wider temperature range (Jauhiainen et al., 2004). The third area of weight loss takes place at temperatures above 500 ºC and it is associated with progressive decomposition of resilient lignin structures, volatilization of heavy products and the progressive carbonization of the solid char. The solid residue at 500 ºC and 800 ºC represents 28.4 and 24.2 wt% of the original mass.
3.2. **Product yields and visual aspects**

The experimental results in Figure 2 evidence a progressive transformation of the raw biomass into different fractions (solid; liquid; gas) as it was heated from 150 to 900 °C. The results in the rotary kiln substantiate those observed in the TGA determinations, although some differences may be observed, which can be attributed to the scale and nature of the technologies. The transformation of the raw biomass in the rotary kiln was very limited at 200 °C and below, with the solid fraction still representing more than 93 wt% of the original mass. The degradation process takes place primarily at temperatures between 250 and 500 °C, resulting in a rapid reduction of the solid yield (31 wt% at 500 °C) and a ensuing increase in the oil and gas fractions (31 wt% and 38 wt%, respectively). The application of temperatures higher than 500 °C caused a progressive but less significant transformation of the solid fraction into condensable products, with the gas fraction remaining essentially stable.

**Figure 2.** Thermal treatment of olive stones: effect of temperature on product yields
3.3. Characterization of solids

3.3.1. Chemical characterization of solids

Table 1 shows the chemical characteristics of the raw biomass and the resulting solids in terms of elemental and proximate composition. The results show a marked increase in the carbon content (C) of the solid fraction as the biomass was heated to 400 ºC. This trend was accompanied by a progressive reduction in proportion of oxygen and hydrogen in the solid fraction. The concentration of nitrogen (N) in the original biomass was comparatively lower and remained fairly constant in that temperature range. The C content in the solid fraction remained fairly constant as the temperature was further increased from 400 ºC to 900 ºC. In that temperature range, the results evidence a progressive reduction in the H and O content. The proximate analyses also show an apparent increase in the ash content caused by volatilization of the organic fraction during the thermal process. Moisture content was rapidly reduced from 7.2 wt% in the original biomass to less than 1.0 wt% in the samples treated at temperatures above 150 ºC. The thermal treatment resulted in a notable reduction of the volatile fraction of the solid and a consequent increase of the fixed carbon content. The lower O/C and H/C ratios, higher fixed carbon contents and lower volatile fractions observed in the samples treated at increasingly higher temperatures have been associated with improved fuel properties, resulting in less smoke and higher net heating values during combustion.

3.3.2. Energy characterization and hydrophobic character of the solids

The results in Table 2 show an increase in calorific value (HHV) of the solid fraction with temperature from 19.1 MJ/kg in the raw material to between 30 and 34 MJ/kg in the samples produced at temperatures above 400 ºC. Similar trends were observed in the case of LHV. In contrast, thermal treatment caused a reduction in the mass density of the resulting solids from 1193 kg/m³ to between 550-600 kg/m³ in the samples produced at temperatures between 350 and 700 ºC. Gains in heating values are comparatively lower than mass losses, which results in a progressive reduction of the energy density of the solids with temperature. The hydrophobic nature of the solids was evaluated from the total moisture retention capacity of the samples (moisture uptake + moisture content). The results evidence a moisture retention capacity around 25 wt% in samples produced at temperatures below 250 ºC. This was progressively reduced to 13-15 wt% in samples produced at higher temperatures.

The thermal degradation of the olive stones has also been investigated by TGA/DSC/MS. The solid fraction has been characterized for its particle size distribution, topographical/ morphological appearance (SEM), pore size distribution, surface area, real mass and energy density. This information is not supplied in this paper.
Table 1. Elemental and proximate analysis of olive stone chars produced at different temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O*</th>
<th>O/C</th>
<th>H/C</th>
<th>Volatile matter</th>
<th>Fixed carbon</th>
<th>Ash</th>
<th>Moisture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Material</td>
<td>47.4</td>
<td>6.5</td>
<td>0.23</td>
<td>46.1</td>
<td>0.97</td>
<td>0.14</td>
<td>82.9</td>
<td>9.2</td>
<td>0.7</td>
<td>7.2</td>
</tr>
<tr>
<td>150 °C</td>
<td>49.3</td>
<td>6.4</td>
<td>0.25</td>
<td>44.1</td>
<td>0.89</td>
<td>0.13</td>
<td>82.4</td>
<td>14.0</td>
<td>0.7</td>
<td>2.9</td>
</tr>
<tr>
<td>200 °C</td>
<td>49.9</td>
<td>6.3</td>
<td>0.17</td>
<td>43.6</td>
<td>0.87</td>
<td>0.13</td>
<td>82.4</td>
<td>16.0</td>
<td>0.5</td>
<td>0.9</td>
</tr>
<tr>
<td>250 °C</td>
<td>51.4</td>
<td>6.3</td>
<td>0.12</td>
<td>42.2</td>
<td>0.82</td>
<td>0.12</td>
<td>79.9</td>
<td>18.7</td>
<td>0.5</td>
<td>0.9</td>
</tr>
<tr>
<td>275 °C</td>
<td>57.2</td>
<td>6.1</td>
<td>0.19</td>
<td>36.7</td>
<td>0.64</td>
<td>0.11</td>
<td>70.4</td>
<td>28.2</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>300 °C</td>
<td>60.4</td>
<td>5.9</td>
<td>0.12</td>
<td>33.5</td>
<td>0.55</td>
<td>0.10</td>
<td>59.4</td>
<td>39.0</td>
<td>1.0</td>
<td>0.6</td>
</tr>
<tr>
<td>350 °C</td>
<td>71.5</td>
<td>5.2</td>
<td>0.12</td>
<td>23.1</td>
<td>0.32</td>
<td>0.07</td>
<td>37.4</td>
<td>60.5</td>
<td>1.6</td>
<td>0.5</td>
</tr>
<tr>
<td>400 °C</td>
<td>75.8</td>
<td>4.7</td>
<td>0.17</td>
<td>19.4</td>
<td>0.26</td>
<td>0.06</td>
<td>28.1</td>
<td>70.1</td>
<td>1.6</td>
<td>0.3</td>
</tr>
<tr>
<td>500 °C</td>
<td>76.0</td>
<td>3.9</td>
<td>0.22</td>
<td>19.8</td>
<td>0.26</td>
<td>0.05</td>
<td>18.2</td>
<td>80.0</td>
<td>1.5</td>
<td>0.3</td>
</tr>
<tr>
<td>700 °C</td>
<td>75.9</td>
<td>2.4</td>
<td>0.42</td>
<td>21.3</td>
<td>0.28</td>
<td>0.03</td>
<td>6.9</td>
<td>90.2</td>
<td>2.2</td>
<td>0.7</td>
</tr>
<tr>
<td>900 °C</td>
<td>74.6</td>
<td>1.3</td>
<td>0.57</td>
<td>23.5</td>
<td>0.31</td>
<td>0.02</td>
<td>4.9</td>
<td>92.0</td>
<td>2.2</td>
<td>0.9</td>
</tr>
</tbody>
</table>

*Estimated by difference

Table 2. HHV, LHV, density, energy densities and hydrophobicity of chars produced at different temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>HHV(^a) (MJ/kg)</th>
<th>LHV(^a) (MJ/kg)</th>
<th>Apparent mass density (kg/m²)</th>
<th>Energy density(^b) MJ/m³</th>
<th>Relative</th>
<th>Energy yield (%)</th>
<th>Moisture uptake (%)</th>
<th>Moisture retention capacity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material</td>
<td>19.1</td>
<td>17.7</td>
<td>1193</td>
<td>21.1</td>
<td>1.00</td>
<td>100.0</td>
<td>17.4</td>
<td>24.6</td>
</tr>
<tr>
<td>150 °C</td>
<td>19.5</td>
<td>18.2</td>
<td>1178</td>
<td>21.4</td>
<td>1.01</td>
<td>97.2</td>
<td>22.2</td>
<td>25.1</td>
</tr>
<tr>
<td>200 °C</td>
<td>20.1</td>
<td>18.8</td>
<td>878</td>
<td>16.5</td>
<td>0.78</td>
<td>97.9</td>
<td>24.5</td>
<td>25.4</td>
</tr>
<tr>
<td>250 °C</td>
<td>20.4</td>
<td>19.1</td>
<td>783</td>
<td>15.0</td>
<td>0.71</td>
<td>94.9</td>
<td>21.0</td>
<td>21.9</td>
</tr>
<tr>
<td>275 °C</td>
<td>22.5</td>
<td>21.3</td>
<td>711</td>
<td>15.1</td>
<td>0.72</td>
<td>86.6</td>
<td>14.9</td>
<td>15.5</td>
</tr>
<tr>
<td>300 °C</td>
<td>24.2</td>
<td>23.0</td>
<td>713</td>
<td>16.4</td>
<td>0.78</td>
<td>80.9</td>
<td>16.1</td>
<td>16.7</td>
</tr>
<tr>
<td>350 °C</td>
<td>29.5</td>
<td>28.4</td>
<td>569</td>
<td>16.2</td>
<td>0.77</td>
<td>63.9</td>
<td>13.0</td>
<td>13.5</td>
</tr>
<tr>
<td>400 °C</td>
<td>30.3</td>
<td>29.3</td>
<td>596</td>
<td>17.5</td>
<td>0.83</td>
<td>56.6</td>
<td>12.5</td>
<td>12.8</td>
</tr>
<tr>
<td>500 °C</td>
<td>32.6</td>
<td>31.8</td>
<td>547</td>
<td>17.4</td>
<td>0.82</td>
<td>53.0</td>
<td>13.9</td>
<td>14.2</td>
</tr>
<tr>
<td>700 °C</td>
<td>33.8</td>
<td>33.3</td>
<td>576</td>
<td>19.2</td>
<td>0.91</td>
<td>48.2</td>
<td>11.9</td>
<td>12.6</td>
</tr>
<tr>
<td>900 °C</td>
<td>32.4</td>
<td>32.1</td>
<td>604</td>
<td>19.6</td>
<td>0.93</td>
<td>44.5</td>
<td>15.7</td>
<td>14.8</td>
</tr>
</tbody>
</table>

\(^a\) as received \(^b\) net energy densities based on LHV

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3.4. Characterization of condensable oils and gases

The visual aspect of the condensable fraction produced at different temperatures is shown in Figure 3 and discussed in Section 3.2. The oil fraction produced at 700 ºC, following completion of the pyrolysis process, was characterized. The water content of this oil, as determined by Karl Fisher, was 62.5 wt%. The oil exhibited a mass density at 15 ºC of 1.063 kg/m³ and a viscosity at 40 ºC of 1.33 cSt. The gross calorific value (HHV) of the oil produced at 700 ºC was 16.9 MJ/kg. Considering that the oil yield at that temperature represents 36.5 wt% of the original material, it may be calculated that the energy yield towards this fraction represents 32.3 % of the energy present in the original biomass. Hence, the energy distribution in the process at 700 ºC (following completion of the pyrolysis process) may be expressed as follows: solid fraction 48.2 %; oil fraction 32.3 %; gas fraction (by difference) 19.5 %.

Figure 4. Composition of gas fraction during the thermal degradation of olive stones

The results in Figure 4 show that the evolution of CO₂ and CO is initiated at 378 ºC, with maxima at 442 and 550 ºC, respectively. The formation of H₂ and unsaturated hydrocarbons (C₂H₄ and C₂H₆) was initiated at higher temperatures (around 530 ºC). Concentration maxima for H₂ and unsaturated hydrocarbons occurred at 636 and 528 ºC, respectively. Other hydrocarbon products, like methane, could not be detected.

4. CONCLUSIONS

- Thermal degradation of olive stones in a rotary furnace takes place primarily at temperatures between 300-500 ºC. The application of lower temperatures has a less remarkable influence on product yields and characteristics.
- The application of increasingly higher temperatures resulted in changes in the chemical, physical and fuel properties of the resulting solids as follows: increase in C content and subsequent reduction in O and H content; reduction in volatile matter and moisture content; apparent concentration of ash content; increase in heating values (LHV/HHV); reduction in apparent mass and energy density; reduction in moisture retention capacity.
- These results evidence an improvement in the fuel properties of the solid fraction as a result of thermal conversion of the original olive stones.

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