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Olive mill wastewater: From a pollutant to green fuels, agricultural water source and bio-fertilizer. Biofuel Production

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- Abstract: Olive mill wastewater (OMWW) management is recognized as the major defy that olive oil industry is facing. Recently, we have established an eco-friendly strategy for OMWW conversion into irrigation water sources, green biofuels and biofertilizers. This work is a part of a series of papers detailing the different steps established in this environmental friendly strategy for OMWW management. It deals with the bio-oil production and characterization during the pyrolysis of OMWW impregnated on olive pomace (OP) in a pyrolyzer pilot.
- 8 Results show a bio-oil production yield of 36 wt.% during the pyrolysis test. This yield 9 could be attributed to the recovery of organic compounds from OMWW through OP 10 impregnation and their conversion to bio-oil. The bio-oil properties show that viscosity 11 and flash point values could reach the European standards. However, the lower heating 12 values (26 MJ/kg) and the acidic character limit its direct use. These values are attributed 13 to the higher water and oxygen contents. The GC/MS analysis confirms these properties 14 showing the presence of phenolic molecules and long chain organic acids. Therefore, 15 OMWW impregnation on OP and pyrolysis could be considered as a promising issue for 16 bio-oil production. However, this bio-oil requires an upgrading step for a better 17 valorization.
- 18

19 **Keywords:** Olive mill wastes; Pyrolysis; Bio-oil; Green fuel; Diesel properties; GC-MS.

20

21 **1.INTRODUCTION**

22 Olive oil production is recognized as one of the main food processing industries in the 23 Mediterranean countries. Each year, about 1.6 million tons of olive oil are extracted in the 24 Mediterranean basin representing more than 96% of the total olive oil extracted worldwide 25 [1]. The leading countries in olive oil production are Spain, Italy, Greece and Tunisia. 26 Typically, three kinds of extraction techniques are commonly used in the world. The pressure 27 process (olive presses), 2-phases separation system and 3-phases separation system. A 2-28 phases system is fully applied in Spain while in Italy, Greece and Tunisia still both systems 29 are used, but mainly the 3-phases system. A 2-phases system generates a humid solid waste (moisture ~ 60 wt.%) called "alperujo". However, the 3-phases system, due to the addition of 30 huge amounts of water during the decanting process, generates a solid residue named olive 31 32 mill solid waste (OMSW) or olive pomace (OP) and a liquid effluent named olive mill 33 wastewater (OMWW). The average amount of OMWW produced during the milling process 34 is 1.2–1.8 m³/t of olives. Therefore, annually over than 30 million m³ of OMWW is generated 35 in the Mediterranean region [2].

36 Sustainable OMWW management is recognized as a real defy for industrials of olive sector as well as for environment protection actors. Different OMWW treatment techniques and 37 38 procedures were mentioned in the literature including flocculation, centrifugation, 39 ultrafiltration, electrochemical oxidation and pellets production [3-7]. However, these 40 techniques were applied at laboratory scale without industrial development due to several constraints such as high economic costs, technical complexity and pollutants emissions. 41 42 Recently, Jeguirim et al. have developed an eco-friendly method for the OMWW treatment 43 was proposed [8-10].



- 44
- 45

46 Figure 1. An Eco-Friendly Strategy for OMWW conversion to green fuels, agricultural water
 47 source and bio-fertilizer [8-10].

This method, detailed in Figure 1, allows the conversion of OMWW into irrigation water source, green fuels and biofertilizers using different procedures. A first step consists on the impregnation of OMWW on dry lignocellulosic biomass such as OP or wood sawdust [9]. This impregnation step allows the retention of the organic and mineral compounds initially present in the OMWW on the dry biomass. The second step includes the convective drying of the impregnated samples and the condensation of the evaporated liquid phase. This recovered

54 water could be used as agriculture water source after tertiary treatment including pH

55 adjustment [10]. The third step is the thermochemical conversion of the dried impregnated 56 samples using the slow pyrolysis process. The latter technique has the advantage to generate solid, liquid and gaseous fractions that could be used in different manners. The solid fraction, 57 58 named biochar, could be used as bio-fertilizers due to its high nutrients concentrations, 59 especially potassium and phosphorus that was recovered during the OMWW impregnation. 60 The gaseous fraction, rich in methane, has a higher calorific contents and could be used as a 61 heating source for the pyrolyzer. The liquid fraction, named bio-oil, could be used as a green fuel or blended with petroleum refinery feedstocks [8]. This green fuel could be used directly 62 63 in the olive mill for heating purposes during the different oil production steps such as olive 64 washing and extraction process.

During the last decades, the biofuel production during organic wastes pyrolysis has received particular attention. Various resources including lignocellulosic biomass, agriculture and agrifood by-products and industrial wastes have been evaluated for bio-oil production [11-15]. These investigations have assessed the bio-oil yields production and also their main properties using different analytical techniques. Generally, the bio-oil yields depend strongly on both the feedstock composition (hemicellulose, cellulose and lignin contents, mineral contents) as well as the operating conditions (residence time, heating rate) [15-16].

The pyrolysis of olive wastes for bio-oil production have been examined in the literature [17-20]. Basically, olive solid wastes were subjected to slow, fast and flash pyrolysis for biofuel production. These experiments showed that the highest bio-oil yields were obtained at 500 °C reaching 30-40 wt. % from dry biomass. These bio-oils were categorized as aromatic, aliphatic and polar sub-fractions. The characterization of the aliphatic sub-fractions using a gas chromatography and infrared analysis indicates a mixture of alkanes and alkenes [19-20].

The OMWW pyrolysis is technically complicated due to the higher moisture content. Therefore, in the current eco-friendly strategy for OMWW treatment, a first step consisting on its impregnation on the OP was proposed [8]. This investigation as a part of a series paper aims to examine the bio-oil recovery during the slow pyrolysis of the impregnated samples and their characterization for a possible use as a green fuel.

83 **2. MATERIALS AND METHODS**

84 2.1.Olive Mill Wastes Preparation

85 The olive mill wastewaters (OMWW) and olive pomace (OP) used in this study were collected from a continuous chain oil mill (three phases centrifugal steps) located in the 86 87 Grombalia city (North East of Tunisia). The OMWW were firstly homogenized and then kept in plastic cans at 4 °C until use. Before each experiment, OMWW sample was centrifuged for 88 89 10 minutes at 3500 rpm in order to remove the contained suspended solids. Afterwards, this 90 sample was physico-chemically characterized by determining its basic parameters. 91 Concerning the OP, they were firstly sieved through a series of mechanical sieves in order to 92 remove large particles. Only the fraction with dimension smaller than 2 mm was retained and 93 used in this study. The sieved OP were dried in the open air until an approximate constant 94 weight and then physico-chemically characterized. Finally, they were afterwards stocked in 95 hermetic bags for further use.

96 **2.2.Impregnated Sample Preparation**

97 The OP impregnation by OMWW was performed in batch mode. It consists in mixing 3.2 kg
98 of OP with 8 L of OMWW using a magnetic stirrer "Yellow line OST Basic" under a stirring
99 speed of 700 rpm and a contact time of 2 hours. This amount corresponds to a dose of 400 g
100 of OP per litre of OMWW. The efficiency of this impregnation process on the retention of

101 OMWW's organic matter and main ions by OP was assessed at the end of the impregnation 102 experiment through tailored physico-chemical measurements.

103 **2.3.Biofuel Production**

104 The bio-oil production using pyrolysis technique was realized in a pyrolyzer pilot. This 105 pyrolyzer contains a vertical tubular furnace (Figure 2).



106 107

Figure 2. Axial plane of the used pyrolyzer

During biofuel production tests, 2 kg of the impregnated sample was positioned in the 108 109 different drawers of the pyrolyzer (Figure 3). Then, N₂ flow was injected constantly at ambient temperature during 30 min in order to remove residual oxygen. Afterwards, the 110 temperature was increased at a range of 5 °C min⁻¹ under N₂ at a flow rate of 10 NL.min⁻¹ 111 112 until the desired value (500 °C). The sample was maintained during 2 h at 500 °C then cooled under nitrogen flow at a flow rate of 1 NL.min⁻¹. During the pyrolysis test, the emitted gases 113 114 reached a condensing system formed by refrigerant connected to the liquid collector where 115 they were cooled by circulating cold water in order to collect the recovered bio-oil.



116 117

Figure 3. Impregnated Sample in the pyrolyzer drawers

118 **2.4.Bio-oil Characterization**

119 2.4.1. Bio-oil Physico-chemical Properties

120 A fuel elements analyser Flash 2000 (The Netherlands), a fuel calorimeter IKA C5000

121 (Germany) and a thermogravimeter TGA 4000 coupled with a gas chromatograph Clarus 680

and a mass spectrometer Clarus 600T (USA) were used for proximate and ultimate analysis of
 the bio-oil according to standards LST EN ISO 16948:2015, LST EN ISO 16994:2016.

- 124 The Acid Value (AC) value of the impregnated olive mill solid waste bio-oil was determined
- by a pH meter pHM210, (Radiometer analytical, Villeurbanne, France) at 20 °C. The pH meter was calibrated with standard buffer solutions, with pH values of 3.00 and 10.00.

127 Bio-oil electrical conductivity was measured using CDM210 conductimeter (Radiometer 128 analytical, Villeurbanne, France). Prior to conductivity test, the apparatus was calibrated with 129 a NaCl buffer solution of 0.01M at a conductivity of 1015 μ S/cm

The viscosity (both dynamic and kinematic) and density of the bio-oil was determined at 20
 °C by using a viscometer Anton-Paar Stabinger 3000 (Austria) according to LST EN ISO
 3104 and LST EN ISO 3675 standards.

- A flash point was measured according to the standard ISO 2719:2013 by a closed cup FP93
 5G2 Pensky–Martens analyzer (ISL, France).
- 135 2.4.2. Gas Chromatography-Mass Spectrometry (GC/MS) analysis

136 *Chemicals and reagents*

Reagents and standards were purchased from Sigma–Aldrich (St Quentin Fallavier, France)
for methoxyamine hydrochloride, phenoxyacetic acid, ferulic acid and squalene, Alfa Aesar

- 139 (by Thermo Fisher, Kandel, Germany) for anhydrous pyridine and MSTFA, Prolabo (Paris,
- 140 France) for myristic and palmitic acid, Merck (Darmstadt, Germany) for linoleic acid, TCI
- 141 (Paris, France) for oleic acid and Acros (by Fisher Scientific, Illkirch, France) for lignoceric
- 142 acid. LC-MS grade MeOH was purchased from Fisher Scientific (Illkirch, France).

143 Derivatization

Bio-oil was diluted 100 times with MeOH and 30 μ L of this sample was evaporated under vacuum after the addition of 50 μ L of 10 μ g/mL methanolic solution of phenoxyacetic acid as internal standard, used for retention time correction. Then, 20 μ L of 30 mg.mL⁻¹

147 methoxyamine hydrochloride in anhydrous pyridine were added and the sample was placed at

148 37 °C for 120 min under agitation at 600 rpm. After this time, 80 μ L of N-methyl-N-149 (trimethylsilyl)trifluoroacetamide (MSTFA) were added and the sample was incubated for 30 150 min at 37 °C and 600 rpm. The sample was allowed to rest for 60 min prior to GC-MS

151 injection.

152 GC-MS Instrument conditions

153 1 µL of derivatized sample was injected into a GC-EI-MS system comprising of a AOC-20i Autoinjector, a Shimadzu GC-2010 gas chromatograph and a Shimadzu GCMS-QP2010 mass 154 155 spectrometer (Shimadzu, Kyoto, Japan) with an electron impact (EI) ion source and 156 quadrupole analyzer. The GC was operated in constant linear velocity mode (40.3 cm.s⁻¹) with helium as a carrier gas. The MS was adjusted using perfluorotributylamine (PFTBA). A SGE 157 Analytical Science BPX5 column (25 m long, 0.15 mm inner diameter, 0.25 µm film 158 159 thickness) was used. The injection temperature in splitless mode was set at 310 °C, the MS 160 transfer line at 330 °C, the ion source adjusted to 200 °C. Helium was used as the carrier gas at a flow rate of 0.97 mL.min⁻¹. The following temperature program was used : injection at 161 110 °C, hold for 4 min, followed by a 10.5 °C.min⁻¹ oven temperature, ramp to 155 °C, then 162 11.5 °C.min⁻¹ oven temperature, ramp to 350 °C and a final 6 min heating at 350 °C. 163

Peaks with an area superior to 100 000 were integrated and annotated. The unknown
compounds were identified by comparing MS-spectra with the NIST mass spectral library
NIST 05 with at least 80 % of similarity.

167

168**3. RESULTS AND DISCUSSION**

169 **3.1.Bio-oil Production**

The established eco-friendly strategy for OMWW valorization aims to produce biofuels and biofertilizers (biochars). Therefore, the operating conditions of the impregnated samples pyrolysis were selected in order to obtain equivalent liquid fraction (bio-oil) and solid fraction (biochar) yields. Thus, based on previous investigations [8], a slow heating rate of 5°C/min and a temperature of 500°C allows the production of 34.4 wt.% of bio-oil and 36 wt. % of biochar. Such yields are typical for the slow pyrolysis of lignocellulosic biomass feedstocks.

The comparison of the obtained results with those reported in the literature for the slow pyrolysis of olive wastes shows closer bio-oil yields. In particular, Pütün et al. [19] studied the effect of final temperature during the olive residue pyrolysis at heating rate of 7 °C.min⁻¹. Authors showed that the bio-oil yield increased from 28.7 wt.% to 32.7 wt.% when the final

180 pyrolysis temperature increased from 400 to 500 °C then decreased to 30.2 wt.% at 700°C.

181 Other scientists have obtained relatively similar bio-oil yields during the olive wastes 182 pyrolysis although the operating conditions were extremely different (rapid and flash 183 pyrolysis). As an example, Demirbas [17] obtained bio-oil yields during olive cakes pyrolysis 184 at 423 °C of 31.0 wt.%, 36.0 wt.% and 41.0 wt.% when applying heating rates of 10 °C/s, 20 185 °C/s, and 40 °C/s, respectively. Zabaniotou et al. [18] showed that the bio-oil yields increased 186 to a maximum value of ~30 wt.% of dry biomass at about 450–550 °C during the pyrolysis of 187 olive residues at heating rate of 200 °C/s.

- 188 The obtained value of bio-oil during this present study is amongst the highest one (36 wt.%).
- 189 This value is attributed to the recovery of some organic compounds during OMWW
- 190 impregnation on OP phase. This statement is confirmed during the pyrolysis of OP in the
- same operating conditions without impregnation with a bio-oil yield of 25.6 wt.%.
- The gas yield during the pyrolysis process is obtained by calculation. The obtained value is29.6 wt %. This value is the typical yield for the slow pyrolysis technique. During this study,

- 194 the gas composition was not analyzed. However, several investigations showed that methane 195 (CH₄), CO and CO₂ are the main products [17-20]. The produced gas could be injected in the 196 burner to provide the required heat for the pyrolysis process.
- 197

198 **3.2.Bio-oil Properties**

199 Table 1 shows the results of the analyses of the bio-oil produced from the slow pyrolysis of 200 the impregnated OP by OMWW.

201 The elemental analysis shows that the obtained bio-oil presents high oxygen (28.9 wt.%) and 202 water contents (15.6 wt.%). Thus, these properties do not allow its direct use as a fuel. 203 According to the EN 14214 standard, which describes the requirements for FAME (fatty acid 204 methyl ester), the most common type of biodiesel, published by the European Committee of Standardization, the upper limit of water content should be less than 500 mg/kg (or 0.05 %) 205 206 [21-22]. Another EN 590 standard for the automotive diesel fuels to be sold in the Europe 207 Union is stricter regarding the properties of commercial diesel. The upper limit of water content should not exceed 200 mg/kg. Therefore, the pyrolysis oil should be upgraded by 208 209 removing water and oxygen content, for instance by catalytic cracking, hydrodeoxygenation, 210 reforming, esterification or supercritical fluids [23]. The high contents of oxygen and water 211 are responsible for the lower calorific value of the pyrolytic oil (23.7 MJ/kg) produced from 212 the OMWW residues via slow pyrolysis. This is almost twice lower than that of the commercial diesel (~43 MJ/kg). Hadhoum et al. [24-25] investigated a direct thermochemical 213 214 hydrothermal liquefaction of OMWW and obtained a HHV for the produced bio-oil in the 215 range of 39.21-43.2 MJ/kg, which is twice the energy density of the pyrolytic oil obtained in 216 this study. Uzun et al. [20] investigated fast pyrolysis of olive oil residues and found that increasing the reaction temperature from 400 to 700 °C, the HHV of the produced bio-oil 217 increased from 30 MJ/kg to 32 MJ/kg. It is important to underline that the water present in the 218 219 pyrolytic oil does not only decrease the lower heating value but also affects the density, 220 viscosity, the acid value, and corrosiveness [26].

221

Tuble 1. Wall physics chemical properties of the produced of on						
Ultimate analysis (wt.%)		Proximate analysis (wt.%)				
Carbon, %	60.5	Ash, %	0.02			
Hydrogen, %	8.5	Water, %	15.6			
Nitrogen, %	2.0	Enougy Contonta				
Sulphur, %	0.04	Energy Contents				
Oxygen, %	28.9	HHV, MJ/kg	26.0			
Chlorine, %	0.005	LHV, MJ/kg	23.7			
Conductivity, µS/cm	11.68	Acid Value, AV	3.81			
Density, kg/m ³	1024.5	Flash point, °C	63.9			
Kinematic viscosity,	2.68	Dynamic	2.76			
mm ² /s	2.00	viscosity, mPa s				

Table 1. Main physico-chemical properties of the produced bio-oil

In fact, one of the most important physical characteristics determining the usability of bio-oil is the AV value. According to the results (Table 1), the impregnated OP bio-oil AV was 3.81,

laying within the range of values reported in literature for bio-oils produced from biomasses

225 (2.90–5.64) [27-28]. This high acidity could be attributed to the release of long chain organic

acids by reaction of deacetylation of cellulose and hemicellulose [29]. The use of this bio-oil

presenting such low AV could be disadvantageous compared to other commercialized fuel

- 228 sources as it could lead to the corrosion of pipelines and engine parts. The acid value of bio-
- 229 oil could be modified by two methods, namely (i) by increasing the heating temperature 230 during the pyrolysis process [30] and (ii) neutralization using alkali solutions such as NaOH
- 231 and KOH [31].

232 The bio-oil electrical conductivity is 11.68 μ S/cm. This value is in the same range as several

- 233 available crude oils analysed in the literature [32]. In addition, this electrical conductivity is 234 also lower than values found in literature for bio-oil obtained during lignocellulosic biomass
- 235 pyrolysis. Such behaviour is attributed to the low ash content. It confirms that the minerals
- 236 initially present in the OMWW are trapped in the biochar. The latter could be used as a
- 237 promising biofertilizer [8].
- 238 The average density of the bio-oil was around 1024.5 kg/m³. This value is much higher than the density of diesel fuel 835 kg/m³. According to the EN 14214 and EN 950 standards, the 239
- density of biodiesel/diesel at 15 °C should be in the range of 860–900 kg/m³ and 820–845 240
- kg/m^3 , respectively. The average density of bio-oil derived from triacylglycerols is 856 kg/m³ 241 242 [26].
- 243 The obtained flash point of the produced bio-oil, representing the lowest temperature at which
- 244 the fuel starts vaporize to form an ignitable mixture when it comes in contact with air, was

245 63.9 °C. The value is within the limits of the above mentioned European standards (EN 950,

- 246 above 55 °C, EN 14214, >101 °C). The flash point of the bio-oil obtained from the OMWW
- 247 during the hydrothermal liquefaction process reported in [26] was in the range of 82–117 °C.
- 248 The mean dynamic and kinematic viscosity at 20 °C of the bio-oil derived from the OMWW 249 during slow pyrolysis was 2.76 mPa.s and 2.68 mm²/s, respectively. Therefore, it corresponds 250 to the limits of the EN 950 standard which is between 2.00-4.5 mm²/s. Generally, the 251 viscosity of a given bio-oil can vary within a large range depending on the biomass feedstock 252 and pyrolysis process. However, the lower the viscosity, the better the pumping, atomization 253 and finer droplets of fuel achieved. Several options to reduce the viscosity of the bio-oil can 254 be used, such as its blending with diesel fuel, the use of catalyst or increase in temperature 255 [33].

256 **3.3.Bio-oil Composition**

257 The analysis of GC-MS chromatogram shows that the bio-oil is principally constituted of lipids as can be seen in Figure 4a-d and Table 2. Free fatty acids (FFAs), in particular 258 259 saturated fatty acids (SFA), but also some mono- and di-unsaturated compounds (MUFAs and 260 DUFAs) are largely represented. Besides, some fatty acids are found under ester forms 261 (glyceryl, methyl and ethyl). Some sterol derivatives like β -sitosterol and methyl ursolate were also found (Figure 3d). The more abundant lipids were palmitic acid (C16:0) and oleic 262 acid (C18:1), and its methyl ester (Figure 4c). 263

- 264 The second more represented class of compounds is phenol derivatives, notably with benzene-1,2-diol (catechol), tyrosol, isoeugenol and homovanillic and ferulic acid (Figure 4b and 265 266 Figure 5). Chemical compound composition of bio-oil obtained after the pyrolysis of olive 267 wastes is very poorly described in literature. Pütün et al. [19] have checked the bio-oil content in small compounds after olive residue pyrolysis. Authors have analysed the composition of 268 269 pentane fraction of the bio-oil by GC-MS. They found straight chain alkanes and alkenes with 270 a range of carbons comprised between C10 and C28/C29. On the other hand, they determined 271 the presence of phenolic compounds in bio-oil by ¹H NMR experiments, but not characterized
- 272 more precisely.

273 As mentioned previously, few data are available on the composition of bio-oil obtained after 274 the olive residue pyrolysis. However, data on olive oil composition or oil extracted from olive pomace (named pomace oil) could be found in literature [34]. The lipid contents in the bio-oil 275 276 obtained in the present study are similar to those obtained for pomace oil. Indeed, Khadem et 277 al. [34] described the presence in their pomace oil (called in the paper whole olive stone oil) 278 of few FFA, MUFA, DUFA and some sterols like β -sitosterol, known as the more abundant 279 sterol in olive oil [35]. Oleic acid is also the predominant fatty acid followed by linoleic, palmitic and stearic acid. However, the presence of ester is not mentioned since the authors 280 281 determined FAs composition with a transesterification method due to the formation of fatty 282 acid methyl ester (FAME). In this present study, the derivatization technique preserves the ester forms of FAs. Relatively same results for SFAs and UFAs with the same GC-MS 283 284 technique were obtained by other groups, in waste pits [36] or pulp, seed and whole olive fruit 285 [37]. Thus, it seems that the slow pyrolysis preserves the lipidic content of OP and OMWW.











Figure 4. GC-MS Chromatogram (TIC : Total Ion Current) of the produced bio-oil from the slow pyrolysis of impregnated OP with OMWW. (a) All chromatogram. (b) Zoom between 3.5 and 15.4 min. (c) Zoom between 15.4 and 17.3 min. (d) Zoom between 17.3 and 25 min.

297 Concerning the phenolic compounds, among the ones annotated using the NIST library with 298 more than 80% of similarity, catechol, isoeugenol and homovanillic acid are known as 299 compounds found in bio-oils of slow or fast pyrolysis of different kinds of wood or plant 300 residues [38-41]. These phenolics come from the decomposition of compounds obtained after 301 lignin depolymerisation by pyrolysis [42].

Tyrosol, hydroxytyrosol, vanillic and ferulic acid are commonly encountered in different olive residues [43-44]. During this GC/MS analysis, peaks that may correspond to hydroxytyrosol at 12.83 min and vanillic acid at 12.98 min were detected but only with 66% and 67% similarity with NIST library

.OCH₃ OCH₃ OH COOH соон Vanillic acid Catechol Homovanillic acid (Benzene-1,2-diol) (4-hydroxy-3-methoxybenzoic acid) (2-(4-hydroxy-3-methoxyphenyl)acetic acid) $\cap \vdash$ OH OH OH OH OCH₃ OCH₃ ÓΗ ÓΗ ĊOOH Tyrosol Hydroxytyrosol Isoeugenol Ferulic acid 306 (2-(4-hydroxyphenyl)ethanol) (2-(3,4-dihydroxyphenyl)ethanol) (2-methoxy-4-propenylphenol) (3-(4-hydroxy-3-methoxyphenyl)acrylic acid)

Figure 5. Main phenolic compounds contained in the produced bio-oil from the slow pyrolysis of impregnated OP with OMWW

- **Table 2.** Products in bio-oil from impregnated sample slow pyrolysis by GC-MS analysis
- 311 (RT : retention time; Peak area $\ge 100\ 000$ and similarity $\ge 80\%$ for compounds annotated with

Compound	RT (min)	Area	NIST similarity %	Family
3-hydroxypyridine	4.64	202 362	88	other
Catechol	7.37	8 781 151	95	phenol
Undecenoic acid (C11:1)	8.00	408 745	80	fatty acid - MUFA
Nonanoic acid (C9:0)	8.08	1 076 202	92	fatty acid - SFA
2-hydroxybenzoic acid	8.46	3 937 152	86	phenol
Butanoic acid, 2-hydroxy-2-methyl-, methyl ester	8.63	3 223 386	86	other
Phenoxyacetic acid (int std)	9.20	1 808 747	standard	IS
2-(2-hydroxyethyl)phenol	9.42	3 791 451	82	phenol
1,2-Benzenediol	9.76	3 707 373	81	phenol
1-Propene-1-thiol	10.03	2 039 745	81	other
3,5-Dimethoxy-4-hydroxybenzaldehyde or Methyl 4-methoxy-3- hydroxybenzoate	10.70	2 391 751	85	phenol
4-Hydroxyphenylethanol (tyrosol)	10.87	1 372 146	91	phenol
2-methoxy-4-propenylphenol	11.00	1 855 963	90	phenol
1,4,6-or 1,4,5-Trimethylnaphthalene	11.26	321 092	82	aromatic
Dodecanoic acid (C12:0)	11.77	399 010	86	fatty acid - SFA
Homovanillic acid	11.95	993 113	81	phenol
8-Heptadecene	12.15	263 282	87	alkene
Heptadecane	12.30	306 029	87	alkane
Azelaic acid	13.23	591 354	86	fatty acid
Myristic acid (C14:0)	13.74	478 939	standard	fatty acid - SFA
Hydrocaffeic acid	14.37	803 280	84	phenol
Hexadecanenitrile (Palmitonitrile)	14.44	476 465	92	fatty acid
Palmitic acid, methyl ester	14.56	4 541 596	95	fatty acid - FAME
n-Pentadecanoic acid (C15:0)	14.64	163 669	81	fatty acid - SFA
(9Z,12Z)-9,12-Octadecadien-1-ol	14.87	223 717	86	fatty acid
Oxacycloheptadec-8-en-2-one (Ambrettolid)	14.92	416 896	86	terpene
Palmitic acid, ethyl ester	15.14	273 192	81	fatty acid
Palmitelaidic acid (C16:1)	15.34	2 059 626	87	fatty acid - MUFA
Palmitic acid (C16:0)	15.50	31 337 446	standard	fatty acid - SFA
trans-Ferulic acid	15.98	321 727	standard	phenol
Linoleic acid, methyl ester	16.05	2 182 596	92	fatty acid - FAME

Oleic acid, methyl ester	16.09	12 409 845	93	fatty acid - FAME
Oleic acid, methyl ester	16.13	4 780 639	92	fatty acid - FAME
Nonadecanenitrile	16.20	503 737	83	fatty acid
Stearic acid, methyl ester	16.27	1 096 206	95	fatty acid - FAME
Heptadecanoic acid (17:0)	16.30	134 092	84	fatty acid - SFA
Oleic acid, ethyl ester	16.61	833 888	91	fatty acid
Linoleic acid (C18:2)	16.88	9 403 400	standard	fatty acid - DUFA
Oleic acid (C18:1 cis)	16.93	71 123 983	standard	fatty acid - MUFA
Oleic acid (C18:1)	16.97	20 649 550	92	fatty acid - MUFA
Stearic acid (C18:0)	17.08	8 219 407	93	fatty acid - SFA
Fatty acid C18:2	17.26	2 201 310	85	fatty acid - DUFA
Fatty acid C18:2	17.30	500 015	86	fatty acid - DUFA
Fatty acid C18:2	17.47	676 247	85	fatty acid - DUFA
Fatty acid C18:2	17.60	2 069 157	94	fatty acid - DUFA
Arachidic acid methyl ester	17.82	271 338	89	fatty acid - FAME
11-Eicosenoic acid (C20:1)	18.38	683 145	86	fatty acid - MUFA
Arachidic acid (C20:0)	18.53	1 078 584	92	fatty acid - SFA
Sucrose	19.40	162 129	standard	sugar
1-Monopalmitoylglycerol (monopalmitin)	19.44	1 145 692	90	fatty acid - MAG
Behenic acid (C22:0)	19.88	634 930	91	fatty acid - SFA
1-Monooleoylglycerol (monoolein)	20.56	4 568 437	93	fatty acid - MAG
1-monosteroylglycerol (monostearin)	20.68	388 228	88	fatty acid - MAG
Squalene	21.09	371 224	standard	terpene
Lignoceric acid (C24:0)	21.13	524 036	standard	fatty acid - SFA
beta-Sitosterol 3-acetate	23.11	854 469	87	sterol
Methyl ursolate	23.97	214 862	81	sterol
beta-Sitosterol	24.20	1 009 726	81	Sterol

313 **4. CONCLUSION**

This study is based on an eco-friendly approach for the valorization of olive mill wastewater (OMWW) through agricultural water recovery and the production of biofuels and biofertilizers. Herein, the physico-chemical properties and the composition of bio-oil collected during the slow pyrolysis of OMWW impregnated olive pomace (OP) was investigated.

319 The bio-oil characterization shows that the electrical conductivity, the ash content, the 320 viscosity and the flash point are close to values defined for commercial diesel. However, the 321 lower energy content and the acidic character limit their direct use as biofuels. These values 322 are attributed to the higher water and oxygen contents in the recovered bio-oil. The GC/MS 323 analyses are in agreement with the obtained properties revealing a very high content in 324 phenols and fatty acids as by-products of aromatic structure carbonization, which explains the 325 high acidity of the bio-oil. Further studies concerning the upgrading of the bio-oil for possible 326 commercial use are considered. Such bio-oil upgrading will help its recovery and therefore 327 make the developed strategy of OMWW treatment economically viable.

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