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 ºC, 20 ºC 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 CO_2 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 CO_2 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, solid biochar 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 ºC), 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.[8] Moreover, olive pomace has negative effects on soil because of its phytotoxicity and antimicrobial properties.[9] 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.[10,11] Thus, it cannot only destroy microbes directly but can also regulate immune function indirectly.[12]

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

121 detector. The proximate analysis gave information about volatile matter, fixed carbon and
122 ash content and the ultimate analysis was used to find out the concentration of carbon,
123 hydrogen, nitrogen, oxygen and sulphur in the sample. In addition, the content of metals
124 in the sample was determined by Inductively Coupled Plasma Spectrometry (IPC).
125 The hemicellulose and Klason lignin contents in the lignocellulosic biomass samples
126 were calculated according to the following experimental methodology. The extractives
127 contents was determined by successively extracting with the Soxhlet system using
128 dichloromethane (6 h), ethanol (16 h) and water (16 h) as an adaptation from TAPPI 204
129 om-97. After extraction, the sample was dried at 110 ºC for 1h and cooled to room
130 temperature in a desiccator. The extractives solubilized by the solvents were determined
131 by mass differences in the solid.[13]
132 Lignin content was determined with the Klason method (TAPPI T 222 om-02). The
133 samples (350 mg) of extractive-free material were added to 3ml of H_2SO_4 (72 %) at 30
134 ºC for 1h, then diluted to 3 % w/w H_2SO_4 and reacted in an autoclave for 1h at 120 ºC.
135 The residue was filtered, washed until neutralization, dried at 110ºC until reaching a
136 constant weight and cooled to room temperature. The weight difference after treatment
137 determined the amount of lignin.[13]
138 For determining hemicellulose contents, 150ml of NaOH solution (0.5 M) were added to
139 1g of extractive-free material and boiled for 3.5 h with recycled water. The product was
140 filtered, washed until neutralization, dried at 110 ºC for 1h and cooled to room
141 temperature. The weight difference after treatment determined the amount of
142 hemicellulose.[14]
143 The proximate analysis, ultimate analysis, metal contents and chemical composition of
144 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 spectroscopy (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).

$$GHG\ emissions = \sum(emissions_{gas} \cdot GWP_{100}) \qquad (1)$$

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 ºC), 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 $\alpha = 0.05$, 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

192 biomass. It is an aromatic, three-dimensional and cross-linked phenol polymer formed by
193 differently bonded “hydroxyl-” and “methoxy-” substituted phenylpropane units.[16] Our
194 objective was to use a reference biomass instead of an unknown one which may have
195 prone to changing. Thus, it would in turn aid us in subsequent studies with lignocellulosic
196 biomass.

197 The main process parameters studied were temperature (ºC), heating rate (ºC ms^{-1}) and
198 vapour residence time (s). Our objective was to evaluate the main products of fast
199 pyrolysis such as alcohols, aldehydes, alkanes, ketones, phenols or cyclic hydrocarbon.
200 The most representative group in this feedstock were phenol derivatives from the
201 depolymerization of lignin. Thus, the optimal conditions were selected on the basis of
202 maximum phenol production. Although its peak area was calculated considering all bio-
203 oil product areas, it can be observed that, in all cases, phenol production represented over
204 80% of the total product distribution whose results are shown in Fig. 1.

205 Fast pyrolysis is characterized by moderate temperatures, high heating rates and short
206 residence times. The effect of temperature was analysed at 400, 500, 600, 700, 800 and
207 900 ºC. As expected, optimum results were obtained at 400 and 500 ºC, which is in good
208 agreement with those reported in the literature.[17–19]

209 The heating rate varied between 5 and 20 ºC ms^{-1}. Higher rates promoted bio-oil
210 production since mass and heat transfer limitations were reduced. Vapour residence time
211 varied between 10 and 25s. Lower times enhanced bio-oil production because secondary
212 reactions were minimised by quickly removing the organic vapours from the reaction
213 zone. However, low residence time may not lead to a high quality liquid product because
214 it favours macromolecule products due to the random breakage of lignin.[1,20] Although the
215 whole range for both parameters was typical in fast pyrolysis, higher phenol production

was obtained at 20 ºC 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

240 triacylglycerol, were lower in the OPMNE sample. This was associated with its low oil
241 content.[22]

242 3.2.2. Thermogravimetric analysis (TGA).

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

264 3.2.3 Scanning electron microscopy (SEM).

265 Fig. 4 shows representative SEM images of the untreated olive pomace and the residues
266 obtained after fast pyrolysis. As can be seen in Fig. 4A, 4C and 4E, the olive pomace
267 before pyrolysis was formed by single particles measuring between 100 and 150 microns.
268 In addition, its surface morphology was very smooth in comparison with the residue with
269 almost no irregularities. However, if we look at Fig. 4B, 4D and 4F, we can see that the
270 structure sample after pyrolysis changed. The particles agglomerated which might have
271 been due to the low melting point of lignin, which facilitated the agglomeration of lignin
272 during pyrolysis.[19] In addition, the pore structure was remarkable and this could be
273 associated with the release of volatile matter.[24] Although all the residues had a porous
274 structure, OPGC (Fig. 4B) was the most porous because the amount of volatile matter and
275 the hemicellulose content were higher in this sample (Table 1).

276 3.3 Py-GC/MS analysis of olive mill wastes.

277 Firstly, olive pomace from different olive mills were compared to evaluate how olive crop
278 location could affect the formation of products in fast pyrolysis. In addition, there were
279 some remarkable differences attributed to the olive mill plant size. *Aceites García de la*
280 *Cruz* is a small size olive mill that processes more homogeneous and more localised olive
281 varieties than *Montes Norte* mill. The latter, as a medium size olive mill, works with a
282 great diversity of olive trees from different locations. Fig. 5 shows the product distribution
283 obtained from the pyrolysis of each olive pomace. The identified compounds were
284 classified into the following groups: alcohols, aldehydes, alkanes, carboxylic acids, cyclic
285 hydrocarbons, ketones, esters, nitrogen compounds, phenols and sugars (see Table S1).
286 In order to better understand these results, a scheme of the possible reaction mechanism
287 for cellulose, hemicellulose and lignin during fast pyrolysis, based on the literature,[3,25]

288 was shown in Fig. 6A. The reaction pathways of the olive oil fast pyrolysis and its
289 influence on the results, as previously commented, are also illustrated in Fig. 6B.

290 The main differences in the fast pyrolysis product distribution concerned alcohols,
291 aldehydes, esters, carboxylic acids and nitrogen compounds. The OPGC sample produced
292 higher amounts of carboxylic acids and aldehydes and lower amounts of alcohols and
293 nitrogen compounds than did the OPMN sample. These differences were mainly
294 attributed to the chemical composition of the samples as can be seen in Table 1. Fig. 6A
295 shows that, at higher temperatures (≥ 400 ºC), cellulose undergoes secondary
296 decomposition to produce furan compounds and light oxygenates. Hemicellulose
297 degradation mainly yields carboxylic acids and non-aromatic ketones. Furthermore,
298 lignin decomposes to methoxyphenols and at higher temperatures (≥ 500 ºC) secondary
299 decompositions favour the formation of aliphatics.[3,26] Therefore, the OPMN sample,
300 which was higher in lignin had more alcohol compounds after the reaction. However, fast
301 pyrolysis of the OPGC sample, with a higher amount of hemicellulose content, promoted
302 the formation of aldehydes and carboxylic acids compounds. These results were in very
303 good agreement with TGA (Fig. 3) and the chemical composition analysis (Table 1).

304 In addition, these differences in alcohols and carboxylic acids could also be associated
305 with the fat content. The olive oil was mainly composed of carboxylic acids such as oleic,
306 maleic or linoleic acids (Fig. 6B), which were decomposed to lighter ones, alcohols and
307 alkenes after fast pyrolysis. Then, in order to verify this, a Py-GC/MS analysis of pure
308 olive oil (Fig. S4) was carried out. As expected, the main products were carboxylic acids,
309 alkanes and alcohols, which were derived from deoxygenation and cracking reactions that
310 took place simultaneously.[26] Therefore, the differences between the OPGC and OPMN
311 samples were also clearly associated with their fat content.

312 Looking at Fig. 5, phenols were the most representative group after fast pyrolysis in the
313 samples under observation. They were oxygenated aromatic compounds of great interest
314 since they had pharmaceutical and cosmetic properties.[6,27] Moreover, they could be
315 separated from the bio-oil for subsequent use as fine chemicals. Their production was
316 attributed to the lignin content in the initial sample because they were the main by-
317 product in lignin decomposition. Here, there were no significant differences between both
318 samples.

319 A second study was carried out to analyse the differences between the OPMN and
320 OPMNE samples. The latter underwent extraction with hexane, in which the remaining
321 oil was partially removed from the olive pomace. Fig. 7 shows the pyrolysis product
322 distribution. Table S1 shows the integrated peak areas for the three olive pomace samples.

323 The main difference was observed in the phenol and esters compounds. In the mineral
324 composition (Table 1), a remarkable difference could be observed in potassium content
325 (774 and 8105 ppm for OPMN and OPMNE, respectively). Hwang et al. reported that
326 phenol production increased with rising potassium, thereby indicating that
327 demethoxylation from lignin was enhanced by this mineral during pyrolysis.[28] Zhang et
328 al. concluded that potassium in biomass changed the composition of the bio-oils
329 obtained: yields of aldehydes, esters and sugars decreased, while furans and phenols
330 increased.[29] Therefore, the differences in phenol production between the OPMN and
331 OPMNE could be attributed to the presence of potassium, as there was ten times more of
332 it in OPMNE of it than in OPMN.

333 3.4 Gas emissions: CO_2 burden

334 A thermogravimetric analysis coupled with a MS spectroscopy was carried out to measure
335 gas emissions in continuous and real time. The experiments were performed from 25 to

336 900 ºC at a heating rate of 10 ºC min^{-1}. It was assumed that the gas given off was mainly
337 composed of H_2, CO, CO_2, CH_4, C_2 hydrocarbons, NOx and SO_2. Those corresponding to
338 individual gases, H_2O, CH_4 and CO_2 were the highest yielded.

339 To calculate the CO_2 burden in light of the IPCC report(15), CO_2 and CH_4 emissions were
340 considered. Then, according to equation 1, GHG emissions were converted into climatic
341 impact (in kg of CO_2 equivalent) considering the Global Warming Potential (1 and 28 for
342 CO_2 and CH_4, respectively). The results obtained are reflected in Table 2.

343 In short, the OPGC sample gave off the lowest amount of greenhouse gases, followed by
344 OPMNE and OPMN. These differences were mainly attributed to lower yields of CH_4
345 and CO_2 in the former (Table 2). Moreover, although yields of CH_4 were lower in
346 comparison with CO_2, CH_4 had more impact on the GWP value due to its high emission
347 metric values. When the samples were received, the drying degree of the OPMN and
348 OPMNE samples were higher than the OPGC one and their fat contents were also lower,
349 as expected in the different working procedures in the olive mills under observation.
350 Therefore, the wastes and by-products generated during olive oil production were highly
351 dependent on the technology used, and it was essential to gain detailed knowledge of all
352 the steps in this process.

353 In addition, we made a comparison between the environmental viability of producing
354 some important chemicals by fast pyrolysis and the corresponding traditional process.
355 Fast pyrolysis was selected due to the high quantity of phenol obtained. The results were
356 compared with those for traditional phenolic production as found in the Ecoinvent
357 database.[30] In this evaluation, only CO_2 emissions were considered due to the limitations
358 of this database. The amount of CO_2 given off in traditional phenol production was 2.10E-
359 01 kg CO_2 kg $phenol^{-1}$, while the CO_2 values obtained in this research were in the range

360 of 2.88E-03 and 3.66E-03 kg CO_2 kg phenol^{-1}. Therefore, from an environmental point
361 of view, fast pyrolysis was considered to be very promising and further studies in this
362 respect should be carried out.

363

364 **4. Conclusions**

365 Fast pyrolysis of three different types of olive pomace samples was carried out to
366 determine how grove location and extraction treatment could influence bio-oil product
367 distribution. Olive pomace was selected as it could provide a use for waste from olive oil
368 due to the importance of this sector in Castilla-La Mancha.
369 Firstly, the fast pyrolysis conditions were optimized using lignin as the reference biomass.
370 Optimum results were obtained at a heating rate of 500 ºC, 20 ºC ms^{-1} and 15s as the
371 vapour residence time.
372 The initial composition of the olive pomace was seen to influence the pyrolysis product
373 distribution and the higher the fat content, the more carboxylic acid was produced. In
374 addition, the chemical composition of the samples (cellulose, hemicellulose and lignin)
375 also determined which products were formed. High lignin content enhanced phenol
376 production, whereas cellulose decomposed to carboxylic acids. In addition, the presence
377 of metals was another important factor to consider because some minerals such as
378 calcium, potassium or magnesium could have acted as catalysts in the process.
379 Finally, olive pomace origin, extraction and the drying methods used at the olive mill
380 determined the amount of greenhouse gases given off. In the samples under observation,
381 OPGC showed the lowest value of kg of CO_2 equivalent due to its low volatile matter and
382 fat content. In comparison with the commercial production of phenol in terms of the
383 amount of CO_2 given off, using wastes from olive pomace could reduce this with further
384 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

1. Kan T, Strezov V, Evans TJ. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. Renew Sustain Energy Rev [Internet]. 2016 May 1 [cited 2019 Jun 27];57:1126–40. Available from: https://www.sciencedirect.com/science/article/pii/S1364032115015683
2. Chen X, Zhang H, Song Y, Xiao R. Prediction of product distribution and bio-oil heating value of biomass fast pyrolysis. Chem Eng Process Intensif. 2018;130:36–42.
3. Qureshi KM, Lup ANK, Khan S, Abnisa F, Daud WMAW. A technical review on semi-continuous and continuous pyrolysis process of biomass to bio-oil. J Anal Appl Pyrolysis. 2018;131:52–75.
4. Mamleev V, Bourbigot S, Le Bras M, Yvon J. The facts and hypotheses relating to the phenomenological model of cellulose pyrolysis: Interdependence of the steps. J Anal Appl Pyrolysis [Internet]. 2009 Jan 1 [cited 2019 Jun 25];84(1):1–17. Available from: https://www.sciencedirect.com/science/article/pii/S0165237008001460
5. Bridwater AV. Review of fast pyrolysis of biomass and product upgrading. Biomass and Bioenergy [Internet]. 2012 Mar 1 [cited 2020 Mar 17];38:68–94. Available from:

https://www.sciencedirect.com/science/article/pii/S0961953411000638

6. Medina E, Romero C, Brenes M. Residual Olive Paste as a Source of Phenolic Compounds and Triterpenic Acids. Eur J lipid Sci Technol. 2018;120(4):1700368.

7. Berbel J, Posadillo A. Review and analysis of alternatives for the valorisation of agro-industrial olive oil by-products. Sustainability. 2018;10(1):237.

8. Parascanu MM, Puig Gamero M, Sánchez P, Soreanu G, Valverde JL, Sanchez-Silva L. Life cycle assessment of olive pomace valorisation through pyrolysis. Renew Energy [Internet]. 2018 Jul 1 [cited 2019 Jun 27];122:589–601. Available from: https://www.sciencedirect.com/science/article/pii/S096014811830171X

9. Volpe M, D'Anna C, Messineo S, Volpe R, Messineo A. Sustainable production of bio-combustibles from pyrolysis of agro-industrial wastes. Sustainability. 2014;6(11):7866–82.

10. Ma N, Ma X. Dietary amino acids and the gut-microbiome-immune axis: physiological metabolism and therapeutic prospects. Compr Rev Food Sci Food Saf. 2019;18(1):221–42.

11. Nie C, He T, Zhang W, Zhang G, Ma X. Branched chain amino acids: beyond nutrition metabolism. Int J Mol Sci. 2018;19(4):954.

12. Wu J, Ma N, Johnston LJ, Ma X. Dietary nutrients mediate intestinal host defense peptide expression. Adv Nutr. 2020;11(1):92–102.

13. Miranda I, Simões R, Medeiros B, Nampoothiri KM, Sukumaran RK, Rajan D, et al. Valorization of lignocellulosic residues from the olive oil industry by production of lignin, glucose and functional sugars. Bioresour Technol [Internet]. 2019 Nov 1 [cited 2019 Nov 18];292:121936. Available from: https://www.sciencedirect.com/science/article/pii/S0960852419311666

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

Thermogravimetric-mass spectrometric analysis on combustion of lignocellulosic biomass. Bioresour Technol [Internet]. 2013 Sep 1 [cited 2019 Nov 18];143:562–74. Available from: https://www.sciencedirect.com/science/article/pii/S0960852413009711

15. Pachauri RK, Meyer L, Hallegatte France S, Bank W, Hegerl G, Brinkman S, et al. Climate Change 2014 [Internet]. Kristin Seyboth (USA). Gian-Kasper Plattner; [cited 2020 Feb 19]. Available from: http://www.ipcc.ch.

16. Montzka SA, Reimannander S, Engel A, Kruger K, Sturges WT, Blake DR, et al. Ozone-Depleting Substances (ODSs) and Related Chemicals, Chapter 1 in Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project-Report No. 52, 516 pp., World Meteorological Organization, Geneva, Switzerland, 2011.| NIST. 2011.

17. Dhyani V, Bhaskar T. A comprehensive review on the pyrolysis of lignocellulosic biomass. Renew Energy [Internet]. 2018 Dec 1 [cited 2019 Jun 27];129:695–716. Available from: https://www.sciencedirect.com/science/article/pii/S0960148117303427

18. Hu X, Gholizadeh M. Biomass pyrolysis: A review of the process development and challenges from initial researches up to the commercialisation stage. J Energy Chem. 2019;

19. Lestander TA, Sandström L, Wiinikka H, Öhrman OGW, Thyrel M. Characterization of fast pyrolysis bio-oil properties by near-infrared spectroscopic data. J Anal Appl Pyrolysis. 2018;133:9–15.

20. Fan L, Zhang Y, Liu S, Zhou N, Chen P, Cheng Y, et al. Bio-oil from fast pyrolysis of lignin: Effects of process and upgrading parameters. Bioresour Technol. 2017;241:1118–26.

21. Akar T, Tosun I, Kaynak Z, Ozkara E, Yeni O, Sahin EN, et al. An attractive agro-industrial by-product in environmental cleanup: Dye biosorption potential of untreated olive pomace. J Hazard Mater. 2009;166(2–3):1217–25.

22. Parascanu MM, Sandoval-Salas F, Soreanu G, Valverde JL, Sanchez-Silva L. Valorization of Mexican biomasses through pyrolysis, combustion and gasification processes. Renew Sustain Energy Rev. 2017;71:509–22.

23. Delgadillo I, Barros A, Nunes A. Quality evaluation of olives, olive pomace and olive oil by infrared spectroscopy. In: Olive Oil-Constituents, Quality, Health Properties and Bioconversions. IntechOpen; 2012.

24. Qiu S, Zhang S, Zhou X, Zhang Q, Qiu G, Hu M, et al. Thermal behavior and organic functional structure of poplar-fat coal blends during co-pyrolysis. Renew Energy. 2019;136:308–16.

25. Puig-Gamero M, Lara-Díaz J, Valverde JL, Sánchez P, Sanchez-Silva L. Synergestic effect in the steam co-gasification of olive pomace, coal and petcoke: Thermogravimetric-mass spectrometric analysis. Energy Convers Manag. 2018;159:140–50.

26. Chen C, Luo Z, Yu C. Release and transformation mechanisms of trace elements during biomass combustion. J Hazard Mater [Internet]. 2019 Dec 15 [cited 2019 Sep 17];380:120857. Available from: https://www.sciencedirect.com/science/article/pii/S0304389419308106?via%3Dihub

27. Asomaning J, Mussone P, Bressler DC. Pyrolysis of polyunsaturated fatty acids. Fuel Process Technol [Internet]. 2014 Apr 1 [cited 2019 Sep 26];120:89–95. Available from: https://www.sciencedirect.com/science/article/pii/S0378382013003780

28. Hwang H, Oh S, Cho T-S, Choi I-G, Choi JW. Fast pyrolysis of potassium impregnated poplar wood and characterization of its influence on the formation as well as properties of pyrolytic products. Bioresour Technol. 2013;150:359–66.
29. Zhang H, Ma Y, Shao S, Xiao R. The effects of potassium on distributions of bio-oils obtained from fast pyrolysis of agricultural and forest biomass in a fluidized bed. Appl Energy [Internet]. 2017;208(April):867–77. Available from: https://doi.org/10.1016/j.apenergy.2017.09.062
30. ecoinvent [Internet]. [cited 2020 Feb 19]. Available from: https://www.ecoinvent.org/

495 **Tables**

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

	Proximate analysis (wt.%)*daf				Ultimate analysis (wt.%)*daf				
Sample	Moisture	Ash	Volatile matter	Fixed carbon*diff	C	H	N	O*diff	S
OPGC	2.12±0.05	4.77±0.05	80.73±0.05	12.38	51.22±0.41	7.17±0.49	1.54±0.01	32.30	-
OPMN	2.75±0.05	8.63±0.05	67.05±0.05	24.32	49.06±0.31	8.76±0.49	1.93±0.02	31.62	-
OPMNE	3.64±0.05	11.90±0.05	63.30±0.05	24.80	47.07±0.11	5.89±0.1	1.92±0.04	33.11	0.11±0.11
P-value	<0.001	<0.001	<0.001	-	<0.001	<0.005	<0.005	-	<0.005

	Mineral content (ppm)								
Sample	Al	Ca	Fe	K	Mg	Na	Zn	Si	Ti
OPGC	-	2995±0.45	-	23±0.53	515±0.31	-	-	100±0.73	31±0.71
OPMN	164±0.55	4156±0.45	-	774±0.53	1335±0.31	189±0.92	-	-	-
OPMNE	234±0.55	8219±0.45	-	8105±0.53	1415±0.31	485±0.92	-	-	-
P-value	<0.001	<0.001	-	<0.001	<0.001	<0.001	-	<0.001	<0.001

	Chemical composition (wt.%)*db (p-value)		
Sample	Klason lignin (%)	Hemicellulose (%)	Extractives (%)
OPGC	21.2±0.5 (0.025)	31.5±0.8 (0.045)	38.0±0.2 (0.007)
OPMN	24.1±0.5 (0.016)	27.6±0.8 (0.037)	38.9±0.2 (0.001)

OPMNE	24.6±0.5 (0.026)	28.5±0.8 (0.036)	34.3±0.2 (0.013)

498 [*daf]: dry and ash free basis; O[diff]: % of oxygen calculated from differences in C, H, N and S; VM:
499 Volatile matter; fixed carbon[diff]: % of fixed carbon calculated from differences in moisture, ash
500 and volatile matter; *[db]: dry basis.
501
502 **Table 2.** GHG emissions produced during pyrolysis.

	GWP (kg CO_2 eq)			P-value
	OPGC	OPMN	OPMNE	
CO_2	3.91E-08±1E-9	3.59E-08±1E-9	3.08E-08±1E-9	<0.001
CH_4	3.56E-07±1E-9	5.19E-07±1E-9	4.51E-07±1E-9	<0.001
TOTAL	3.95E-07±1E-9	5.55E-07±1E-9	4.81E-07±1E-9	

503
504