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Bio-oils from microwave assisted pyrolysis of kraft lignin operating at reduced residual pressure / Bartoli, Mattia; Rosi, Luca; Frediani, Piero; Frediani, Marco. - In: FUEL. - ISSN 0016-2361. - ELETTRONICO. - 278:(2020), p. 118175. [10.1016/j.fuel.2020.118175]

Availability:

This version is available at: 11583/2837237 since: 2020-06-25T11:58:01Z

Publisher:

Elsevier

Published

DOI:10.1016/j.fuel.2020.118175

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<http://dx.doi.org/10.1016/j.fuel.2020.118175>

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1 Biooils from microwave assisted pyrolysis of Kraft lignin operating at reduced residual 2 pressure

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7 Abstract

8 In this work, MAP of Kraft lignin at reduced residual pressure was studied. MAP experiments were
9 carried out at different pressure (1 bar, 0.13 bar, 0.013 bar) with and without a fractionating system
10 in a multimode MW batch reactor using carbon like MW absorber. The most relevant achievements
11 were gained at residual pressure of 0.013 kPa with a 37 wt% of biooil collected without fractionating
12 and at the same pressure with fractionating when process was carried out in 9 min. Compositions of
13 biooils were evaluated through ¹H-NMR, FT-IR ATR and a quantitative GC-MS method that allowed
14 to evaluation concentration of Biooils compounds. Analysis showed high concentration of
15 multisubstituted aromatic ring and light linear/cyclic compounds (C2-C5) from advanced thermal
16 degradation of lignin structure side chains.

17 **Key words:** microwave-pyrolysis-Kraft lignin-quantitative GC-MS-Biooil

18 Highlights

- 19 • MAP of Kraft lignin at reduced pressure was studied.
- 20 • Relationship between biooils production and residual pressure was investigate.
- 21 • Biooils were produce up to 43.6 wt%.
- 22 • A mechanism for lignin degradation under reduced residual pressure was proposed

23 1.Introduction

24 Nowadays, use of natural renewable resources have grown up as a sustainable alternative to oil based
25 ones driving from governance policies[1]. Use of biomasses is of the most attractive way to replace
26 fossil sources and lignin could play a very relevant role[2]. Lignin is second most abundant natural
27 polymer[3], back to cellulose, and the only natural renewable source of aromatic compounds[4].
28 Commonly, lignin is isolated like organosolved, sulphonate or as Kraft derivative from biomass
29 feedstock derived from pulp and mills industry and from bioethanol production[5, 6]. For its many
30 application, Kraft lignin gained an addressable global market of more than 40Mton/year [7]. Indeed,
31 it is used like low energy solid fuels[8] and it is currently employed like dispersant in high
32 performance conglomerate[9], for water treatment[10] and chemicals productions[11]. Aromatics
33 production from lignin represent the great challenge in lignin management and the most studied
34 methodologies to achieve this result are thermochemical treatments[12], in particularly pyrolysis[13,

35 14]. In the last decade, microwave assisted pyrolysis (MAP) was employed for process a great variety
36 of several biomasses [15-19] into fuels and chemicals[20]. Also, MW heating technique[21] had been
37 proofed like a very effective way to convert lignin into aromatic chemicals[22] together with the
38 magnification of aromatic recovery using reduced residual pressure[23]. In this work, MAP of Kraft
39 lignin at reduced pressure was studied for magnification of multisubstituted single aromatic rings and
40 depletion of non aromatic and high molecular compounds using different residual pressure values.
41 MAP experiments were carried out in a multimode microwave oven with and without a fractionating
42 checking the influence of different residence time and residual pressure. Biooils obtained were
43 analysed through different techniques (¹H-NMR, FT IR-ATR, quantitative GC-MS) to define their
44 compositions and rheological properties.

45 **2. Materials and Methods**

46 *2.1. Materials*

47 Lignin was furnished by BioChemTex-Mossi Ghisolfi Group and it was dried until constant weight
48 to remove moisture and store in nitrogen atmosphere at 269 K.

49 The carbon powder, employed as MW absorber was the solid from MAP of tires, metal wires depleted
50 (C: 89.01 %, H: 0.83%, N: 0.48%, S: 2.0%), a more detailed characterization of the carbon powder
51 was previously reported [24, 25].

52 Analytical standard for GC-MS and acetonitrile employed (99.99%, GC grade) were purchased from
53 Sigma Aldrich and used as received.

54 DMSO-d₆ (Aldrich 99.8%) were supplied by Sigma Aldrich and used without any purification.

55 *2.2 Instruments*

56 Kinematic viscosity was detected according to the ASTM method D 2854-00 using an Ostwald
57 viscosimeter thermostated at 298.14 K with a Julabo model ME-18 V. Cyclohexane, chlorobenzene
58 and 1,4-dimethylbenzene were used as standards[26].

59 Density was determined with a pycnometer thermostated at 298.14 K.

60 FT-IR analyses were performed with a Shimadzu model IRAffinity-1, equipped with a Golden Gate
61 single reflection diamond ATR accessory supplied by Specac for liquids analysis and a sapphire cell
62 for gas analysis.

63 ¹H-NMR spectra were recorded with a NMR Varian Mercury 400 using dimethylsulfoxide-d₆
64 (DMSO-d₆). Residual hydrogens of the solvent were employed as internal standard and spectra were
65 referenced to tetramethylsilane (TMS).

66 The water content was evaluated through ¹H-NMR spectroscopy using the standard addition method.

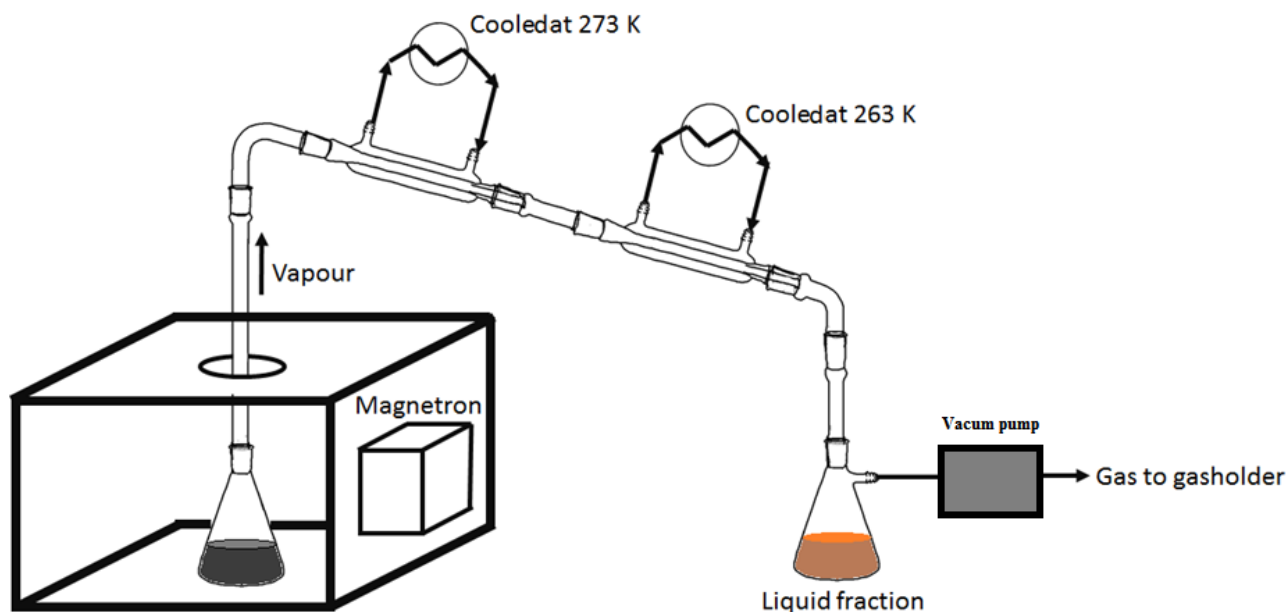
67 Three spectra were recorded on the same sample: pure solvent; after the addition of a weighed sample

68 of Biooil, and after the addition of a known amount of Milli Q water. Areas in each set of three spectra
69 were normalized to the area of the residual hydrogen of the solvent that was used as internal standard.
70 Gas chromatographic analyses were performed using a Shimadzu GC–MS QP5050A equipped with
71 a capillary column PetrocolTM DH 24160-U, (100 m length, 0.25 mm diameter, 0.5 μ m stationary
72 phase) using a 1:30 split ratio operating at 298 K for 15 min, then heated at 2.5 K/min up to 523 K
73 and kept at this temperature for 15 min. A quadrupole mass (MS) detector, with a 70 eV electron
74 ionization ions generator, operating in the range 40–450 m/z was used. Other noteworthy peaks were
75 not detected at higher temperature. Total ion chromatography (TIC) was obtained with a signal/noise
76 ratio of five, and composition was reported as percent peak areas without any response factors
77 correction. Compounds were tentatively identified using the NIST mass spectral library.
78 Samples for GC-MS analysis (standard and biooils) were prepared with addition of diphenyl (1 mg)
79 and biooil 100 mg in 1 mL of acetonitrile. Solutions of analytical standards were prepared according
80 to the same procedure, at a concentration of 1.0 mg/mL in acetonitrile.

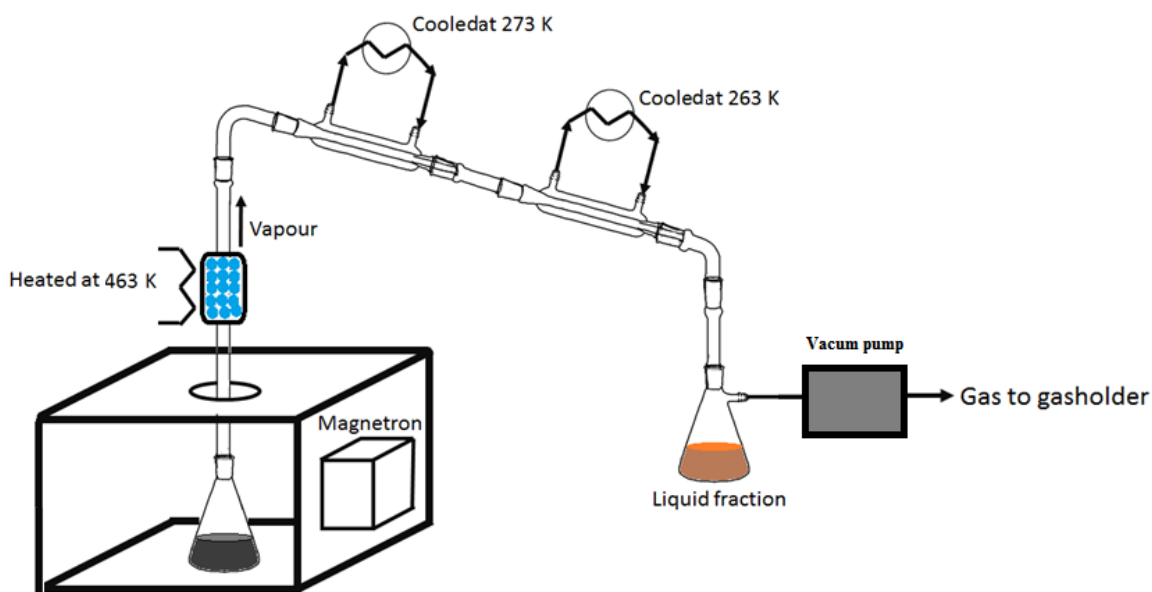
81 *2.2 Pyrolysis details*

82 Pyrolysis were carried out in a MW oven working at 2.45 GHz, equipped with four external
83 microwave generators (max electric absorption 8 kW, max MW power inside the oven 6 kW),
84 designed and supplied by Bi.Elle s.r.l. (Italy). The oven was equipped with a wide angle measuring
85 infrared thermometer, which provides information on the overall temperature inside the oven but not
86 the temperature on the sample surface. Two experimental set-ups were used, **Figure 1**, and in all of
87 them samples were placed in a 1000cm³ borosilicate Erlenmeyer flask inside the oven and connected
88 with two condensing systems cooled at 298K and 263K respectively. Liquids were collected in a flask
89 and gas in a gas holder.

90 **Figure 1:** Experimental set-up used to carry out the MAP at reduce residual pressure



Set-up A



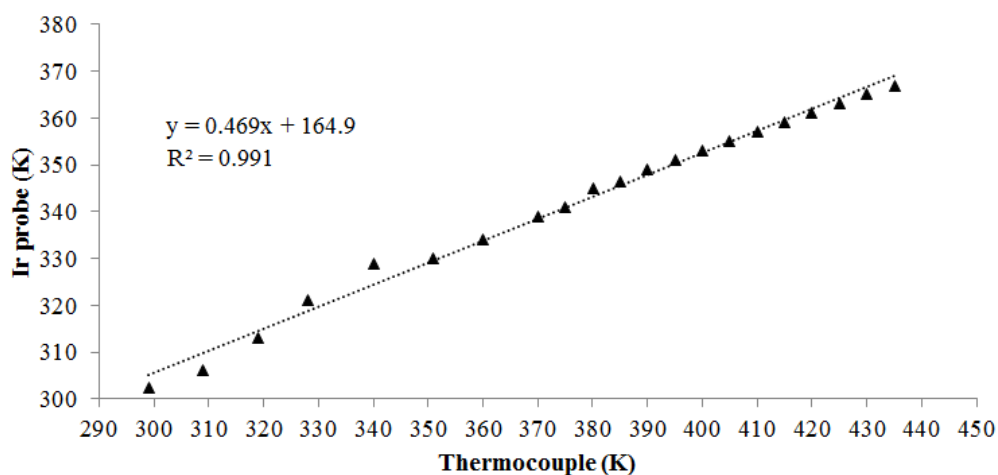
Set-up B

91

92 In the set-up named A, a membrane vacuum pump was inserted between the liquid collecting system
 93 and the gas holder to realize a reduced pressure inside the oven. The gas leaving the reactor through
 94 the vacuum pump was sent to the gas holder. The second equipment, called set-up B, used the same
 95 MW oven and vacuum system, but a fractionating column was placed between the oven and the
 96 condensing system. The column had a length of 0.2 m² internal diameter of 30.0mm, it was filled
 97 with glass spheres having a diameter of 4.0mm. In a typical experiment Kraft lignin were
 98 mechanically mixed with the MW absorber prior the pyrolysis, than heated, in a nitrogen atmosphere,
 99 according to parameters reported in Table 1.

100 In all experiments temperature values were measured through a calibrated IR probe, **Figure 2**,
 101 according with Undri et al.[27].

102 **Figure 2:** Calibration curve for temperature monitoring during MAP experiments [28]



103

104 3.Result and discussion

105 3.1 Experimental conditions

106 MAP of Kraft lignin was carried on in a multimode MWe oven with a power of 3KW using carbon
 107 like MW absorber and different residual pressure as reported in **Table 1**.

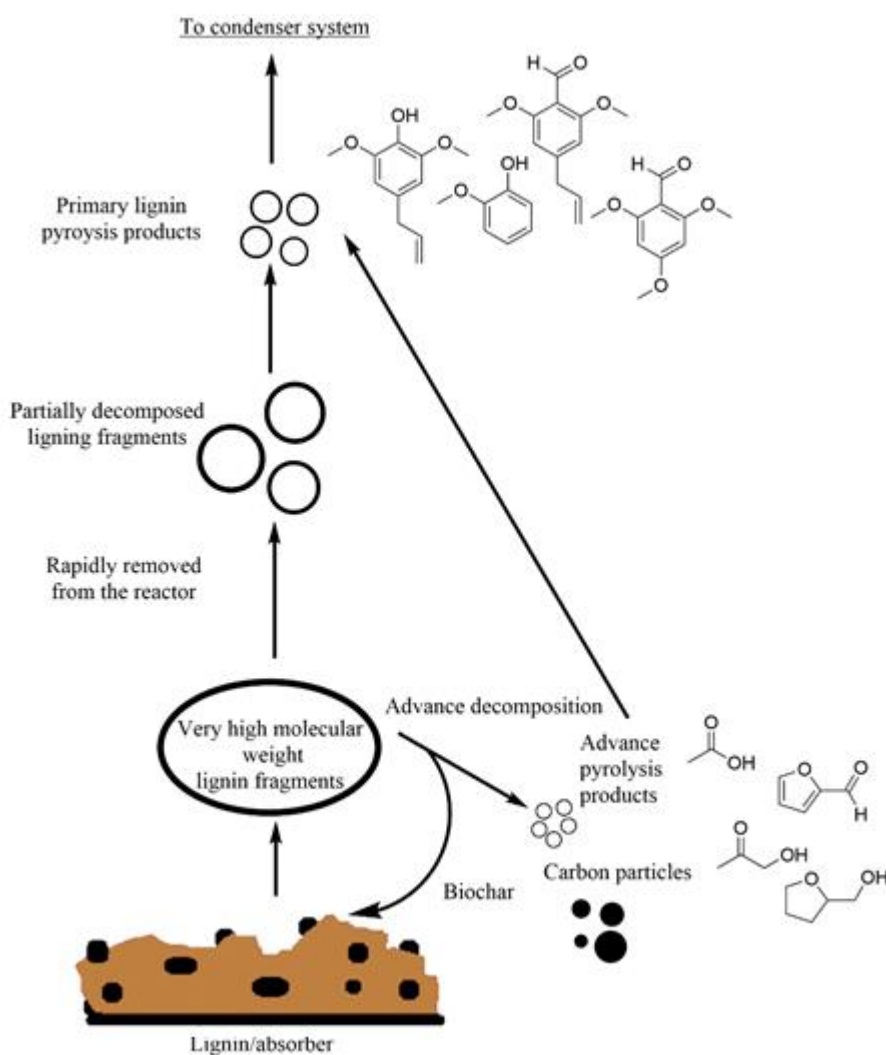
108 **Table 1:** Experimental conditions and mass balance of MAP of Kraft lignin experients

	Set-ups	Lignin [g]	Absorber [g]	Lignin/Absorber	t [min]	T [K]	Pressure [bar]	Yields [wt%]		
								Biochar	Biooil	Gas
ID1	A	118.8	60.0	1.98	20	723	1.0	36.8	43.6	19.5
ID2	B	100.5	50.2	2.00	16	681	1.0	47.6	26.4	26.1
ID3	A	101.2	50.6	2.00	13	638	0.13	45.0	27.5	27.6
ID4	B	100.0	50.1	2.00	19	721	0.13	41.4	25.5	33.1
ID5	A	100.0	50.3	1.99	9	720	0.013	33.2	37.7	29.1
ID6	B	100.1	50.1	2.00	15	618	0.013	58.4	27.1	14.5

109

110 **ID1** was carried out at pressure of 1 bar to a preliminary estimation on MAP yields and compounds.
 111 In this experiment a biooil yield of 43.6 wt% and a biochar yield of 36.8% were reached. **ID2** was
 112 carried out at the same pressure but with a fractionating system observing a lower biooil yields (26.4
 113 wt%) together with an increment of biochar (47.6 wt%) and gas (26.1 wt%) production according
 114 with Undri et al.[24]. Surprisingly, **ID3** and **ID4** (residual pressure of 0.13 bar) showed a very close
 115 biooils yields to **ID2** was observed respectively 27.5% and 25.5%. This was probably due thermal
 116 degradation reactions like shown in **Figure 3**.

117 **Figure 3:** Hypothesized gas-phase degradation pathways for high molecular weight lignin fragments.



118

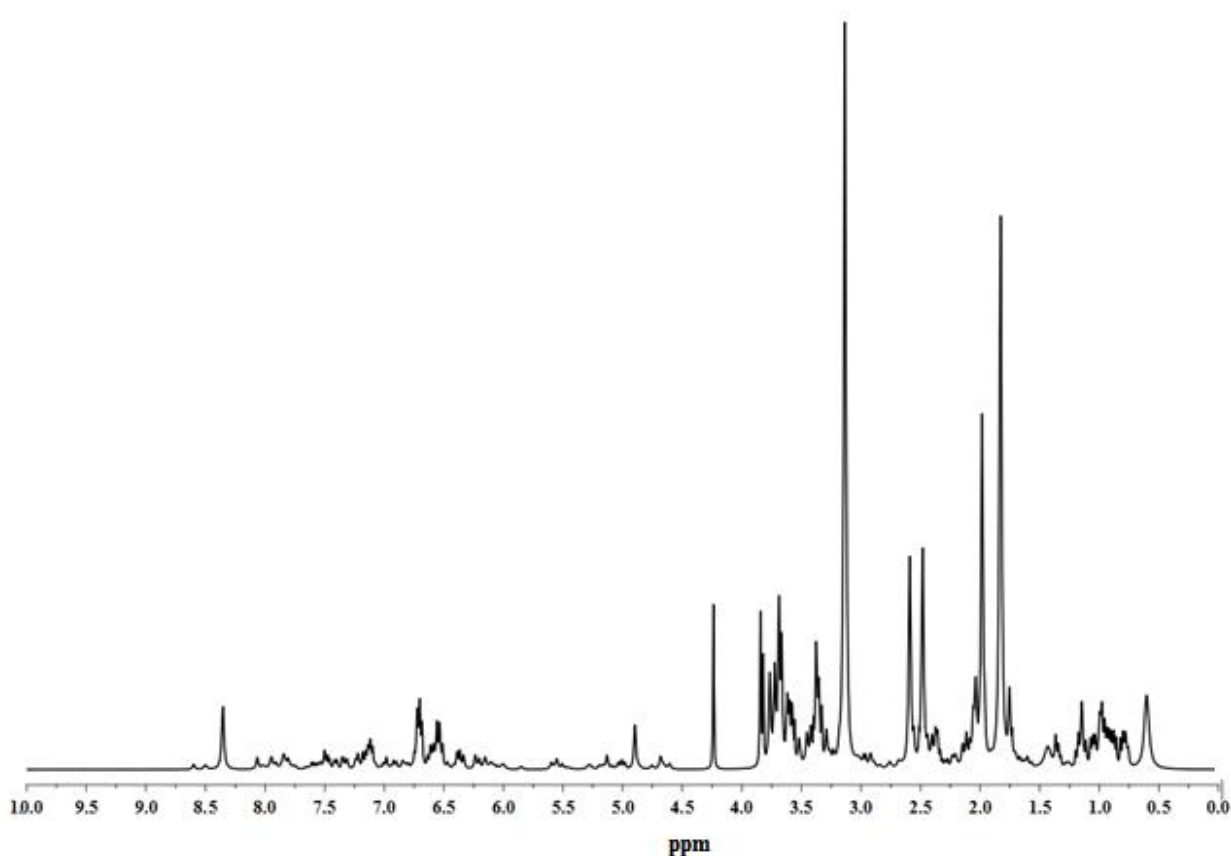
119 According to our hypothesis, very high molecular weight lignin fragments can be dragged up from
120 bulk by the gas streaming and reduce pressure applied to the system with tiny carbon particles. In the
121 gas phase they might be involved in further degradation reaction[29, 30] and they can be form light
122 lignin pyrolysis products and other carbon particles[23]. Moreover, carbon particles can induce
123 further cracking reactions with additional production of char and advance pyrolysis compounds[31].
124 We hypothesize that **ID3-ID4** high weight lignin fragments were not remove fast enough to massively
125 conversion to single ring aromatic compounds. For this reason, production of biochar in **ID3-ID4** was
126 magnified (45-47 wt%). Contrary in **ID5**, an increased yield in biooil was observed. This is might
127 due to reduce residence time due to pressure adopted (0.013 bar). In this case, process conditions
128 might allow the rapidly evolution of the high molecular weight lignin fragments to primary lignin
129 degradation products (*i.e. guaiacol*, methylated phenols) with a decrease of advance degradation
130 products such as water and light organic molecules according with the various mechanism reported
131 by Kawamoto[32]. This was supported by very short process time (9 min), high biooil yield (up to

132 37.7%) and reduce biochar formation (down to 33.2 wt%). The presence of fractionating system in
133 **ID6** forbidden this chemical pathway because a very high biochar yield was reported for this
134 experiment (58.4%). In this experiment a further degradation on the inner surface of condenser system
135 occurred.

136 3.2 NMR analysis

137 NMR techniques are a very versatile methods to analyser biooil[33].In this work NMR was used to
138 perform a preliminary estimation of organic composition and water content through ^1H -NMR
139 experiments, as an example in **Figure 4** is shown ^1H -NMR spectrum of **ID5**.

140 **Figure 4:** ^1H -NMR spectrum of **ID5**, water signal is depleted



141

142 The resonances were attributed according to the following ranges δ 13.0-12.0 (mobile proton of
143 carboxylic acid); 10.0-9.0 (aldehyde); 9.0-6.5 (aromatic, furan, and C=CH-OCC); 6.5-5.0 (phenolic
144 "OH" or C=CH olefins); 5.0-3.3 (CH₂-O-C; or CH₂-OOC; or Ar-CH₂-Ar); 3.3-2.0 (CH₃, CH₂, and
145 CH on aromatic ring); 2.0-1.6 (CH, CH₂ of alkyl groups; CH₂ and CH in β position to an aromatic
146 ring); 1.6-1.0 (CH₂, CH₃ of alkyl groups, CH₃ in β position and CH₂ and CH in γ position to an
147 aromatic ring or ethereal oxygen); 1.0-0.5 (CH₃ of alkyl groups or CH in γ position or further of an
148 alkyl chain linked to an aromatic ring) and values of normalized area are reported in **Table 2**.

149 **Table 2:** Percentage of organic functional groups determined from ^1H -NMR analysis of bio-oils.

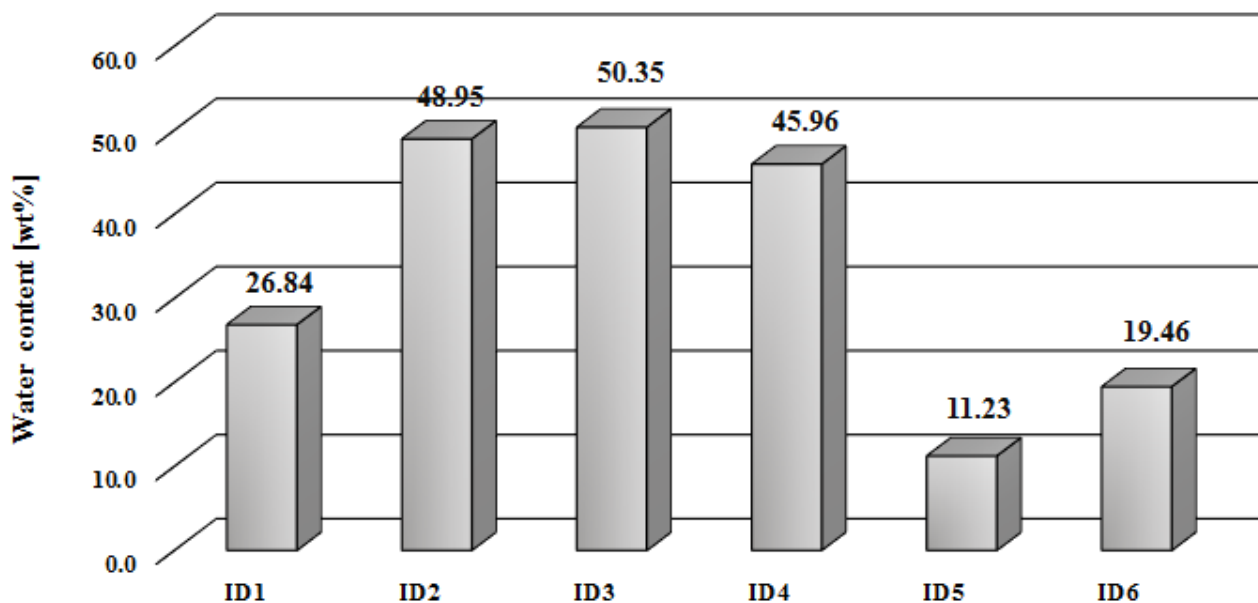
	Carboxylic protons	Aldehydic protons	Aromatic, furan, and C=CH-OCC	ArOH and C=CH olefin	CH ₂ -O-C; CH ₂ -OOC; ring-join methylene, and Ar-CH ₂ -Ar	Protons of CH ₃ , CH ₂ , and CH on aromatic ring and in α position to carboxylic groups	CH, CH ₂ of alkyl groups; CH ₂ and CH in β position to an aromatic ring	CH ₃ in β position and CH ₂ and CH in γ position to an aromatic ring or ethereal	CH ₃ of alkyl groups or in γ position or further of an alkyl chain linked to an aromatic ring
δ (ppm)	13.0-10.0	10.0-9.0	9.0-6.5	6.5-5.0	4.5-3.3	3.3-2.0	2.0-1.6	1.6-1.0	1.0-0.0
ID1	0.01	0.01	5.55	2.94	7.57	60.81	16.41	2.88	3.84
ID2	0.01	0.01	6.02	1.77	13.99	51.76	20.55	2.86	3.02
ID3	0.01	0.02	7.58	1.97	19.05	44.31	20.59	3.79	2.70
ID4	0.01	0.27	3.65	1.52	33.08	26.05	29.58	2.71	3.14
ID5	0.00	0.02	11.82	3.66	19.12	32.79	18.77	6.05	7.78
ID6	0.01	0.08	6.71	2.63	26.21	34.82	23.71	2.80	3.05

150

151 Compounds abundances from ¹H-NMR showed a high percentage of substituted aromatic compounds
 152 in comparison with data previous reported [16]. In particularly a great amount of aromatic compounds
 153 with one or more alkyl groups. Moreover ¹H-NMR analysis showed the presence of ethers derivatives
 154 (Ar-O-R, R-O-R) particularly in **ID4** (up to 33.08%), unsaturated compounds and a few aldehyde
 155 derivatives in all samples. Signals of mobile protons of carboxylic compounds were difficult to detect
 156 but signals of protons in α position to carboxylic groups were abundant (region 2.5-2.3 ppm)
 157 particularly in **ID1**.

158 Water content of biooils was evaluated by using internal standard technique as reported and data are
 159 shown in **Figure 5**.

160 **Figure 5:** Water content evaluate through ¹H-NMR analysis of biooils from MAP of Kraft lignin
 161 from experiments



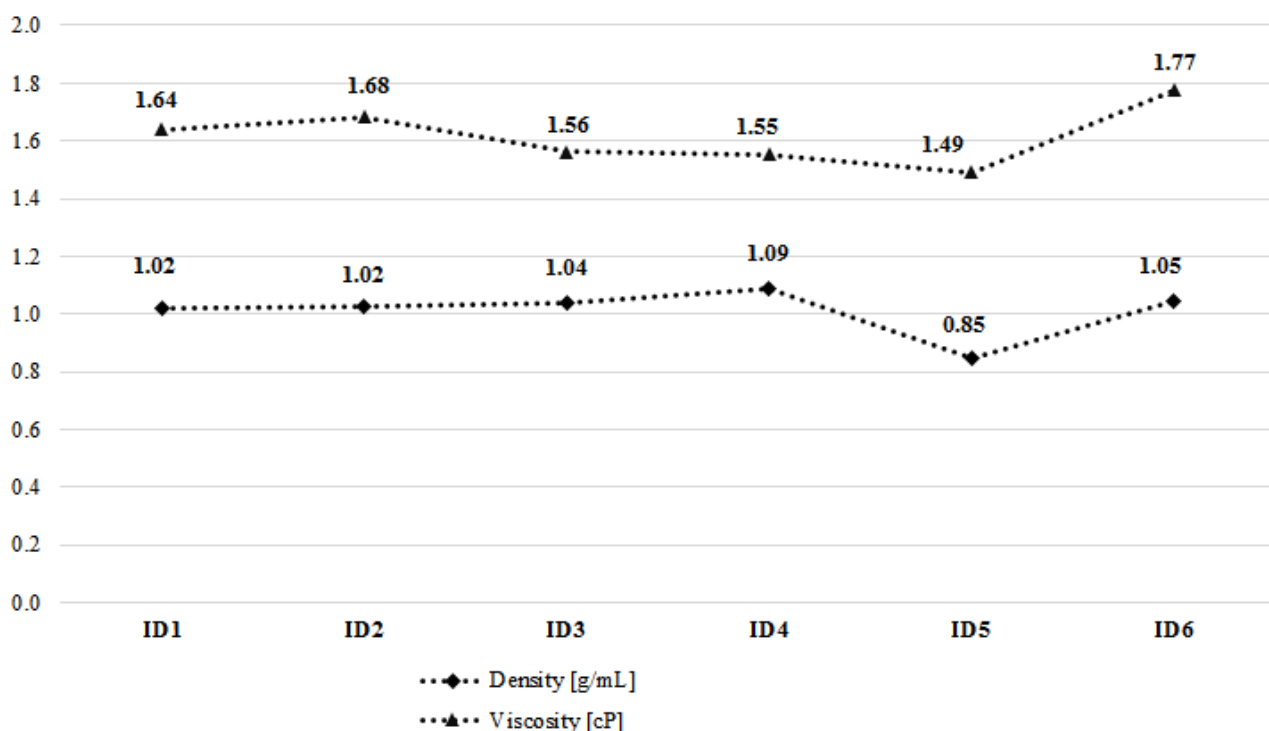
162

163 A water percentage of 26.8 wt% was detected in **ID1** in according with data reported in literature for
 164 pyrolysis of lignin[13, 34, 35]. A very high water contents were detected in **ID2-ID4** according with
 165 experimental set-ups and degradation pathways proposed in **Figure 3**. . Very low water content were
 166 detected in **ID5** (11.2%), lower than similar biooils reported in literature [36, 37]. Contrary to **ID2-**
 167 **ID4** in **ID6** a low content of water was detected and it was imputable to residual pressure (0.013 bar)
 168 that forbidden the efficiently condensation of water produced during MAP.

169 3.3 Rheological properties

170 All biooils collected were deep dark brown liquid at room temperature. In **Figure 6** rheological data
 171 of biooils are shown.

172 **Figure 6:** Trends of viscosity and density values of biooils



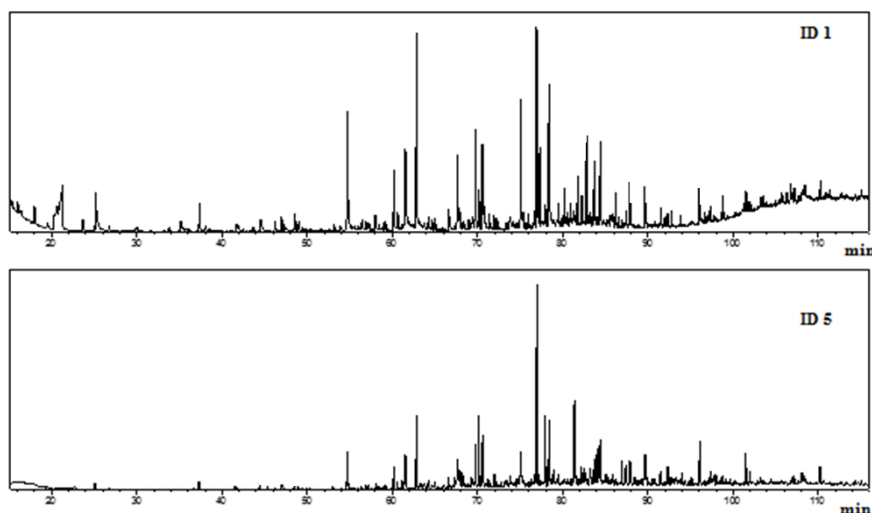
173

174 All density and viscosity values were strong influenced by water content. They were close to 1 mg/mL
 175 with exception of **ID6** that was significantly lower (0.85 g/mL) in according with low content of water
 176 and higher content of organic compounds. Viscosity values were lower than reported for biooils from
 177 different lignocellulosic materials[38].

178 3.4 Quantitative analysis of biooils through GC-MS technique

179 Like showed in **Figure 7** biooils are composed by a remarkably number of compounds.

180 **Figure 7:** As case of examples are showed GC-MS chromatograms of **ID1** and **ID5**



181

182 Previous methods gave a fast but not detailed of biooils for this reason a quantitative GC-MS method
 183 was employed to evaluate the concentration of different compounds. Relative response factors (RRF)
 184 and concentrations of compounds into biooil were calculated in according with the equation reported

185 by Undri et al. [39] and methodology proposed by Bartoli et al.[40] (Supplementary materials) and
 186 result are reported in **Table 3**.

187 **Table 3:** Quantitative GC-MS analysis of biooils using diphenile as internal standard

	r.t. [min]	RRF ^a	Concentration [mg/mL]					
			ID1	ID2	ID3	ID4	ID5	ID6
<i>Non aromatic compounds</i>								
Acetaldehyde	11.6	0.04	10.5	0.0	7.2	0.0	0.0	0.0
Formic acid	16.0	0.05	18.2	0.0	0.0	0.0	0.0	0.0
Acetic acid	21.3	0.18	137.9	39.7	57.6	55.8	0.0	95.5
1-Hydroxy-2-Propanone	24.9	0.09	8.8	13.6	105.3	103.8	0.0	136.8
Acetic acid anhydride	25.2	0.13	41.9	0.0	0.5	0.0	20.9	28.6
2-Methylfuran	41.6	0.20	0.0	8.0	0.0	0.0	10.1	0.0
2-Cyclopenten-1-one	41.7	0.22	8.9	0.0	8.5	12.7	0.0	14.1
Furfural	42.1	0.13	0.0	0.0	3.5	2.6	0.0	19.0
2-Oxopropyl acetate	44.4	0.19	0.0	4.8	0.0	7.4	0.0	13.3
2-Furanmethanol	44.6	0.18	20.3	16.9	26.2	25.6	14.7	43.4
2-Oxepanone	47.2	0.27	0.0	0.0	0.0	20.8	0.0	0.0
Butyrolactone	47.3	0.19	0.0	11.0	0.0	0.0	9.4	0.0
2(5H)-Furanone	47.5	0.18	0.0	0.0	20.0	0.0	0.0	45.6
2-Methyl-2-cyclopenten-1-one	48.5	0.30	0.0	4.8	1.9	4.3	0.0	6.9
3-Methyl-2-cyclopenten-1-one	49.0	0.32	3.2	3.7	3.0	3.5	0.0	8.4
Pentanal	54.1	0.35	0.0	0.0	49.9	10.9	0.0	61.0
Butanoic acid anhydride	54.7	0.38	49.0	0.0	0.0	0.0	0.0	0.0
2-Methyl-cyclopentanone	56.8	0.28	0.0	0.0	10.1	24.7	0.0	0.0
3-Methyl-1,2-cyclopentanedione	58.1	0.32	0.0	7.3	8.6	0.0	0.0	13.1
Limonene	60.1	0.67	0.0	2.1	0.0	0.0	6.1	3.5
<i>Aromatic compounds</i>								
Toluene	37.33	0.16	22.9	21.4	1.3	4.0	20.0	4.2
o-Xylene	47.3	0.38	4.4	4.0	0.0	0.0	3.2	0.0
Phenol	53.1	0.34	3.5	39.2	15.5	25.0	47.6	34.3
o-Cresol	60.2	0.38	17.5	17.8	4.7	0.0	17.0	10.2
Indene	60.6	0.57	4.3	2.0	0.0	0.0	4.5	3.0
p-Cresol	61.5	0.38	39.2	40.7	0.0	21.0	50.0	79.1
Guiacol	62.8	0.43	43.0	1.6	25.0	47.4	65.1	2.3
2,4-Xylenol	66.6	0.48	3.8	9.9	0.0	0.0	0.0	0.0
2,3-Xylenol	66.8	0.48	3.3	1.5	2.4	0.0	5.3	0.0
4-Ethylphenol	67.6	0.49	14.7	1.1	5.1	8.4	18.1	9.0
2,5-Xylenol	67.8	0.49	2.9	15.9	0.0	0.0	0.0	0.0
Pyrocatechol	69.4	0.33	0.0	14.9	16.9	0.0	0.0	11.1
Homoguaiacol	69.8	0.45	22.0	24.0	16.8	20.4	31.4	27.0
Naphthalene	70.2	0.71	6.5	1.4	1.1	3.1	35.9	6.6
2,3-Dihydro-benzofuran	70.6	0.57	15.6	6.3	0.5	0.0	0.0	0.0

3-Methylbenzaldehyde	70.6	0.48	0.0	0.0	0.0	0.0	27.8	0.0
2-Methyl-benzaldehyde	70.6	0.48	0.0	0.0	0.0	15.6	0.0	24.4
3-Methoxy-1,2-benzenediol	73.8	0.35	8.8	8.1	12.6	0.0	17.3	10.5
4-Ethyl-2-methoxyphenol	75.1	0.56	22.1	25.2	0.0	9.8	11.3	8.9
4-Hydroxy-2-methylacetophenone	76.9	0.55	38.4	0.0	0.0	0.0	0.0	0.0
1-Methylnaphthalene	77.9	0.86	0.0	1.1	0.0	0.0	26.4	2.7
Syringol	78.4	0.45	46.6	36.9	0.0	27.0	53.7	32.6
1,2,4-Trimethoxybenzene	81.5	0.55	0.0	0.0	0.0	4.3	16.4	8.2
4-Methoxy-3-(methoxymethyl)-phenol	83.7	0.66	11.2	0.0	0.0	0.0	0.0	0.0
1,6-Dimethyl-naphthalene	84.2	1.06	0.0	0.0	0.0	0.0	12.6	0.0
Isoeugenol	84.4	0.68	12.4	0.0	0.0	7.8	35.9	0.0
3-Methyl-1,1'-biphenyl	87.0	1.16	0.0	0.0	0.0	0.0	11.9	0.0
Acetoveratrone	89.7	0.68	6.3	0.0	0.0	0.0	15.8	0.0
4-Allylsyringol	91.5	0.76	0.0	0.0	0.0	0.0	19.2	4.7
Diethyl Phthalate	92.3	0.87	0.0	0.0	38.9	0.0	0.0	4.8
TOTAL ASSIGNMENT (%)^b			93.8	83.0	95.3	83.5	94.8	95.7

188

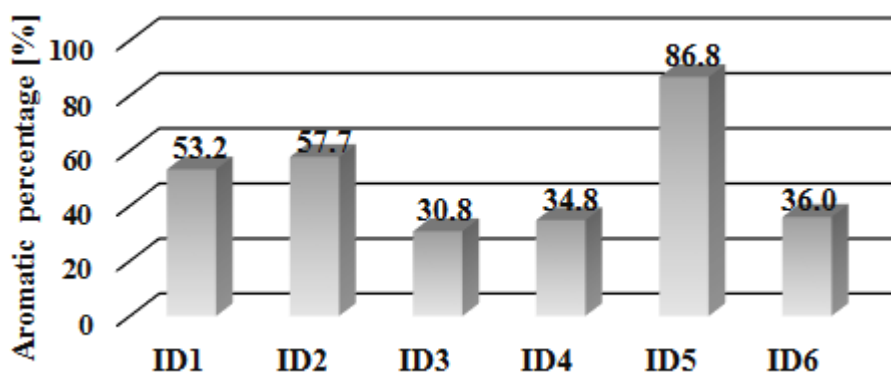
189 a) RRF_{found} were used when available (Table 2 SM) otherwise RRF_{calc} using Eq. 2 were employed.

190 b) Total assignment was calculated with formula: $100 * (\text{summa of weight of all assignment compounds}) / (\text{weight of biooil-water content})$

192

193 A great amount of aromatic compounds were detected in according with primary pyrolytic products
 194 from MAP of lignin. Notwithstanding, aromatic percentage into biooils was significantly different by
 195 each other like shown in Figure 8 according with mechanism proposed in Figure 3.

196 **Figure 8:** Aromatic percentage calculated on the weight of total assignment compounds.



197

198 Different percentage of aromatics was strongly related with set-up and residual pressure used during
 199 MAP experiments. In ID1-ID2 a residual pressure of 1 bar was used and a little increased in aromatic
 200 compounds yield was detected when fractionating system was employed (around 4%). A similar
 201 trend was detected in ID3-ID4 but in this case, a great amount of non aromatic compounds were
 202 detected. This was in agreement with the larger production of carbon in those two experiments like
 203 reported in Table 1. Contrary to other experiments, when a residual pressure of 0.013 bar was used a

204 great percentage of aromatic compounds was detected in **ID5** indeed in **ID6** a similar concentration
 205 to **ID4** was achieved. In according with pathway propose in **Figure 1**, fractionating system may be
 206 promote a degradation of high molecular weight compounds to advance pyrolysis products like acetic
 207 acid (95.5 mg/mL) or 1-Hydroxy-2-propanone (136.8 mg/ml) that were not present in **ID5**. Therein
 208 these compounds were massively present in **ID1-ID4** with a concentration of the acetic acid up to
 209 145.2 mg/mL (**ID1**) and a concentration of the 1-Hydroxy-2-propanone up to 105.3 mg/mL (**ID3**). A
 210 similar trend was observed for 2-Cyclopenten-1-one, 2-Methyl-2-cyclopenten-1-one, 2-Methyl-2-
 211 cyclopenten-1-one that may be derived from degradative cyclization reaction of lignin aromatic side
 212 chains. In **ID5**, the concentration of aromatic was the highest achieved with a massively presence of
 213 polyfunctionalized aromatic compounds.

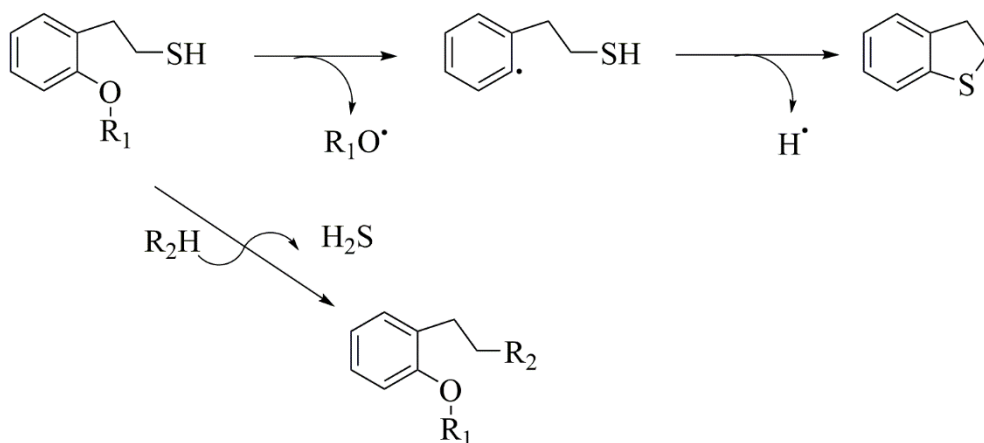
214 The composition of aromatic compounds fraction of biooils comprised a little percentage of multiple
 215 rings aromatic compounds like Naphtalene and its derivatives produced by radical rearrangement of
 216 single rings aromatic compounds.

217 The greater amount of aromatic fraction was compose by phenol and its methoxylated and
 218 methylated derivatives like Guaiacol, Syringol, Cresols and their alkylated and methoxylated
 219 derivatives.

220 A low amount of long alkyl chain (three or more carbon atom) compounds were detected like
 221 Eugenol, Isoeugenol or 4-Allylsyringol. This was imputable to a decomposition process that
 222 involved these chains with a production of non aromatic compounds in according with Yang[34].

223 In the biooils produced in this study, 2,3-Dihydro-benzo[b]thiophene was detected qith a
 224 concentration of 5.1 mg/mL in **ID5**; (see **Table SM 3** on Supporting materials). This was a proof
 225 that a part of original sulphur content of Kraft lignin was retained into biooils like polycyclic
 226 organic compounds and it did not convert light alkyl derivatives like showed in **Figure 7**.

227 **Figure 9:** Radical degradation of sulphide functions on an aromatic moiety of Kraft lignin



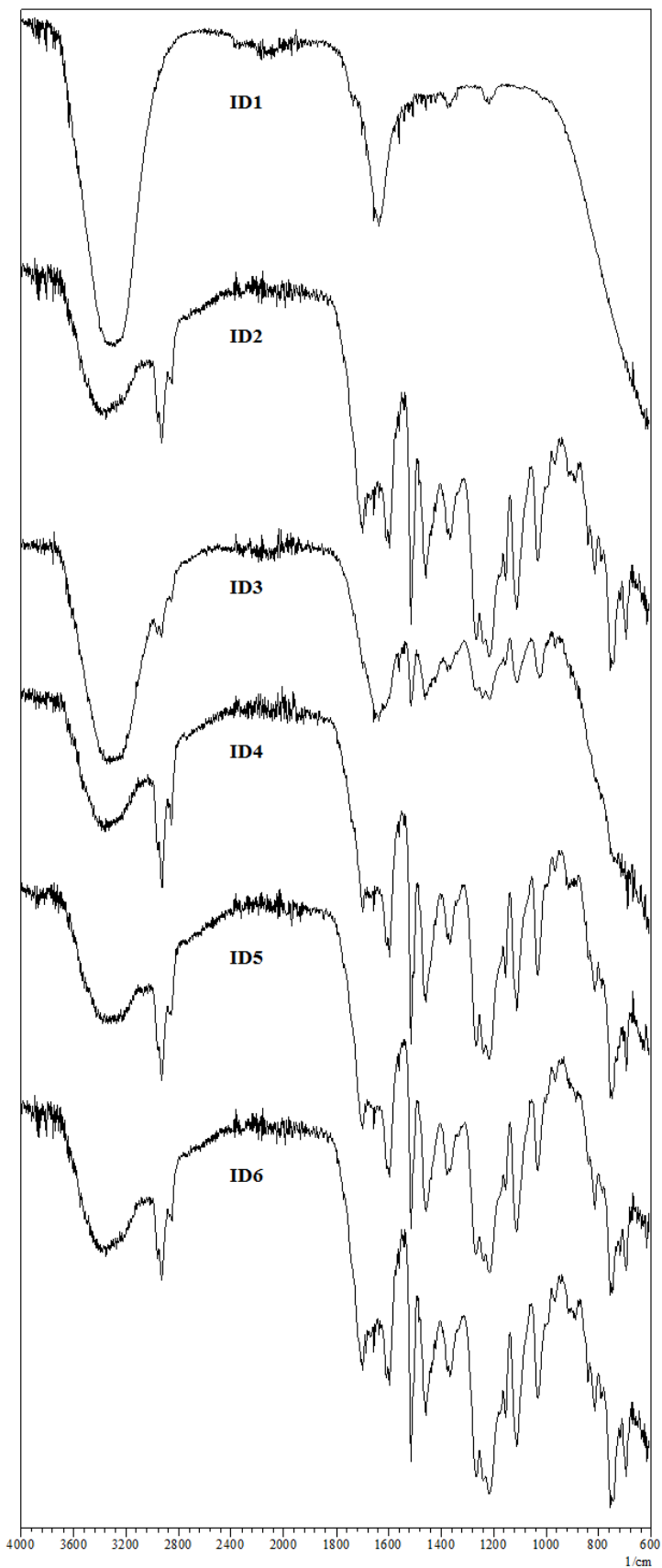
228
 229

230 A proper comparison between aromatic yields obtained with those reported in literature is not an easy
231 task cause the analytical methods generally used that are based on the merely chromatographic area
232 percentage. Under this approximation, Guo et al.[41] reported an biooils aromatic concentration up
233 to 90% using a fast thermal pyrolysis process and similar results could be also obtained using catalytic
234 MAP processes[42]. Contrary to the study mentioned above, de Wild et al.[43] used a quantitative
235 methods to quantify the aromatics after catalytic thermochemical lignin conversion and the results
236 obtained are comparable with those achieved MAP at residual pressure.

237 **3.5 FT IR-ATR analysis**

238 Biooils were analysed through FT-IR ATR technique and spectra are shown in **Figure 10**.

239 **Figure 10:** FT-IR ATR spectra of all biooils



240

241 Broad bands in the range of $3750\text{-}3500\text{ cm}^{-1}$ attested the presence of water (ν_{OH}) and carboxylic acids
242 (ν_{COO}). The presence of aliphatic chains were confirmed by bands in the range and $2950\text{-}2750\text{ cm}^{-1}$

243 (ν_{C-H}) meanwhile bands in the range of 3250-3000 (stretching of CH of methylenic groups) cm^{-1} were
244 not observed due to overlapping with the close bands of ν_{OH} . Presence of carbonyl moieties was
245 evidenced by bands in the range of 1875-1750 cm^{-1} ($\nu_{C=O}$). Band in the close range of 1660-1600 cm^{-1}
246 ($\nu_{C=C}$) were particularly appreciable in **ID2-ID6** as the same for bands in the range of 1300-1100
247 cm^{-1} (ν_{C-O} and δ_{O-H}). These bands confirm the presence of aromatic compounds detected in previous
248 analysis.

249 **4. Conclusion**

250 MAP Kraft lignin was performed in a multimode MW oven at different residual pressure with and
251 without a fractionating system to check the influence of residence time on biooils composition. Two
252 experiments were performed at 1 bar of pressure (**ID1** and **ID2**) and the highest amount of biooil was
253 achievement in **ID1** with set-up A (46.3%) but with high water content (26.8%). Experiments **ID3-**
254 **ID4** were performed at residual of 0.13 bar and a lower biooils yields were detected. Different
255 behaviour respect to polystyrene was observed[23] and a generic mechanism to explain it was
256 proposed. In **ID5** a very poor in water biooil (11.2%) was produce with a residual pressure of 0.013
257 bar with good yield (37.7%) in a very short time (9 min). Results from **ID2**, **ID4**, and **ID6** showed
258 that contrary analogue process reported by Undri et al.[24] and Bartoli et al.[23] in the case of Kraft
259 lignin an upgrading of liquid fraction did not occurred and a reduced quality (higher water content,
260 density and viscosity) and quantity of biooil were obtained.

261 Deep dark brown low density (close to 1 mg/ml) and viscosity (close to 1.6 cP) liquid biooils were
262 obtained. In the case of **ID5** a density of 0.85 mg/mL and a viscosity of 1.45 cP were achievement.

263 Quantitative GC-MS analysis of biooils were performed using RRF and concentrations of more the
264 one hundred compounds were determined.

265 MAP of Kraft lignin at 1 bar with set-up was proved like a very promising way to obtained a biooil
266 rich in acetic acid (145.2 mg/mL) and relatively poor in water. Indeed MAP of Kraft lignin at reduce
267 pressure of 0.013 without any fractionating system was proofed like a sound way to convert lignin in
268 a rich aromatics mixture.

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