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Bio-oils from microwave assisted pyrolysis of kraft lignin operating at reduced residual pressure

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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 absorberThe most relevant achievements

11 were gained at residual pressure of 0.013 kPa whit 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 ^{1}H-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,

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

2.Materials and Methods

2.1. Materials

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

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

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

DMSO-d_6 (Aldrich 99.8%) were supplied by Sigma Aldrich and used without any purification.

2.2 Instruments

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

Density was determined with a pycnometer thermostated at 298.14 K.

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

^{1}H-NMR spectra were recorded with a NMR Varian Mercury 400 using dimethylsulfoxide-d_6 (DMSO-d_6). Residual hydrogens of the solvent were employed as internal standard and spectra were referenced to tetramethylsilane (TMS).

The water content was evaluated through ^{1}H-NMR spectroscopy using the standard addition method. Three spectra were recorded on the same sample: pure solvent; after the addition of a weighed sample

2

of Biooil, and after the addition of a known amount of Milli Q water. Areas in each set of three spectra were normalized to the area of the residual hydrogen of the solvent that was used as internal standard. Gas chromatographic analyses were performed using a Shimadzu GC–MS QP5050A equipped with a capillary column Petrocol[TM] DH 24160-U, (100 m length, 0.25 mm diameter, 0.5 µm stationary 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 and kept at this temperature for 15 min. A quadrupole mass (MS) detector, with a 70 eV electron ionization ions generator, operating in the range 40–450 m/z was used. Other noteworthy peaks were not detected at higher temperature. Total ion chromatography (TIC) was obtained with a signal/noise ratio of five, and composition was reported as percent peak areas without any response factors correction. Compounds were tentatively identified using the NIST mass spectral library.

Samples for GC-MS analysis (standard and biooils) were prepared with addition of diphenyl (1 mg) and biooil 100 mg in 1 mL of acetonitrile. Solutions of analytical standards were prepared according to the same procedure, at a concentration of 1.0 mg/mL in acetonitrile.

2.2 Pyrolysis details

Pyrolysis were carried out in a MW oven working at 2.45 GHz, equipped with four external microwave generators (max electric absorption 8 kW, max MW power inside the oven 6 kW), designed and supplied by Bi.Elle s.r.l. (Italy). The oven was equipped with a wide angle measuring infrared thermometer, which provides information on the overall temperature inside the oven but not the temperature on the sample surface. Two experimental set-ups were used, **Figure 1**, and in all of them samples were placed in a 1000cm^3 borosilicate Erlenmeyer flask inside the oven and connected with two condensing systems cooled at 298K and 263K respectively. Liquids were collected in a flask and gas in a gas holder.

Figure 1: Experimental set-up used to carry out the MAP at reduce residual pressure
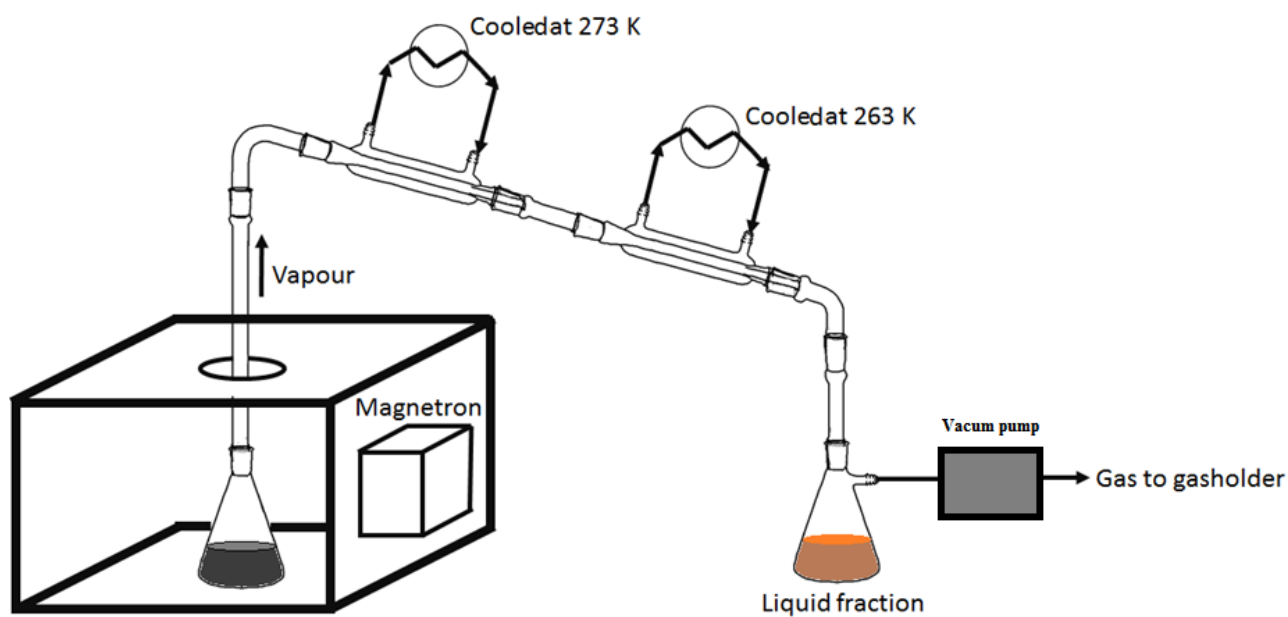
Set-up A
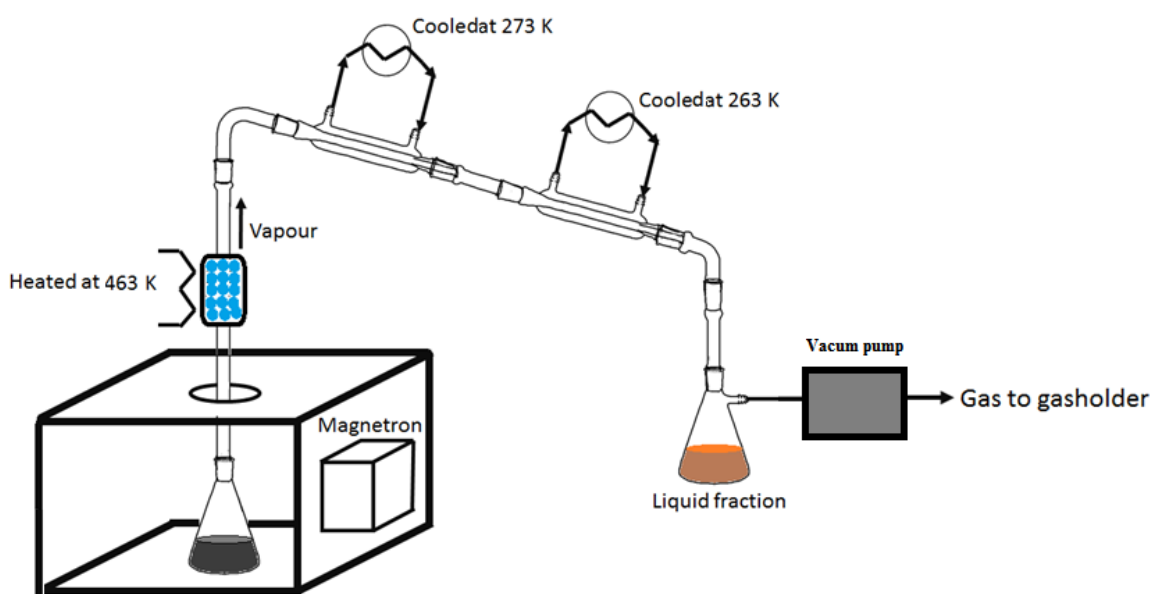
Set-up B

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]

$y = 0.469x + 164.9$

$R^2 = 0.991$

103
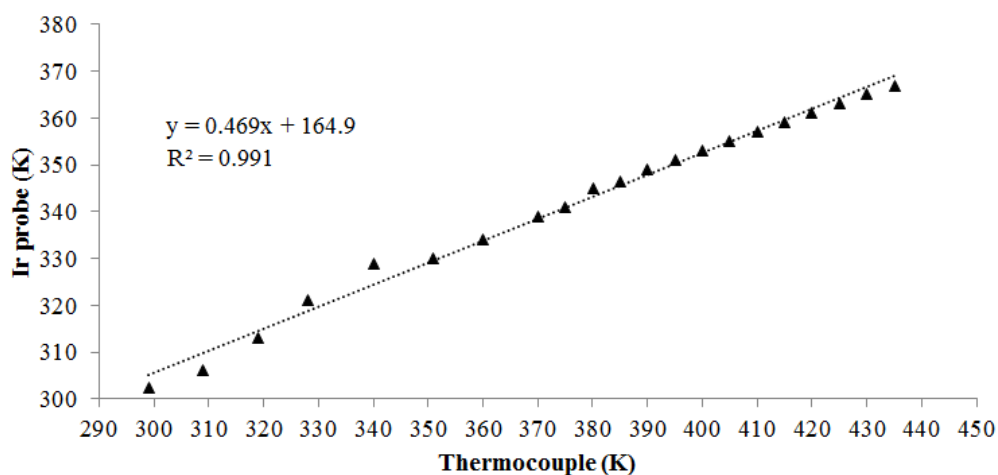
3.Result and discussion

104

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 increament 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.
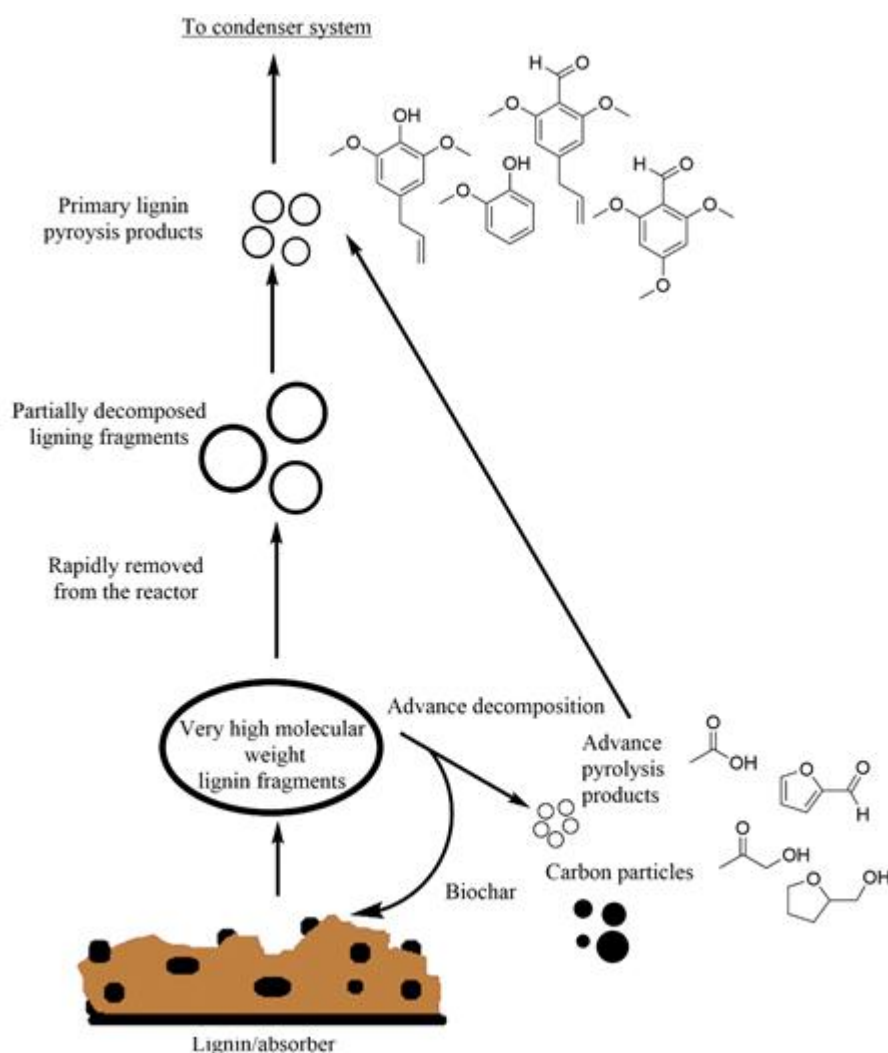
118

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*. *guaicol*, 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

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

3.2 NMR analysis

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

Figure 4: ^{1}H-NMR spectrum of **ID5**, water signal is depleted
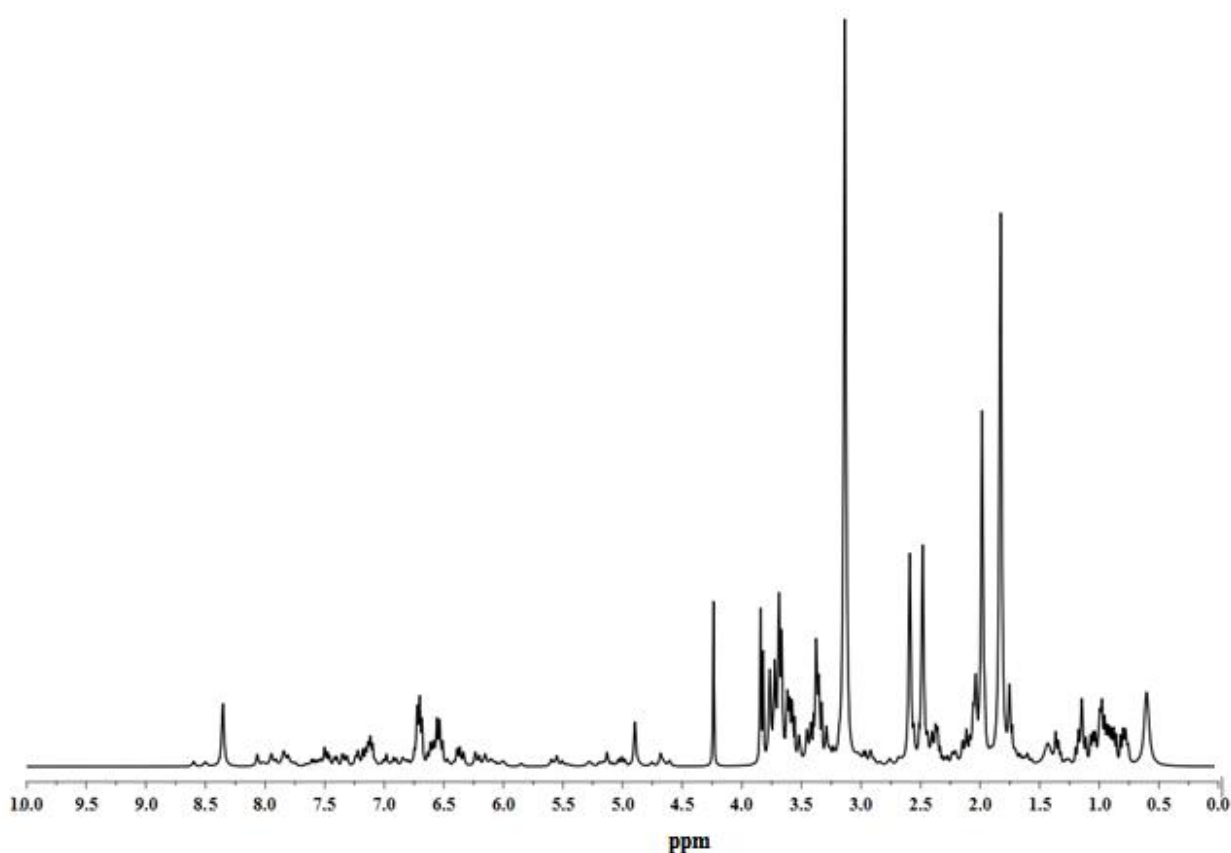
The resonances were attributed according to the following rangesδ 13.0-12.0 (mobile proton of carboxylic acid); 10.0-9.0 (aldehyde); 9.0-6.5 (aromatic, furan, and C=CH-OCC); 6.5-5.0 (phenolic "OH" or C=CH olefins); 5.0-3.3 (CH_2-O-C; or CH_2-OOC; or Ar-CH_2-Ar); 3.3-2.0 (CH_3, CH_2, and CH on aromatic ring); 2.0-1.6 (CH, CH_2 of alkyl groups; CH_2 and CH in β position to an aromatic ring); 1.6-1.0 (CH_2, CH_3 of alkyl groups, CH_3 in β position and CH_2 and CH in γ position to an aromatic ring or ethereal oxygen); 1.0-0.5 (CH_3 of alkyl groups or CH in γ position or further of an alkyl chain linked to an aromatic ring)and values of normalized area are reported in **Table 2**.

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

7

	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 oxygen	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

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

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

Figure 5: Water content evaluate through ^{1}H-NMR analysis of biooils from MAP of Kraft lignin from experiments

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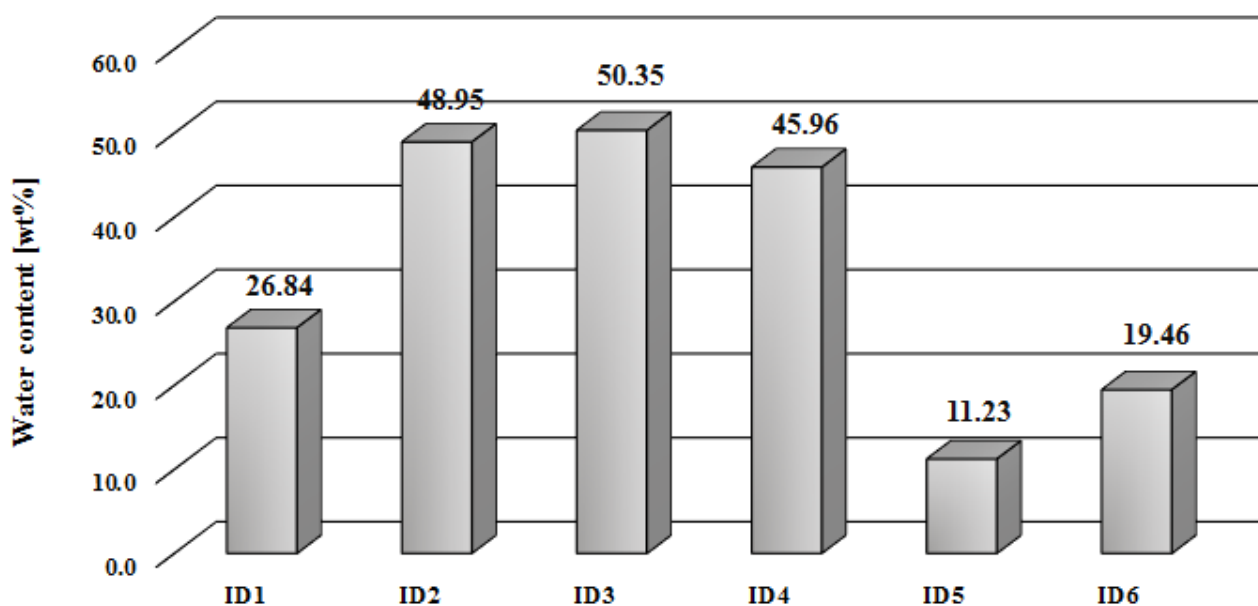
A water percentage of 26.8 wt% was detected in **ID1** in according with data reported in literature for

pyrolysis of lignin[13, 34, 35]. A very high water contents were detected in **ID2-ID4** according with

experimental set-ups and degradation pathways proposed in **Figure 3.** . Very low water content were

detected in **ID5** (11.2%), lower than similar biooils reported in literature [36, 37]. Contrary to **ID2-**

ID4 in **ID6** a low content of water was detected and it was imputable to residual pressure (0.013 bar)

that forbidden the efficiently condensation of water produced during MAP.

3.3 Rheological properties

All biooils collected were deep dark brown liquid at room temperature. In **Figure 6** rheological data

of biooils are shown.

Figure 6: Trends of viscosity and density values of biooils
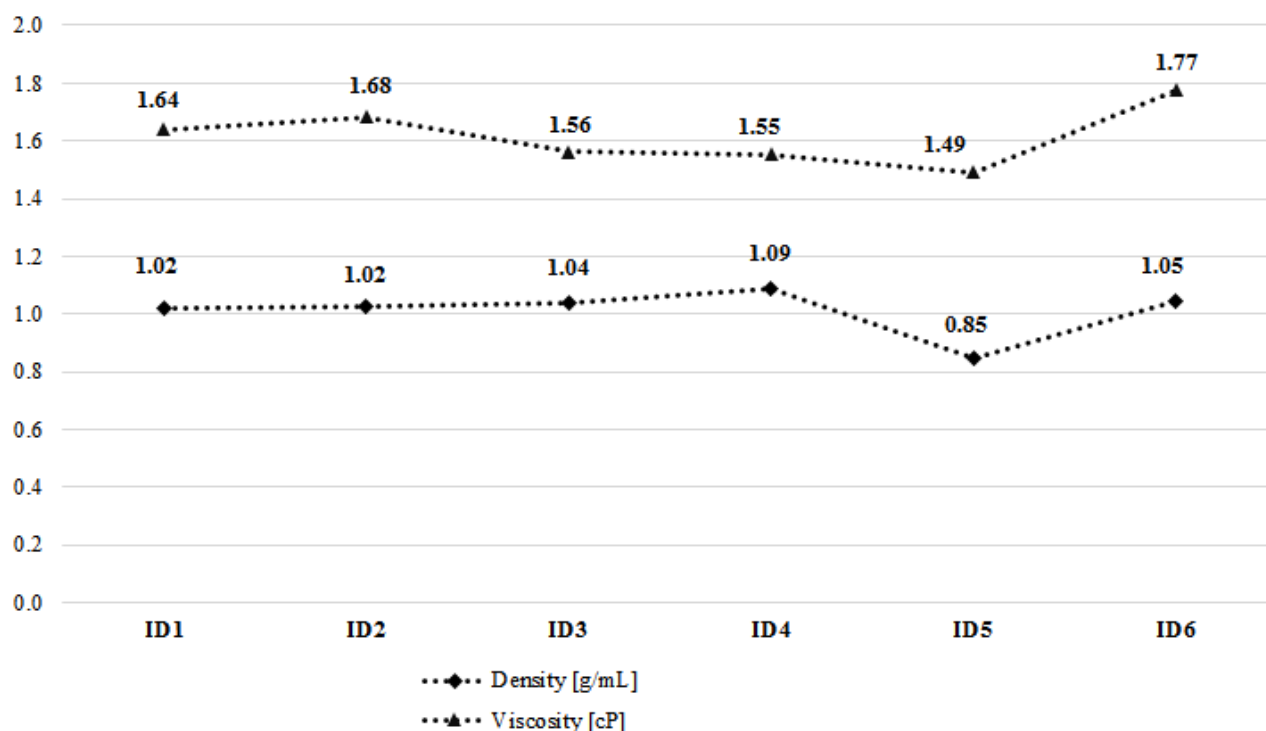
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174 All density and viscosity values were strong influenced by water content. They were close to 1 mg/mL

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**
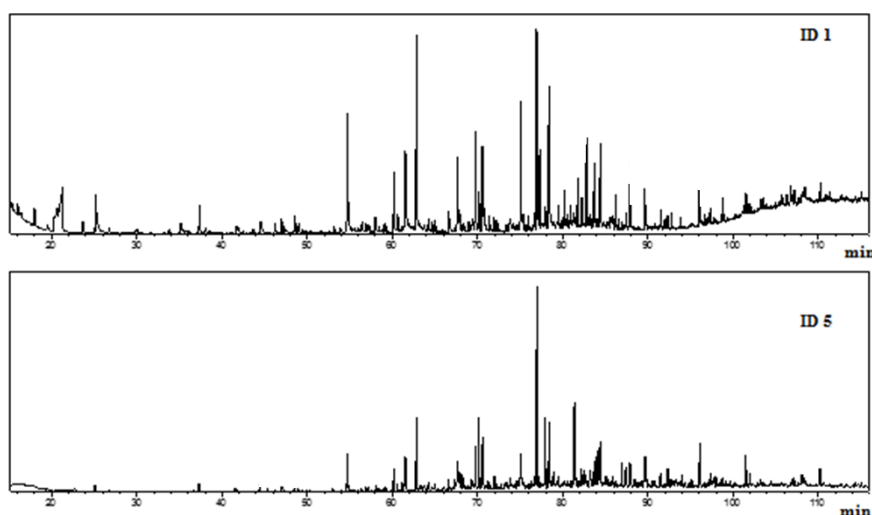
181

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

10

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

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
Non aromatic compounds								
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
Aromatic compounds								
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

11

Compound		RRF[a]	ID1	ID2	ID3	ID4	ID5	ID6
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*(summa of weight of all assignment compounds)/(weight of biooil-

191 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.
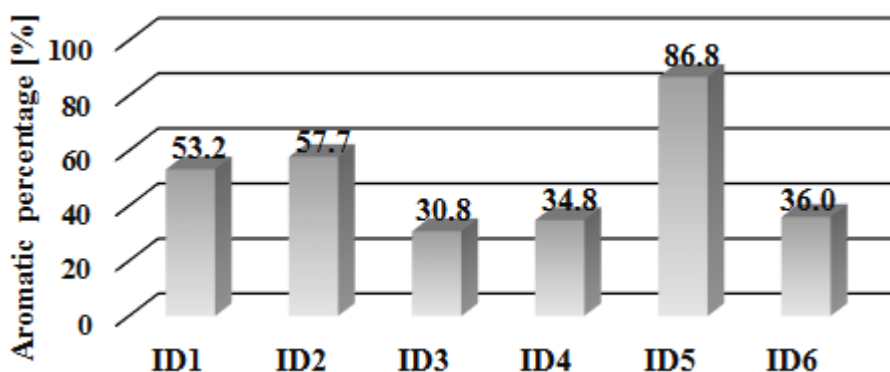
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198 Different percentage of aromatics was strongly related with set-up and residual pressure used during

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

12

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

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

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

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

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

**Figure 9:** Radical degradation of sulphide functions on an aromatic moiety of Kraft lignin
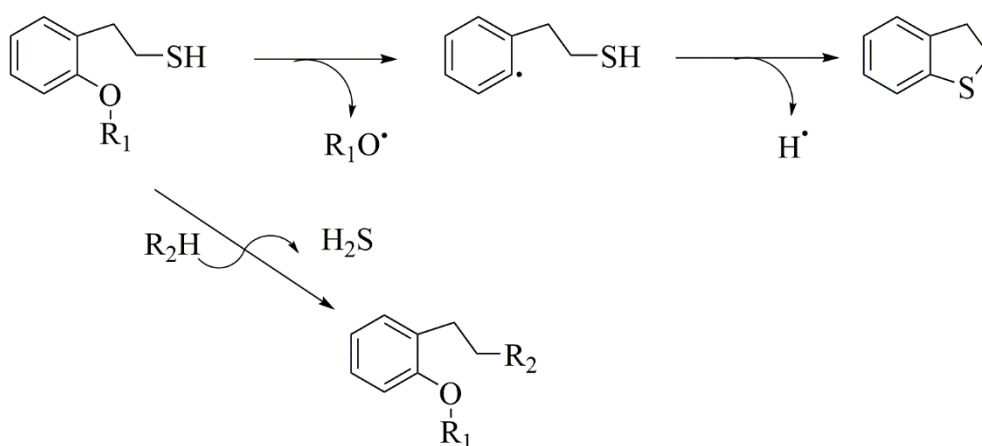
A proper comparison between aromatic yields obtained with those reported in literature is not an easy task cause the analytical methods generally used that are based on the merely chromatographic area percentage. Under this approximation, Guo et al.[41] reported an biooils aromatic concentration up to 90% using a fast thermal pyrolysis process and similar results could be also obtained using catalytic MAP processes[42]. Contrary to the study mentioned above, de Wild et al.[43] used a quantitative methods to quantify the aromatics after catalytic thermochemical lignin conversion and the results obtained are comparable with those achieved MAP at residual pressure.

3.5 FT IR-ATR analysis

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

Figure 10: FT-IR ATR spectra of all biooils

4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600
1/cm
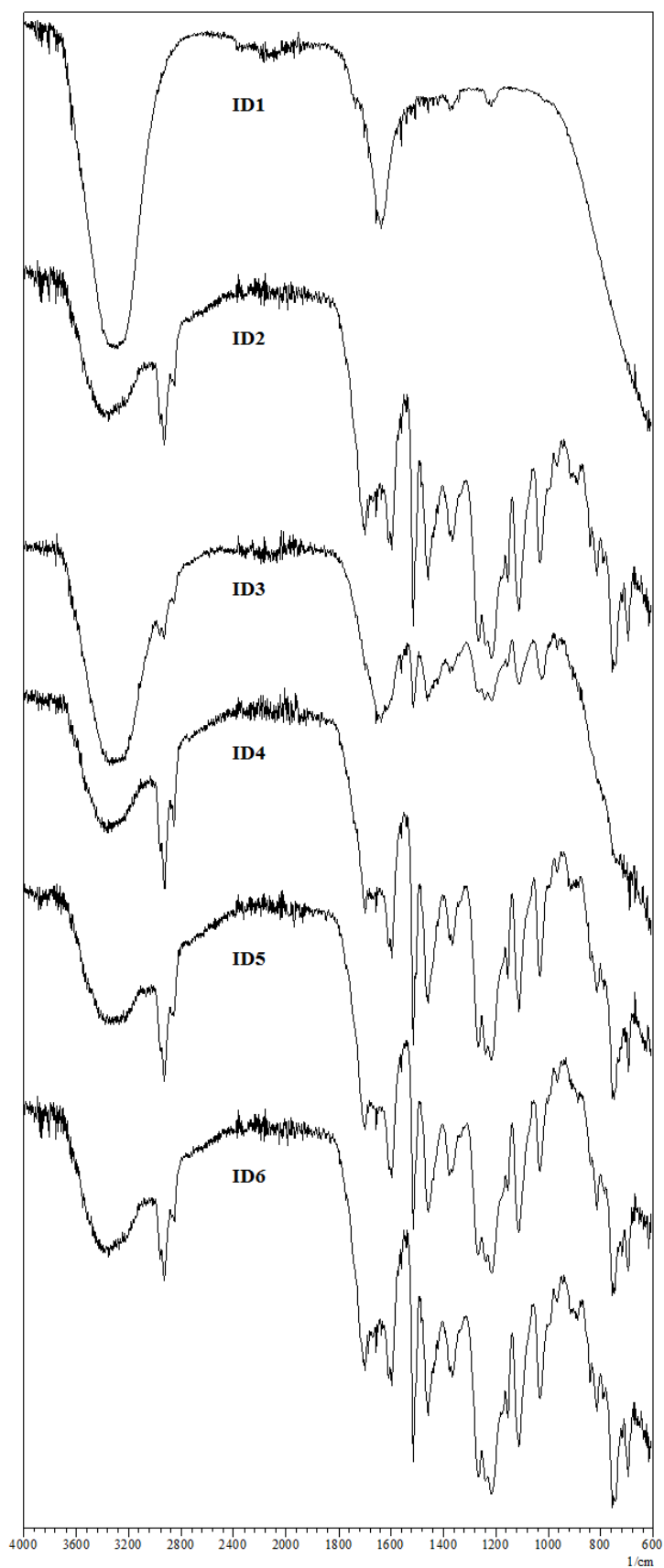
240

241 Broad bands in the range of 3750-3500 cm^{-1} attested the presence of water (ν_{OH}) and carboxylic acids

242 (ν_{COO}). The presence of aliphantic chains were confirmed by bands in the range and 2950-2750 cm^{-1}

15

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^{-}

246 ^{1} ($\nu_{C=C}$) 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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