FAST PYROLYSIS AS AN ALTERNATIVE TO THE VALORIZATION OF
OLIVE MILL WASTES

F. Dorado, P. Sanchez, A. Alcazar-Ruiz, L. Sanchez- Silva*

Department of Chemical Engineering, University of Castilla –La Mancha, Avda.
Camilo José Cela 12, 13071 Ciudad Real, Spain

*Corresponding author phone: +34 926 29 53 00 ext. 6307; fax: +34 926 29 52 56;
e-mail: marialuz.sanchez@uclm.es
Abstract

BACKGROUND: The valorization of organic wastes through fast pyrolysis appears to be a highly promising option for decreasing pollutants and reducing consumption of natural resources. For this purpose, three different olive pomace samples were studied to determine how olive crop location and the extraction process could influence bio-oil product distribution. Olive pomace was selected as the feedstock due to the importance of the olive oil industry in Spain.

RESULTS: In this study, the conditions of fast pyrolysis were optimized using lignin as a reference, with the optimum conditions being 500 °C, 20 °C ms⁻¹ as the heating rate and 15s as the vapour residence time. The olive pomace results determined that not only their chemical composition, but also their fat content had a remarkable effect on product distribution obtained after fast pyrolysis. However, whereas high lignin content enhanced phenol production, cellulose decomposed to carboxylic acids. In addition, due to current global warming, the CO₂ burden of the three samples was calculated using MS spectroscopy. The OPGC sample gave off the lowest amount of greenhouse gases, followed by OPMNE and OPMN.

CONCLUSIONS: The higher fat content in the sample enhanced carboxylic acid production. The difference in phenol production between OPMN and OPMNE could be attributed to the presence of potassium. From an environmental point of view, the use of olive pomace wastes could reduce CO₂ emissions with further research and by developing experimental processes.

Keywords: Olive pomace; fast pyrolysis process; bio-oil; greenhouse emissions.
1. Introduction

Biomass pyrolysis is defined as the thermal decomposition of the biomass organic matrix in non-oxidising atmospheres to produce liquid bio-oil, solidbiochar and non-condensable gas products.\(^1\) Depending on the final target of the products and operating conditions, pyrolysis can be slow, intermediate or fast. The latter is a promising method for converting lignocellulosic biomass into useful energy forms, mainly bio-oil. It is carried out at moderate temperatures (400-600 °C), high heating rates (103-104 C/s) and with short vapour residence times (0.5-15 s).\(^2\) These operational conditions limit the secondary cracking reaction of products, and thereby increase bio-oil yield. Optimizing the process parameters (mainly temperature, heating rate and residence time) is crucial because they strongly affect the yield and composition of pyrolysis products. In recent years, the influence of these parameters on product composition for different biomass has been analysed in a great deal of research.\(^3,4\) Temperature has important effects on product yields, because it affects the amount and composition of volatile components. Also, the heating rate of biomass particles is the main parameter for differentiating between slow and fast pyrolysis.\(^4\) A higher heating rate promotes cracking reactions and produced greater amount of bio-oil than char. Finally, product yields from biomass pyrolysis are affected by vapour residence time with shorter times favouring bio-oil production and minimising cracking reactions, while higher residence time are conducive to the formation of char.\(^5\)

Many studies focused on converting lignocellulosic biomass through pyrolysis. However, relatively few studies have focused on olive pomace applications.\(^6,7\) Olive pomace is the main subproduct from olive oil extraction, which is a key economic sector in countries such as Spain, Italy and Greece. Its composition may vary depending on the olive variety and the processing method. It has a high moisture content, slightly acidic pH values and
high amounts of organic matter (lignin, hemicellulose and cellulose). In addition, it contains water-soluble fats, proteins, water-soluble carbohydrates and water-soluble phenolic substances. Moreover, olive pomace has negative effects on soil because of its phytotoxicity and antimicrobial properties. This antimicrobial properties, employed by antimicrobial proteins, could help an immune function maintaining a complex microbial environment and preventing the invasion of pathogens owing to their antimicrobial and immunomodulatory effects. Thus, it cannot only destroy microbes directly but can also regulate immune function indirectly.

These environmental problems could be significantly reduced if the olive pomace were treated and revalued. However, there is an evident lack of detailed works on the use of olive pomace as a feedstock in fast pyrolysis. This is not surprising, as the main valorization of this residue focuses on olive pomace oil production, but as it is an economical derivative in, its use as biomass feedstock could be of great interest. It should be remarked that the study of olive pomace in fast pyrolysis is quite challenging, as its composition can change for many reasons. For instance, olive crop location, the olive variety or the different processes carried out at the olive mill for extracting the oil can influence its composition, but even when these conditions remain the same, it can change from season to season, due to random factors such as weather. To the best of our knowledge, these determining issues have been considered in detail for the first time in literature in this work.

Therefore, the aim of this study was, firstly, to analyse the operational conditions of fast pyrolysis using a pyrolyzer coupled with a GC/MS analyser. To carry out this objective, the effect that temperature, heating rate and vapour residence time had on bio-oil yield was studied using by lignin as the reference. Moreover, once the optimal parameters were selected, three different types of olive pomace were compared to analyse how olive crop
location and the olive oil extraction methodology influenced bio-oil product distribution.

Finally, GHG emissions were evaluated for each olive pomace sample studied.

2. Materials and methods

2.1 Materials

In this study, three samples of olive pomace from the 2019 harvest were analysed and there were two main differences between them. The first concerned their locations: one was obtained from Aceites Garcia de la Cruz olive oil mill from Madridejos (Toledo, Spain) named as OPGC, whereas the other two samples were from Montes Norte olive oil mill from Mora (Toledo, Spain). The geographical location of these olive oil mills can be seen in Fig. S1. Samples named as OPMN and OPMNE were obtained before and after extraction, respectively. In addition, the fat value data for each sample was recorded by each olive mill plant. The OPGC sample showed a higher fat content (4.9 %) than the OPMN and OPMNE samples (2.8 and 1.7 %, respectively).

All the samples were dried in an oven for 24 h, and then milled and sieved to obtain an average particle size ranging from 100 to 150 µm.

2.2 Equipment and procedures

The olive pomace samples were first characterized by an elemental analyser and then a thermogravimetric analyser (TGA), atomic emission spectroscopy inductively coupled plasma (ICP-AES), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

A proximate analysis and ultimate analysis were carried out according to standards UNE 15104:2011, UNE-EN ISO18123, UNE 32-004-84 and UNE 32-002-95 in the elemental analyser, Thermo Fischer Scientific Flash 2000, equipped with a thermal conductivity
detector. The proximate analysis gave information about volatile matter, fixed carbon and
ash content and the ultimate analysis was used to find out the concentration of carbon,
hydrogen, nitrogen, oxygen and sulphur in the sample. In addition, the content of metals
in the sample was determined by Inductively Coupled Plasma Spectrometry (IPC).
The hemicellulose and Klason lignin contents in the lignocellulosic biomass samples
were calculated according to the following experimental methodology. The extractives
contents was determined by successively extracting with the Soxhlet system using
dichloromethane (6 h), ethanol (16 h) and water (16 h) as an adaptation from TAPPI 204
om-97. After extraction, the sample was dried at 110 ºC for 1h and cooled to room
temperature in a desiccator. The extractives solubilized by the solvents were determined
by mass differences in the solid.13
Lignin content was determined with the Klason method (TAPPI T 222 om-02). The
samples (350 mg) of extractive-free material were added to 3ml of H2SO4 (72 %) at 30
 ºC for 1h, then diluted to 3 % w/w H2SO4 and reacted in an autoclave for 1h at 120 ºC.
The residue was filtered, washed until neutralization, dried at 110ºC until reaching a
constant weight and cooled to room temperature. The weight difference after treatment
determined the amount of lignin.13
For determining hemicellulose contents, 150ml of NaOH solution (0.5 M) were added to
1g of extractive-free material and boiled for 3.5 h with recycled water. The product was
filtered, washed until neutralization, dried at 110 ºC for 1h and cooled to room
temperature. The weight difference after treatment determined the amount of
hemicellulose.14
The proximate analysis, ultimate analysis, metal contents and chemical composition of
each biomass are shown in Table 1.
The IR spectra were performed with a Perkin-Elmer FTIR Spectrum-two spectrophotometer provided with a Universal Attenuated Total Reflectance Accessory (UATR). The spectra accumulated 64 scans with a range between 500 and 4000 cm\(^{-1}\) and a resolution of 4 cm\(^{-1}\).

The scanning electron microscope (SEM) was carried out using a Phenom ProX desktop scanning electron microscope, the objective of which was to compare the surface features and morphology of the olive pomace before and after fast pyrolysis.

A thermogravimetric analysis coupled with mass spectrometry (TGA-MS) was employed in this study to identify non-condensable gases and, subsequently, calculate greenhouse gas emissions. The experiments were carried out with a thermogravimetric analyser (TGA-DSC 1, METTLER TOLEDO). The CO\(_2\) burden was calculated following the IPCC report.\(^{15}\) Then, the Global Warming Potential value over a 100-year time horizon (GWP\(_{100}\)) was considered by converting GHG emissions into climatic impact (carbon dioxide equivalent), according to equation (1).

\[
GHG\ emissions = \sum (emissions_{gas} \cdot GWP_{100}) \quad (1)
\]

where GHG emissions were expressed in CO\(_2\) equivalent units. GWP\(_{100}\) values were taken from the latest version of the Intergovernmental Panel on Climate Change (IPCC) for converting emissions into CO\(_2\) equivalents. These values were 1 and 28 for CO\(_2\) and CH\(_4\), respectively.\(^{13}\)

2.3 Experimental procedure for carrying out fast pyrolysis

Py-GC/MS experiments were carried out using a Pyroprobe 6200 pyrolyzer (CDS analytical) connected to a 7890B/5977B GC/MS analyser (Agilent Technologies) with a transfer line (length: 1m; temperature: 340 °C), as shown in Fig. S2.
1 mg ± 0.05 mg of olive pomace sample was placed in the middle of the quartz tube (2
mm in diameter and 20mm long) with a quartz wool base and it was inserted into the
platinum Pyroprobe autosampler. Pyrolysis took place at 500 ºC, at a heating rate of 20
ºC/ms for 15 s. The experiments were carried out in triplicate for each sample to ensure
reproducibility.

The GC/MS injector temperature was kept at 280 ºC. An Elite-35MS capillary column
(30 m x 0.25 µm) was used for chromatographic separation. Helium (99.999%) was
selected as the carrier gas with a constant flow rate of 1mL min⁻¹ and a 1:80 split ratio,
the purpose of which was to separate and identify the chemical composition of the bio-
oil. The oven temperature was programmed from 40ºC (3 min) to 280ºC at a heating rate
of 5 ºC min⁻¹. The chromatograms were integrated, and the relative peak areas were
calculated and subsequently identified according to the NIST library. Only peaks with a
>80% matching quality with the library were considered.

2.4 Data analysis

Statistical analysis was performed through a one-way analysis of variance (ANOVA) in
order to assess statistical differences between the different olive pomace samples, at a
significance level of α = 0.05, using STATGRAPHICS Centurion (Statgraphics
Technologies, Inc.).

3. Results and discussion

3.1 Effects of fast pyrolysis conditions

To optimize fast pyrolysis, the effect of the operational conditions on product distribution
was analysed. In this study, lignin alkali (CAS 8068-05-1) from Sigma Aldrich was used
as the feedstock. Lignin is one of the three main building blocks of lignocellulosic
biomass. It is an aromatic, three-dimensional and cross-linked phenol polymer formed by
differently bonded “hydroxyl-” and “methoxy-” substituted phenylpropane units. Our
objective was to use a reference biomass instead of an unknown one which may have
prone to changing. Thus, it would in turn aid us in subsequent studies with lignocellulosic
biomass.

The main process parameters studied were temperature (°C), heating rate (°C ms⁻¹) and
vapour residence time (s). Our objective was to evaluate the main products of fast
pyrolysis such as alcohols, aldehydes, alkanes, ketones, phenols or cyclic hydrocarbon.
The most representative group in this feedstock were phenol derivatives from the
depolymerization of lignin. Thus, the optimal conditions were selected on the basis of
maximum phenol production. Although its peak area was calculated considering all bio-
oil product areas, it can be observed that, in all cases, phenol production represented over
80% of the total product distribution whose results are shown in Fig. 1.

Fast pyrolysis is characterized by moderate temperatures, high heating rates and short
residence times. The effect of temperature was analysed at 400, 500, 600, 700, 800 and
900 °C. As expected, optimum results were obtained at 400 and 500 °C, which is in good
agreement with those reported in the literature. The heating rate varied between 5 and 20 °C ms⁻¹. Higher rates promoted bio-oil
production since mass and heat transfer limitations were reduced. Vapour residence time
varied between 10 and 25s. Lower times enhanced bio-oil production because secondary
reactions were minimised by quickly removing the organic vapours from the reaction
zone. However, low residence time may not lead to a high quality liquid product because
it favours macromolecule products due to the random breakage of lignin. Although the
whole range for both parameters was typical in fast pyrolysis, higher phenol production
was obtained at 20 °C ms\(^{-1}\) and 15 s, and these parameters were selected to carry out further studies.

3.2 Biomass characterization

3.2.1 FTIR analysis

Fig. 2 shows the FTIR spectra for the three samples (OPGC, OPMN and OPMNE). This characterization was carried out to recognise the main functional groups of the biomass such as alcohols, alkenes, esters, ketones, phenols and aromatics, among others. This kind of biomass is mainly composed of cellulose, hemicellulose and lignin. Thus, the presence of these components determined the main bands of the spectra, among which lignin was the most abundant whose main phenylpropane monomers could be categorized as guaiacyl, syringyl and p-hydroxyphenyl units.\(^{16}\)

In all cases, the peak between 3600 and 3000 cm\(^{-1}\) was related to the stretching vibration of O-H (alcohols and phenols). The one from 3000 to 2700 cm\(^{-1}\) was associated with the stretching vibration of C-H in the lignin structure.\(^{20}\) The peak in the region between 1440 and 1380 cm\(^{-1}\) corresponded to the asymmetric bending of the lignin structure.\(^{19}\) Moreover, those peaks near 1250 cm\(^{-1}\) might have been caused by the presence of C-O-C in the cellulose biopolymer chain. The band between 1100 and 900 cm\(^{-1}\) showed a high intensity peak which might have been related to C-O-H stretching vibrations linkages in cellulose and hemicellulose or the presence of C-O-R alcohols or esters.\(^{20}\) Finally, the peak around 600 cm\(^{-1}\) was associated with aromatic compounds.\(^{20,21}\) According to the results, the three biomasses showed similar spectra due to their close compositions. However, the intensity of the peaks between 3100 and 2800 cm\(^{-1}\), assigned to the C-H stretching modes from the methylene and methyl groups of fatty acids and triacylcerols, and the sharp peak located at 1743 cm\(^{-1}\), ascribed to the free fatty acids in the
triacylglycerol, were lower in the OPMNE sample. This was associated with its low oil content.\textsuperscript{22}

3.2.2. Thermogravimetric analysis (TGA).

Fig. 3 shows the DTG profile for the pyrolysis of the three types of olive pomace (OPGC, OPMN and OPMNE). As reported elsewhere, the DTG curves for lignocellulosic biomass revealed three common degradation stages. The first was attributed to moisture evaporation; it was carried out at low temperatures (<150 °C) and the three biomasses showed the same weight loss. The second in which, temperatures ranged from 150 to 500 °C, represented the main pyrolysis stage and was associated with devolatilization. Finally, the third stage concerned char formation (>500 °C). If we look at the second stage of the DTG curve, three shoulders can be observed which could be attributed to the individual decomposition of the main components of lignocellulosic biomass: hemicellulose, cellulose and lignin. According to previous studies,\textsuperscript{23} changes found between 230-250 °C could be associated with hemicellulose decomposition. In the OPGC sample there was a more marked peak than in the OPMN and OPMNE samples, as its hemicellulose content was higher (Table 1). The peak from 370 to 410 °C may have corresponded to cellulose degradation. In addition, olive oil decomposition might have been a factor, given that it takes place in this temperature range. This was corroborated with a TGA experiment with pure olive oil (Fig. S3). Therefore, the marked peak observed in the OPGC sample can also be attributed to its higher fat content. This experimental outcome was remarkable in that it indicated that the pyrolysis of the remaining olive oil in the olive pomace could have overlapped with the pyrolysis of the biomass. Finally, lignin decomposition occurred at higher temperatures (> 500 °C) and, at this final stage, the lowest degradation rate was seen in comparison with previous ones.
3.2.3 Scanning electron microscopy (SEM).

Fig. 4 shows representative SEM images of the untreated olive pomace and the residues obtained after fast pyrolysis. As can be seen in Fig. 4A, 4C and 4E, the olive pomace before pyrolysis was formed by single particles measuring between 100 and 150 microns. In addition, its surface morphology was very smooth in comparison with the residue with almost no irregularities. However, if we look at Fig. 4B, 4D and 4F, we can see that the structure sample after pyrolysis changed. The particles agglomerated which might have been due to the low melting point of lignin, which facilitated the agglomeration of lignin during pyrolysis. In addition, the pore structure was remarkable and this could be associated with the release of volatile matter. Although all the residues had a porous structure, OPGC (Fig. 4B) was the most porous because the amount of volatile matter and the hemicellulose content were higher in this sample (Table 1).

3.3 Py-GC/MS analysis of olive mill wastes.

Firstly, olive pomace from different olive mills were compared to evaluate how olive crop location could affect the formation of products in fast pyrolysis. In addition, there were some remarkable differences attributed to the olive mill plant size. *Aceites García de la Cruz* is a small size olive mill that processes more homogeneous and more localised olive varieties than *Montes Norte* mill. The latter, as a medium size olive mill, works with a great diversity of olive trees from different locations. Fig. 5 shows the product distribution obtained from the pyrolysis of each olive pomace. The identified compounds were classified into the following groups: alcohols, aldehydes, alkanes, carboxylic acids, cyclic hydrocarbons, ketones, esters, nitrogen compounds, phenols and sugars (see Table S1). In order to better understand these results, a scheme of the possible reaction mechanism for cellulose, hemicellulose and lignin during fast pyrolysis, based on the literature.
was shown in Fig. 6A. The reaction pathways of the olive oil fast pyrolysis and its influence on the results, as previously commented, are also illustrated in Fig. 6B.

The main differences in the fast pyrolysis product distribution concerned alcohols, aldehydes, esters, carboxylic acids and nitrogen compounds. The OPGC sample produced higher amounts of carboxylic acids and aldehydes and lower amounts of alcohols and nitrogen compounds than did the OPMN sample. These differences were mainly attributed to the chemical composition of the samples as can be seen in Table 1. Fig. 6A shows that, at higher temperatures (≥ 400 ºC), cellulose undergoes secondary decomposition to produce furan compounds and light oxygenates. Hemicellulose degradation mainly yields carboxylic acids and non-aromatic ketones. Furthermore, lignin decomposes to methoxyphenols and at higher temperatures (≥ 500 ºC) secondary decompositions favour the formation of aliphatics. Therefore, the OPMN sample, which was higher in lignin had more alcohol compounds after the reaction. However, fast pyrolysis of the OPGC sample, with a higher amount of hemicellulose content, promoted the formation of aldehydes and carboxylic acids compounds. These results were in very good agreement with TGA (Fig. 3) and the chemical composition analysis (Table 1).

In addition, these differences in alcohols and carboxylic acids could also be associated with the fat content. The olive oil was mainly composed of carboxylic acids such as oleic, maleic or linoleic acids (Fig. 6B), which were decomposed to lighter ones, alcohols and alkenes after fast pyrolysis. Then, in order to verify this, a Py-GC/MS analysis of pure olive oil (Fig. S4) was carried out. As expected, the main products were carboxylic acids, alkanes and alcohols, which were derived from deoxygenation and cracking reactions that took place simultaneously. Therefore, the differences between the OPGC and OPMN samples were also clearly associated with their fat content.
Looking at Fig. 5, phenols were the most representative group after fast pyrolysis in the samples under observation. They were oxygenated aromatic compounds of great interest since they had pharmaceutical and cosmetic properties.\textsuperscript{5,27} Moreover, they could be separated from the bio-oil for subsequent use as fine chemicals. Their production was attributed to the lignin content in the initial sample because they were the main by-product in lignin decomposition. Here, there were no significant differences between both samples.

A second study was carried out to analyse the differences between the OPMN and OPMNE samples. The latter underwent extraction with hexane, in which the remaining oil was partially removed from the olive pomace. Fig. 7 shows the pyrolysis product distribution. Table S1 shows the integrated peak areas for the three olive pomace samples. The main difference was observed in the phenol and esters compounds. In the mineral composition (Table 1), a remarkable difference could be observed in potassium content (774 and 8105 ppm for OPMN and OPMNE, respectively). Hwang et al. reported that phenol production increased with rising potassium, thereby indicating that demethoxylation from lignin was enhanced by this mineral during pyrolysis.\textsuperscript{28} Zhang et al. concluded that potassium in biomass changed the composition of the bio-oils obtained: yields of aldehydes, esters and sugars decreased, while furans and phenols increased.\textsuperscript{29} Therefore, the differences in phenol production between the OPMN and OPMNE could be attributed to the presence of potassium, as there was ten times more of it in OPMNE of it than in OPMN.

3.4 Gas emissions: CO\textsubscript{2} burden

A thermogravimetric analysis coupled with a MS spectroscopy was carried out to measure gas emissions in continuous and real time. The experiments were performed from 25 to
900 °C at a heating rate of 10 °C min⁻¹. It was assumed that the gas given off was mainly composed of H₂, CO, CO₂, CH₄, C₂ hydrocarbons, NOx and SO₂. Those corresponding to individual gases, H₂O, CH₄ and CO₂ were the highest yielded.

To calculate the CO₂ burden in light of the IPCC report (15), CO₂ and CH₄ emissions were considered. Then, according to equation 1, GHG emissions were converted into climatic impact (in kg of CO₂ equivalent) considering the Global Warming Potential (1 and 28 for CO₂ and CH₄, respectively). The results obtained are reflected in Table 2.

In short, the OPGC sample gave off the lowest amount of greenhouse gases, followed by OPMNE and OPMN. These differences were mainly attributed to lower yields of CH₄ and CO₂ in the former (Table 2). Moreover, although yields of CH₄ were lower in comparison with CO₂, CH₄ had more impact on the GWP value due to its high emission metric values. When the samples were received, the drying degree of the OPMN and OPMNE samples were higher than the OPGC one and their fat contents were also lower, as expected in the different working procedures in the olive mills under observation. Therefore, the wastes and by-products generated during olive oil production were highly dependent on the technology used, and it was essential to gain detailed knowledge of all the steps in this process.

In addition, we made a comparison between the environmental viability of producing some important chemicals by fast pyrolysis and the corresponding traditional process. Fast pyrolysis was selected due to the high quantity of phenol obtained. The results were compared with those for traditional phenolic production as found in the Ecoinvent database.30 In this evaluation, only CO₂ emissions were considered due to the limitations of this database. The amount of CO₂ given off in traditional phenol production was 2.10E-01 kg CO₂ kg phenol⁻¹, while the CO₂ values obtained in this research were in the range
of 2.88E-03 and 3.66E-03 kg CO2 kg phenol\(^{-1}\). Therefore, from an environmental point of view, fast pyrolysis was considered to be very promising and further studies in this respect should be carried out.

4. **Conclusions**

Fast pyrolysis of three different types of olive pomace samples was carried out to determine how grove location and extraction treatment could influence bio-oil product distribution. Olive pomace was selected as it could provide a use for waste from olive oil due to the importance of this sector in Castilla-La Mancha.

Firstly, the fast pyrolysis conditions were optimized using lignin as the reference biomass. Optimum results were obtained at a heating rate of 500 °C, 20 °C ms\(^{-1}\) and 15s as the vapour residence time.

The initial composition of the olive pomace was seen to influence the pyrolysis product distribution and the higher the fat content, the more carboxylic acid was produced. In addition, the chemical composition of the samples (cellulose, hemicellulose and lignin) also determined which products were formed. High lignin content enhanced phenol production, whereas cellulose decomposed to carboxylic acids. In addition, the presence of metals was another important factor to consider because some minerals such as calcium, potassium or magnesium could have acted as catalysts in the process.

Finally, olive pomace origin, extraction and the drying methods used at the olive mill determined the amount of greenhouse gases given off. In the samples under observation, OPGC showed the lowest value of kg of CO2 equivalent due to its low volatile matter and fat content. In comparison with the commercial production of phenol in terms of the amount of CO2 given off, using wastes from olive pomace could reduce this with further research and experiments.
Acknowledgments

The authors wish to thank the Regional Government of Castilla-La Mancha for their financial support (Project SBPLY/17/180501/000238).

References


López-González D, Fernandez-Lopez M, Valverde JL, Sanchez-Silva L.


Table 1. Ultimate analysis, proximate analysis, mineral content and chemical composition of the olive pomace samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Moisture (wt.%)</th>
<th>Ash (wt.%)</th>
<th>Volatile matter (wt.%)</th>
<th>Fixed carbon (wt.%)</th>
<th>C (wt.%)</th>
<th>H (wt.%)</th>
<th>N (wt.%)</th>
<th>O (wt.%)</th>
<th>S (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPGC</td>
<td>2.12±0.05</td>
<td>4.77±0.05</td>
<td>80.73±0.05</td>
<td>12.38</td>
<td>7.17±0.49</td>
<td>1.54±0.01</td>
<td>32.30</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>OPMN</td>
<td>2.75±0.05</td>
<td>8.63±0.05</td>
<td>67.05±0.05</td>
<td>24.32</td>
<td>49.06±0.31</td>
<td>8.76±0.49</td>
<td>1.93±0.02</td>
<td>31.62</td>
<td>-</td>
</tr>
<tr>
<td>OPMNE</td>
<td>3.64±0.05</td>
<td>11.90±0.05</td>
<td>63.30±0.05</td>
<td>24.80</td>
<td>47.07±0.11</td>
<td>5.89±0.1</td>
<td>1.92±0.04</td>
<td>33.11</td>
<td>0.11±0.11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al (ppm)</th>
<th>Ca (ppm)</th>
<th>Fe (ppm)</th>
<th>K (ppm)</th>
<th>Mg (ppm)</th>
<th>Na (ppm)</th>
<th>Zn (ppm)</th>
<th>Si (ppm)</th>
<th>Ti (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPGC</td>
<td>-</td>
<td>2995±0.45</td>
<td>-</td>
<td>23±0.53</td>
<td>515±0.31</td>
<td>-</td>
<td>100±0.73</td>
<td>31±0.71</td>
<td></td>
</tr>
<tr>
<td>OPMN</td>
<td>164±0.55</td>
<td>4156±0.45</td>
<td>-</td>
<td>774±0.53</td>
<td>1335±0.31</td>
<td>189±0.92</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>OPMNE</td>
<td>234±0.55</td>
<td>8219±0.45</td>
<td>-</td>
<td>8105±0.53</td>
<td>1415±0.31</td>
<td>485±0.92</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Klason lignin (%)</th>
<th>Hemicellulose (%)</th>
<th>Extractives (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPGC</td>
<td>21.2±0.5 (0.025)</td>
<td>31.5±0.8 (0.045)</td>
<td>38.0±0.2 (0.007)</td>
</tr>
<tr>
<td>OPMN</td>
<td>24.1±0.5 (0.016)</td>
<td>27.6±0.8 (0.037)</td>
<td>38.9±0.2 (0.001)</td>
</tr>
</tbody>
</table>
Table 2. GHG emissions produced during pyrolysis.

<table>
<thead>
<tr>
<th></th>
<th>GWP (kg CO₂ eq)</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OPGC</td>
<td>OPMN</td>
</tr>
<tr>
<td>CO₂</td>
<td>3.91E-08±1E-9</td>
<td>3.59E-08±1E-9</td>
</tr>
<tr>
<td>CH₄</td>
<td>3.56E-07±1E-9</td>
<td>5.19E-07±1E-9</td>
</tr>
<tr>
<td>TOTAL</td>
<td>3.95E-07±1E-9</td>
<td>5.55E-07±1E-9</td>
</tr>
</tbody>
</table>