

1 Article

2 **Characterization of Fast Pyrolysis Bio-oil from**
3 **Hardwood and Softwood Lignin**4 **Zahra Echresh Zadeh**¹, **Ali Abdulkhani**² and **Basudeb Saha**^{1, *}5 ¹ School of Engineering, London South Bank University, 103 Borough Road, London SE1 0AA, UK;
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12 **Abstract:** The depletion of fossil fuel reserves and the increase of greenhouse gases (GHG) emission
13 have led to moving towards alternative, renewable, and sustainable energy sources. Lignin is one
14 of the significant, renewable and sustainable energy sources of biomass and pyrolysis is one of the
15 most promising technologies that can convert lignocellulosic biomass to bio-oil. This study focuses
16 on the production and characterization of bio-oil from hardwood and softwood lignin *via* pyrolysis
17 process using a bench-scale batch reactor. In this study, a mixed solvent extraction method with
18 different polarities was developed to fractionate different components of bio-crude oil into three
19 fractions. The obtained fractions were characterized by using gas chromatography and mass
20 spectrometry (GCMS). The calculated bio-oil yields from Sigma Kraft lignin and Chouka Kraft
21 lignin were about 30.2% and 24.4%, respectively. The organic solvents, e.g. toluene, methanol, and
22 water were evaluated for chemical extraction from bio-oil, and it was found that the efficiency of
23 solvents is as follows: water > methanol > toluene. In both types of the bio-oil samples, phenolic
24 compounds were found to be the most abundant chemical groups which include phenol, 2-methoxy,
25 2-methoxy-6-methylphenol and phenol, 4-ethyl-2-methoxy that is due to the structure and the
26 originality of lignin, which is composed of phenyl propane units with one or two methoxy groups
27 (O-CH₃) on the aromatic ring.

28 **Keywords:** Bioenergy; Bio-oil; Characterization; Extraction; Lignin; Pyrolysis.
2930 **1. Introduction**

31 Fossil fuel sources are being depleted due to increased industrialization, and biomass is
32 considered to be a sustainable and renewable source of energy for the future [1]. Conversion of
33 biomass to biofuel has established significant consideration for the development of a renewable and
34 environmentally friendly source of energy for alternative fossil fuels since it does not contribute to
35 global warming [2,3]. A large number of biomass conversion technologies have been developed for
36 the production of biofuels, including biodiesel from vegetable oils [4] and bioethanol from sugar-
37 containing plants [5], which are considered as the first-generation of biofuels. Biofuels produced from
38 lignocellulose feedstock [6] are considered second-generation biofuels as they come from non-food
39 crops. The production of first generation biofuels determines significant costs due to limited
40 feedstock species, while the second generation biofuels overcome the problem of feedstock
41 availability related to the first generation biofuels and present a further preferable variety of
42 feedstocks[7–10]. Furthermore, the third generation of biomass have been derived from marine
43 biomasses such as algae and can be classified into two categories: microalgae and seaweeds[11]. The
44 third generation of biomass is a noble alternative to prevent the growth of food market prices
45 occurred because of the usage of farmable land for the production of first and second-generation
46 biofuels. The studies indicate that a wide variety of biomass can be used as feedstock for the

47 production of second-generation biofuels[12]. Different types of biological or thermochemical
48 conversion technologies can be employed to convert biomass to value-added products in the absence
49 of oxygen. For instance, anaerobic digestion is a biological process where the wet biomass such as
50 food waste and sewage sludge is converted to biogas in the absence of oxygen[13,14]. Whereas wood
51 and other forms of biomass can be converted to biofuel using thermochemical routes such as
52 combustion, gasification, and pyrolysis [1,14–16]. Pyrolysis is known as a process of thermal
53 degradation of organic materials to vapour in the absence of oxygen, where the large hydrocarbon
54 molecules decomposed to several smaller ones. [6]. If the pyrolysis performs in the presence of
55 subcritical water, it is generally called hydrous pyrolysis or hydrothermal carbonization (HTC) or
56 wet pyrolysis[20]. One of the advantages associated with wet pyrolysis is that wet materials such as
57 municipal solid waste (MSW) can be used as feedstocks. The solid product of wet pyrolysis is known
58 as hydrochar [21]. On the other hand, in the dry pyrolysis, the solid product is known as bio-char,
59 which is rich in carbon content, whereas the volatile product of this process is condensed to a liquid
60 fraction called tar or bio-oil along with a mixture of the non-condensable gasses. In general, dry
61 pyrolysis has three different variations: fast, intermediate, or mild and slow pyrolysis. The mode and
62 the conditions of pyrolysis can affect the relative proportions of the gas, liquid, and solid products.
63 The cellulose, hemicellulose, and lignin are the three main components of biomass, and all these three
64 main components of biomass are determined as the elements of hydrogen, carbon, and oxygen
65 [22]and high energy content can be relieved by pyrolysis process [23,24]. Lignin occurs throughout
66 the plant cell-wall, and in comparison to cellulose and hemicellulose, carries the highest specific
67 energy content [25] and is a by-product of the bleaching process of wood pulp. It is an aromatic
68 polymer composed of phenyl propane units that are connected through the ether and condensed (C-
69 C) linkages [26]. The worldwide annual production of lignin exceeds 70 million tons from the pulp
70 and paper industry, which is used as boiler fuel in the pulp and paper industry. Gaining the
71 knowledge and understanding the properties of lignin, such as reactivity, thermal stability, and
72 monomeric properties to obtain the optimal lignin applications for future development are far more
73 worthwhile than use it only as boiler fuel in the paper industry. Hence, lignin deserves more than
74 only be used as boiler fuel [27] since lignin is burned in the recovery boiler to compensate for the
75 energy and chemicals that are used in the pulping process. Other possible applications of lignin are
76 the concurrent production of lignosulfonate and bioethanol from spent liquor in the pulping process
77 [28]. Bio-oil production from lignin seems to be a promising solution to a sustainable source of energy,
78 however some technical issues such as energy efficiency and quality of the bio-oil remain to be
79 addressed.

80 Lignin pyrolysis chemistry can be investigated *via* the analysis of the products obtained from fast
81 pyrolysis at different temperatures. The composition of pyrolysis products strongly depends on the
82 source and quality of the biomass (lignin) as well as on the process parameters. In this study, two
83 different types of commercial Kraft lignin were selected. One type of Kraft Lignin is supplied by
84 Sigma Aldrich, which is produced from softwood and the other type supplied by Chouka Wood and
85 Paper Industry, Talesh, Iran, which is produced from hardwood. The softwood lignin consists of
86 about 75% coniferyl alcohol and 20% sinapyl alcohol and 5% *p*-coumaryl alcohol [29], which in total
87 has fewer methoxy groups than hardwood Kraft. Bio-crude oil from the pyrolysis of biomass is a
88 dark brown liquid with a pungent odor. It is a complex mixture and contains more than 400 different
89 chemical components such as organic acids, ketones, alcohol esters, furans, sugar derivatives,
90 phenols as well as aliphatic and aromatic hydrocarbons. Bio-oil has poor properties due to the
91 complexity of composition, which causes the limitation of the application range. In order to
92 determine the composition and understand the properties of bio-oil, the characterization of bio-oil is
93 necessary [30]. Hence, to improve the application and enhancing industrialization of bio-oil, different
94 separation methods can be used. The employed separation methods can be considered either as a
95 method to obtain chemicals from bio-oil or as an analysis method of bio-oil for research purposes
96 [31]. Distillation, adsorption, and emulsion are stated in the literature as the separation methods of
97 bio-oil to chemical families. However, bio-oil fractions can be separated by using solvent extraction
98 that can be considered as one of the effective methods of separation of bio-oil chemicals. Also, one of

99 the advantages of this method is the low cost of separation. Various types of organic solvents include
 100 hexane, toluene, dichloromethane, ethyl acetate, methanol, acetone, pentane, butanone, and diethyl-
 101 ether were examined to obtain the best possible route for this study. In the present study, a mixed
 102 solvent extraction method with different polarities was developed to fractionate different
 103 components of bio-crude oil into three fractions. The obtained fractions were characterized by using
 104 gas chromatography and mass spectrometry (GCMS). The main aim of this study is to identify the
 105 most efficient solvent extraction route to separate and analysis highly valued chemicals. The selection
 106 of the appropriate organic solvents for the multistep solvent extraction method is a crucial procedure
 107 to obtain the main chemicals of bio-oil such as phenol, phenol, 2-methoxy, and 2, 6-dimethoxy for
 108 both direct application and further separation. Other types of characterization techniques, e.g.
 109 elemental analysis, water content, pH, and bomb calorimetry, to obtain heating values were
 110 performed.

111 2. Materials and Methods

112 2.1 Materials

113 Two commercial Kraft lignins, one supplied by Sigma Aldrich (softwood lignin), and the other
 114 supplied by Chouka Wood and Paper Industry, Talesh, Iran, (hardwood lignin), were employed for
 115 this study. The lignins were dried in an oven for 12 hours at 373 K to remove moisture prior to
 116 pyrolysis experiments.

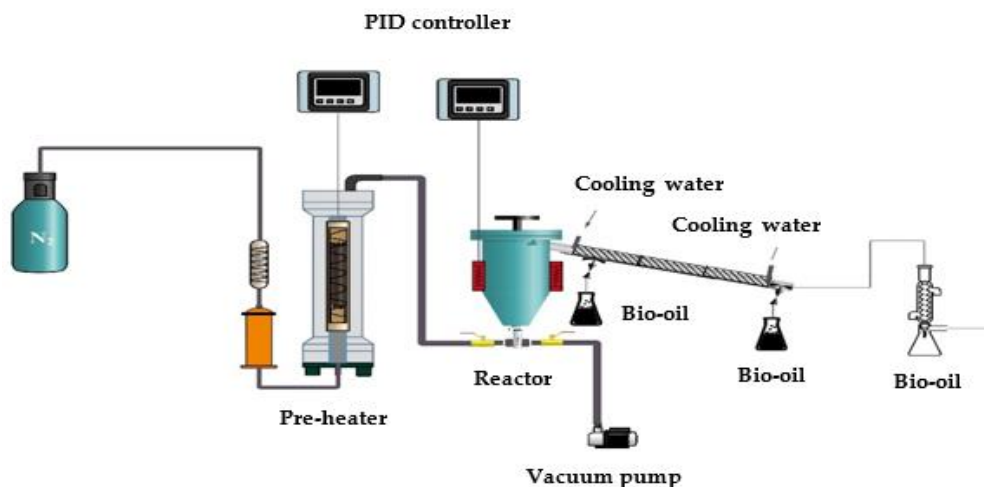
117 2.2 Crude Bio-oil Production

118 In this study, a fixed bed, bench-scale pyrolysis reactor was designed for bio-oil production,
 119 whereas the feedstock was fed in the reactor, and the heat was supplied externally. Electrical power
 120 was used to provide the heat, and nitrogen gas was used as a carrier gas to provide inert conditions
 121 inside the reactor.
 122 The experimental setup comprised of two preheaters to preheat the carrier gas before entering the
 123 reactor. A CaO store to remove the moisture from the carrier gas and a cylindrical stainless steel
 124 reactor vessel, which was heated by hot oil jacket and occupied around 10% with silica sand bed to
 125 maintain a homogenous temperature across the reactor. Also, the reactor vessel was attached with a
 126 PID controller and a double condenser. The attached thermocouples recorded the inside temperature
 127 of the reactor. The experiments were conducted at a temperature of 773 K for two types of lignins
 128 (Sigma Aldrich softwood lignin and Chouka hardwood lignin). The feedstocks were dried in an oven
 129 for 12 hours at 373 K to remove moisture before the pyrolysis process. In each experiment, firstly the
 130 weights of the glassware and condensers were recorded before and after the experiment to obtain
 131 an accurate weight of the bio-oil, using weigh by difference method. Approximately 100 g of lignin
 132 was weighed and loaded inside the sample container and then placed inside the reactor when the
 133 thermocouple indicated the temperature of 773 K (Figure 1). Nitrogen gas (N₂) was introduced at the
 134 rate of 500 ml/min to the reactor after passing through two preheaters to obtain oxygen-free
 135 conditions. The outlet of the pyrolysis reaction was directed into a water-cooled condenser, and the
 136 condensed liquid bio-oil was collected at three different collection points. Figure 1 illustrates the
 137 schematic of the experimental setup for bio-oil production. On completion of the experiment, to
 138 obtain the liquid mass yield, the condensers and glassware were weighed again, and the difference
 139 was calculated and the bio-oils that were collected at the collection points, considered as the liquid
 140 yield. To recover the bio-oil, which was attached to the condenser walls, the condensers were washed
 141 with acetone, and then the solvent was allowed to evaporate. After that the liquid and solid products
 142 were weighted, and the following equations were used to calculate the product yield.

$$\text{Liquid Yield (\%)} = (\text{Weight of Liquid (g)}) / (\text{Weight of Lignin Fed to Reactor (g)}) \times 100 \quad (\text{Eq1})$$

$$\text{Char Yield (\%)} = (\text{Weight of Solid (g)}) / (\text{Weight of Lignin Fed to Reactor (g)}) \times 100 \quad (\text{Eq2})$$

$$\text{Gas Yield (\%)} = 100 - (\text{Liquid Yield (\%)} + \text{Char Yield (\%)}) \times 100 \quad (\text{Eq3})$$



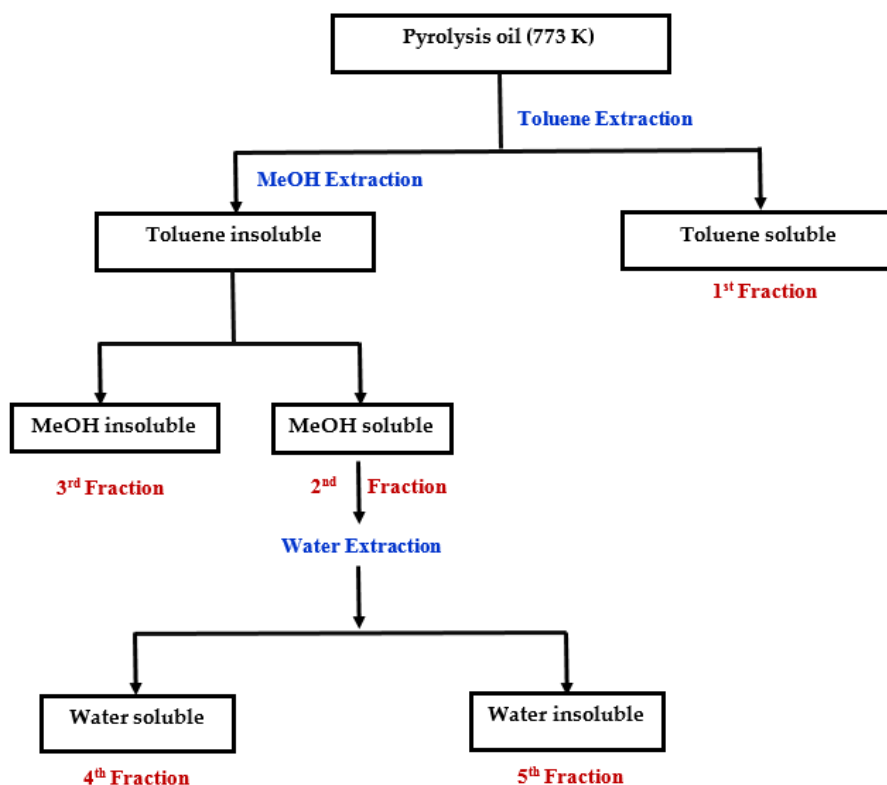
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Figure 1. Schematic of experimental set-up for bio-oil production

145 *2.3. Characterisation of Bio-oil*

146 *2.3.1 Fractionation of Bio- oil*

147 The principle of solvent extraction is based on solvent polarity, and the solvation capability of
 148 the materials excited in the bio-oil. Hence, the polarity is used as the driving force for the fractionation
 149 of bio-oil. One of the advantages of the solvent extraction method is that each of the separated
 150 fractions can be appointed to a certain chemical family. Therefore, the grouping of bio-oil components
 151 into chemical families is a useful method for characterisation of bio-oil with about 400 different
 152 components. Solvent extraction can be considered as an upgrading technique in the development of
 153 bio-oil upgrading approaches. After evaluating numerous types of solvents such as butanone,
 154 hexane, ethyl acetate, toluene, methanol, dichloromethane, and diethyl ether to extract the light oil
 155 from heavy oil the protocol which, is presented in Figure 2, was the best-considered route for this
 156 purpose. This route contains three organic solvents, in which the degree of polarity changes from top
 157 to down the route (Figure 2). The polarity of toluene is lower than methanol and methanol's polarity
 158 is lower than water. Bio-crude oil was prepared at a temperature of 773 K. In this method, 4 ml of oil
 159 was mixed with 115 ml of toluene to obtain toluene soluble and toluene insoluble fractions. The main
 160 aim of this step is to separate the wood-extractive compounds that interfere with the heavy
 161 compounds precipitating process. The filter paper was used to separate the insoluble waxy materials
 162 suspended in the toluene soluble fraction. Toluene soluble is the first extracted fraction of bio-oil,
 163 which can be injected to GCMS for compositional analysis (see 1st fraction in Figure 2). The toluene
 164 insoluble fraction was treated with 115 ml of methanol to separate the char, non-polar waxy materials
 165 and other very heavy oligomeric compounds as the MeOH insoluble fraction. The MeOH soluble
 166 fraction was filtrated and then placed in the rotary evaporator to remove the solvent. According to
 167 Figure 2, MeOH is the 2nd fraction that was injected into the GCMS. The residue from the rotary
 168 evaporator was dried in an oven at a temperature of 378 K overnight. Then the residue was weighed,
 169 and 150 ml of ice-cooled distilled water was added per 10 g of MeOH-oil mixture. The distilled water
 170 was added dropwise with continuous agitation to provide the water-soluble (4th fraction) and water-
 171 insoluble (5th fraction) according to Figure 2.



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Figure 2. Fractionation protocol of bio-oil for light oil and chemicals

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2.3.2 GCMS Analysis of Obtained Fractionations of Bio- oil

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The chemical compositions of the entire obtained fractions for the two types of bio-oil were determined by gas chromatography with mass spectra (GCMS) Shimadzu GCMS-QP2010S with manual injection. The column was a mild-polarity phase, 14% cyanopropylphenyl polysiloxane; 30 m, 0.25 mm inner diameter, 0.25 μm film thickness. The GC oven temperature was held at 323 K for 2 min then programmed to 563 K at 278 K min^{-1} . The injector temperature was 568 K with split mode, and the injection dose was 1 μL . The carrier gas flow rate was 0.90 ml/min to maintain a high-quality separation of the components. The mass scanning range was adjusted at 80-700 m/z and the electron ionization system with ionization energy of 70 eV was used.

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2.3.3 Elemental Analysis (CHNO) and Heating Values

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A CE-440 elemental analyser was used to obtain the percentage of hydrogen, carbon, sulphur and oxygen. The heating values were obtained using the Bomb Calorimetry (G.CUSSONS with PT104 data logger) method.

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2.3.4 Water Content and pH

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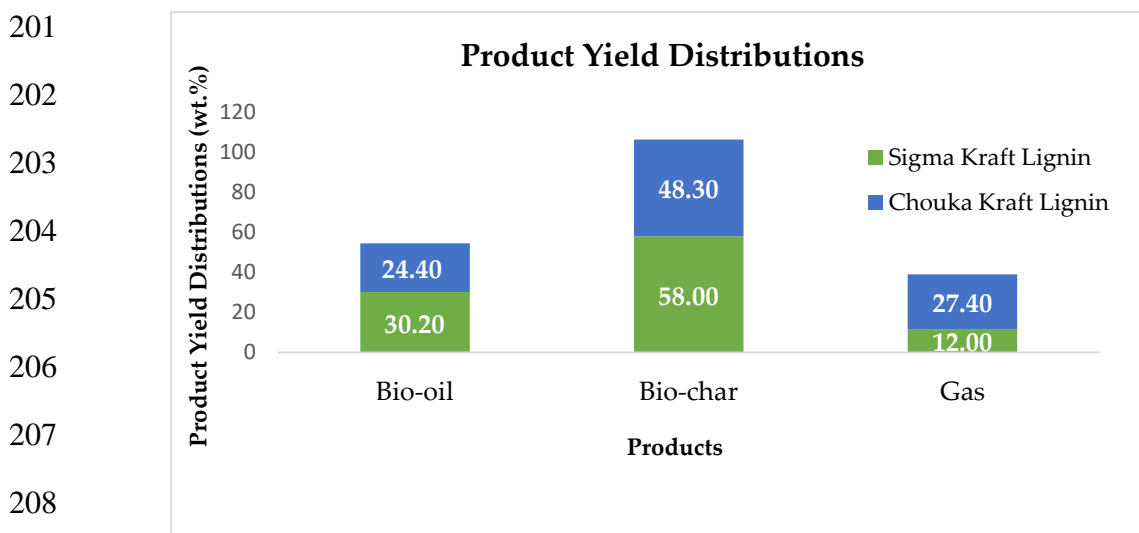
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The water content of bio-oil was analysed by Karl–Fisher titration Mettler Toledo. The used solvent for this method was dry methanol, and this solvent can dissolve all the compounds of bio-oil. In this approach, one drop (0.0060 g) of bio-oil was added to the glass bottle containing Karl-Fisher solvent and after entering the exact weighed injected bio-oil drop. The reported data is the average of three runs for each sample. The pH values of the bio-oil samples were measured by using PHM240 at 298 K. Methanol was used to clean the probe after each run. The reported data is the average of two readings for each sample.

197 3. Results and discussions

198 3.1 Distribution of product yield

199 The distribution of product yield results from thermal fast pyrolysis of two types of lignin is
200 presented in Figure 3.



209 **Figure 3.** Product yield distributions (wt. %) of fast pyrolysis of Sigma Kraft (softwood) and
210 Chouka Kraft (hardwood) lignin

211 The results indicate that the product yield distribution is affected by the type of lignin. The bio-oil
212 yield and bio-char yield of the Sigma Kraft lignin (softwood) was higher than the Chouka Kraft lignin
213 (hardwood). However, the gas yield of Chouka Kraft was higher than the Sigma Kraft lignin. One of
214 the possible reasons could be different lignin processing conditions used by different wood and pulp
215 industries since, in this study, two Kraft lignins were supplied by two different commercial
216 companies. This assumption was confirmed by elemental analysis of the bio-oil samples, where the
217 bio-oil from Sigma Kraft lignin presented higher carbon and oxygen and lower sulphur and oxygen
218 in comparison to the bio-oil from Chouka Kraft lignin. The low bio-oil yield could be as a result of
219 longer reaction time and a high lignin loading. However, it is essential to investigate the effect of
220 reaction time and the loading amount of lignin on the production of bio-oil from technical lignin.

221 3.2 Properties of Bio-oil

222 3.2.1 Elemental Analysis (CHNO) and Heating Values

223 The elemental analysis of two different bio-oils was performed to investigate carbon, hydrogen,
224 sulphur and oxygen content of fast pyrolysis bio-oil samples. In addition, the standard measurement
225 of the energy content of a fuel, which is known as heating value, was determined. Table 1, bio-oil
226 from Sigma Kraft Lignin contains higher carbon and hydrogen by 68.50% and 6.63% respectively
227 whereas the bio-oil from Chouka Kraft Lignin presented lower values for carbon and hydrogen.
228 However, both lignins contain an acceptable amount of carbon and hydrogen in comparison to the
229 values reported by other researchers [32]. Moreover, the bio-oil obtained from Sigma Kraft Lignin
230 presents a lower sulphur content than Chouka Kraft Lignin. However, this sulphur results from the
231 Kraft pulping process where the woodchips are converted into pulp through the bleaching process
232 by washing the wood with white liquor ($\text{Na}_2\text{S}/\text{NaOH}$). In this process, the lignin is separated from
233 wood chips by breaking the bonds that link lignin, hemicellulose, and cellulose[33]. The lignin
234 obtained by Kraft process contains considerable amounts of sulphur compounds including
235 lignosulfates, which is considered as one of the disadvantages of the Kraft process[34].

236 As stated in the literature, the oxygen content of bio-oil varies in the range of 35-40% [35]. The
 237 lowest amount of oxygen was found for Sigma Kraft Lignin (22.91%). The presence of oxygen in bio-
 238 oil confirms the necessity of upgrading of bio-oil for a better quality bio-oil. Since the presence of
 239 oxygen in the bio-oil is considered as the main difference between bio-oil and fossil fuels, which
 240 results in poor properties of bio-oil such as corrosiveness, low energy density, and thermal stability.

241 Heating values were determined by using the oxygen-bomb calorimeter method and it was
 242 found that both lignin bio-oils have a high heating value (HHV), was 29.97 MJ/kg for Sigma Kraft
 243 Lignin and was 28.63 MJ/kg for Chouka Kraft Lignin. The bio-oil lower heating values were found to
 244 be 28.56 MJ/kg for Sigma Kraft Lignin and 27.33 MJ/kg for bio-oil from Chouka Kraft Lignin. As stated
 245 in the literature [33], the lower heating values of bio-oil in comparison to fossil fuels, which, is
 246 between 41 and 43 MJ/kg is almost half of fossil fuels due to oxygen and water contents. This explains
 247 the requirement of upgrading to reduce the oxygen and water contents and improve the bio-oil
 248 properties.

249 Table 1. Elemental analysis (CHNO) and heating values of the bio-oil samples

Sample ID	Carbon%	Hydrogen%	Sulphur%	Oxygen%	HHV (MJ/kg)	LHV (MJ/kg)
Sigma Kraft Lignin	68.50	6.63	1.96	22.91	29.97	28.56
Chouka Kraft Lignin	64.80	6.13	2.09	26.98	28.63	27.33

250 3.2.2 Water Content and pH Values

251 The presence of water in bio-oil is unavoidable and it is due to the moisture content of the raw
 252 materials and dehydration reactions during the pyrolysis process[36]. As stated in the literature, the
 253 water content of bio-oil is reported to be 15-35% [33]. The existence of water in bio-oil has a negative
 254 effect on the storage, which causes phase separation and also reduces the heating values In Table 2,
 255 the water content of Sigma Kraft Lignin (10.43%) seems to be lower than the Chouka Kraft Lignin (12.
 256 00%). The pH values are presented in Table 2. The pH value for bio-oil of Sigma Kraft Lignin was
 257 5.33, whereas for Chouka Kraft lignin was 4.57, as shown in Table 2. Therefore, the bio-oil requires
 258 upgrading to fulfil the standard requirement of fuels to be accepted in any application.

259 Table 2. Physical properties of two different samples of fast pyrolysis bio-oil at 773 K

260

Sample ID	Properties	
	Water Content %	pH
Sigma Kraft Lignin	10.43	5.33
Chouka Kraft Lignin	12.00	4.57

261 3.3 GCMS Analysis of Sigma Kraft and Chouka Kraft Lignin Bio-oil Fractions

262 The fractionation method was developed by examining several different types of organic
 263 solvents to separate different chemicals at each stage. To determine the chemical composition of the
 264 extracted fraction, GCMS analysis was performed. The injected fractions for each type of fast
 265 pyrolysis bio-oil, e.g. toluene soluble, MeOH soluble and water-soluble were analysed, and the
 266 results obtained from fractionation of bio-crude oil are presented below.

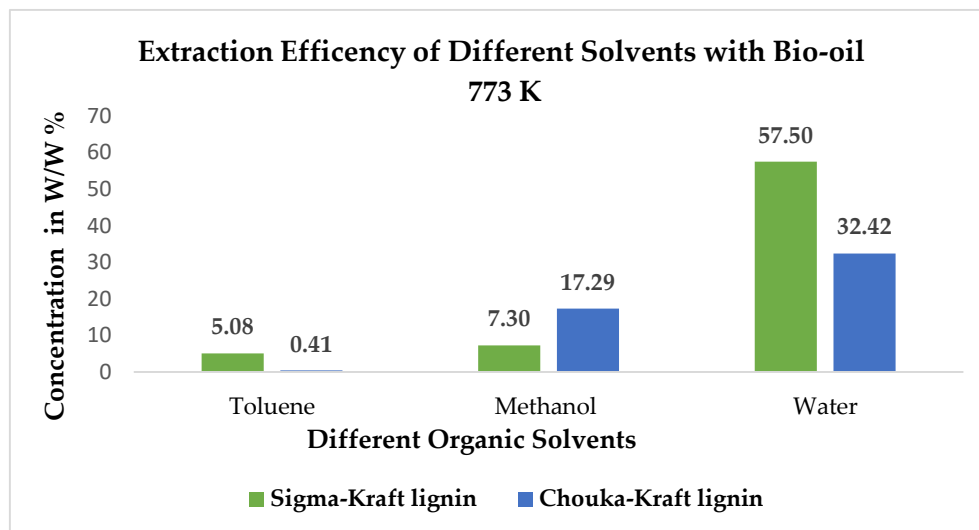
267 GCMS analysis identified more than 40 compounds detected in bio-oil by the solvent extraction
 268 method and the identified compounds were recorded by a probability match of more than 90% using
 269 the GCMS software NIST library. The identified compounds were entirely phenolics and aromatics

270 groups detected by GCMS in the pyrolysis of bio-oil from two different commercial lignins. The
 271 analysis of the identified compounds was performed by checking the mass report of the GCMS results
 272 for each bio-oil from different feedstock (Sigma Kraft lignin and Chouka Kraft lignin). Then the mass
 273 report for each bio-oil was analysed by checking three extracted fractions, e.g. toluene soluble, MeOH
 274 soluble and water-soluble. The extracted data was reported in graphs of abundancy against retention
 275 time for each fraction (supplementary materials, Figures S1 and S2) and the corresponding
 276 components for each graph were presented in Tables 3 and 4.

277 3.3.1 Effect of Organic Solvents on the Extraction of Total Chemicals

278 The effect of solvents on the extraction of chemical compounds in bio-oil is investigated in this
 279 study. Figure 4, illustrates the total mass percentage of the chemicals extracted by three different
 280 organic solvents from two different types of bio-oil (Sigma Kraft lignin and Chouka Kraft lignin) at a
 281 temperature of 773 K. As shown in Figure 4, water has the highest affinity for chemicals at this
 282 fraction for both types of bio-oil. The identified compounds in the pyrolysis oil from lignin were
 283 totally phenolics compounds. The phenolic compounds are polar compounds, which extracted with
 284 a solvent with a higher polarity such as water or methanol. The chemicals that exist in bio-oil are
 285 mostly oxygenated compounds which have high polarity and solubility in water and polar solvents.
 286 Therefore, fewer compounds dissolved in the toluene due to its low polarity, which limits the
 287 solubility of the oxygenated compounds. These findings are in accordance with the previous studies
 288 reported by literature which confirms that more chemicals can be extracted from bio-oil with solvents
 289 with higher polarity [37]. As shown in Figure 4, for bio-oil produced from Sigma Kraft Lignin,
 290 methanol extracted 7.30%, water 57.50% and toluene 5.08% of the bio-oil chemicals. For Chouka Kraft
 291 Lignin, methanol separated 17.29%, water 32.42% and toluene 0.41% of the bio-oil chemicals.

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293

294 **Figure 4.** The effect of solvent on the extraction of chemicals

295 3.3.2 GCMS Analysis of Sigma Kraft Lignin and Chouka Kraft Lignin Bio-oil Fractions

296 Lignin is a by-product of the bleaching process of wood pulp, and it is an aromatic polymer
 297 composed of phenyl propane units that are connected through the ether and condensed (C- C)
 298 linkages. Lignin pyrolysis chemistry is investigated *via* the analysis of products obtained from fast
 299 pyrolysis. The composition of pyrolysis products strongly depends on the source and quality of the
 300 biomass (lignin) as well as on the process parameters. In this study, two different types of commercial
 301 Kraft lignin were selected. One supplied by Sigma Aldrich, which is produced from softwood and
 302 the other supplied by Chouka Wood and Paper Industry, Talesh, Iran, which originated from

303 hardwood. The Sigma Kraft lignin consists of about 75% coniferyl alcohol and 20% sinapyl alcohol
304 and 5% *p*-coumaryl alcohol [29], which in total has fewer methoxy groups than hardwood Kraft.

305 3.3.2.1 GCMS Analysis of Sigma Kraft Lignin Bio-oil Fractions

306 The peak identification and chemical compositions of bio-oil from Sigma Kraft Lignin, e.g.
307 toluene soluble, MeOH soluble and water-soluble are presented in Table 3, and each fraction is
308 discussed as follows.

309 3.3.2.1.1 Sigma Kraft Lignin-Toluene Soluble

310 Toluene can be considered as an effective solvent in separating different types of the chemical
311 group with lower polarity. As can be seen from Table 3, phenolic and aromatic compounds were
312 separated by toluene fraction. Phenolic compounds have lower polarity than acids and furans and
313 according to the functional group and previously reported studies phenolic family was considered
314 the components, which include 1, 2-benzenediol, phenol, 3-ethylphenol, 2, 6-dimethoxyphenol [35].
315 The toluene fraction analysis of sigma Kraft Lignin shows the separation of different phenolic
316 components such as phenol, phenol, 2-methoxy, and 2-methoxy-6-methylphenol, guaiacol and 1, 2-
317 benzenediol. According to the structure and the originality of lignin, which is composed of phenyl
318 propane units with one or two methoxy groups (O-CH₃) on the aromatic ring, the deformation of
319 lignin provides lower molecular weight compounds that composed of monomers of lignin. Hence,
320 it is clear that the distribution of the extracted chemicals resulted from the pyrolysis of lignin would
321 be mostly on phenolics compounds.

322 3.3.2.1.2 Sigma Kraft Lignin- Methanol (MeOH) Soluble

323 It was found that phenolics and aromatics compounds were the main extracted compounds in
324 MeOH fraction detected by GCMS. However, the polarity of phenolic groups is lower than other
325 chemical groups such as acids, furans and hence according to the principle of dissolution, the
326 extraction efficiency of phenolic compounds is better by solvent with higher polarity. Hence, more
327 phenolics were extracted by methanol in comparison to toluene. However, the phenolics and
328 aromatics were the two most observed compounds in this fraction due to the originality of lignin,
329 which composed of phenyl propane units. A small number of other components such as sugars,
330 esters, and alcohols were also identified in this fraction due to the higher polarity of these
331 compounds. In addition, methanol insoluble fractions were extracted as a homogenous char-powder
332 fraction. However, as mentioned above, according to Figure 2 which illustrates the fractionation
333 protocol of bio-oil with different solvent, the main aim of the treatment of bio-oil fractions with
334 methanol after toluene, is to remove the char and non-polar compounds.

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336 3.3.2.1.3 Sigma Kraft Lignin- Water Soluble

337 The cloudy-yellow water-soluble fractions were mainly composed of acids, sugars, alcohols,
338 ethers, aromatics, and phenolics, which comprised of more polar compounds of the pyrolysis oils. In
339 other words, all the compounds in pyrolysis oils, eluted with GCMS analysis were found in the water-
340 soluble fraction. However, fewer compounds were identified by water extraction of Sigma-Kraft
341 lignin bio-oil. According to Table 3, 4-hydroxy-3-methoxyphenyl, which is the G units (Guaiacyl) of
342 softwood and resulted from coniferyl alcohol precursor was identified in these fractions and this
343 confirms the origin of the Sigma Kraft lignin, which comes from softwood.

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348 Table 3. Peak identification of fast pyrolysis products of Sigma Kraft Lignin

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	Peak No	Component	RT (min)	Chemical Family
Toluene Soluble 773 K	1	Phenol	13.94	Phenolics
	2	Phenol, 2-methoxy	14.44	Phenolics
	3	Phenol, 3-methyl	15.30	Phenolics
	4	Phenylmethyl alcohol	16.33	Phenolics
	5	2-Methoxy-6-methylphenol	17.36	Phenolics
	6	Phenol, 4-ethyl-2-methoxy	18.99	Phenolics
	7	Phenol, 2,3,6-trimethyl	19.55	Phenolics
	8	Phenol, 2-methoxy-4-propyl	21.69	Phenolics
	9	1,2-Benzenediol	22.27	Phenolics
	10	1,2,4-Trimethoxybenzene	24.63	Aromatics
	11	Benzene methanol, 4-hydroxy	26.02	Aromatics
	12	Vanillyl methyl ketone	27.75	Aromatics
	13	Phenol, 4-(ethoxymethyl)-2-methoxy	30.60	Phenolics
MeOH Soluble 773 K	1	Phenol	13.97	Phenolics
	2	Phenol, 2-methoxy	14.34	Phenolics
	3	Fumaric acid, 2-ethylcyclohexyl isobutyl ester	15.03	Esters
	4	Phenol, 3-methyl	16.32	Phenolics
	5	2-Methoxy-6-methylphenol	17.23	Phenolics
	6	Phenol, 2-ethyl	18.72	Phenolics
	7	4-Ethyl guaiacol	19.46	Phenolics
	8	Phenol, 2-ethyl-5-methyl	19.85	Phenolics
	9	Phenol, 2-methoxy-4-propyl	21.62	Phenolics
	10	1,2-Benzenediol	22.25	Phenolics
	11	Phenol, 2-methoxy-4-propenyl	24.25	Phenolics
	12	3-Methoxy-4-hydroxy acetophenone	26.67	Aromatics
	13	Vanillyl methyl ketone	27.68	Aromatics
	14	Methyl-(2-hydroxy-3-ethoxy-benzyl)ether	30.54	Aromatics
Water Soluble 773 K	1	Acetic acid	2.36	Acids
	2	Propane, 1-(1-methylethoxy)	4.14	Ethers
	3	Phenol, 2-methoxy	14.23	Phenolics
	4	2-Methoxy-6-methylphenol	17.12	Phenolics
	5	1,2-Benzenediol	22.27	Phenolics
	6	1,3-Benzenediol, 2-methyl-	24.25	Phenolics
	7	Acetoguaiacon	26.68	Aromatics
	8	4-Hydroxy-3-methoxyphenyl	27.69	Aromatics
	9	Phenol, 4-(ethoxymethyl)-2-methoxy	30.59	Phenolics

350

351 3.3.2.2 GCMS Analysis of Chouka Kraft Lignin Bio-oil Fractions

352 The second type of lignin was provided by Chouka Wood and Paper Industry, Talesh, Iran,
 353 which was produced from hardwood. The lignin content of hardwood generally is less than
 354 softwood. The monomeric lignin precursor of softwood is guaiacyl only while the precursors of
 355 hardwood lignin are guaiacyl and syringyl units [38]. Thus, the hardwood contains higher methoxy
 356 groups than softwood that results in the condensed-type linkage between phenyl propane units in
 357 hardwood [39].

358 The peak identification and chemical compositions of bio-oil from Chouka Kraft Lignin, including
 359 toluene soluble, MeOH soluble and water-soluble are presented in Table 4.

360

361 Table 4. Peak identification of the fast pyrolysis products of Chouka Kraft Lignin

	Peak No	Component	RT (min)	Chemical Family
Toluene Soluble 773 K	1	Formic acid phenyl ester	14.07	Aromatics
	2	Benzenemethanol	15.44	Aromatics
	3	Phenol, 3-methyl	16.47	Phenolics
	4	2-Methyl-4-nitro-5-pyrrolidin-1-yl-phenylamine	18.79	Aromatics
	5	Phenol, 2-ethyl-6-methyl	20.97	Phenolics
Methanol Soluble 773 K	1	Phenol	14.02	Phenolics
	2	Phenol, 3-methyl	15.40	Phenolics
	3	Phenol, 4-methyl	16.42	Phenolics
	4	Phenol, 2,3-dimethyl	17.69	Phenolics
	5	Phenol, 2,5-dimethyl	18.73	Phenolics
Water Soluble 773 K	1	Phenol	12.87	Phenolics
	1	Phenol, 2,6-dimethyl	16.62	Phenolics
	2	Phenol, 4-(2-methylpropyl)	19.26	Phenolics
	3	1,2,3-Trimethoxybenzene	20.34	Phenolics
	4	2,3,6-Trimethylphenol	22.55	Phenolics
	5	Phenol, 3,4-dimethoxy	25.32	Phenolics
	6	1,2,4-Trimethoxybenzene	27.30	Phenolics
	7	Benzene, 1,2,3-trimethoxy-5-methyl	29.15	Phenolics
	8	2,6-Dimethyl-4-nitrophenol	33.38	Phenolics
9	Methyl 14-methylpentadecanoate	12.87	Esters	

362

363 3.3.2.2.1 Chouka Kraft Lignin-Toluene Soluble

364 The result of the toluene fraction of bio-oil from Chouka Kraft lignin is shown in Table 4. The
 365 non-polar compounds with high molecular weight were expected to be separated by toluene soluble
 366 fraction. However, the phenolics were the dominant chemical groups for this fraction of bio-oil
 367 obtained from Chouka Kraft Lignin. As stated in the literature, toluene is also considered as an
 368 efficient solvent for extraction of phenolic and aromatic compounds [31]. In addition, there were no
 369 peaks corresponding to small hydrocarbon (C2-C5) products, which most probably due to the low
 370 carbohydrate content of the lignin. However, the origin of the Chouka lignin comes from hardwood
 371 and hardwood has less lignin content in comparison to softwood. Hence, Sigma Kraft lignin

372 (softwood) shows a better distribution of chemicals in the fractionation approach in comparison to
373 Chouka Kraft lignin. Furthermore, among the three solvents, toluene shows a better affinity to the
374 chemicals presents in Chouka Kraft lignin in comparison to bio-oil from Sigma Kraft lignin as more
375 compounds were extracted by this solvent (Table 3 and Table 4).

376 3.3.2.2.2 Chouka Kraft Lignin-Methanol Soluble

377 The result of the methanol fraction of bio-oil from Chouka Kraft lignin is shown in Table 4. As can be
378 seen, less number of compounds were identified by methanol in comparison to methanol fractions of
379 Sigma Kraft lignin.

380

381 3.3.2.2.3 Chouka Kraft Lignin-Water Soluble

382 Water-soluble fractions of Chouka Kraft lignin bio-oil are presented in Table 4. Generally, fewer
383 compounds were extracted by toluene extraction in comparison to Sigma Kraft lignin bio-oil. It
384 appears that Chouka Kraft lignin bio-oil contains compounds with a higher polarity which were
385 extracted by water fraction. The polarity of methanol and water is higher than toluene which
386 methanol and water show a good performance in the extraction of compounds with higher polarity.

387 3.4. Applications and Future Perspective for the Production of Fuels and Chemicals

388 There has been a growing demand in bio-oil production in the last two decades due to potential
389 shortages of petroleum resources, hence in recent years, the ecological advantages of bio-oil have
390 played an important role in this production. Bio-oil produced from biomass can be considered
391 essentially as a renewable source of energy which contains low nitrogen and sulphur, maintains a
392 closed carbon cycle with no net increase in atmospheric CO₂ levels compared to fossil fuels [40].
393 However, the properties of bio-oil have significant problems during its use as a fuel in boilers,
394 engines, and gas turbines. Oxygen content, poor volatility, high viscosity, coking, and corrosiveness
395 have so far limited the range of bio-oil applications [33]. Combustion behavior of bio-oil due to the
396 presence of high content of non-volatile components in bio-oil has an important impact on the
397 performance of bio-oils during combustion and consequently on the applications for energy
398 production. The most important feature of bio-oil is being liquid which makes the storage, usage and
399 transportation such as easy process [41]. Bio-oil can be used as fuel oil or diesel in many applications
400 such as boilers, engines and turbines for electricity generation and as a raw material for the
401 production of adhesives such as phenol-formaldehyde-type resins, wood flavours, etc. [42,43]. Lignin
402 pyrolysis bio-oil can be used for the synthesis of phenolic resins without any fractionation [41].
403 Hence, a very useful application of phenolic compounds in bio-oil is to extract phenols from bio-oil,
404 since phenolics compounds are valuable chemicals and can be used in a wide range of applications.
405 Resin manufacturing is one of the virtual applications of phenolic compounds and is normally
406 synthesised by acid or base catalysed reactions between phenols and aldehydes to produce phenol-
407 formaldehyde (PF) resin. Phenolic resins are used in many industries such as electronic laminating
408 and wood composite industries. The application of phenolic-rich bio-oil in synthesis of phenol-
409 formaldehyde resin to replace the petroleum-based phenol is one of the potential applications in this
410 field [41].

411 4. Conclusions

412 The main aim of this study is to focus on solving a real-world problem for sustainable production
413 of bioenergy from a renewable source of feedstock. For this purpose, this study focused on the
414 production and characterization of fast pyrolysis bio-oil from two different types of technical lignin
415 samples. Selective extraction method was used to obtain chemicals from bio-oil and also as a method
416 of analysis to determine the chemical composition of bio-oil by GCMS. Other types of characterization
417 techniques, e.g. elemental analysis, water content, pH and bomb calorimetry, were performed. This
418 study can be concluded as follows:

419 A fixed bed, bench-scale pyrolysis reactor was designed to produce bio-oil from two commercial
 420 lignins. The bio-oil yield from Sigma Kraft lignin and Chouka Kraft lignin was calculated to be about
 421 30.24 % and 24.36%, respectively. Three organic solvents, such as toluene, methanol and water were
 422 evaluated for chemical extraction from bio-oil, and it was found that the efficiency of solvents is as
 423 follows: water > methanol > toluene. The fractions obtained by solvent extraction describes the bio-
 424 oil as a mixture of ten chemical families, e.g. phenolics, aromatics, furans, ketones, alcohol, acids,
 425 sugars, ethers, esters and aldehydes. However, in this study, only bio-oil from lignin has been
 426 presented.

427 In the current study, for both types of bio-oil samples, phenolic compounds were found to be
 428 the most abundant chemical groups, which include phenol, 2-methoxy, 2-methoxy-6-methylphenol
 429 and phenol, 4-ethyl-2-methoxy.

430 The application of phenolic-rich bio-oils for the synthesis of phenol-formaldehyde resin shows
 431 its strong potential for the replacement of phenols sourced from fossil fuels. However, the future
 432 study on bio-oil from catalytic pyrolysis of lignin enhances the potential for liquid fuel applications.

433

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439

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