VALORIZATION OF OLIVE OIL INDUSTRY SUBPRODUCTS: ASH AND OLIVE POMACE FAST PYROLYSIS

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Abstract

Environmental problems have encouraged investigation of renewable energies. The organic waste treating through fast pyrolysis seems to be a highly promising option for decreasing pollutants. Olive pomace, a major source of waste in countries with high production of olive oil (mainly Spain, Italy, and Greece), is a clear target for valorisation. Dried olive pomace together with the ashes obtained during the drying process was blended to study the influence of the inorganic metals inherently present in the ashes (K, Na, Ca and Mg) for fast pyrolysis product distribution. The results determined that these metals increased yields of phenolic compounds until a maximum was reached, whereas carboxylic acid yield fell due to the action of metals. In addition, aromatic hydrocarbons and polyphenols were obtained for those samples with a large amount of ash. Moreover, the formation of organic acids, such as acetic acid, requires a smaller proportion of ash in the blend. Finally, it has been found that the ashes could be used as a catalyst for producing better quality bio-oil, thereby avoiding extra costs and thus valorizing the industrial treatment olive pomace.

1. Introduction

As a result of the rising world population and continuous industrialization from developing countries, the demand for energy and its resources will considerably increase in the near future. Crude petroleum fuels at present cover about 40% of the world energy demand while at the beginning of the 20th century they accounted for only around 4% (Cabeza et al., 2018). Depletion of fossil fuels, growing environmental concern for reducing pollution and political commitment have encouraged research into developing some alternative renewable sources of energy to reduce greenhouse gas emissions. Thus, biomass as an energy source has emerged as one possible option which has a great potential for future applications (Dhyani and Bhaskar, 2018; Parascanu et al., 2018; Valenti et al., 2020). Lignocellulosic biomass is one of the resources of most interest to researchers, due to its abundance (about 180 million tons per year) and as it is an organic, renewable, natural resource (Kumar et al., 2008). It comes from food waste, and therefore, it does not compete with food production (Tripathi et al., 2016). In addition, it is considered to be an attractive feedstock for producing renewable energy and biofuels depending on the treatment while simultaneously reducing dependence on fossil fuels (Saraeian et al., 2019).

Olive oil production and related industries are very important in the Mediterranean area in terms of wealth, health and tradition, which account for approximately 90% of world olive oil production (Souilem et al., 2017; Yuzbasi and Selçuk, 2011). Spain ranks first in terms of olive oil area and production, which represents around 60% of the total area in the European Union and about 45% worldwide (Ministerio de Agricultura, 2020). According to the most recent data published in the Statistical Yearbook (2018), Andalusia is the Spanish region which more land dedicates to cultivate olives representing around

63%, followed with Castilla-La Mancha which dedicates approximately 15% of the total (MAPAMA, 2018).

In recent years, traditional olive oil mills have been replaced by extraction systems that use an industrial decanter to separate all the different phases by centrifugation (Dermeche et al., 2013). In this research, a two-phase decanter was used to pre-treat the raw material (Gómez-de la Cruz et al., 2015). This produced olive oil and wet pomace with high moisture content (50-70 %) and the content must be dried to treat it further (Miranda et al., 2019). Fig. 1, modified from (Gómez-de la Cruz et al., 2017), illustrates the trommel-rotary drying process used for producing dried olive pomace.
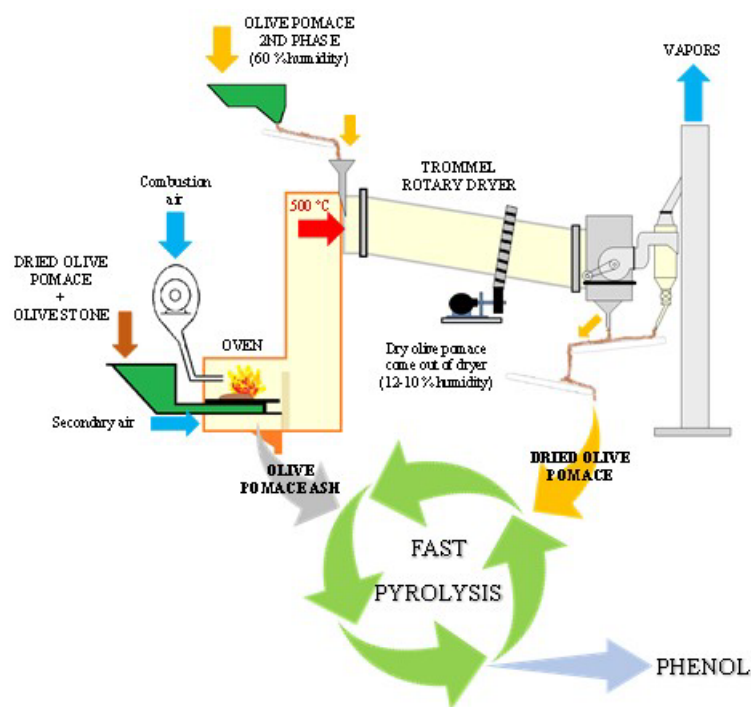

Figure 1. Integral valorization scheme of olive pomace wastes by fast pyrolysis.

Dried olive pomace contains high amount of organic matter, water-soluble fats, proteins, water-soluble carbohydrates, and water-soluble phenolic substances. It is also rich in potassium and poor in phosphorus and micronutrients (Parascanu et al., 2018).

However, it has environmentally harmful effects due to its phytotoxicity and antimicrobial properties (Volpe et al., 2014). This could be significantly reduced if the olive pomace were treated and revalued. As it was found for other biomasses, it could be converted into chemicals and energy mainly through thermochemical technologies (Puig-Gamero et al., 2020).

Pyrolysis is a thermochemical process that has attracted a great deal of interest due to its flexibility under operating conditions, technological versatility and adaptability to a wide variety of raw materials and products (Tripathi et al., 2016; W. Van Swaaij, S. Kersten, 2015). Three pyrolysis processes can be differentiated depending on the operating conditions, each of which is oriented to the production of desirable products. Fast pyrolysis leads to high bio-oil production (approximately 75 % wt.), which generally contains high added value chemicals such as phenolic compounds (Fan et al., 2017; Isahak et al., 2012). The operating conditions of fast pyrolysis process can easily be adjusted to maximize bio-oil production, as well as the quality of the obtained products (Al Arni, 2018). However, low quality and unstable bio-oil with a high content of acidic components is obtained in fast pyrolysis (Yildiz et al., 2015). These problems could be overcome by using a catalyst, which could increase costs. In this sense, olive pomace ashes, obtained from the olive pomace treatment (Fig. 1), are known to contain a high amount of alkaline and alkaline earth metals (AAEMs) which could act as alkaline activators (Alonso et al., 2019).

The effect of alkaline and alkaline earth metal ions on fast pyrolysis has attracted significant attention due to their inherent presence in these raw materials (Blasi et al., 2009; Várhegyi et al., 1997). Liu et al. (Liu et al., 2014) showed that potassium catalyzes pyrolytic reactions and promotes the formation of acetic acid from hemicellulose and methanol from lignin. Zhao et al. (Zhao and Li, 2016) studied the effect of using sodium

chloride as a catalyst in the pyrolysis of rice husk and concluded that better quality bio-oil was obtained. Alonso et al. (Alonso et al., 2019) characterized olive biomass ashes to determinate their potential as alkaline activators for preparing geopolymers.

However, there are no studies on the use of olive pomace ashes in catalytic fast pyrolysis. Therefore, the main aim of this research was to investigate the influence of different inherent metals (K, Na, Ca and Mg) on the final composition of the bio-oil produced in the fast pyrolysis of olive pomace. These metals were not externally added, but rather, were inherently present in the ashes produced in the drying of olive pomace. Therefore, the potential use of ashes as catalysts will be studied in this paper, trying to valorize the industrial pretreatment process of olive pomace.

2. Materials and methods

2.1 Materials

Olive pomace and olive pomace ashes were supplied by Montes Norte olive oil mill (Mora, Castilla-La Mancha, and Spain). As the olive pomace was dried, ashes were obtained. Different blends of both materials were prepared in varying proportions in each sample. Samples were defined depending on the proportion of olive pomace (O) and olive pomace ashes (A), from the drying stage in the trammel-type rotary dryer. To give an example, sample 75O_25A contained 75% of olive pomace and 25% ash. The other samples were named with the same nomenclature. After preparation, they were oven-dried for 24h, milled and sieved to obtain an average particle size ranging from 100 to 150 μm.

2.2 Methods

Ultimate and proximate analysis were performed to determine the composition of the different materials, according to standards UNE 15104:2011, UNE-EN ISO18123, UNE 32-004-84 and UNE 32-002-95. An elemental analyser, Thermo Fischer Scientific Flash 2000, equipped with a thermal conductivity detector. The proximate analysis gave information on moisture, ash, volatile matter and fixed carbon content. Also, the ultimate analysis was applied to find out the concentration of carbon, hydrogen, nitrogen, oxygen and sulphur in the sample. In addition, metal content was determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) with Varian 720-ES equipment that was previously calibrated using standard stock solutions.

The content of the extractives, hemicellulose and Klason lignin in the samples was calculated according to the following method: first, the content of the extractives was determined with an extraction process in which a Soxhlet system was used successively with 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 110ºC for 1h and cooled to room temperature in a desiccator. The amount of extractives solubilized by the solvents was determined from the mass difference in the solid (Miranda et al., 2019; TAPPI, 2018).

Lignin content was determined by the Klason method (TAPPI T 222 om-02). The samples (0.35 g) of extractive-free material were added to 3mL of H_2SO_4 (72 %) at 30ºC for 1h, then diluted to 3% w/w H_2SO_4 and reacted in an autoclave for 1h at 120ºC. The residue obtained was filtered, washed until neutralization, dried at 110ºC to a constant weight and then cooled to room temperature. The weight difference, determined after treatment, defined the amount of lignin (Miranda et al., 2019; TAPPI, 2018).

To determine the hemicelluloses content, 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 110ºC for 1h and cooled to room temperature. The weight difference after treatment was used to determine the amount of hemicellulose (López-González et al., 2013).

Table 1 shows the proximate, ultimate, metal content and chemical composition analysis of the olive pomace, whereas Table 2 shows the proximate and metal content analysis of the olive pomace and ashes blends.

Table 1. Properties of the olive pomace (100O_0A)

Proximate analysis (wt.%) *daf	
Moisture	2.75
Ash	8.63
Volatile matter	67.05
Fixed carbon	24.32
Ultimate analysis (wt. %)*daf	
C	49.06
N	1.93
O*diff	31.62
S	-
Metal content (wt. %)	
Ca	0.64
K	3.90
Mg	0.36
Na	2.29
Chemical composition (wt.%)*db	
Klason lignin	24.10
Hemicellulose	27.60
Extractives	38.90

*daf: dry and ash free basis; O^{diff}: % of oxygen calculated from the difference in C, H, N and S; VM: Volatile matter; fixed carbon^{diff}: % of fixed carbon calculated from the difference in moisture, ash and volatile matter; *db: dry basis.

Table 2. Proximate and metal content analyses of the different blends.

Proximate analysis (wt.%)[*daf]				
Blend	Moisture	Ash	Volatile matter	Fixed carbon [*diff]
75O_25A	4.18	27.08	59.35	9.39
50O_50A	4.84	43.24	48.86	3.07
25O_75A	5.15	61.48	33.23	0.15
0O_100A	6.12	76.22	17.29	0.36
Metal content (wt. %)				
Blend	Ca	K	Mg	Na
75O_25A	3.18	7.10	1.42	2.77
50O_50A	5.63	9.89	2.48	2.97
25O_75A	7.25	14.75	3.73	0.58
0O_100A	10.93	19.90	5.38	2.31

[*daf]: dry and ash free basis;

2.3 Fast pyrolysis experiments

Pyroprobe gas chromatography-mass spectrometer (Py-GC/MS) experiments for all the samples under study 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: 1 m; temperature: 340ºC).

1mg ± 0.05 mg of the different blends was placed in the middle of a quartz tube (2mm diameter and 20mm long) with a quartz wool base which was then fed into the platinum Pyroprobe autosampler. Pyrolysis was at 500 ºC, with a heating rate of 20 ºC/ms for 15s. The experiments were carried out three times for each sample.

The GC/MS injector temperature was kept at 280ºC. 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 and a 1:80 split ratio, the purpose of which was to separate and identify the chemical composition in the bio-oil. The oven temperature was programmed from 40ºC (3 min) to 280ºC at a heating rate of 5ºC/min. The chromatograms were integrated and the relative peak areas were calculated and subsequently identified using the NIST library as a reference. Only the peaks with a matching quality of over 75% were considered.

3. Results and discussion

3.1 Samples characterization

The characterisation results from the olive pomace, including the proximate and ultimate analysis, metal content and chemical composition are presented in Table 1. As expected, in the dried olive pomace sample, there was a low moisture content (2.75 wt.%). Water content was one of the main parameters under consideration in biomass pyrolysis, as it hinders the process if it is higher than 10wt.% (Hassan et al., 2020). High volatile matter (67.05wt.%) was observed which indicated the devolatilization of the biomass (Varma and Mondal, 2017). Regarding the chemical composition analysis, hemicellulose was the major fraction which made up 27.6wt.% of the total composition, whereas Klason lignin represented 24.1wt.% of the biomass and another group, composed of organic extractives, comprised 38.9 wt.%. These results were similar to those found in other works. For instance, Miranda et al. (2019), obtained a composition of 27wt.% in Klason lignin and 34.4wt.% in extractives, for olive pomace from a two-phase olive mill (Miranda et al., 2019). The chemical analyses by the ICP-OES technique detected certain amounts of alkali (K, Na) and alkali earth (Ca, Mg) metals, the most abundant of which was K (3.90 wt.%). Metal content was an important factor to take into account, as these

metals can catalyse several reactions involved in pyrolysis, and thus influence their performance and the final distribution of products (Chagas et al., 2016).

The proximate and metal content analysis of the different blends are shown in Table 2. The metal content analysis reveals that the most abundant inorganic elements in the biomass ashes were K and Ca, which represented 19.90 and 10.93 wt.%, respectively. There was also Mg (5.38 wt.%) and Na (2.31 wt.%) albeit in lower proportions. The metal content in the different blends was very approximately proportional to their quantity in the raw samples, olive pomace and ashes. Therefore, apart from K, the amount of Ca became significant as the amount of ashes increased in the blends. However, other metals such as Na and Mg, which were present in a lower proportion also needed to be considered as there is evidence they influence the pyrolysis product yield (Hernando et al., 2017; Hernando et al., 2016).

3.2 Effect of ash on product distribution

Fig. 2 shows the peak area (%) of the different compounds obtained during fast pyrolysis of the blends. The products detected were separated as the functional groups of alcohols, cyclic hydrocarbons, aldehydes, alkanes, carboxylic acids, ketones, esters, nitrogen compounds, phenols and sugars. Table S1 gives a detailed breakdown of the chemical compositions of the bio-oils produced by fast pyrolysis for the different samples.
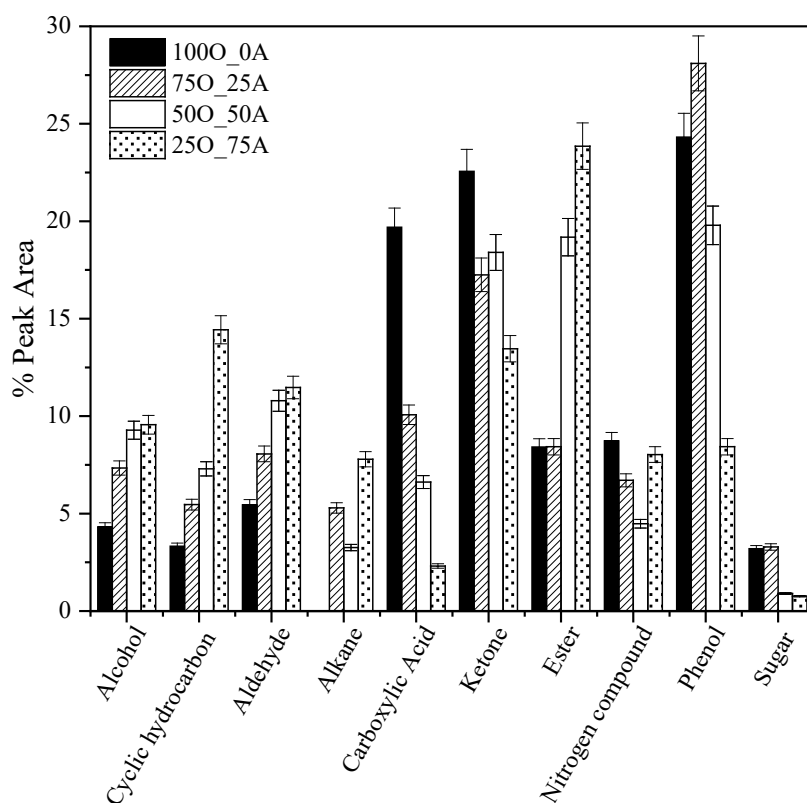
Figure 2. Comparison of the different functional groups obtained during fast pyrolysis of the blends.

As seen in Fig. 2, the composition of the bio-oil obtained during fast pyrolysis was highly influenced by the ash content in the sample. Thus, several changes are observable in the product distribution as the proportion of ash increases. The most representative functional group are phenolic compounds in samples with higher proportion of olive pomace in blend. Phenols, which are one of the most important products in bio-oil, are mainly produced by lignin decomposition (Wang et al., 2015). The yield of phenols increases as the proportion of ash rises due to the increase in metal content. These metals promote dehydration and demethoxylation reactions of lignin, which take place at 500ºC (Duan et al., 2019; Kawamoto, 2017). In addition, when ash proportion is 25 wt.%, phenolic content peaks (28.10%). However, if the amount of ash increases excessively, this promotes cracking and deoxygenation reactions, leading to a decrease in the

production of phenolic compounds and resulting in an increase in the proportion of alkanes and cyclic hydrocarbons in the bio-oil (Chen et al., 2019), as observed in Fig.2. It also explains why there are few alkanes and cyclic hydrocarbons when the amount of ash is low: a higher proportion of metals is necessary for initiating cracking and deoxygenation reactions.

Interestingly, levoglucosan (LGV), a typical product of biomass pyrolysis, was not observed (Table S1). The reasons for this are twofold: firstly, fast pyrolysis was carried out at a relatively high temperature (500 ºC), at which it keeps decomposing to form phenolic and alcoholic compounds (Chen et al., 2019). Secondly, the metals introduced by the ashes (mainly K and Ca) would have catalysed its degradation into other products (Liu et al., 2014; Patwardhan et al., 2010; Yildiz et al., 2015). In fast pyrolysis, cellulose generally first evolves into LVG and, then, it undergoes a dehydration reaction to evolve into anhydrosugars which are eventually transformed into linear aldehydes from ring scission reactions (Zhang et al., 2017), and these are catalysed by K. In addition, the presence of K can also hinder the formation of LVG and increase that of aldehydes, due to a competing fragmentation reaction (Trendewicz et al., 2015). This explains why the amount of aldehydes increases with the proportion of ash in the samples (from 5.45 to 11.47%).

Acids represent one of the main products obtained in bio-oils. Moreover, they have a significant effect on pH value, as they are an indicator of bio-oil quality (Zhang et al., 2017). As observed in Fig. 2, the yield of carboxylic acids decreased proportionally with the amount of ashes in the blends. Again, this is related to the increase in inherent metal content (Hernando et al., 2017). It also explains the increase in the yield of esters, due to the transformation of carboxylic acids into esters through esterification. As for

sugars, isosorbide is mainly present in the bio-oil whose yields decreased due to the addition of ash, through the action of K and Ca (Leng et al., 2017).

Regarding the formation of alcoholic compounds, they were favoured by the increase in the amount of ash. As mentioned above, and according to the literature, the presence of alkali metals suppresses the formation of LVG and, instead, promotes cellulose to undergo reactions of ring scission, isomerization, decarbonylation, decarboxylation or dehydration to form alcoholic compounds (Zhao and Li, 2016). Regarding the ketones, yields decreased as the amount of ash increased. If we look at this group in Table S1, it can be seen that K catalyzes the conversion of short ketones into ring shaped ketones due to its ability to convert cellulose into cyclic ketones (Zhang et al., 2017).

Finally, a consistent regularity in the quantity of nitrogen compounds (found in several chemical forms including amides, nitriles and aromatic amines) was observed. They came from the degradation of amino acids and proteins in the biomass (Schmeltz et al., 1972). Compared to oxygenated compounds, nitrogenates are far less affected by AEEMs (Chagas et al., 2016) and are not altered by them.

3.3. Deoxygenation selectivity.

Generally, catalytic fast pyrolysis of lignocellulosic biomass helps produce lower oxygenated bio-oils with higher stability and heating values (Fermoso et al., 2016; Kabir and Hameed, 2017). The pyrolysis products in contact with the catalyst may undergo a series of complex reactions such as catalytic cracking, oligomerisation, cyclisation, aromatisation and deoxygenation. The latter may be a result of the decarbonylation, decarboxylation or dehydration reactions, which lead to the formation of CO, CO_2 and H_2O, respectively (Hernando et al., 2017). Dehydration is the main deoxygenation route

under thermal conditions, followed by decarboxylation and decarbonylation (Hernando et al., 2016). However, a high degree of deoxygenation produces large amounts of aromatic hydrocarbons (Mukarakate et al., 2014). The presence of AAEMs in the blends have been put forward as a potential catalyst for carbonization reactions (Eom et al., 2013). In addition, the catalytic effect of mineral matter was not as effective in bio-oil deoxygenation, since it promoted an excessive amount of char formation, and in some cases retained over 40% of the energy from the initial biomass (Fermoso et al., 2017; Hernando et al., 2017).

Fig 3. shows how the distribution of blends displays the three possible routes of deoxygenation. The dehydration group is formed with the functional groups that involve the formation of water during the reaction. Moreover, with decarboxylation and decarbonylation, the functional groups included were those contributing to the formation of CO and CO_2 in their reactions, respectively.
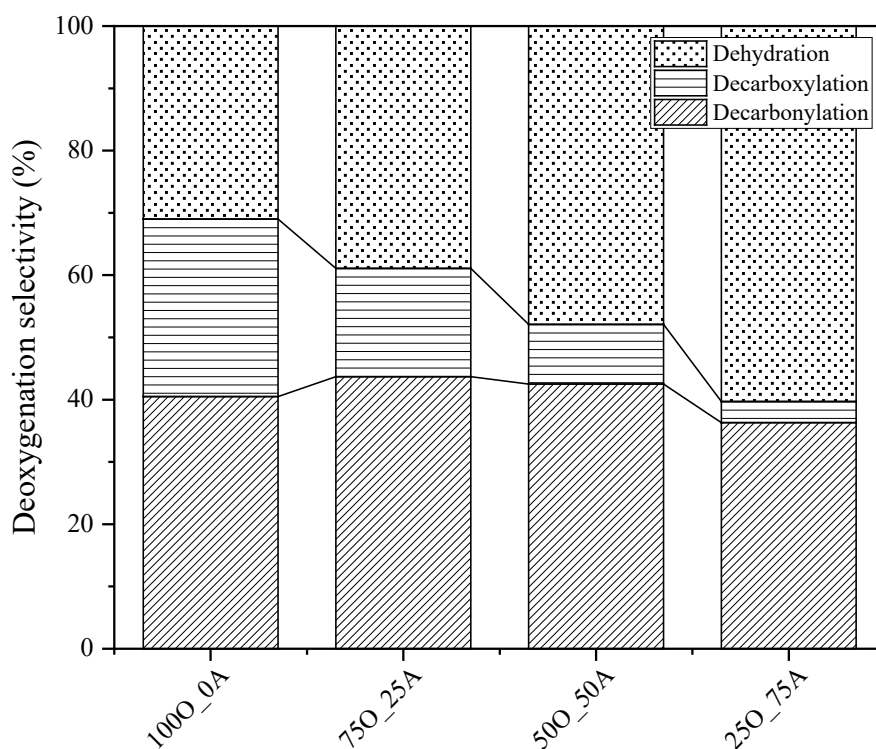
Figure 3. Deoxygenation selectivity obtained in the fast pyrolysis of the olive pomace and ashes blends.

In Fig. 3 it can be observed that in the absence of ash, i.e. with the raw material, decarbonylation seems to be the predominant pathway (40.5%), followed by dehydration (31%) and, finally, decarboxylation (28.5%). In addition, it can clearly be seen that the increase in ash in the sample favours decarbonylation and, especially, dehydration. When the blends have significant ash content, dehydration is promoted, and a high decrease in decarboxylation can be observed (from 28.5 to 3.4%). Furthermore, when the proportion of ashes in the sample is higher, there are high amounts of AAEMs. K may have interacted with the oxygen atoms to excite the hydrogen bonds during fast pyrolysis, which makes hydroxyl groups from phenol compounds unstable, thus causing dehydration reactions (Leng et al., 2017). In contrast, the percentage of decarboxylation decreased overwhelmingly when the ash content in the sample increased. These data reveal that dehydration became the main deoxygenation pathway observed when ash was used as the catalyst.

3.4. Comparison of the main products obtained with ash.

3.4.1. Comparison of cyclic hydrocarbons

Fig. 4. shows the cyclic hydrocarbons obtained in fast pyrolysis for the blends. 1,3,5-Cycloheptatriene and toluene were the main products detected.
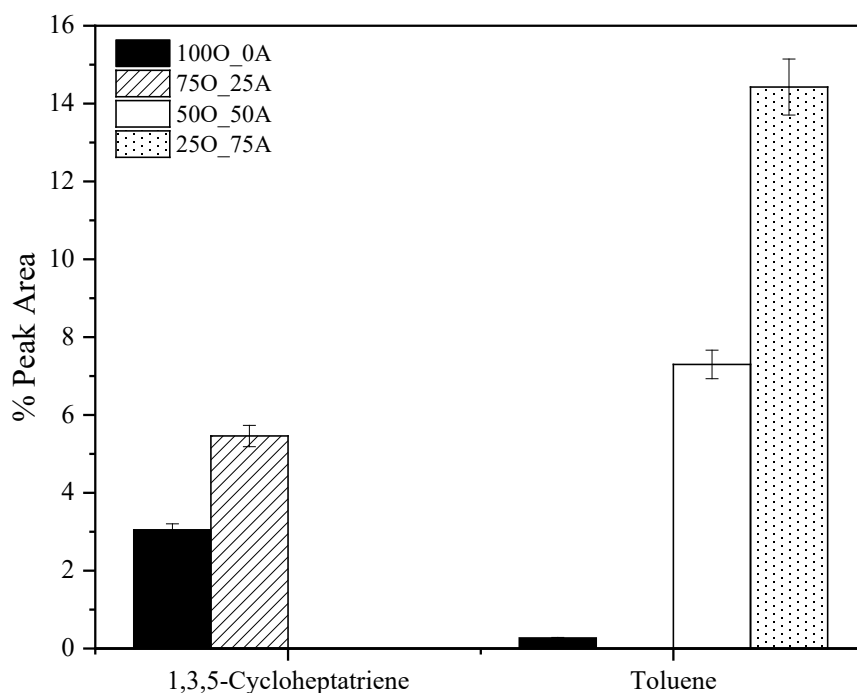
1,3,5-Cycloheptatriene was seen to be the main component obtained in the pyrolysis of the raw material and when there was more olive pomace than ash (75O_25A). Furthermore, toluene became the main component in blends with high amount of ash, especially in blend 25O_75A in which it accounted for 14.43 % of the total percentage of the sample. These results indicated that AAEMs caused this increase. The catalytic effect was observed in the increase in aromatic hydrocarbons and the decrease in phenols and the yields of nitrogen compounds remained the same or slightly decreased (Chagas et al., 2016). Du et al. (2013) also obtained aromatic compounds by increasing the catalyst to biomass ratio. Thus, it may be concluded that the formation mechanism for these cyclic hydrocarbons could be different from that for the aromatics (Kim et al., 2015). This shows that the intermediate compounds that form aromatic hydrocarbons are more active when there is a high proportion of ash in the blend. The inorganic substances in the ash,

especially K and Ca, catalysed the conversion of the cyclic ring leading to an increase in the degree of aromaticity.

3.4.2. Comparison of phenols

The comparison of the phenols obtained during fast pyrolysis of the samples with different proportions of ash and olive pomace is shown in Fig. 5. The most representative group in this feedstock was phenol, from the thermal degradation of the lignocellulosic structural material of the samples (Ducom et al., 2020). Lignin is a complex-dimensional amorphous macromolecule made from the polymerization of three phenylpropane units. Its main phenylpropane monomers could be categorized as guaiacyl, syringyl and p-hydroxyphenyl in proportions which depend on the origin of the molecule (Darvell et al., 2010; Dhyani and Bhaskar, 2018). The phenolic compounds in the bio-oil are mainly phenol, phenol 2-methoxy, 2-methoxy-4-vinylphenol, phenol 2,6-dimethoxy, 3-allyl-6-methoxyphenol and (E)-2,6-dimethoxy-4-(prop-1-en-1-yl)phenol. Some studies have demonstrated that: phenol and 2-Methoxy-4-vinylphenol are by-products from the pyrolysis of p-hydroxyphenyl lignin; phenol 2-methoxy is a by-product from the pyrolysis of guaiacyl lignin; and, phenol 2,6-dimethoxy and (E)-2,6-dimethoxy-4-(prop-1-en-1-yl)phenol come from the pyrolysis of syringyl lignin (Ducom et al., 2020).
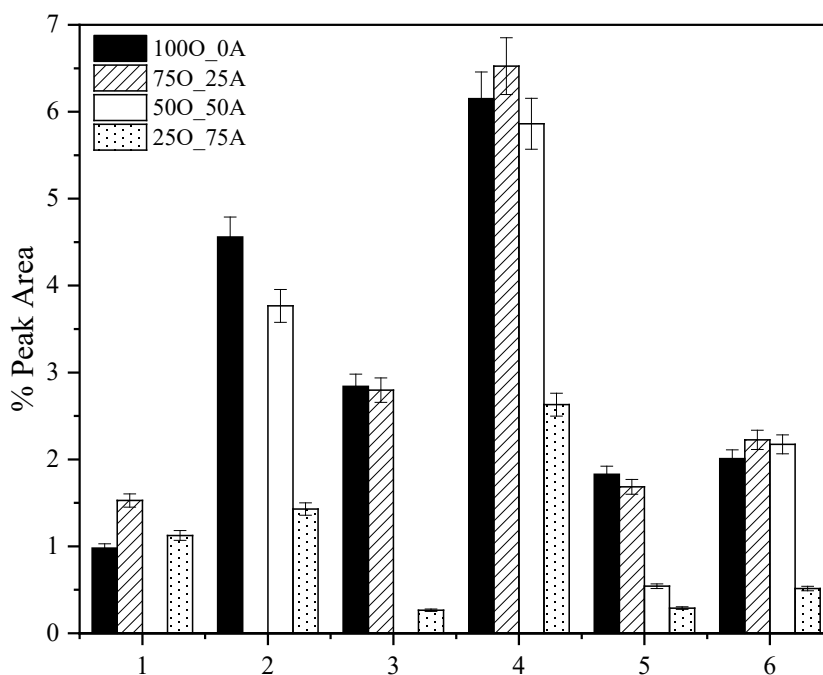
Figure 5. Comparison of the phenols obtained by means of fast pyrolysis products for the blends: (1) Phenol, (2) Phenol, 2-methoxy, (3) 2-Methoxy-4-vinylphenol, (4) Phenol 2,6-dimethoxy, (5) 3-Allyl-6-methoxyphenol and (6) (E)-2,6-Dimethoxy-4-(prop-1-en-1-yl) phenol.

Phenol 2,6-dimethoxy (4) was the main component in the phenols detected from the fast pyrolysis of biomass. It reduced by over half as a result of the increase in ash in the blend composition, from 6.15% in the raw sample to 2.63% in blend 25O_75A from the total amount of the sample. A maximum of 6.52% for blend 75O_25A was reached when the amount of inorganic matter was that needed to promote the cracking of lignin. Phenol 2-methoxy (2) is produced mainly in raw materials and it decreased significantly with the ash content in the blend in which there was a higher amount of AAEMs, specially K (Zhang et al., 2017). 2-Methoxy-4-vinylphenol (3) was mainly obtained for blends with high amounts of olive pomace, while it reduced strongly when ash content rose in the blend. As for phenol (1), a constant amount of it was detected for all the samples under

observation. There was a significant decrease in the selectivity of 3-Allyl-6-methoxyphenol (5) and (E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol (6) with high amounts of ash in the blend. Firstly, lignin depolymerised into small polymers and then, cracked into monophenols. According to Zhang et al., the addition of ash in the blends promotes the production of polyphenols from small polymers due to the catalytic effect of K (Zhang et al., 2017).

3.4.3. Comparison of carboxylic acids

Fig 6. shows a comparison of the carboxylic acid products obtained during fast pyrolysis of the evaluated blends. These included acetic acid (AA), oxalic acid and oleic acid.
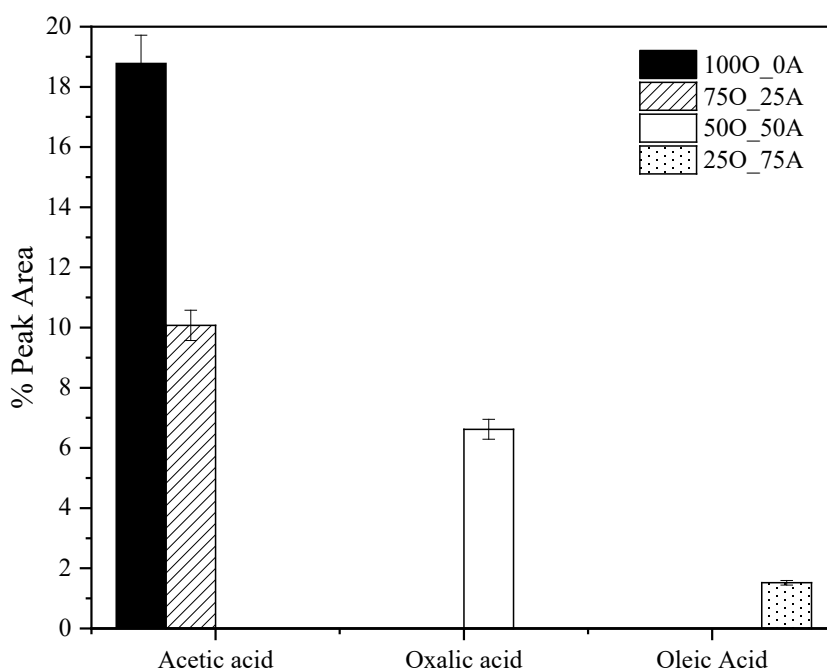

Figure 6. Comparison of carboxylic acids obtained in the fast pyrolysis of the blends.

Fig 6. shows the most representative compounds of carboxylic acid. Note that, as explained before, the yield of carboxylic acids decreased as ash content rose. Thus, fast pyrolysis led to improvements in the quality of the bio-oil produced due to the decrease

in these acids (Zhao and Li, 2016). In addition, high production of acetic acid was seen with pyrolysis of the raw material (18.78%). However, by adding a small amount of ash (75O_25A), the carboxylic acid produced was AA but in a smaller yield (10.07 %). Di Blasi et al. observed the same trend in AA yields using K (Blasi et al., 2009), which was the main metal in the ash. According to the literature, the main explanatory factor behind the higher yield of AA was the high hemicellulose content in the raw material, which underwent a ring scission reaction to produce the acid (Chen et al., 2019; Oh et al., 2017). For sample 100O_0A, there was a maximum yield of AA due to the high amount of hemicellulose (27.60 wt.%), as seen in Table 1. Other compounds appeared when the ash content such as oxalic acid, increased, which was obtained from the oxidative conversion of the cellulose in the raw material promoted by Na. This is generally used to produce rayon and for other type of uses such as clothing or leather manufacture, among others (Zhang and Huber, 2018). Finally, with the highest content of ash used (25O_75A), performance of carboxylic acids decreased greatly and they were mainly composed by oleic acid which is the main component of olive oil, which is also made up of linoleic, palmitic and stearic acid, and this is obtained from a partial degradation of the olive oil (Ducom et al., 2020; Jeguirim et al., 2020). According to the results, when a small quantity of ash is employed, AA is the predominant carboxylic acid obtained, whereas if a large amount of ash is used, it is mainly oleic acid that is yielded.

4. Conclusion

Fast pyrolysis experiments were performed to investigate the presence of metals in the blends to evaluate the composition of the products obtained. Results revealed that dehydration became the main deoxygenation pathway obtained when ash was used as the catalyst. The inorganic matter in the blends catalysed the conversion of the cyclic ring to aromatic hydrocarbons. Mainly, phenolic compounds were obtained, which peaked when

ash content was 25%. However, when ash content increased, cracking and deoxygenation reactions were promoted leading to a decrease in phenolic compounds. There were also improvements in the quality of the bio-oil obtained from blends of olive oil industry subproducts. The effect of ash blending ratio was investigated, revealing that a catalytic fast pyrolysis process could decrease the production of carboxylic acids as ash content grew higher.

Acknowledgments

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