Article

Characterization of Fast Pyrolysis Bio-Oil from Hardwood and Softwood Lignin

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Abstract: The depletion of fossil fuel reserves and the increase of greenhouse gases (GHG) emission have led to moving towards alternative, renewable, and sustainable energy sources. Lignin is one of the significant, renewable and sustainable energy sources of biomass and pyrolysis is one of the most promising technologies that can convert lignocellulosic biomass to bio-oil. This study focuses on the production and characterization of bio-oil from hardwood and softwood lignin via pyrolysis process using a bench-scale batch reactor. In this study, a mixed solvent extraction method with different polarities was developed to fractionate different components of bio-crude oil into three fractions. The obtained fractions were characterized by using gas chromatography and mass spectrometry (GCMS). The calculated bio-oil yields from Sigma Kraft lignin and Chouka Kraft lignin were about 30.2% and 24.4%, respectively. The organic solvents, e.g., toluene, methanol, and water were evaluated for chemical extraction from bio-oil, and it was found that the efficiency of solvents is as follows: water > methanol > toluene. In both types of the bio-oil samples, phenolic compounds were found to be the most abundant chemical groups which include phenol, 2-methoxy, 2-methoxy-6-methylphenol and phenol, 4-ethyl-2-methoxy that is due to the structure and the originality of lignin, which is composed of phenyl propane units with one or two methoxy groups ($O-CH_3$) on the aromatic ring.

Keywords: bioenergy; bio-oil; characterization; extraction; lignin; pyrolysis

1. Introduction

Fossil fuel sources are being depleted due to increased industrialization, and biomass is considered to be a sustainable and renewable source of energy for the future [1]. Conversion of biomass to biofuel has established significant consideration for the development of a renewable and environmentally friendly source of energy for alternative fossil fuels since it does not contribute to global warming [2,3]. A large number of biomass conversion technologies have been developed for the production of biofuels, including biodiesel from vegetable oils [4] and bioethanol from sugar-containing plants [5], which are considered as the first-generation of biofuels. Biofuels produced from lignocellulose feedstock [6] are considered second-generation biofuels as they come from non-food crops. The production of first generation biofuels determines significant costs due to limited feedstock species, while the second generation biofuels overcome the problem of feedstock availability related to the first generation biofuels and present a further preferable variety of feedstocks [7–10]. Furthermore, the third generation of biomass have been derived from marine biomasses such as algae and can be classified into two categories: microalgae and seaweeds [11]. The third generation of biomass is a noble alternative to prevent the growth of food market prices occurred because of the usage of farmable landing for the production of first and second-generation biofuels. The studies indicate that a wide variety of biomass can be used as feedstock for the production of second-generation biofuels [12]. Different

types of biological or thermochemical conversion technologies can be employed to convert biomass to value-added products in the absence of oxygen. For instance, anaerobic digestion is a biological process where the wet biomass such as food waste and sewage sludge is converted to biogas in the absence of oxygen [13,14], whereas wood and other forms of biomass can be converted to biofuel using thermochemical routes such as combustion, gasification, and pyrolysis [1,14–19]. Pyrolysis is known as a process of thermal degradation of organic materials to vapor in the absence of oxygen, where the large hydrocarbon molecules decomposed to several smaller ones [6]. If the pyrolysis performs in the presence of subcritical water, it is generally called hydrous pyrolysis or hydrothermal carbonization (HTC) or wet pyrolysis [20]. One of the advantages associated with wet pyrolysis is that wet materials such as municipal solid waste (MSW) can be used as feedstocks. The solid product of wet pyrolysis is known as hydrochar [21]. On the other hand, in the dry pyrolysis, the solid product is known as bio-char, which is rich in carbon content, whereas the volatile product of this process is condensed to a liquid fraction called tar or bio-oil along with a mixture of the non-condensable gasses. In general, dry pyrolysis has three different variations: fast, intermediate, or mild and slow pyrolysis. The mode and the conditions of pyrolysis can affect the relative proportions of the gas, liquid, and solid products. The cellulose, hemicellulose, and lignin are the three main components of biomass, and all these three main components of biomass are determined as the elements of hydrogen, carbon, and oxygen [22] and high energy content can be relieved by pyrolysis process [23,24]. Lignin occurs throughout the plant cell-wall, and in comparison to cellulose and hemicellulose, carries the highest specific energy content [25] and is a by-product of the bleaching process of wood pulp. It is an aromatic polymer composed of phenyl propane units that are connected through the ether and condensed (C–C) linkages [26]. The worldwide annual production of lignin exceeds 70 million tons from the pulp and paper industry, which is used as boiler fuel in the pulp and paper industry. Gaining the knowledge and understanding the properties of lignin, such as reactivity, thermal stability, and monomeric properties to obtain the optimal lignin applications for future development are far more worthwhile than use it only as boiler fuel in the paper industry. Hence, lignin deserves more than only be used as boiler fuel [27] since lignin is burned in the recovery boiler to compensate for the energy and chemicals that are used in the pulping process. Other possible applications of lignin are the concurrent production of lignosulfonate and bioethanol from spent liquor in the pulping process [28]. Bio-oil production from lignin seems to be a promising solution to a sustainable source of energy, however some technical issues such as energy efficiency and quality of the bio-oil remain to be addressed.

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

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

2. Materials and Methods

2.1. Materials

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

2.2. Crude Bio-Oil Production

In this study, a fixed bed, bench-scale pyrolysis reactor was designed for bio-oil production, whereas the feedstock was fed in the reactor, and the heat was supplied externally. Electrical power was used to provide the heat, and nitrogen gas was used as a carrier gas to provide inert conditions inside the reactor.

The experimental setup comprised of two preheaters to preheat the carrier gas before entering the reactor. A CaO store to remove the moisture from the carrier gas and a cylindrical stainless steel reactor vessel, which was heated by hot oil jacket and occupied around 10% with silica sand bed to maintain a homogenous temperature across the reactor. In addition, the reactor vessel was attached with a PID controller and a double condenser. The attached thermocouples recorded the inside temperature of the reactor. The experiments were conducted at a temperature of 773 K for two types of lignins (Sigma Aldrich softwood lignin and Chouka hardwood lignin). The feedstocks were dried in an oven for 12 h at 373 K to remove moisture before the pyrolysis process. In each experiment, firstly the weights of the glassware and condensers were recorded before and after the experiment to obtain an accurate weight of the bio-oil, using weigh by difference method. Approximately 100 g of lignin was weighed and loaded inside the sample container and then placed inside the reactor when the thermocouple indicated the temperature of 773 K (Figure 1). Nitrogen gas (N_2) was introduced at the rate of 500 ml/min to the reactor after passing through two preheaters to obtain oxygen-free conditions. The outlet of the pyrolysis reaction was directed into a water-cooled condenser, and the condensed liquid bio-oil was collected at three different collection points. Figure 1 illustrates the schematic of the experimental setup for bio-oil production. On completion of the experiment, to obtain the liquid mass yield, the condensers and glassware were weighed again, and the difference was calculated and the bio-oils that were collected at the collection points, considered as the liquid yield. To recover the bio-oil, which was attached to the condenser walls, the condensers were washed with acetone, and then the solvent was allowed to evaporate. After that the liquid and solid products were weighted, and the following equations were used to calculate the product yield.

$$\text{Liquid Yield (\%)} = (\text{Weight of Liquid (g)})/(\text{Weight of Lignin Fed to Reactor (g)}) \times 100 \qquad (1)$$

$$\text{Char Yield (\%)} = (\text{Weight of Solid (g)})/(\text{Weight of Lignin Fed to Reactor (g)}) \times 100 \qquad (2)$$

$$\text{Gas Yield (\%)} = 100 - (\text{Liquid Yield (\%)} + \text{Char Yield (\%)}) \times 100 \qquad (3)$$
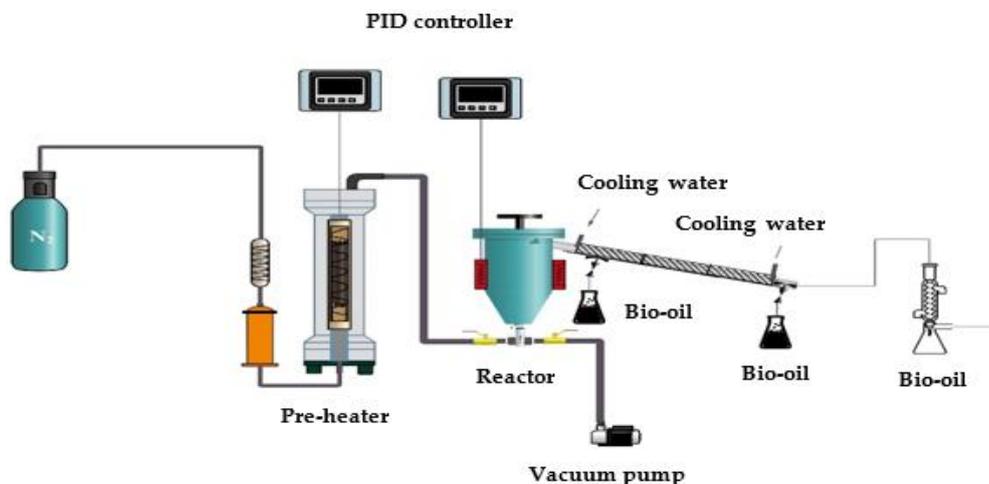

Figure 1. Schematic of experimental set-up for bio-oil production.

2.3. Characterisation of Bio-Oil

2.3.1. Fractionation of Bio-Oil

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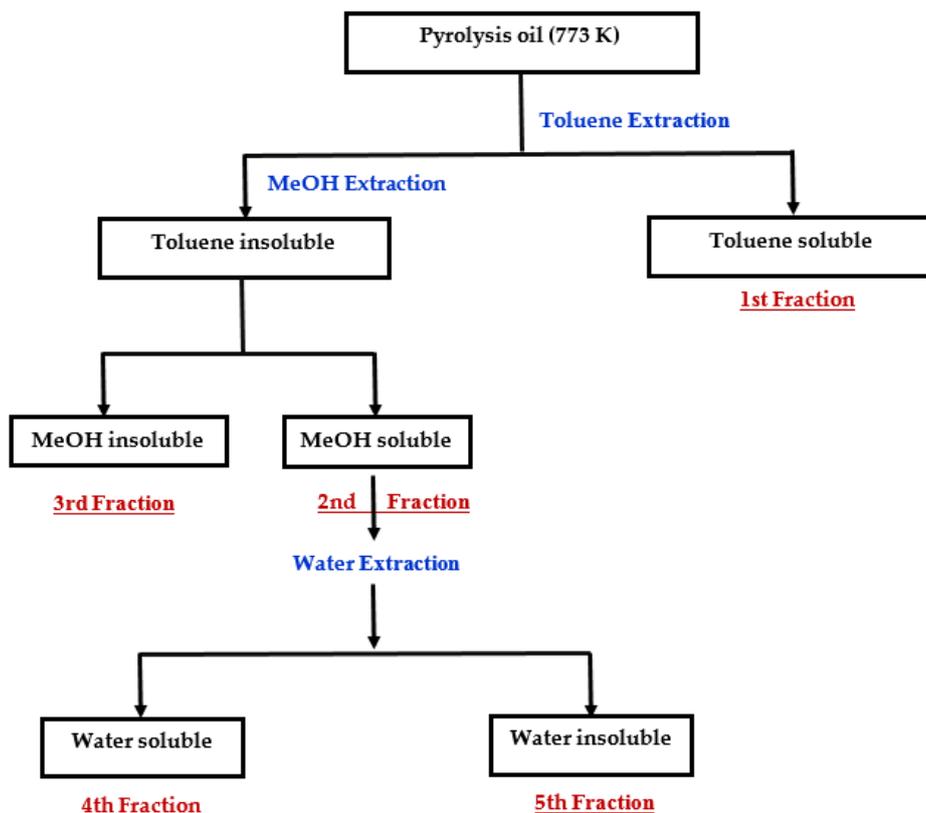
**Figure 2.** Fractionation protocol of bio-oil for light oil and chemicals.

2.3.2. GCMS Analysis of Obtained Fractionations of Bio-Oil

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, Tokyo, Japan) 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.

2.3.3. Elemental Analysis (CHNO) and Heating Values

A CE-440 elemental analyzer (Exeter Analytical, Coventry, UK) was used to obtain the percentage of hydrogen, carbon, sulfur and oxygen. The heating values were obtained using the Bomb Calorimetry (Cussons, Manchester, UK) (G.CUSSONS with PT104 data logger) method.

2.3.4. Water Content and pH

The water content of bio-oil was analyzed by Karl-Fisher titration (Mettler Toledo, Leicester, UK). 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 PHM 240 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.

3. Results and Discussions

3.1. Distribution of Product Yield

The distribution of product yield results from thermal fast pyrolysis of two types of lignin is presented in Figure 3.
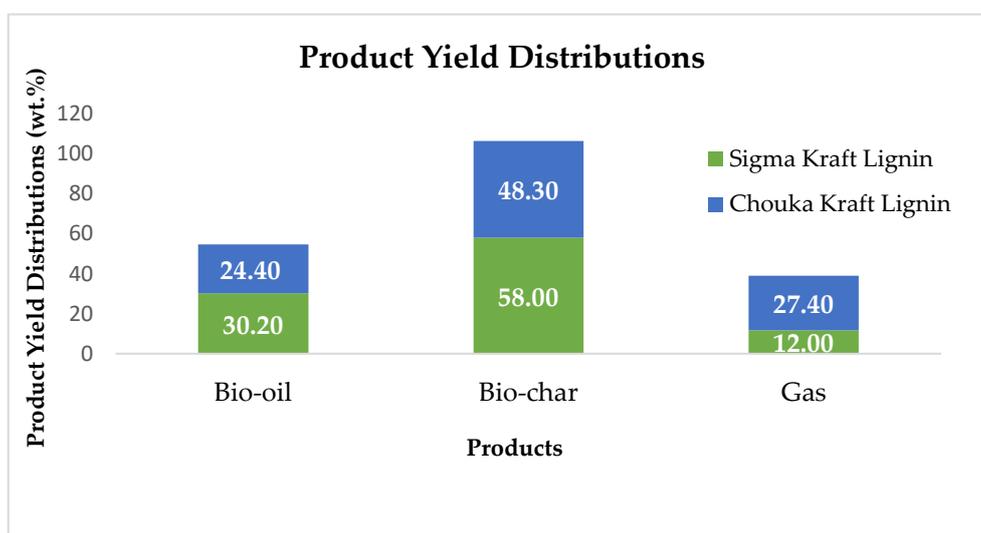
Figure 3. Product yield distributions (wt.%) of fast pyrolysis of Sigma Kraft (softwood) and Chouka Kraft (hardwood) lignin.

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

3.2. Properties of Bio-Oil

3.2.1. Elemental Analysis (CHSO) and Heating Values

The elemental analysis of two different bio-oils was performed to investigate carbon, hydrogen, sulfur and oxygen content of fast pyrolysis bio-oil samples. In addition, the standard measurement of the energy content of a fuel, which is known as heating value, was determined. Table 1, bio-oil from Sigma Kraft Lignin contains higher carbon and hydrogen by 68.50% and 6.63% respectively whereas the bio-oil from Chouka Kraft Lignin presented lower values for carbon and hydrogen. However, both lignins contain an acceptable amount of carbon and hydrogen in comparison to the values reported by other researchers [32]. Moreover, the bio-oil obtained from Sigma Kraft Lignin presents a lower sulfur content than Chouka Kraft Lignin. However, this sulfur results from the Kraft pulping process where the woodchips are converted into pulp through the bleaching process by washing the wood with white liquor (Na_2S/NaOH). In this process, the lignin is separated from wood chips by breaking the bonds that link lignin, hemicellulose, and cellulose [33]. The lignin obtained by Kraft process contains

considerable amounts of sulfur compounds including lignosulfates, which is considered as one of the disadvantages of the Kraft process [34].

Table 1. Elemental analysis (carbon, hydrogen, sulfur and oxygen) 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

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

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

3.2.2. Water Content and pH Values

The presence of water in bio-oil is unavoidable and it is due to the moisture content of the raw materials and dehydration reactions during the pyrolysis process [36]. As stated in the literature, the water content of bio-oil is reported to be 15–35% [33]. The existence of water in bio-oil has a negative effect on the storage, which causes phase separation and also reduces the heating values. In Table 2, the water content of Sigma Kraft Lignin (10.43%) seems to be lower than the Chouka Kraft Lignin (12.00%). The pH values are presented in Table 2. The pH value for bio-oil of Sigma Kraft Lignin was 5.33, whereas for Chouka Kraft lignin was 4.57, as shown in Table 2. Therefore, the bio-oil requires upgrading to fulfil the standard requirement of fuels to be accepted in any application.

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

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

3.3. GCMS Analysis of Sigma Kraft and Chouka Kraft Lignin Bio-Oil Fractions

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

GCMS analysis identified more than 40 compounds detected in bio-oil by the solvent extraction method and the identified compounds were recorded by a probability match of more than 90% using the GCMS software NIST library. The identified compounds were entirely phenolics and aromatics groups detected by GCMS in the pyrolysis of bio-oil from two different commercial lignins. The

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

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

	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-hydoxy-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

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

The effect of solvents on the extraction of chemical compounds in bio-oil is investigated in this study. Figure 4, illustrates the total mass percentage of the chemicals extracted by three different organic solvents from two different types of bio-oil (Sigma Kraft lignin and Chouka Kraft lignin) at a temperature of 773 K. As shown in Figure 4, water has the highest affinity for chemicals at this fraction for both types of bio-oil. The identified compounds in the pyrolysis oil from lignin were totally phenolics compounds. The phenolic compounds are polar compounds, which extracted with a solvent with a higher polarity such as water or methanol. The chemicals that exist in bio-oil are mostly oxygenated compounds which have high polarity and solubility in water and polar solvents. Therefore, fewer compounds dissolved in the toluene due to its low polarity, which limits the solubility of the oxygenated compounds. These findings are in accordance with the previous studies reported by

literature which confirms that more chemicals can be extracted from bio-oil with solvents with higher polarity [37]. As shown in Figure 4, for bio-oil produced from Sigma Kraft Lignin, methanol extracted 7.30%, water 57.50% and toluene 5.08% of the bio-oil chemicals. For Chouka Kraft Lignin, methanol separated 17.29%, water 32.42% and toluene 0.41% of the bio-oil chemicals.

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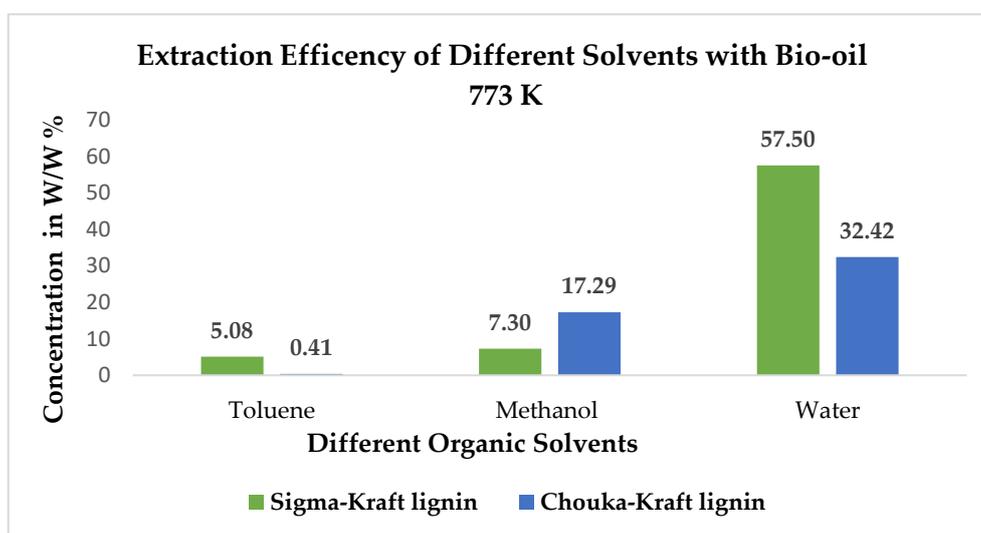
Figure 4. The effect of solvent on the extraction of chemicals.

3.3.2. GCMS Analysis of Sigma Kraft Lignin and Chouka Kraft Lignin Bio-Oil Fractions

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

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

GCMS Analysis of Sigma Kraft Lignin Bio-Oil Fractions

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

Sigma Kraft Lignin-Toluene Soluble

Toluene can be considered as an effective solvent in separating different types of the chemical group with lower polarity. As can be seen from Table 3, phenolic and aromatic compounds were separated by toluene fraction. Phenolic compounds have lower polarity than acids and furans and according to the functional group and previously reported studies phenolic family was considered the components, which include 1, 2-benzenediol, phenol, 3-ethylphenol, 2, 6-dimethoxyphenol [35]. The toluene fraction analysis of sigma Kraft Lignin shows the separation of different phenolic components such as phenol, phenol, 2-methoxy, and 2-methoxy-6-methylphenol, guaiacol and 1, 2-benzenediol. According to the structure and the originality of lignin, which is composed of phenyl propane units with one or two methoxy groups ($O-CH_3$) on the aromatic ring, the deformation of lignin provides lower molecular weight compounds that composed of monomers of lignin. Hence, it is clear that the distribution of the extracted chemicals resulted from the pyrolysis of lignin would be mostly on phenolics compounds.

Sigma Kraft Lignin-Methanol (MeOH) Soluble

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

Sigma Kraft Lignin-Water Soluble

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

GCMS Analysis of Chouka Kraft Lignin Bio-Oil Fractions

The second type of lignin was provided by Chouka Wood and Paper Industry, Talesh, Iran, which was produced from hardwood. The lignin content of hardwood generally is less than softwood. The monomeric lignin precursor of softwood is guiacyl only while the precursors of hardwood lignin are

guiacyl and syringyl units [38]. Thus, the hardwood contains higher methoxy groups than softwood that results in the condensed-type linkage between phenyl propane units in hardwood [39].

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

Chouka Kraft Lignin-Toluene Soluble

The result of the toluene fraction of bio-oil from Chouka Kraft lignin is shown in Table 4. The non-polar compounds with high molecular weight were expected to be separated by toluene soluble faction. However, the phenolics were the dominant chemical groups for this fraction of bio-oil obtained from Chouka Kraft Lignin. As stated in the literature, toluene is also considered as an efficient solvent for extraction of phenolic and aromatic compounds [31]. In addition, there were no peaks corresponding to small hydrocarbon (C2-C5) products, which most probably due to the low carbohydrate content of the lignin. However, the origin of the Chouka lignin comes from hardwood and hardwood has less lignin content in comparison to softwood. Hence, Sigma Kraft lignin (softwood) shows a better distribution of chemicals in the fractionation approach in comparison to Chouka Kraft lignin. Furthermore, among the three solvents, toluene shows a better affinity to the chemicals presents in Chouka Kraft lignin in comparison to bio-oil from Sigma Kraft lignin as more compounds were extracted by this solvent (Tables 3 and 4).

Chouka Kraft Lignin-Methanol Soluble

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

Chouka Kraft Lignin-Water Soluble

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

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

There has been a growing demand in bio-oil production in the last two decades due to potential shortages of petroleum resources, hence in recent years, the ecological advantages of bio-oil have played an important role in this production. Bio-oil produced from biomass can be considered essentially as a renewable source of energy which contains low nitrogen and sulfur, maintains a closed carbon cycle with no net increase in atmospheric CO_2 levels compared to fossil fuels [40]. However, the properties of bio-oil have significant problems during its use as a fuel in boilers, engines, and gas turbines. Oxygen content, poor volatility, high viscosity, coking, and corrosiveness have so far limited the range of bio-oil applications [33]. Combustion behavior of bio-oil due to the presence of high content of non-volatile components in bio-oil has an important impact on the performance of bio-oils during combustion and consequently on the applications for energy production. The most important feature of bio-oil is being liquid which makes the storage, usage and transportation such as easy process [41]. Bio-oil can be used as fuel oil or diesel in many applications such as boilers, engines and turbines for electricity generation and as a raw material for the production of adhesives such as phenol-formaldehyde-type resins, wood flavors, etc. [16,42]. Lignin pyrolysis bio-oil can be used for the synthesis of phenolic resins without any fractionation [41]. Hence, a very useful application of phenolic compounds in bio-oil is to extract phenols from bio-oil, since phenolics compounds are valuable chemicals and can be used in a wide range of applications. Resin manufacturing is one of the virtual applications of phenolic compounds and is normally synthesized by acid or base catalyzed reactions between phenols and

aldehydes to produce phenol-formaldehyde (PF) resin. Phenolic resins are used in many industries such as electronic laminating and wood composite industries. The application of phenolic-rich bio-oil in synthesis of phenol-formaldehyde resin to replace the petroleum-based phenol is one of the potential applications in this field [41].

4. Conclusions

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

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

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

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

Author Contributions: Main and second authors designed the pyrolyser and produced the bio-oil in the laboratory, Z.E.Z.; prepared the original draft and performed the GCMS tests, Z.E.Z.; Performed elemental analysis and heating values tests and analysis, A.A.; First Supervisor, reviewed manuscript, gave comments, edited contents and supervised the PhD student at LSBU, B.S.; All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Jeong, Y.W.; Choi, S.K.; Choi, Y.S.; Kim, S.J. Production of biocrude-oil from swine manure by fast pyrolysis and analysis of its characteristics. *Renew. Energy* **2015**, *79*, 14–19. [CrossRef]
2. Bu, Q.; Lei, H.; Wang, L.; Yadavalli, G.; Wei, Y.; Zhang, X.; Zhu, L.; Liu, Y. Biofuel production from catalytic microwave pyrolysis of Douglas fir pellets over ferrum-modified activated carbon catalyst. *J. Anal. Appl. Pyrolysis* **2015**, *112*, 74–79. [CrossRef]
3. Huang, Y.; Wei, L.; Crandall, Z.; Julson, J.; Gu, Z. Combining Mo-Cu/HZSM-5 with a two-stage catalytic pyrolysis system for pine sawdust thermal conversion. *Fuel* **2015**, *150*, 656–663. [CrossRef]
4. Aboelazayem, O.; Gadalla, M.; Saha, B. Biodiesel production from waste cooking oil via supercritical methanol: Optimisation and reactor simulation. *Renew. Energy* **2018**, *124*, 144–154. [CrossRef]

5. Hamzeh, Y.; Ashori, A.; Mirzaei, B.; Abdulkhani, A.; Molaei, M. Current and potential capabilities of biomass for green energy in Iran. *Renew. Sustain. Energy Rev.* **2011**, *15*, 4934–4938. [CrossRef]

6. Kim, J.Y.; Lee, H.W.; Lee, S.M.; Jae, J.; Park, Y.K. Overview of the recent advances in lignocellulose liquefaction for producing biofuels, bio-based materials and chemicals. *Bioresour. Technol.* **2019**, *279*, 373–384. [CrossRef] [PubMed]

7. Damartzis, T.; Zabaniotou, A. Thermochemical conversion of biomass to second generation biofuels through integrated process design-A review. *Renew. Sustain. Energy Rev.* **2011**, *15*, 366–378. [CrossRef]

8. Sims, R.E.H.; Mabee, W.; Saddler, J.N.; Taylor, M. An overview of second generation biofuel technologies. *Bioresour. Technol.* **2010**, *101*, 1570–1580. [CrossRef] [PubMed]

9. Suurs, R.A.A.; Hekkert, M.P. Competition between first and second generation technologies: Lessons from the formation of a biofuels innovation system in the Netherlands. *Energy* **2009**, *34*, 669–679. [CrossRef]

10. Naik, S.N.; Goud, V.V.; Rout, P.K.; Dalai, A.K. Production of first and second generation biofuels: A comprehensive review. *Renew. Sustain. Energy Rev.* **2010**, *14*, 578–597. [CrossRef]

11. Alaswad, A.; Dassisti, M.; Prescott, T.; Olabi, A.G. Technologies and developments of third generation biofuel production. *Renew. Sustain. Energy Rev.* **2015**, *51*, 1446–1460. [CrossRef]

12. Liew, W.H.; Hassim, M.H.; Ng, D.K.S. Review of evolution, technology and sustainability assessments of biofuel production. *J. Clean. Prod.* **2014**, *71*, 11–29. [CrossRef]

13. International Energy Agency. *Deploying Renewables 2011: Best and Future Policy Practice*; OECD Publishing: Paris, France, 2011.

14. Gopu, C.; Gao, L.; Volpe, M.; Fiori, L.; Goldfarb, J.L. Valorizing municipal solid waste: Waste to energy and activated carbons for water treatment via pyrolysis. *J. Anal. Appl. Pyrolysis* **2018**, *133*, 48–58. [CrossRef]

15. Park, H.J.; Dong, J.I.; Jeon, J.K.; Park, Y.K.; Yoo, K.S.; Kim, S.S.; Kim, J.; Kim, S. Effects of the operating parameters on the production of bio-oil in the fast pyrolysis of Japanese larch. *Chem. Eng. J.* **2008**, *49*, 3187–3204. [CrossRef]

16. Bridgwater, A.V.; Peacocke, G.V.C. Fast pyrolysis processes for biomass. *Renew. Sustain. Energy Rev.* **2000**, *4*, 1–73. [CrossRef]

17. Yu, X.; Hassan, M.; Ocone, R.; Makkawi, Y. A CFD study of biomass pyrolysis in a downer reactor equipped with a novel gas-solid separator-II thermochemical performance and products. *Fuel Process. Technol.* **2015**, *133*, 51–63. [CrossRef]

18. Chen, D.; Yin, L.; Wang, H.; He, P. Reprint of: Pyrolysis technologies for municipal solid waste: A review. *Waste Manag.* **2015**, *37*, 116–136. [CrossRef]

19. Echresh, Z.; Abdulkhani, A.; Saha, B. Analytical pyrolysis study of different lignin biomass. In Proceedings of the 27th European Biomass Conference and Exhibition Proceedings, Lisbon, Portugal, 26 May 2019; pp. 1241–1245.

20. Peterson, A.A.; Vogel, F.; Lachance, R.P.; Fröling, M.; Antal, M.J.; Tester, J.W. Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies. *Energy Environ. Sci.* **2008**, *1*, 32–65. [CrossRef]

21. Libra, J.A.; Ro, K.S.; Kammann, C.; Funke, A.; Berge, N.D.; Neubauer, Y.; Titirici, M.M.; Fühner, C.; Bens, O.; Kern, J.; et al. Hydrothermal carbonization of biomass residuals: A comparative review of the chemistry, processes and applications of wet and dry pyrolysis. *Biofuels* **2011**, *2*, 89–124. [CrossRef]

22. Shirmohammadli, Y.; Moradpour, P.; Abdulkhani, A.; Efhamisisi, D.; Pizzi, A. Water resistance improvement by polyethyleneimine of tannin-furfuryl alcohol adhesives. *Int. Wood Prod. J.* **2019**, *10*, 16–21. [CrossRef]

23. Tsai, W.T.; Lee, M.K.; Chang, Y.M. Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor. *J. Anal. Appl. Pyrolysis* **2006**, *76*, 230–237. [CrossRef]

24. Kim, S.S.; Kim, J.; Park, Y.H.; Park, Y.K. Pyrolysis kinetics and decomposition characteristics of pine trees. *Bioresour. Technol.* **2010**, *101*, 9797–9802. [CrossRef] [PubMed]

25. Abdelaziz, O.Y.; Hulteberg, C.P. Physicochemical characterisation of technical lignins for their potential valorisation. *Waste Biomass Valoriz.* **2017**, *8*, 859–869. [CrossRef]

26. Abdulkhani, A.; Karimi, A.; Mirshokraie, A.; Hamzeh, Y.; Marlin, N.; Mortha, G. Isolation and chemical structure characterization of enzymatic lignin from populus deltoides wood. *J. Appl. Polym. Sci.* **2010**, *118*, 469–479. [CrossRef]

27. Karimi, S.; Abdulkhani, A.; Karimi, A.; Ghazali, A.H.B.; Ahmadun, F.R. The effect of combination enzymatic and advanced oxidation process treatments on the colour of pulp and paper mill effluent. *Environ. Technol.* **2010**, *118*, 469–479. [CrossRef] [PubMed]

28. Abdulkhani, A.; Amiri, E.; Sharifzadeh, A.; Hedjazi, S.; Alizadeh, P. Concurrent production of sodium lignosulfonate and ethanol from bagasse spent liquor. *J. Environ. Manag.* **2019**, *231*, 819–824. [CrossRef] [PubMed]

29. Liu, Q.; Wang, S.; Zheng, Y.; Luo, Z.; Cen, K. Mechanism study of wood lignin pyrolysis by using TG–FTIR analysis. *J. Anal. Appl. Pyrolysis* **2008**, *82*, 170–177. [CrossRef]

30. Xu, Y.; Hu, X.; Li, W.; Shi, Y. Preparation and characterization of bio-oil from biomass. In *Progress in Biomass and Bioenergy Production*; InTech Publisher: Rijeka, Croatia, 2011; Volume 1, pp. 198–222.

31. Yang, X.; Lyu, H.; Chen, K.; Zhu, X.; Zhang, S.; Chen, J. Selective extraction of bio-oil from hydrothermal liquefaction of salix psammophila by organic solvents with different polarities through multistep extraction separation. *BioResources* **2014**, *9*, 5219–5233. [CrossRef]

32. David, E.; Kopac, J. Pyrolysis of rapeseed oil cake in a fixed bed reactor to produce bio-oil. *J. Anal. Appl. Pyrolysis* **2018**, *134*, 495–502. [CrossRef]

33. Czernik, S.; Bridgwater, A.V. Overview of applications of biomass fast pyrolysis oil. *Energy Fuels* **2004**, *18*, 590–598. [CrossRef]

34. De la Torre, M.J.; Moral, A.; Hernández, M.D.; Cabeza, E.; Tijero, A. Organosolv lignin for biofuel. *Ind. Crops Prod.* **2013**, *45*, 58–63. [CrossRef]

35. Ren, S.; Ye, X.P.; Borole, A.P. Separation of chemical groups from bio-oil water-extract via sequential organic solvent extraction. *J. Anal. Appl. Pyrolysis* **2017**, *123*, 30–39. [CrossRef]

36. Bridgwater, A.V. Principles and practice of biomass fast pyrolysis processes for liquids. *J. Anal. Appl. Pyrolysis* **1999**, *51*, 3–22. [CrossRef]

37. Hu, H.S.; Wu, Y.L.; Yang, M. De Fractionation of bio-oil produced from hydrothermal liquefaction of microalgae by liquid-liquid extraction. *Biomass Bioenergy* **2018**, *108*, 487–500. [CrossRef]

38. Asmadi, M.; Kawamoto, H.; Saka, S. Characteristics of softwood and hardwood pyrolysis in an ampoule reactor. *J. Anal. Appl. Pyrolysis* **2017**, *124*, 523–535. [CrossRef]

39. Abdulkhani, A.; Mirshokraie, A.; Karimi, A.; Hamzeh, Y. Chemical structure characterization of lignin from populus deltoides. In Proceedings of the 16th International Symposium on Wood, Fiber and Pulping Chemistry (ISWFPC 2011), Tianjing, China, 8–10 June 2011.

40. Yang, H.; Yao, J.; Chen, G.; Ma, W.; Yan, B.; Qi, Y. Overview of upgrading of pyrolysis oil of biomass. *Energy Proced.* **2014**, *61*, 1306–1309. [CrossRef]

41. Kim, J.S. Production, separation and applications of phenolic-rich bio-oil—A review. *Bioresour. Technol.* **2015**, *178*, 90–98. [CrossRef]

42. Lu, Q.; Li, W.Z.; Zhu, X.F. Overview of fuel properties of biomass fast pyrolysis oils. *Energy Convers. Manag.* **2009**, *50*, 1376–1383. [CrossRef]