

A comparative production and characterisation of fast pyrolysis bio-oil from *Populus* and *Spruce* woods

Zahra Echresh Zadeh ^a, Ali Abdulkhani ^b and Basudeb Saha^{a*}

^a School of Engineering, London South Bank University, 103 Borough Road, London SE1 0AA, UK.

^b Department of Wood and Paper Sciences and Technology, Faculty of Natural Resources, University of Tehran, Karaj, Iran.

ABSTRACT

This study focuses on the production and characterisation of fast pyrolysis bio-oil from hardwood (*Populus*) and softwood (*Spruce*) using a bench-scale pyrolysis reactor at two different temperatures. In this study, a mixed solvent extraction method with different polarities was developed to extract different components of bio-crude oil into three fractions. The obtained fractions were characterized by using gas chromatography and mass spectrometry (GC-MS). The effect of temperature on the production of bio-oil and on the chemical distribution in bio-oil was examined. The maximum bio-oil yield (71.20%) was obtained at 873 K for bio-oil produced from softwood (*Spruce*). In contrast, at a temperature of 773 K, the bio-oil yields were 62.50% and 65.40% for bio-oil obtained from hardwood (*Populus*) and softwood (*Spruce*) respectively. More phenolic compounds were extracted at a temperature of 773 K for bio-oil derived from softwood (*Spruce*) whereas the bio-oil obtained from hardwood (*Populus*) produced mostly furans, acids and sugar compounds at this temperature. For both types of bio-oil, a wide variety of chemical groups were identified at a temperature of 873 K in comparison to 773 K.

KEYWORDS

Biomass; Bio-oil; Characterisation; Extraction; Organic solvents; Pyrolysis.

1. INTRODUCTION

With the increase of world's population and the depletion of fossil fuel reserves, it is necessary to find new technologies and alternative energy sources that can be renewable and sustainable. Conversion of biomass to bio-oil has established significant consideration for the development of a renewable and environmentally friendly source of energy for alternative fuels since it does not contribute to greenhouse gases emission. Biomass is an organic material that is derived from plants or animals and can be used in bio-oil production. Biomass can be divided into two main groups: virgin biomass, which includes wood, plants (lignocellulose), and waste biomass. Waste biomass includes municipal solid waste (MSW) and agricultural waste [1]. Wood and other forms of biomass can be converted to biofuel using two different approaches one involving biochemical methods such as fermentation and anaerobic digestion and the other one including thermo-chemical methods such as combustion, gasification, and pyrolysis [2–4]. Enzymatic conversion and pyrolysis are the most common methods for converting both soft and hardwood feedstock [5]. Pyrolysis is known as a process of thermal degradation of low-density organic materials in the absence of oxygen [6,7]. In other words, pyrolysis is a thermal decomposition of large hydrocarbon molecules to several smaller ones. The vapour is condensed to produce bio-oil and non-condensable gas phase, mainly containing CO, CO₂ and minor amounts of H₂ and CH₄ [8]. The most significant aspect of pyrolysis product is the volatile product, which after cooling and condensation is converted to liquid bio-oil [9]. Bio-crude oil from the pyrolysis of biomass is a dark brown liquid with a pungent odour. It is a complex mixture, which 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 [10,11]. The chemical compositions of bio-oil are defined by several factors including biomass type, process parameters (temperature, heating rate, residence time, pressure, and gaseous environment) as well as vapour filtration and condensation (filter type, condensing method, and medium, cooling rate). However, the pyrolysis process requires accurate control of temperature and short residence time to achieve high yield bio-oil. In addition, bio-oil properties of different bio-oil produced from different biomass and under different process conditions may perhaps differ from one another [12].

Defining the reaction pathway of pyrolysis process would enable the process development moves from initial research towards the commercial stage. Pyrolysis behaviour was mostly studied based on three main biomass components, i.e. cellulose, hemi-cellulose and lignin. Also, numerous reactions take place i.e. dehydration, depolymerisation, decarboxylation, and isomerization [13]. During the pyrolysis process, the primary reactions include char formation, depolymerisation and fragmentation to form some intermediates. The secondary reactions also take place during the pyrolysis process after the formation of unstable primary products. Char formation occurs by condensation of benzene ring during the pyrolysis

process, whereas depolymerisation reaction occurs by cracking bonds between monomers [14]. Nevertheless, pyrolysis is a complex process, which results in production of three main products. Operating parameters such as pyrolysis temperature and type of the pyrolysis process can affect the main reaction pathways. In Figure 1, the overall pathways involved in the mechanism of pyrolysis are presented.

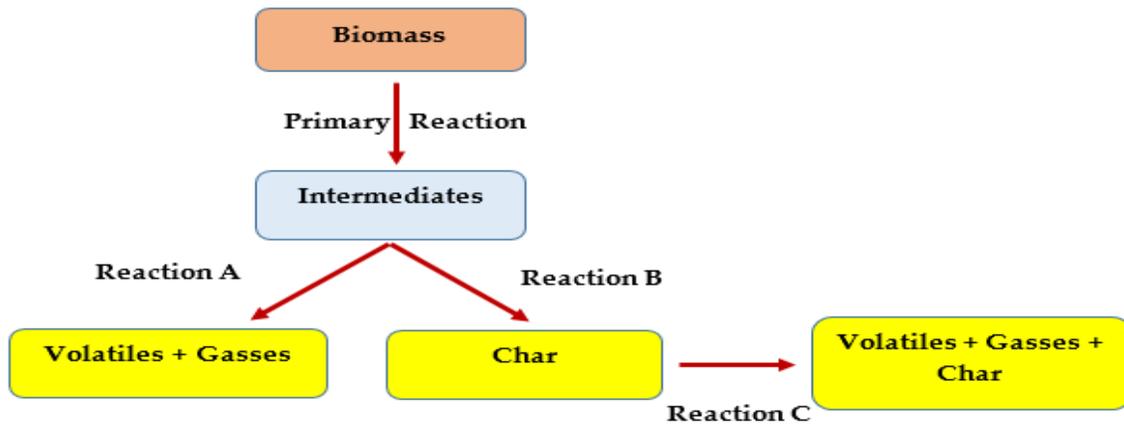


Figure 1. The overall pathways of pyrolysis process (adapted from [43])

The woody biomass is classified into two groups, e.g. hardwood and softwood. Hardwoods are angiosperms (fruit or nut) whereas the softwoods are gymnosperms (cones). Angiosperms have flowers and produce seeds enclosed within a carpel. Gymnosperms have no flowers or fruits, and have unenclosed or “naked” seeds on the surface of scales or leaves.

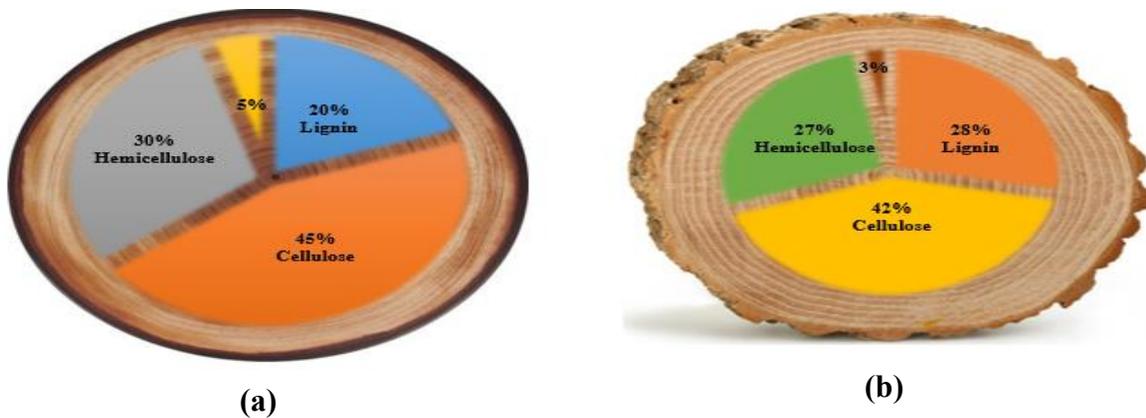


Figure 2. Percentage content of main constituents of woody biomass in a wood cell, (a) hardwood, (b) softwood (adapted from [1])

Softwood comes from coniferous trees, which is green all year round and hardwood comes from deciduous trees, which is produced from broad leaf trees that lose their leaves in winter.

Therefore, hardwood and softwood have nothing to do with density. However, softwood generally contains higher lignin content (26–34%) than hardwood (23–30%) [15,16]. In this study, two groups of the woody biomass were used for the production of bio-oils, *Populus* chips (hardwood) and *Spruce* chips (softwood) [17]. Figure 2 presents the percentage content of main components of lignocellulosic biomass in softwood and hardwood.

According to the published studies in the literature for the production of bio-oil from biomass, most of the studies are mainly focused on bio-oil production process, and many aspects of fast pyrolysis of biomass process such as characterisation of bio-oil parameters require further study and improvement [7]. Hence, the novelty of this work is to perform intensive bio-oil characterisation for the separation of chemicals. Bio-oil has poor properties due to the complexity and inconsistency of composition, which causes the limitation of application range [18]. Hence, to determine the composition and understand the properties of bio-oil characterisation of bio-oil is necessary [19]. To improve the application and industrialisation of bio-crude 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 [20]. The bio-oil chemicals can be separated by using a solvent extraction method that can be considered as one of the effective methods of separation, which separates different chemicals at each stage. The present study is focused on solving a real-world problem for the sustainable production of bioenergy from renewable sources of feedstock. However, commercialisation has not been achieved for thermochemical conversion of biomass yet. A few pilot plants for bio-ethanol synthesis have been built, ranging from 0.3 to 67 MW [21]. A number of techno-economic studies for bio-oil production have been published in the literature using different analysis methods [22]. However, the production cost of bio-oil per energy unit (GJ) was estimated at \$4.04/GJ, whereas conventional petroleum fuel had shown \$10.7/GJ [23]. The demand for utilisation of lignocellulosic biomass has induced with obtaining a detailed analysis of bio-oil for understanding its chemical and physical properties to find the optimal application. Bio-oil has poor properties due to the complexity of its composition, which causes the limitation of its commercial application. In order to determine the composition and to understand the properties of bio-oil, a detailed characterisation of bio-oil is necessary [19]. The characterisation of bio-oil is essential for defining design parameters, developing kinetic models, scaling up, and decision making related to the production of by-products and upgrading [24]. The product of pyrolysis depends on the design of the pyrolysis reactor, the physical and chemical characterisation of the biomass, and operating parameters such as pyrolysis temperature, heating rate and residence time in the reaction zone [25]. The biomass type and the operating parameters of pyrolysis significantly affect the chemical composition of the produced bio-oil. According to the published literature on bio-oil characterisation, the heating values of bio-oil (range between 41 and 43 MJ kg⁻¹) are almost half in comparison to fossil fuels due to the presence of oxygen and water content. This explains the requirement

of bio-oil upgrading to reduce the oxygen and water content and improve the bio-oil properties [26]. The water content of bio-oil is reported to be 15–35% [26]. The presence of water in bio-oil reduces the heating values and enhances the phase separation. In addition, water content in bio-oil is considered to be a drawback as it contributes to a low pH value. A typical pH value of bio-oil is about 2.5. The oxygen content of bio-oil varies in the range between 35 and 40% [26] and is considered as the main difference between bio-oil and petroleum-based fuels, which results in poor bio-oil properties.

The main aim of this study is to investigate the production of bio-oil from two different woodchips and evaluate the design of the pyrolysis reactor. To identify the most efficient solvent extraction route for separating and analysing highly valued chemicals, 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 characterised by using gas chromatography and mass spectrometry (GC-MS). Other types of characterisation techniques e.g. elemental analysis, water content, viscosity and pH measurements, and bomb calorimetry were performed.

This work highlights a fast pyrolysis process to obtain higher-value products from bio-oil yields obtained at two process temperatures using two different types of biomass. A multiple-step solvent extraction method was used for improving the yield and composition of chemicals from the fast-pyrolysis bio-oil. The novelty of this work is to perform intensive bio-oil characterisation for the separation of chemicals from two different sources of feedstock. A comparative production and detailed characterisation of fast pyrolysis bio-oil from *Populus* and *Spruce* woods is the main emphasis of this research.

2. MATERIALS AND METHODS

2.1. Materials

The bio-oil used in this study was obtained from two different feedstock. Two woodchips samples, one hardwood tree named *Populus* and other type softwood tree named *Spruce*, kindly supplied by the Department of Wood and Paper Sciences, University of Tehran. The produced bio-oil was fractionated with three different organic solvents, which include toluene, methanol (MeOH), and water. Toluene and methanol were purchased from Merck, UK.

2.2. Experimental procedures

2.2.1. Bio-oil production

In this study, a bench-scale, fixed bed pyrolysis reactor was designed for bio-oil production, whereas the feedstock was fed in the reactor and heat was supplied externally. Electrical

power was used to provide the heat and nitrogen gas was used as a carrier gas to provide the oxygen-free conditions inside the reactor.

Figure 3 illustrates the schematic of the experimental set-up for bio-oil production. The experimental setup consists of two preheaters to preheat the carrier gas before entering the reactor. To remove any moisture from the carrier gas stream, a CaO store was placed before the preheater. A stainless-steel cylindrical reactor vessel, which was heated by a hot oil jacket and occupied about 10% with silica sand bed to keep a homogenous temperature across the reactor, PID controller and double condenser. Bio-oil was formed by sudden cooling of the pyrolysis vapours. Thus, an efficient cooling arrangement is essential to condense the vapours into bio-oil. The reactor vessel was made of stainless steel 316 to achieve desired pyrolysis temperature without structural deformation. The height and diameter of the reactor vessel were selected to be 30 cm and 10 cm, respectively. The inert conditions for pyrolysis process were reached by passing nitrogen gas and defining the vapour residence time. The attached thermocouples recorded inside temperature of the reactor.

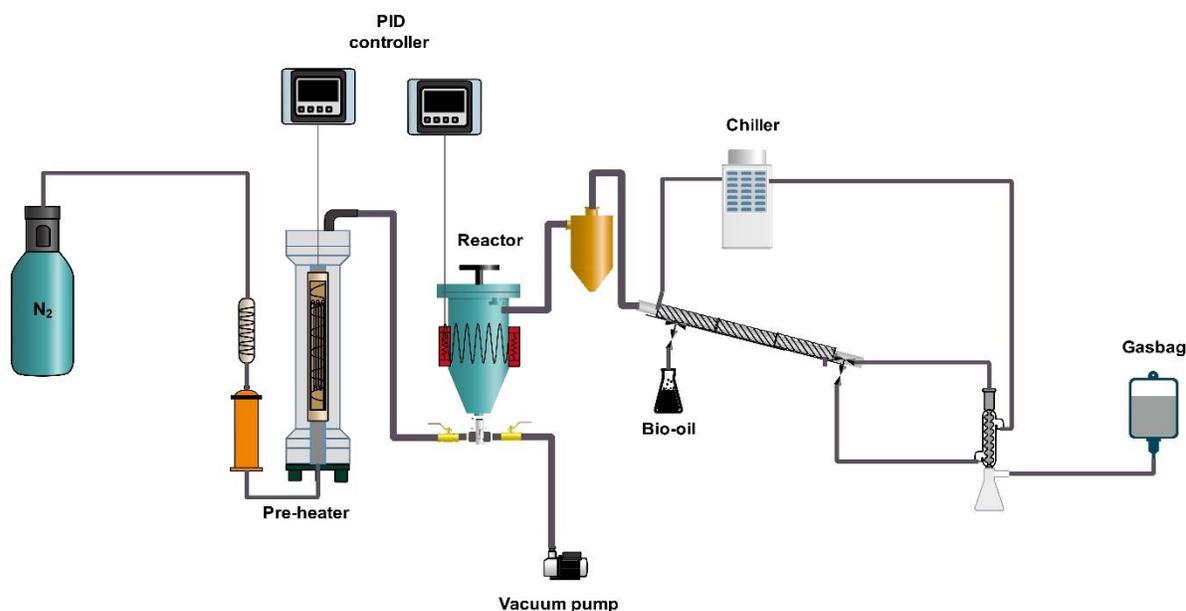


Figure 3. Schematic of the experimental setup for bio-oil production

The experiments were conducted at a temperature of 773 K and 873 K for two types of woodchips. Before the pyrolysis process, the feedstocks were dried in the oven for 12 hours at 373 K to remove moisture. Approximately 44.66 g of woodchips with a particle size of ~18 mm were weighed and loaded inside the sample container and then placed inside the reactor (Figure 3). Nitrogen gas (N₂) was passed at a flow rate of 500 ml min⁻¹ to the reactor after passing through two preheaters to obtain the inert conditions for pyrolysis process and

to achieve the reaction temperature. 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 and the incondensable gases were collected in a gasbag. According to the literature [27], the vapour residence time for the fast pyrolysis process should not exceed 5 s. However, it is a key parameter in the fast pyrolysis process since the main objective of this process is to maximise the liquid yield. Hence, a short vapour residence time (~2 s), fast condensation process to maximise the bio-oil yield, accurate heating system, proper gas flow rate to maintain oxygen-free conditions inside the reactor and preheating of the nitrogen gas to achieve the desired pyrolysis temperature have been considered for pyrolysis system. On completion of the experiment, the liquid and solids products were weighed and the product yield was calculated.

2.2.2. Bio-oil fractionation method

The principle of solvent extraction is based on solvent polarity, and the solvation capability of the materials present in the bio-oil, where the polarity of the solvents increased top to bottom of the route [26]. Hence, the polarity is used as the driving force for the fractionation of the bio-oil.

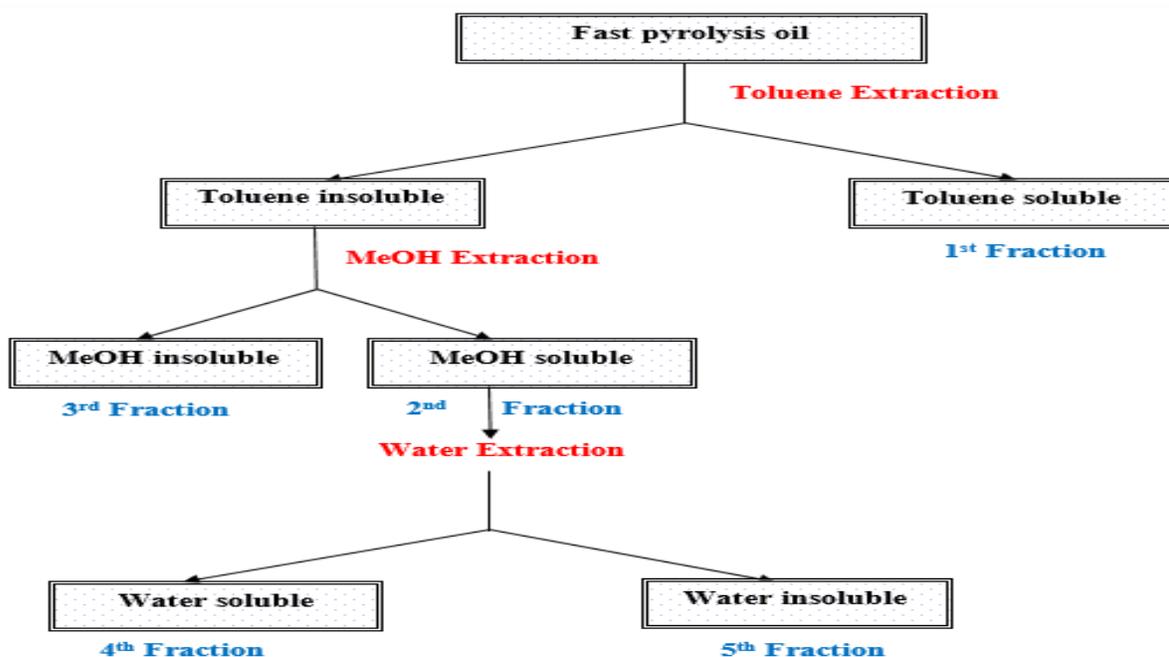


Figure 4. Fractionation protocol of bio-oil for light oil and chemicals

Numerous types of solvents such as butanone, hexane, ethyl acetate, toluene, methanol, dichloromethane and diethyl ether were evaluated to extract the light oil from heavy oil the multi-step pathway, which is presented in Figure 4, was the best-considered route for this purpose. This route contains three solvents, toluene, primary extraction, MeOH secondary

extraction, and water tertiary extraction where the degree of polarity changes from top to bottom of the route (Figure 4) [26]. The composition of bio-oil samples have been obtained by a mixed solvent extraction method with different polarities, which has been developed to fractionate different components of bio- oil into three fractions. The obtained fractions have been characterised by using gas chromatography and mass spectrometry (GC-MS).

In this method, 4 ml of oil was mixed with 115 ml of toluene to obtain toluene soluble and toluene insoluble. Toluene soluble is the first extracted fraction of bio-oil, which can be injected to GC-MS for compositional analysis (1st fraction in Figure 4). Then the toluene insoluble fraction was treated with 115 ml of methanol to MeOH soluble and insoluble.

The MeOH insoluble fraction extracted as a homogenous char-powder fraction and the MeOH soluble fraction was filtrated and then placed in a rotary evaporator to remove the solvent and then 1 μ L was injected to GC-MS. 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) as illustrated in Figure 4. Figure 5 presents the obtained bio-oil fractions for GC-MS analysis.



Figure 5. Illustration of bio-oil fractions by (a) toluene soluble, (b) toluene insoluble, (c) methanol soluble, (d) methanol insoluble, (e) water soluble, (f) water insoluble

2.2.2.1 Composition analysis of bio-oil

The chemical composition of the entire obtained fractions for two types of bio-oils was determined by gas chromatography with mass spectra Shimadzu GC-MS-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 a ramp of 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 0.95 ml min^{-1} to maintain a high-quality separation of the components. The mass scanning range was set 80-700 m/z and the electron ionization system with ionization energy of 70 eV was used [28].

2.2.3 pH, viscosity and water content measurements

The quality of bio-oil in combustion applications is regulated by ASTM D7544 standard. American Society for Testing and Materials (ASTM, D7544-12) standard method were used to determine the water content, elemental analysis, and viscosity of bio-oil [29].

The pH values of bio-oil samples at temperatures 773 K and 873 K were measured by using PHM240 at 298 K. The reported data is the average of two readings for each sample. The viscosity values of the bio-oil samples were measured by using Bohlin Gemini 2 at 313 K. The value of the viscosity of the bio-oil is used to examine the stability of the bio-oil during the storage.

Karl-Fisher titration Mettler Toledo following the ASTM E203 standard test method was used for determining the water content of bio-oil samples. The used solvent for this method was dry methanol and this solvent can dissolve all the compounds of bio-oil [30]. In this approach, one drop (0.0060 g) of bio-oil was added to the glass bottle containing the Karl-Fisher solvent and after entering the exact weight of the injected bio-oil drop. The reported data is the average of three runs for each sample.

2.2.4 Elemental analysis (CHNO) and heating values

A CE-440 elemental analyser was used to obtain the percentage of hydrogen, carbon, sulphur, and oxygen. For elemental analysis, 15 μL of each bio-oil sample was taken and placed inside a metal container and then the container hard-pressed and the samples were weighed and placed inside the CE-440 elemental analyser for analysis. The heating values were obtained using Bomb Calorimetry method [31].

3. RESULTS AND DISCUSSION

3.1 Product yield distributions

The distribution of product yield results from thermal fast pyrolysis of two types of wood is presented in Figure 6. Pyrolysis temperature is the most important parameter that affects the yield of the products. The results indicate that with an increase in temperature, the bio-oil and bio-gas yields increase for both types of the feedstocks while the char yields were observed to decrease since the char materials decompose at higher temperatures as stated in the literature [32]. The maximum bio-oil yield was obtained at a higher temperature of 873 K for bio-oil produced from softwood (*Spruce*) by 71.19%. In contrast, at a temperature of 773 K, the bio-oil yields from hardwood (*Populus*) and softwood (*Spruce*) were 62.54% and 65.42%, respectively.

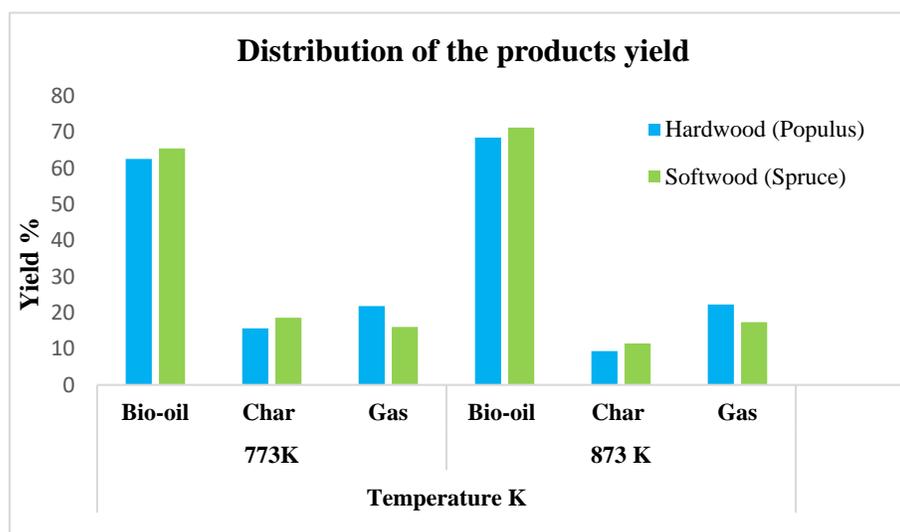


Figure 6. Product yield distributions (%) of fast pyrolysis of softwood (*Spruce*) and hardwood (*Populus*) at two different temperatures

3.2 Characterization of bio-oil

The physical properties of bio-oil including water content, pH value, and viscosity are presented in Table 1. According to Table 1, the percentage of the water content of hardwood (*Populus*) bio-oil at 873 K was the highest value among the bio-oil samples (54.60%), while for the same sample at lower temperature was 35.88%. However, for the bio-oil from softwood (*Spruce*) at a temperature of 873 K, a lower percentage of water content (41.79) was observed. As reported in the literature, the water content of bio-oil is reported to be 15-35% [30]. The presence of water in bio-oil is due to moisture content of the woodchips and the dehydration reactions during the fast pyrolysis process. Studies reported that thermal decomposition of lignocellulosic biomass involves complex mechanisms due to numerous types of structures and the multiplicity of possible reactions. Generally, due to complexity of biomass composition, the pyrolysis behaviour mostly studied based on three main biomass components, i.e. cellulose, hemi-cellulose and lignin. Cellulose is the most abundant

biopolymer, a linear macromolecular polysaccharide that composed of a long-chain of glucose units linked by β -1,4-glycosidic bonds, and contains several inter-molecular hydrogen [33]. The glycosidic bonds linking the glucose units in cellulose are not strong and cleave under high temperature conditions such as pyrolysis process [34]. The main products of pyrolysis of cellulose are acids, alcohols, anhydrosugars, char, and gases. The degradation of hemicellulose mainly occurred at a low temperature and the major weight loss took place at 493–588 K with higher CO₂ and char yields [35]. In contrast, the polymer molecular structure of lignin is very difficult to be degraded into phenyl propane monomers. Lignin is a complex three dimensional polymer in which guaiacyl-, syringyl- and *p*-hydroxy phenyl propane- type units are interconnected. Furthermore, the bio-oil includes two phases: one non-aqueous phase, called bio-oil, consisting of high molecular weight molecules, and the other is an aqueous phase, the aqueous phase is a result of the moisture present in the biomass and from products of reactions that occur during the pyrolysis process[27,36].

Table 1. Physical properties of two different samples of bio-oil at temperatures of 773 K and 873 K

Sample ID	Properties		
	Water Content %	pH	Viscosity (cP)
Hardwood (<i>Populus</i>) 773 K	35.88	2.57	36.94
Hardwood (<i>Populus</i>) 873 K	54.60	2.71	71.10
Softwood (<i>Spruce</i>) 773 K	48.63	2.43	86.61
Softwood (<i>Spruce</i>) 873 K	41.79	2.51	95.48

However, the existence of water in bio-oil has an undesirable effect on the storage, which causes phase separation and also reduces the heating values of bio-oil as a source of fuel.

In addition, the pH values of bio-oil from hardwood and softwood are between 2.4 and 2.8. The presence of water and organic acids in the bio-oil results in a low pH values, which is the main reason of the corrosion property of bio-oil in storage and possible applications. It can be resulted that upgrading of bio-oil is essential in order to achieve the standard requirement of fuels to be accepted in any application.

The ASTM D7544 standard method was used to obtain the viscosity of the bio-oil samples. The presence of water, sugars and acids in bio-oil from wood chips resulted in a lower values and a less viscous product. In addition, the viscosity of the bio-oil samples increases as the temperature of the pyrolysis increased. Thus, a higher viscosity was reported for bio-oil at 873 K and particularly, for softwood (*Spruce*) bio-oil. However, the viscosity of heavy oil is

about 180 cP at 323 K, while the viscosity of bio-oil from biomass is between 40 and 100 cP [37].

The elemental analysis of two different bio-oils was performed to examine carbon, hydrogen, sulphur and oxygen content and also the heating values of fast pyrolysis bio-oil samples from hardwood (*Populus*) and softwood (*Spruce*) at temperatures of 773 and 873 K. As stated in the literature, the oxygen content of bio-oil varies in the range of 35-40% [38]. The lowest amount of oxygen was found for softwood (*Spruce*) 873 K (37.22%) and the highest amount was found for softwood (*Spruce*) 773 K (62.80%), which confirms the necessity of upgrading of the 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 [38]. According to Table 2, bio-oil produced from softwood (*Spruce*) at 873 K contains higher carbon (55.81%) whereas the bio-oil from hardwood (*Populus*) at 773 K contains slightly higher hydrogen (6.64%). The results indicate that bio-oil from softwood (*Spruce*) at the two temperatures contains higher sulphur content than the hardwood (*Populus*) bio-oil samples.

Heating values were determined by using the oxygen-bomb calorimetry method and it was found that bio-oil from softwood (*Spruce*) at 873 K presents a higher heating value by 23.60 MJ/kg in comparison to other bio-oil samples. However, the heating values of bio-oil are affected by the composition of hydrogen and carbon of the bio-oil, which defined the energy content of bio-oil. According to Table 2, the lower heating values of bio-oil in comparison to fossil fuels, which is between 41 and 43 MJ/kg, this value is almost half of fossil fuels value, due to oxygen and water contents, which confirms the necessity of upgrading of bio-oil to reduce the oxygen and water contents and improve the bio-oil properties.

Table 2. Elemental analysis (CHNO) and heating values of the bio-oil samples

Sample ID	Carbon %	Hydrogen %	Sulphur %	Oxygen %	HHV (MJ/kg)	LHV (MJ/kg)
Hardwood (<i>Populus</i>) 773 K	42.90	6.64	0.06	50.40	21.30	19.85
Hardwood (<i>Populus</i>) 873 K	51.30	6.32	0.06	42.32	21.37	20.30
Softwood (<i>Spruce</i>) 773 K	30.30	6.47	0.43	62.80	14.41	13.04
Softwood (<i>Spruce</i>) 873 K	55.81	6.27	0.70	37.22	23.60	22.27

3.3 Composition analysis of bio-oil fractions

Solvent extraction can be considered as an upgrading technique in the development of bio-oil upgrading approaches. The fractions obtained by solvent extraction describes the bio-oil as a mixture of ten chemical families, which include phenolics, aromatics, furans, ketones,

alcohol, acids, sugars, ethers, esters and aldehydes. Therefore, the grouping of bio-oil components into chemical families is a useful method for the characterisation of bio-oil with about a hundred different components. The fractionation method was developed by examining several different types of organic solvents to separate different chemicals. To determine the chemical composition of 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 analysed and the results obtained from fractionation of bio-oil are presented below.

GCMS analysis identified the 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 extracted data was reported in graphs of abundance against retention time for each fraction in Figures 7-12, and the corresponding components for each graph were presented in Tables 3-8. The grouping of chemical families was performed according to their functional groups and structural formula [38].

3.3. 1 GC-MS Analysis of hardwood (*Populus*) bio-oil fractions

The wood chips of *Populus* were used in the bio-oil production and the peak identification and chemical compositions of bio-oil from *Populus* hardwood chips at two different temperatures of 773 K and 873 K include toluene soluble, MeOH soluble and water-soluble are presented in Figures 7, 8 and 9 and the corresponding components for each identified peak for each fraction are presented in Table 3, 4 and 5.

3.3. 1.1 Hardwood (*Populus*) - toluene soluble (773 K and 873 K)

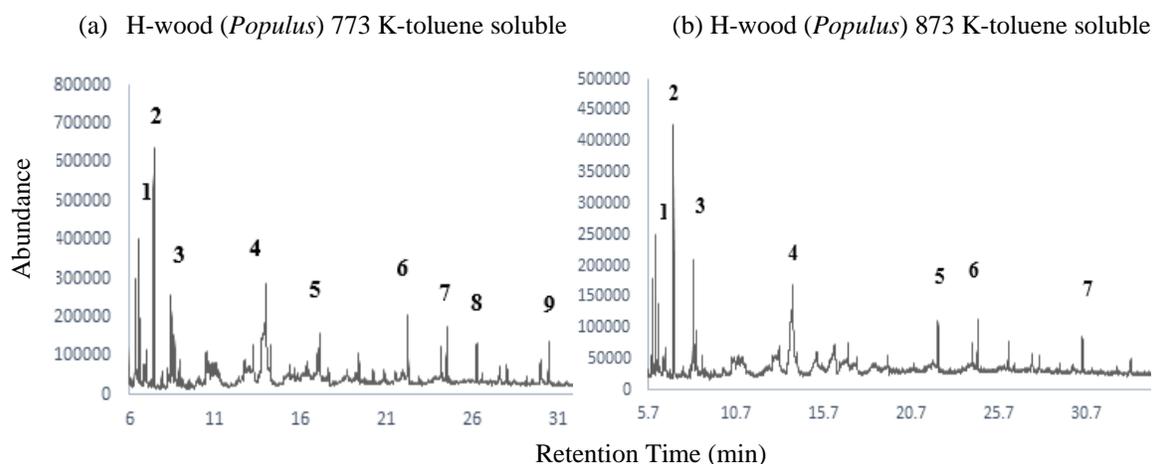


Figure 7. GC-MS chromatogram resulting from Hardwood (*Populus*)-toluene soluble fractions of bio-oil at temperatures of (a) 773 K and (b) 873 K

According to Figure 6, which illustrates the distribution of chemical families includes furans, esters, phenolics, aromatics, and ketones. This suggests that wood chips consist of cellulose, hemicellulose and lignin and the depolymerisation of wood produces more compounds with different polarities. It is clear that compounds with carbon C₅ and C₆ are extracted in these fractions at two different temperatures. The intensity of the produced compounds at temperature 773 K is higher than 873 K fraction (Figure 7).

Table 3. GC-MS chromatogram resulting from Hardwood (*Populus*)-toluene soluble fractions of bio-oil corresponding components

	Peak No	Component	Formula	Chemical Family
Toluene Soluble at 773 K	1	Ethylbenzene	C ₈ H ₁₀	Aromatics
	2	Furfural	C ₅ H ₄ O ₂	Furans
	3	5-Methyl-5-hexen-2-one	C ₇ H ₁₂ O	Ketones
	4	Phenol	C ₆ H ₆ O	Phenolics
	5	Phenol, 2-methoxy-4-methyl	C ₈ H ₁₀ O ₂	Phenolics
	6	Phenol, 3,4-dimethoxy	C ₈ H ₁₀ O ₃	Phenolics
	7	Benzene, 1,2,4-trimethoxy	C ₉ H ₁₂ O ₃	Phenolics
	8	1,2,3-Trimethoxy-5-methylbenzene	C ₁₀ H ₁₄ O ₃	Phenolics
	9	Methoxyeugenol	C ₁₁ H ₁₄ O ₃	Phenolics
Toluene Soluble at 873 K	1	Benzene, ethyl	C ₈ H ₁₀	Aromatics
	2	Furfural	C ₅ H ₄ O ₂	Furans
	3	3,4-Dimethyl-3-pentene-2-one	C ₇ H ₁₂ O	Ketones
	4	Phenol	C ₆ H ₆ O	Phenolics
	5	2,4-Dimethoxyphenol	C ₈ H ₁₀ O ₃	Phenolics
	6	Phenol, 2-methoxy-4-propenyl	C ₁₀ H ₁₂ O ₂	Phenolics
	7	Methoxyeugenol	C ₁₁ H ₁₄ O ₃	Phenolics

3.3.2.2 Hardwood (*Populus*) -methanol soluble (773 K and 873 K)

Figure 8 illustrates the chemical distribution of methanol soluble fractions of bio-oil from *Populus* hardwood chips at two different temperatures of 773 K and 873 K and the corresponding components for each identified peak for each temperature are presented in Table 4. As can be seen the complexity of the sample is visible in the spectrum results presented below. As stated in the literature, methanol has good performance in separating

polar compounds [39] and according to Figure 8, and Table 4, ketones, phenolics, aromatics and furans were found as the main decomposition products of the *Populus* hardwood chips bio-oil. The intensity of the extracted products is higher at a temperature of 773 K. However, more volatile compounds were identified in these fractions, which is due to condensed structure of lignin in hardwood resulted from higher methoxy groups. Hazardous materials, such as N-compounds were identified in this fraction, which results from biomass processing and pre-treatment prior to the pyrolysis process [36].

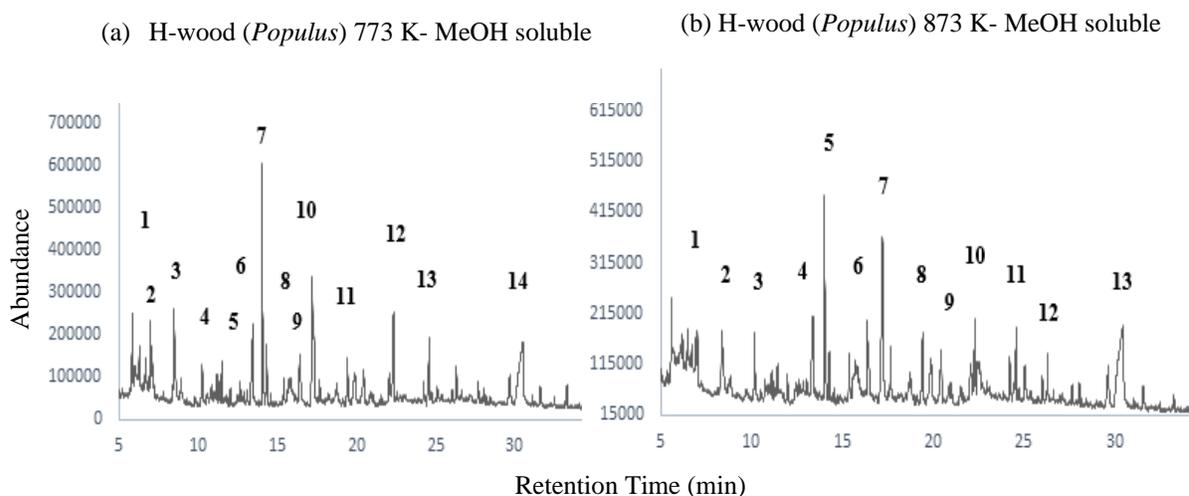


Figure 8. GC-MS chromatogram resulting from Hardwood (*Populus*)-methanol soluble fractions of bio-oil at temperatures of (a) 773 K and (b) 873 K

Table 4. GC-MS chromatogram resulting from Hardwood (*Populus*)-MeOH soluble fractions of bio-oil corresponding components

Methanol Soluble at 773 K	Peak No	Component	Formula	Chemical Family
	1	2-Propanone, 1-hydroxy	C ₃ H ₆ O ₂	Ketones
	2	Furfural	C ₅ H ₄ O ₂	Furans
	3	3-Methyl-4-penten-2-one	C ₆ H ₁₀ O	Ketones
	4	1,1-Dimethoxypropane	C ₅ H ₁₂ O ₂	Aldehydes
	5	Propargyl acrylate	C ₆ H ₆ O ₂	Acids
	6	3-Methylcyclopentane-1,2-dione	C ₆ H ₈ O ₂	Furans
	7	Phenol	C ₆ H ₆ O	Phenolics
	8	Phenol, 2-methoxy	C ₇ H ₈ O ₂	Phenolics
	9	Phenol, 3-methyl	C ₇ H ₈ O	Phenolics
	10	2-Methoxy-6-methylphenol	C ₈ H ₁₀ O ₂	Phenolics
	11	Phenol, 4-ethyl-2-methoxy	C ₉ H ₁₂ O ₂	Phenolics
	12	Phenol, 3,4-dimethoxy	C ₈ H ₁₀ O ₃	Phenolics
	13	Benzene, 1,2,4-trimethoxy	C ₉ H ₁₂ O ₃	Phenolics
	14	D-Mannoheptulose	C ₇ H ₁₄ O ₇	Sugars
Methanol Soluble at 873 K	Peak No	Component	Formula	Chemical Family
	1	2-Propanone, 1-hydroxy	C ₃ H ₆ O ₂	Ketones
	2	3-Methyl-4-penten-2-one	C ₆ H ₁₀ O	Ketones
	3	3-Ethyl-2,4-dioxapentane	C ₅ H ₁₂ O ₂	Aldehydes
	4	3-Methyl-1,2-cyclopentanedione	C ₆ H ₈ O ₂	Furans
	5	Phenol	C ₆ H ₆ O	Phenolics
	6	Phenol, 3-methyl	C ₇ H ₈ O	Phenolics
	7	Propylamine, 3-(furan-2-yl)-1-methyl	C ₈ H ₁₃ NO	Furans
	8	Phenol, 4-ethyl-2-methoxy-	C ₉ H ₁₂ O ₂	Phenolics
	9	2-Methyl-4-pentenoic acid	C ₆ H ₁₀ O ₂	Acids
	10	Phenol, 3,4-dimethoxy	C ₈ H ₁₀ O ₃	Phenolics
	11	Vanillin	C ₈ H ₈ O ₃	Phenolics
	12	Benzene, 1,2,3-trimethoxy-5-methyl	C ₁₀ H ₁₄ O ₃	Phenolics
13	Hexose	C ₆ H ₁₂ O ₆	Sugars	

3.3.2.3 Hardwood (*Populus*)-water soluble (773 K and 873 K)

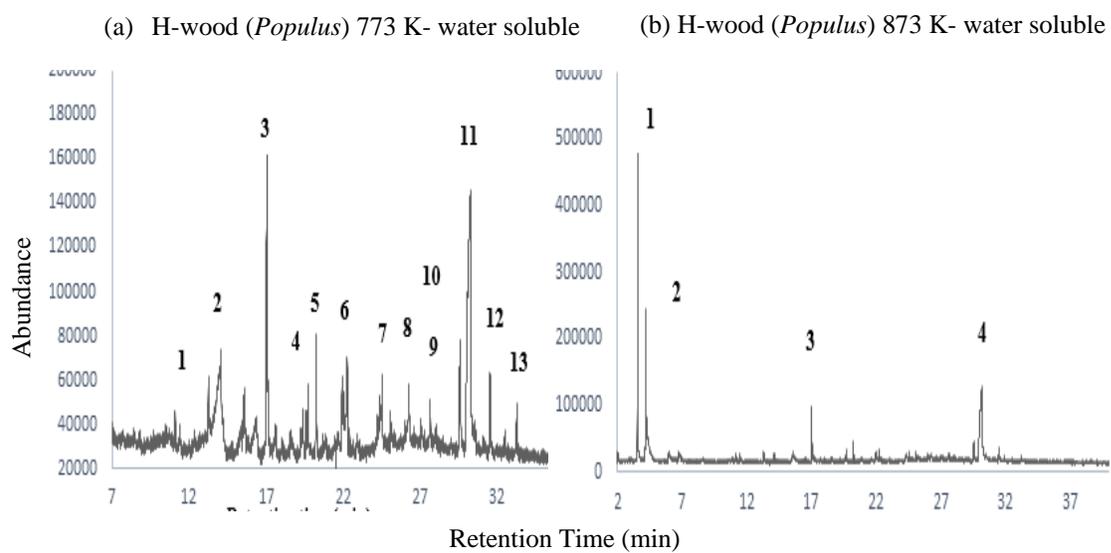


Figure 9. GC-MS chromatogram resulting from Hardwood (*Populus*)-water soluble fractions of bio-oil at temperatures of (a) 773 K and (b) 873 K

Table 5. GC-MS chromatogram resulting from Hardwood (*Populus*)-water soluble fractions of bio-oil corresponding components

	Peak No	Component	Formula	Chemical Family
Water Soluble at 773 K	1	3-Methyl-1,2-cyclopentanedione	C ₆ H ₈ O ₂	Furans
	2	Monophenol	C ₆ H ₆ O	Phenolics
	3	2-Methoxy-6-methylphenol	C ₈ H ₁₀ O ₂	Phenolics
	4	Oxetane, 2-methyl-4-propyl	C ₇ H ₁₄ O	Alcohols
	5	2-Methyl-4-pentenoic acid	C ₆ H ₁₀ O ₂	Acids
	6	Phenol, 3,4-dimethoxy	C ₈ H ₁₀ O ₃	Phenolics
	7	Phenol, 4-methoxy-3-(methoxymethyl)	C ₉ H ₁₂ O ₃	Phenolics
	8	1,3-Dihydroxy-2-methylbenzene	C ₇ H ₈ O ₂	Aromatics
	9	Vanillin methyl ketone	C ₁₀ H ₁₂ O ₃	Aromatics
	10	2,2-Dimethyl-1,3-propanediol diacetate	C ₉ H ₁₆ O ₄	Alcohols
	11	Ethylene lactic acid	C ₃ H ₆ O ₃	Acids
	12	3-Hydroxy-3-methylpentanoic acid	C ₆ H ₁₂ O ₃	Acids
	13	2,6-Dihydroxy-4-methoxyphenyl	C ₁₁ H ₁₄ O ₄	Aromatics
Water Soluble at 873 K	1	Methylbenzene	C ₇ H ₈	Aromatics
	2	2-Propanone, 1-hydroxy	C ₃ H ₆ O ₂	Ketones
	3	Hydroxymethylcyclopropane	C ₄ H ₈ O	Furans
	4	Hexose	C ₆ H ₁₂ O ₆	Sugars

Figure 9 illustrates the chemical distribution of water-soluble fractions of bio-oil from *Populus* hardwood chips at two different temperatures of 773 K and 873 K and the corresponding components for each identified peak for each temperature are presented in Table 5. It appears that water has a good performance in extraction of the compounds presents in bio-oil from *Populus* hardwood chips at temperature of 773 K (Figure 9) in comparison to other temperature. Since the intensity and the number of extracted compounds is higher at this temperature. Sugars, phenolics, aldehydes, aromatics, acids, alcohols, and furans were found as the main decomposition products of the *Populus* hardwood chips bio-oil in water-soluble fractions. Compounds with higher polarity include acids and alcohols were found in these fractions according to Table 5.

3.3. 2 GCMS analysis of softwood (*Spruce*) bio-oil fractions

The wood chips of *Spruce* were used in the bio-oil production and the peak identification and chemical compositions of bio-oil from *Spruce* softwood chips at two different temperatures of 773 K and 873K include toluene soluble, MeOH soluble and water-soluble are presented in Figures 10, 11, and 12 and the corresponding components for identified peak for each fraction are presented in Table 6, 7, and 8.

3.3. 2.1 Softwood (*Spruce*) -toluene soluble (773 K and 873 K)

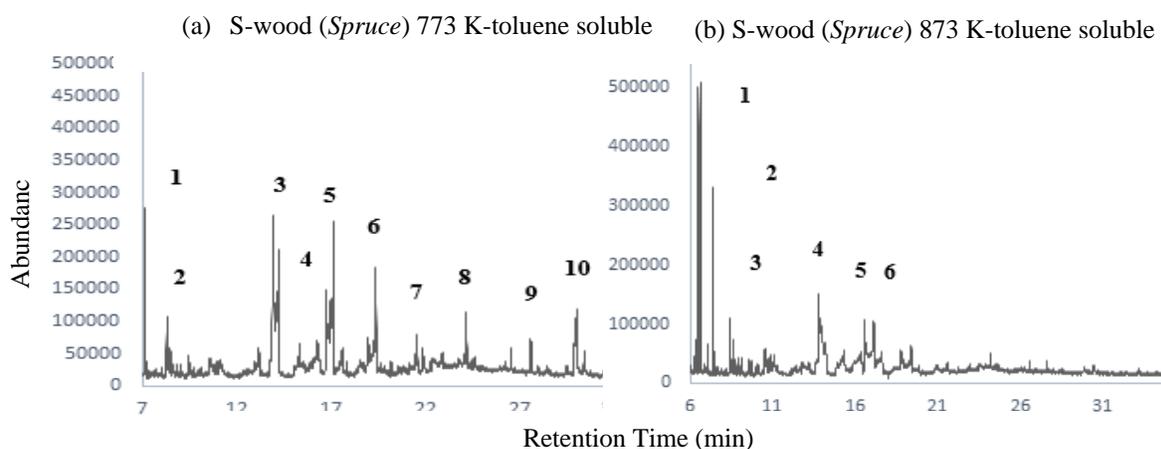


Figure 10. GC-MS chromatogram resulting from Softwood (*Spruce*) - toluene soluble fractions of bio-oil at temperatures of (a) 773 K and (b) 873 K

Figure 10 shows the chemical distribution of toluene soluble fractions of bio-oil from *Spruce* Softwood chips at two different temperatures of 773 K and 873 K and the corresponding components for each identified peak for each temperature are presented in Table 6.

According to Figure 10, a variety of compounds from different chemical families identified in these fractions. However, the intensity of the identified compounds is higher at a temperature of 773 K and more phenolic compounds were identified at this temperature.

Table 6. GC-MS chromatogram resulting from Softwood (*Spruce*) - toluene soluble fractions of bio-oil corresponding components

	Peak No	Component	Formula	Chemical Family
Toluene Soluble at 773 K	1	Furfural	C ₅ H ₄ O ₂	Furans
	2	Dimethyl diketone	C ₄ H ₆ O ₂	Ketones
	3	Phenol, 2-methoxy	C ₇ H ₈ O ₂	Phenolics
	4	Phenol, 2-methoxy-4-methyl	C ₈ H ₁₀ O ₂	Phenolics
	5	2-Methoxy-6-methylphenol	C ₈ H ₁₀ O ₂	Phenolics
	6	Phenol, 4-ethyl-2-methoxy	C ₉ H ₁₂ O ₂	Phenolics
	7	Phenol, 2-methoxy-4-propyl	C ₁₀ H ₁₄ O ₂	Phenolics
	8	2-Methoxy-4-propenylphenol	C ₁₀ H ₁₂ O ₂	Phenolics
	9	2-Propanone,1-(4-hydroxy-3-methoxyphenyl)	C ₁₀ H ₁₂ O ₃	Aromatics
	10	Methyl-(2-hydroxy-3-ethoxy-benzyl)ether	C ₁₀ H ₁₄ O ₃	Aromatics
Toluene Soluble at 873 K	1	Methyl 2-ethyl-2-propylhexanoate	C ₁₂ H ₂₄ O ₂	Esters
	2	Furfural	C ₅ H ₄ O ₂	Furans
	3	3-Methyl-2-heptanone	C ₈ H ₁₆ O	Ketones
	4	Phenol, 2-methoxy	C ₇ H ₈ O ₂	Phenolics
	5	2-Methoxy-6-methylphenol	C ₈ H ₁₀ O ₂	Phenolics
	6	Phenol, 2-methoxy-4-methyl	C ₈ H ₁₀ O ₂	Phenolics

3.3. 2.2 Softwood (*Spruce*) -methanol soluble (773 K and 873 K)

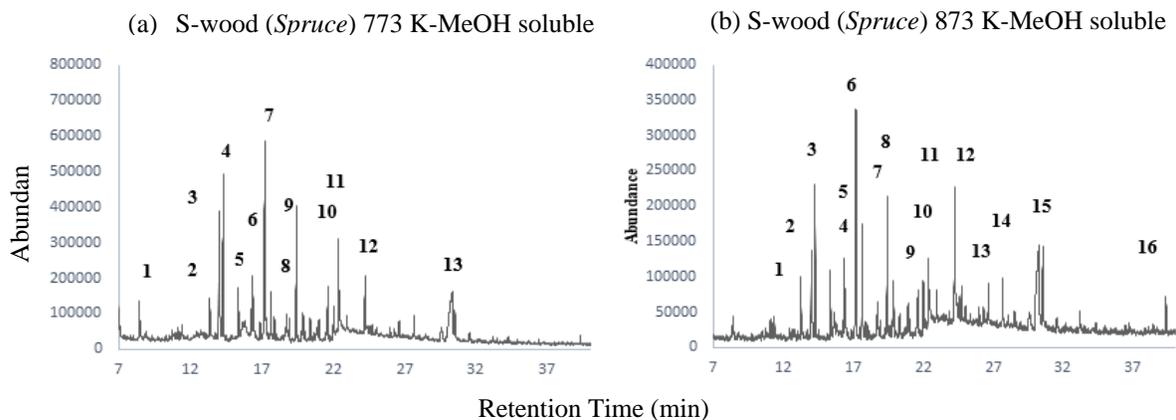


Figure 11. GC-MS chromatogram resulting from Softwood (*Spruce*)-methanol soluble fractions of bio-oil at temperatures of (a) 773 K and (b) 873 K

Table 7. GC-MS chromatogram resulting from Softwood (*Spruce*)-MeOH soluble fractions of bio-oil corresponding components

	Peak No	Component	Formula	Chemical Family
Methanol Soluble 773 K	1	2-Methyl-2-cyclopentenone	C ₆ H ₈ O	Furans
	2	3-Methyl-1,2-cyclopentanedione	C ₆ H ₈ O ₂	Furans
	3	Phenol	C ₆ H ₆ O	Phenolics
	4	Phenol, 2-methoxy-	C ₇ H ₈ O ₂	Phenolics
	5	Phenol, 3-methyl	C ₇ H ₈ O	Phenolics
	6	Phenol, 4-methy	C ₇ H ₈ O	Phenolics
	7	2-Methoxy-6-methylphenol	C ₈ H ₁₀ O ₂	Phenolics
	8	Phenol, 2,3-dimethyl	C ₈ H ₁₀ O	Phenolics
	9	Phenol, 4-ethyl-2-methoxy-	C ₉ H ₁₂ O ₂	Phenolics
	10	Phenol, 2-methoxy-4-propyl	C ₁₀ H ₁₄ O ₂	Phenolics
	11	1,2-Benzenediol	C ₆ H ₆ O ₂	Phenolics
	12	Phenol, 2-methoxy-4-propenyl	C ₁₀ H ₁₂ O ₂	Phenolics
	13	Methyl-(2-hydroxy-3-ethoxy-benzyl)ether	C ₁₀ H ₁₄ O ₃	Aromatics
Methanol Soluble 873 K	1	3,3,5-Trimethylcyclohexyl methacrylate	C ₁₃ H ₂₂ O ₂	Esters
	2	Phenol	C ₆ H ₆ O	Phenolics
	3	Phenol, 2-methoxy	C ₇ H ₈ O ₂	Phenolics
	4	Phenol, 3-methyl	C ₇ H ₈ O	Phenolics
	5	Phenol, 2-methyl-	C ₇ H ₈ O	Phenolics
	6	2-Methoxy-6-methylphenol	C ₈ H ₁₀ O ₂	Phenolics
	7	Phenol, 2,3-dimethyl-	C ₈ H ₁₀ O	Phenolics
	8	Phenol, 4-ethyl-2-methoxy	C ₉ H ₁₂ O ₂	Phenolics
	9	Phenol, 2-ethyl-5-methyl	C ₉ H ₁₂ O	Phenolics
	10	1,2-Benzenediol	C ₆ H ₆ O ₂	Phenolics
	11	Phenol, 3,4-dimethoxy	C ₈ H ₁₀ O ₃	Phenolics
	12	Phenol, 2-methoxy-4-propenyl	C ₁₀ H ₁₂ O ₂	Phenolics
	13	4-Acetyl-2-methoxyphenyl acetate	C ₁₁ H ₁₂ O ₄	Aromatics
	14	Vanillin methyl ketone	C ₁₀ H ₁₂ O ₃	Aromatics
	15	Methyl-(2-hydroxy-3-ethoxy-benzyl)ether	C ₁₀ H ₁₄ O ₃	Aromatics
	16	2,3,5-Trimethyl-phenanthrene	C ₁₇ H ₁₆	Aromatics

Figure 11 presents the chemical distribution of methanol soluble fractions of bio-oil from Spruce softwood chips at two different temperatures of 773 K and 783 K and the corresponding components for each identified peak for each temperature are presented in Table 7. It is obvious that methanol performed a good extraction for this type of bio-oil. A wide variety of compounds include C₃-C₁₀ were extracted in these fractions. More phenolic compounds were identified at these two temperatures. It appears that methanol has good performance in extraction of different chemical families in both hardwood and softwood fractions. It can be seen that methanol extracted over 90% of total chemicals in bio-oil due to high polarity (polarity of toluene: 2.7 and polarity of methanol: 6.6) [40]. The chemicals that exist in bio-oil are mostly oxygenated compounds, which have high polarity and solubility in water and polar solvents.

3.3. 2.3 Softwood (*Spruce*) –water soluble (773 K and 873 K)

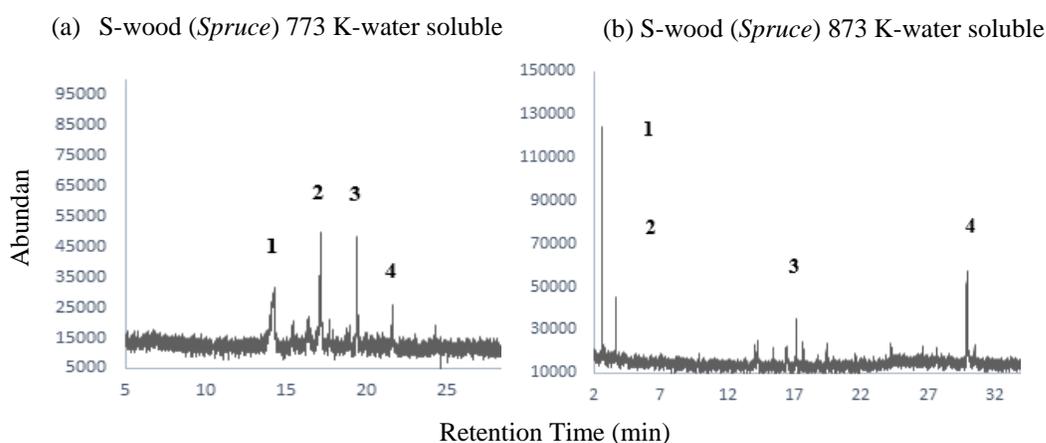


Figure 12. GC-MS chromatogram resulting from Softwood (*Spruce*)-water soluble fractions of bio-oil at temperatures of (a) 773 K and (b) 873 K

Figure 12 shows the chemical distribution of water-soluble fractions of bio-oil from *Spruce* Softwood chips at two different temperatures of 773 K and 873 K and the corresponding components for each identified peak for each temperature are presented in Table 8. As it can be seen from Table 8 that less compounds were identified by water-soluble fraction for softwood bio-oil. This is because the vast majority of the compounds were extracted by toluene and then methanol followed by water fraction and hence lower fraction of compounds appears in the water fraction. However, the extracted compounds were found to be the compounds with high polarity. According to Table 8, more phenolic compounds were

identified by water-soluble fraction at 773 K compared to 873 K. However, the intensity of the two temperatures is low among the other fractions of softwood extractions.

Table 8. GC-MS chromatogram resulting from Softwood (*Spruce*)-water soluble fractions of bio-oil corresponding components

	Peak No	Component	Formula	Chemical Family
Water Soluble at 773 K	1	Phenol, 2-methoxy	C ₇ H ₈ O ₂	Phenolics
	2	Phenol, 2-methoxy-4-methyl	C ₈ H ₁₀ O ₂	Phenolics
	3	Phenol, 4-ethyl-2-methoxy	C ₉ H ₁₂ O ₂	Phenolics
	4	Phenol, 2-methoxy-4-propyl	C ₁₀ H ₁₄ O ₂	Phenolics
Water Soluble at 873 K	1	2-Propanone, 1-hydroxy	C ₃ H ₆ O ₂	Ketones
	2	Methylbenzene	C ₇ H ₈	Aromatics
	3	2-Methoxy-6-methylphenol	C ₈ H ₁₀ O ₂	Phenolics
	4	Hexose	C ₆ H ₁₂ O ₆	Sugars

3.3.3 Effect of temperature on chemical distribution in bio-oil

The classification of the identified compounds into chemical families was performed according to their functional groups and structural formula. The grouping of bio-oil compounds in chemical families is a very useful method, which allows working with a few chemical groups instead of hundreds of compounds. The detected compounds were classified into 10 different chemical families, which include phenolics, aromatics, furans, ketones, alcohol, acids, sugars, ethers, esters, and aldehydes. The classification of the identified components of bio-oil was reported in the literature [20,31,39] and according to the functional group and structure of each compound, the classification was achieved carefully. Figures 13 and 14 illustrate the overall functional group distribution of chemical families from two different types of bio-oil e.g. hardwood (*Populus*) and softwood (*Spruce*) chips.

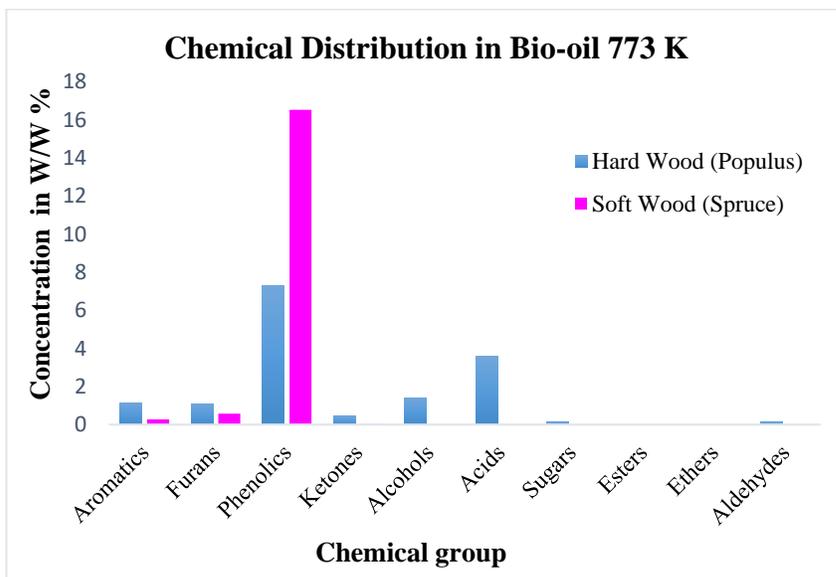


Figure 13. The effect of temperature on chemical distribution in bio-oil at 773 K

According to Figure 13, the phenolic compounds were the major identified chemical groups for the softwood (*Spruce*) bio-oil at 773 K, whereas the bio-oil produced from hardwood (*Populus*), furanic, acid and sugar compounds were the most produced compounds at this temperature. However, the intensity of the phenolic and ketonic compounds was higher for the softwood (*Spruce*) bio-oil at this temperature. In other words, bio-oil produced from hardwood (*Populus*) shows a wider distribution of functional groups, but with less intensity than bio-oil produced from softwood (*Spruce*) at 773 K as presented in Figure 13. For both types of bio-oil, wide varieties of chemical groups were identified at a temperature of 873 K in comparison to 773 K.

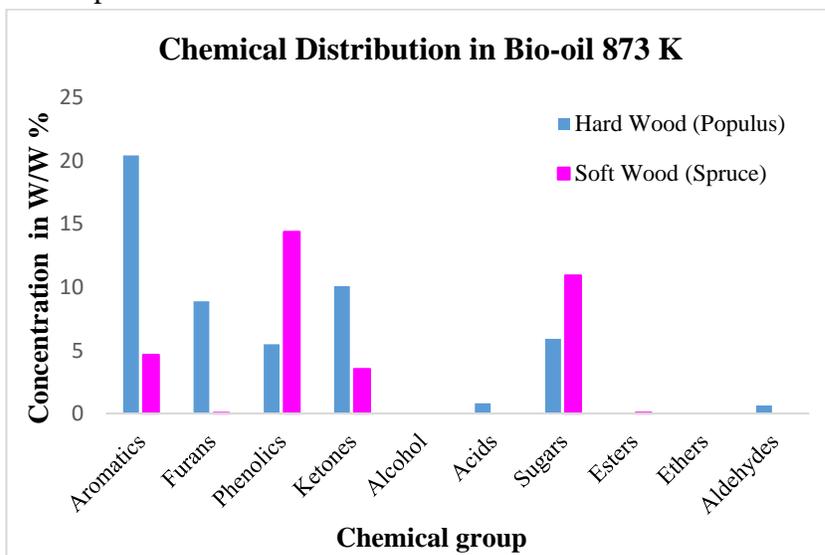


Figure 14. The effect of temperature on chemical distribution in bio-oil at 873 K

As shown in Figure 14, aromatics, ketones, furans and sugars were the most abundant compounds for bio-oil from hardwood (*Populus*) at this temperature. However, phenolics and sugar compounds were the dominant chemical groups for softwood bio-oil at this temperature. Furans are volatile cyclic compounds which resulted from cellulose degradation and are used in the production of resins, lacquers and agrochemicals [41-43].

4. CONCLUSIONS

This study focused on the production and characterisation of fast pyrolysis bio-oil produced from two different types of biomass samples at two different temperatures of 773 K and 873 K. The woodchips - one from hardwood (*Populus*) and the other type from softwood (*Spruce*) were used to produce bio-oil using a bench-scale pyrolysis reactor. The selective extraction method was developed to obtain chemicals from bio-oil and also as a method of analysis to determine the chemical composition of bio-oil by GC-MS. Other types of characterization techniques e.g. elemental analysis, water content, pH and viscosity measurements, and bomb calorimetry were employed for this study.

The effect of temperature on the production of bio-oil and on the chemical distribution in bio-oil was examined. The bio-oil yields from hardwood (*Populus*) at 773 K and 873 K were calculated to be 62.50% and 68.40% respectively. For softwood (*Spruce*) the bio-oil yields at 773 K and 873 K were 65.40% and 71.20% respectively. It was found that more phenolic compounds were extracted at a temperature of 773 K for bio-oil obtained from softwood (*Spruce*), whereas the bio-oil extracted from hardwood (*Populus*) produced furans, acids and sugar compounds. However, for both types of bio-oils, a wide variety of chemical groups were identified at a temperature of 873 K in comparison to 773 K. The results indicate that pyrolysis of softwood (*Spruce*) produced a higher yield of bio-oil at higher temperature (873 K), however more selective chemicals (phenolics) can be obtained at a temperature of 773 K. It can be concluded that the efficiency of methanol in extracting chemical groups was higher than water and toluene. It was found that methanol extracted over 90% of total chemicals in bio-oil due to high polarity. The chemicals that exist in bio-oil are mostly oxygenated compounds, which have high polarity and solubility in polar solvents. This study highlighted an appropriate method for solving a real world problem for sustainable production of bioenergy from renewable source of feedstock.

For future work, biochar could be used as a source of activated carbon for production of supercapacitor to produce electrodes. The gaseous products of pyrolysis process could be utilised as a source of energy for pyrolysis process. However, the effect of the use of product gas on pyrolysis process and the essential equipment required for this purpose must be studied in detail.

ACKNOWLEDGEMENT

The authors would like to acknowledge London South Bank University for partial funding of this project. The authors are also thankful to the Department of Wood and Paper Technology, University of Tehran, for their help and support during some experimental work.

REFERENCES

- [1] Stefanidis SD, Kalogiannis KG, Iliopoulou EF, Michailof CM, Pilavachi PA, Lappas AA. A study of lignocellulosic biomass pyrolysis via the pyrolysis of cellulose, hemicellulose and lignin. *J Anal Appl Pyrolysis* 2014;105:143-150. <https://doi.org/10.1016/j.jaap.2013.10.013>.
- [2] Park HJ, Dong JI, Jeon JK, Park YK, Yoo KS, Kim SS, et al. Effects of the operating parameters on the production of bio-oil in the fast pyrolysis of Japanese larch. *Chem Eng J* 2008;143:124-132. <https://doi.org/10.1016/j.cej.2007.12.031>.
- [3] Jeong YW, Choi SK, Choi YS, Kim SJ. Production of biocrude-oil from swine manure by fast pyrolysis and analysis of its characteristics. *Renew Energy* 2015;79:14–9. <https://doi.org/10.1016/j.renene.2014.08.041>.
- [4] Bridgwater A V., Peacocke GVC. Fast pyrolysis processes for biomass. *Renew Sustain Energy Rev* 2000;4:1–73. [https://doi.org/10.1016/S1364-0321\(99\)00007-6](https://doi.org/10.1016/S1364-0321(99)00007-6).
- [5] Papari S, Hawboldt K. A review on the pyrolysis of woody biomass to bio-oil: Focus on kinetic models. *Renew Sustain Energy Rev* 2015;52:1580-1595. <https://doi.org/10.1016/j.rser.2015.07.191>.
- [6] 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. <https://doi.org/10.1016/j.fuproc.2015.01.002>.
- [7] Chen D, Yin L, Wang H, He P. Reprint of: Pyrolysis technologies for municipal solid waste: A review. *Waste Manag* 2015;37:116–36. <https://doi.org/10.1016/j.wasman.2015.01.022>.
- [8] Guo D, Wu S, Lyu G, Guo H. Effect of molecular weight on the pyrolysis characteristics of alkali lignin. *Fuel* 2017;193:45-53. <https://doi.org/10.1016/j.fuel.2016.12.042>.
- [9] Saidur R, Abdelaziz EA, Demirbas A, Hossain MS, Mekhilef S. A review on biomass as a fuel for boilers. *Renew Sustain Energy Rev* 2011;15:2262-2289. <https://doi.org/10.1016/j.rser.2011.02.015>.
- [10] Isahak WNRW, Hisham MWM, Yarmo MA, Yun Hin TY. A review on bio-oil production from biomass by using pyrolysis method. *Renew Sustain Energy Rev* 2012;16: 5910-5923. <https://doi.org/10.1016/j.rser.2012.05.039>.
- [11] Wu YM, Zhao ZL, Li H Bin, He F. Low temperature pyrolysis characteristics of major components of biomass. *Ranliao Huaxue Xuebao/Journal Fuel Chem Technol* 2009;37:427–32. [https://doi.org/10.1016/S1872-5813\(10\)60002-3](https://doi.org/10.1016/S1872-5813(10)60002-3).
- [12] Lu Q, Li WZ, Zhu XF. Overview of fuel properties of biomass fast pyrolysis oils.

- Energy Convers Manag 2009;50:1376-1383.
<https://doi.org/10.1016/j.enconman.2009.01.001> .
- [13] Kissinger HE. Reaction Kinetics in Differential Thermal Analysis. *Anal Chem* 1957;29: 1702–1706. <https://doi.org/10.1021/ac60131a045>.
- [14] Hu X, Gholizadeh M. Biomass pyrolysis: A review of the process development and challenges from initial researches up to the commercialisation stage. *J Energy Chem* 2019;39:109-143. <https://doi.org/10.1016/j.jechem.2019.01.024>.
- [15] Amaral SS, De Carvalho Junior JA, Costa MAM, Neto TGS, Dellani R, Leite LHS. Comparative study for hardwood and softwood forest biomass: Chemical characterization, combustion phases and gas and particulate matter emissions. *Bioresour Technol* 2014;164:55-63. <https://doi.org/10.1016/j.biortech.2014.04.060>.
- [16] Abdulkhani A, Hosseinzadeh J, Ashori A, Dadashi S, Takzare Z. Preparation and characterization of modified cellulose nanofibers reinforced polylactic acid nanocomposite. *Polym Test* 2014;35:73-79. <https://doi.org/10.1016/j.polymertesting.2014.03.002>.
- [17] Echresh Z, Abdulkhani A, Saha B. A comparative structural characterisation of different lignin biomass. *ECOS 2019 - Proc. 32nd Int. Conf. Effic. Cost, Optim. Simul. Environ. Impact Energy Syst.*, 2019.
- [18] Zadeh ZE, Abdulkhani A, Aboelazayem O, Saha B. Recent insights into lignocellulosic biomass pyrolysis: A critical review on pretreatment, characterization, and products upgrading. *Processes* 2020;8:799. <https://doi.org/10.3390/pr8070799>.
- [19] Xu Y, Hu X, Li W, Shi Y. Preparation and Characterization of Bio-oil from Biomass. *Prog. Biomass Bioenergy Prod.*, 2011. <https://doi:10.5772/16466>.
- [20] 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. <https://doi:10.15376/biores.9.3.5219-5233>.
- [21] He J, Zhang W. Techno-economic evaluation of thermo-chemical biomass-to-ethanol. *Appl Energy* 2011;88:1224-1233. <https://doi.org/10.1016/j.apenergy.2010.10.022>.
- [22] Rogers JG, Brammer JG. Estimation of the production cost of fast pyrolysis bio-oil. *Biomass and Bioenergy* 2012;36:208-217. <https://doi.org/10.1016/j.biombioe.2011.10.028>.
- [23] Treedet W, Suntivarakorn R. Design and operation of a low cost bio-oil fast pyrolysis from sugarcane bagasse on circulating fluidized bed reactor in a pilot plant. *Fuel Process Technol* 2018;179:17-31. <https://doi.org/10.1016/j.fuproc.2018.06.006>.
- [24] Zhang L, Liu R, Yin R, Mei Y. Upgrading of bio-oil from biomass fast pyrolysis in China: A review. *Renew Sustain Energy Rev* 2013;24:66-72. <https://doi.org/10.1016/j.rser.2013.03.027>.
- [25] Tsai WT, Lee MK, Chang JH, Su TY, Chang YM. Characterization of bio-oil from induction-heating pyrolysis of food-processing sewage sludges using chromatographic analysis. *Bioresour Technol* 2009;100(9):2650-2654. <https://doi.org/10.1016/j.biortech.2008.11.023>.
- [26] Zadeh ZE, Abdulkhani A, Saha B. Characterization of fast pyrolysis bio-oil from hardwood and softwood lignin. *Energies* 2020;13:887. <https://doi.org/10.3390/en13040887>.

- [27] Bridgwater A V. Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy* 2012;38:68–94. <https://doi.org/10.1016/j.biombioe.2011.01.048>.
- [28] Echresh Z, Abdulkhani A, Saha B. Analytical pyrolysis study of different lignin biomass. *Eur. Biomass Conf. Exhib. Proc.*, 2019. <https://doi.org/10.5071/27thEUBCE2019-3BV.7.23>.
- [29] Alvarez-Chavez BJ, Godbout S, Palacios-Rios JH, Le Roux É, Raghavan V. Physical, chemical, thermal and biological pre-treatment technologies in fast pyrolysis to maximize bio-oil quality: A critical review. *Biomass and Bioenergy* 2019;128:105333. <https://doi.org/10.1016/j.biombioe.2019.105333>.
- [30] Czernik S, Bridgwater A V. Overview of applications of biomass fast pyrolysis oil. *Energy and Fuels* 2004;18:590-598. <https://doi.org/10.1021/ef034067u>.
- [31] Khuenkao N, Tippayawong N. Production and characterization of bio-oil and biochar from ablative pyrolysis of lignocellulosic biomass residues. *Chem Eng Commun* 2019;207:153-160. <https://doi.org/10.1080/00986445.2019.1574769>.
- [32] Garg R, Anand N, Kumar D. Pyrolysis of babool seeds (*Acacia nilotica*) in a fixed bed reactor and bio-oil characterization. *Renew Energy* 2016;96:167-171. <https://doi.org/10.1016/j.renene.2016.04.059>.
- [33] Hamzeh Y, Ashori A, Khorasani Z, Abdulkhani A, Abyaz A. Pre-extraction of hemicelluloses from bagasse fibers: Effects of dry-strength additives on paper properties. *Ind Crops Prod* 2013;43:365-371. <https://doi.org/10.1016/j.indcrop.2012.07.047>.
- [34] Dai L, Wang Y, Liu Y, Ruan R, Yu Z, Jiang L. Comparative study on characteristics of the bio-oil from microwave-assisted pyrolysis of lignocellulose and triacylglycerol. *Sci Total Environ* 2019;659:95-100. <https://doi.org/10.1016/j.scitotenv.2018.12.241>.
- [35] Couhert C, Commandre JM, Salvador S. Is it possible to predict gas yields of any biomass after rapid pyrolysis at high temperature from its composition in cellulose, hemicellulose and lignin? *Fuel* 2009;88:408-417. <https://doi.org/10.1016/j.fuel.2008.09.019>.
- [36] Yu S, Park J, Kim M, Ryu C, Park J. Characterization of biochar and byproducts from slow pyrolysis of hinoki cypress. *Bioresour Technol Reports* 2019;6:.. <https://doi.org/10.1016/j.biteb.2019.03.009>.
- [37] Valle B, Remiro A, García-Gómez N, Gayubo AG, Bilbao J. Recent research progress on bio-oil conversion into bio-fuels and raw chemicals: a review. *J Chem Technol Biotechnol* 2019;94:670-689. <https://doi.org/10.1002/jctb.5758>.
- [38] Ren S, Ye XP, Borole AP. Separation of chemical groups from bio-oil water-extract via sequential organic solvent extraction. *J Anal Appl Pyrolysis* 2017;123:30-39. <https://doi.org/10.1016/j.jaap.2017.01.004>.
- [39] Hu HS, Wu YL, Yang M De. Fractionation of bio-oil produced from hydrothermal liquefaction of microalgae by liquid-liquid extraction. *Biomass and Bioenergy* 2018;108:487-500. <https://doi.org/10.1016/j.biombioe.2017.10.033>.
- [40] Gollakota ARK, Reddy M, Subramanyam MD, Kishore N. A review on the upgradation techniques of pyrolysis oil. *Renew Sustain Energy Rev* 2016;58:1543–68. <https://doi.org/10.1016/j.rser.2015.12.180>.
- [41] Ghafari R, DoostHosseini K, Abdulkhani A, Mirshokraie SA. Replacing formaldehyde by furfural in urea formaldehyde resin: effect on formaldehyde emission

and physical–mechanical properties of particleboards. *Eur J Wood Wood Prod* 2016;74:609–616. <https://doi.org/10.1007/s00107-016-1005-6>.

[42] Hamzeh Y, Abyaz A, Niaraki MOSM, Abdulkhani A. Application of surfactants as pulping additives in soda pulping of bagasse. *BioResources* 2009;4: 1267-1275.

[43] Mallick D, Mahanta P, Moholkar VS. Co-gasification of coal and biomass blends: Chemistry and engineering. *Fuel* 2017;204:106-128. <https://doi.org/10.1016/j.fuel.2017.05.006>.