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Hydrothermolysis of organosolv lignin for the production of bio-oil rich in monoaromatic phenolic compounds

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ABSTRACT

Bio-oils rich in monoaromatic phenolic compounds were produced by a hydrothermal treatment in a batch reactor from organosolv lignin derived from beech wood. Reaction temperatures and times were varied (270 – 350 °C and 10 – 120 min, respectively). Increase in the temperature at a particular reaction time had a positive impact on the bio-oil yields, which varied from 8.0 wt.% to 14.6 wt.%, based on the original amount of dry lignin. GC-MS analysis of bio-oils revealed that the yields of monoaromatic compounds ranged from 22 - 65 wt.% of bio-oil depending on the reaction conditions. Syringol (8.9 - 22.8 wt.% of bio-oil), guaiacol (2.6 - 9.3 wt.% of bio-oil), pyrocatechol (0 - 12.4 wt.% of bio-oil), 3-methoxycatechol (0 - 21 wt.% of bio-oil), 4-methylsyringol (0.5 - 5.9 wt.% of bio-oil), and syringaldehyde (0 - 9 wt.% of bio-oil) were identified as the major aromatic compounds. In addition to bio-oil, gaseous components, water solubles, char, and undegraded lignin were formed in the experiments. The mass balances of the experiments were constructed. The results show that monoaromatics can be produced at a moderate yield through uncatalysed lignin hydrothermolysis; char formation remains as an obstacle, however, and its prevention calls for the usage of catalysts and/or organic solvents.

KEYWORDS

Bio-oil, Hydrothermal degradation, Lignin, Monoaromatics

1. Introduction

A biorefinery refers to a facility that integrates processes and technologies to convert biomass to energy and value-added products such as fuels and chemicals [1]. Chemical pulp mills have a high potential for becoming future biorefineries. They utilize a large amount of lignocellulosic biomass for the production of chemical pulp. Currently, the majority of chemical pulp mills produce paper grade pulp, consisting of cellulose and hemicelluloses in a typical yield of 90% and 50% on the initial raw material, while the lignin fraction, together with the degraded carbohydrates, is dissolved in the cooking liquor after degradation and fragmentation reactions. The resulting black liquor is concentrated by the evaporation of water before it is incinerated. In this way, the cooking chemicals are recycled and the energy content of the dissolved lignocellulose fraction is utilized as steam and power for the energy supply of the pulp mill [2, 3].

Lignin is considered a side product of pulp industry. Kraft lignin and lignosulfonates are commercially available whereas organosolv lignin is produced for research purposes on small scale. In the kraft process, NaOH and Na_2S are utilized to degrade and dissolve lignin from wood in a water/alkali mixture at *ca.* 170 °C [4]. Recent developments have enabled the commercial extraction of kraft lignin with *e.g.* Lignoboost technology [5] through acidification of black liquor with CO_2 and H_2SO_4 followed by precipitation, filtration

and washing. Acid sulfite pulping utilizes hydrated SO_2 together with mono or divalent counter ions such Na^+, Mg^{2+} and Ca^{2+} to solubilize lignin from wood at 120 – 180 °C. Lignin obtained from acid sulfite process is known as lignosulfonate due to incorporation of sulfonate groups in its structure. The organic sulfur content of kraft lignin is 1 – 3 wt.%, in contrast to 4 – 8 wt.% in lignosulfonates. Lignosulfonates have a high molar mass ranging from 12,000 to 60,000 $gmol^{-1}$. Organosolv lignin is produced by treating wood with aqueous organic solvents such as ethanol or methanol at elevated temperature. The Alcell process, a well-known organosolv process, utilizes 50% aqueous ethanol mixture at 190 °C and 28 bar with a digestion time of 1 hour. The organic sulfur content of organosolv lignin is negligible, the molar mass is low and the distribution is narrow, ranging from less than 1,000 to 4,000 g mol^{-1} [4].

From the annual production of 50 million tons of lignin only a small fraction [6] is recovered as low-value products such as flocculating and dispersing agents. These applications can be seen as an underutilization of lignin's potential; [7, 8] additionally, commercial products from lignin available today include vanillin from sulfite lignin and dimethyl sulfoxide (DMSO) from kraft lignin. [9, 10, 11]

As a renewable source for aromatics, lignin is an obvious choice: it is widely available and therefore it has the potential of becoming an alternative feedstock for aromatic chemicals, currently obtained from petroleum (*e.g.* phenols). A hindrance for utilizing lignin as a chemical feedstock is its complex, amorphous structure. The lignin polymer is an aromatic network composed of three basic monolignols, namely p-coumaryl alcohol (H), coniferyl alcohol (G), and sinapyl alcohol (S) [12, 13]. These units are connected to each other with a number of different ether and carbon-carbon bonds among which the ether bonds are in majority [14, 4]. Along with these bonds, lignin is presumably covalently linked to hemicelluloses forming so-called lignin carbohydrate complexes [14].

Despite all the challenges which lignin presents due to its structural complexity, there has been a substantial interest in finding techniques to utilize lignin as a raw material for higher value products. The techniques applied for lignin conversion include pyrolysis, gasification, liquefaction and chemical degradation such as acid, base and metal catalyzed reactions [15, 16]. Among the liquefaction techniques hydrothermal treatment has recently gained attraction [17]. This process exploits water at subcritical (liquid water at 100 - 374 ˚C) and supercritical (water above 221 bar and 374 ˚C) conditions to convert lignin to low molecular weight chemicals such as phenol, guaiacol, and catechols. The solvent properties of water vary along with changes in conditions, *e.g.* the values of dielectric constant, ion product, pH, and density are heavily dependent on the temperature and pressure [18]. As an example, the dielectric constant of water decreases from 78 at 25 ˚C to 21 at 300 ˚C, with a further decrease to 4.1 at 500 ˚C [19]. Low dielectric constant results in increased solubility of organic hydrophobic substances; this is manifested in results published by Zhang *et al*. [20]: the solubility of pine kraft lignin in

water is very limited at ambient conditions (2.7 %), whereas it dissolves completely in supercritical water. In addition to changes in the dielectric constant, the higher ion product (K_w) of water under subcritical conditions (10^{-12} (mol $kg^{-1})^2$, *ca.* 350 ˚C) compared to water at room temperature (10^{-14} (mol $kg^{-1})^2$, *ca.* 25 ˚C) leads to an increased concentration of H^+ and OH^- ions, thus promoting acid or base catalyzed reactions [17, 19].

Recently, several attempts [20 – 26] have been reported for converting lignin into low molecular weight phenolic compounds using hydrothermal techniques. In most of these studies emphasis is given to supercritical and near supercritical water. At short residence time, supercritical water can result in a higher yield of phenolic compounds, such as guaiacol, compared to subcritical water; however, the compounds are highly reactive in supercritical water and undergo rapid repolymerization [21, 22]. Consequently, in several studies [20 – 22] the yield of the solid residue of lignin degradation in supercritical water is mentioned to be higher compared to depolymerization experiments carried out in subcritical water [22]; nevertheless, contradicting results have also been published [23]. The degradation rate of some abundant phenolic compounds such as guaiacol and catechol has been observed to be faster in supercritical conditions compared to subcritical and near supercritical conditions [21, 23]. Saisu *et al* [24] and Okuda *et al* [25] have suggested that the addition of phenol to water could supress the formation of residual solids during hydrothermal treatment of lignin. However, complete suppression of solid residue is still a challenge under non-catalytic hydrothermal conditions.

The objective of this work is to investigate the potential of hydrothermolysis at subcritical conditions as a method for converting beech organosolv lignin to monoaromatic phenolic compounds. The reasons for prioritizing organosolv lignin over kraft lignin are sulfur free nature, narrow polydispersity, and limited carbohydrate contamination. The presence of sulfur complicates the subsequent derivatization of kraft lignin and hinders its use as a substrate for producing biofuels. Special attention is given to separating residual lignin from char and calculating mass balances, enhancing the understanding of the product distribution at various reaction conditions. Also, yields of water soluble compounds as well as effects of reaction conditions on the formation of monoaromatic phenolic compounds are studied. These aspects are largely missing from earlier publications in this area [20 – 23], which report mostly experiments with softwood alkali lignin and in which the separation techniques fail to separate residual lignin from char; instead, in many occasions residual lignin has been extracted with an organic solvent and included in the bio-oil yield.

2. Materials and Methods

2.1. Materials

All degradation experiments of this study were performed with beech wood organosolv lignin (supplied by Fraunhofer Institute, Germany). Lignin model compounds, including phenol (99.5%), guaiacol (98%), catechol (99.0%), 4-methylcatechol (95.0%), syringaldehyde (98.0%), 4-methylsyringol (97.0%), 3-methoxycatechol (99.0%), 4-methylguaiacol (98.0%), and syringol (99.0%) were purchased from Sigma Aldrich and used as standard compounds for locating the peaks and plotting calibration curves to calculate individual response factors in GC-MS. Anisole (purity 99.0%) purchased from Sigma Aldrich was used as an internal standard. Tetrahydrofuran (THF; 99.9%), and ethylacetate (99.7%) were also purchased from Sigma Aldrich and used either for extraction or solubilizing bio-oil for analysis. Acetic anhydride (99.6%, VWR chemicals BDH Prolabo), methanol (99.8%, Sigma Aldrich), and ethanol (99.5%, Altia Oyj) were used in acetylation and purification of lignin. Sodium hydroxide (99.2%, VWR chemicals BDH Prolabo) was used for separating undegraded lignin from char. Sulfuric acid (95.0 – 97.0%, Sigma Aldrich) was used for acidification. All chemicals were used as received except sodium hydroxide and sulfuric acid which were diluted to required concentrations in distilled water.

2.2. Experimental Methods

2.2.1. Hydrothermal degradation of lignin

Hydrothermal degradation of lignin was performed in a stainless steel (T316) Parr 4575 batch reactor of 500 ml volume, equipped with a 4848 reactor controller. Reactions were conducted by charging the reactor with 5 g of organosolv lignin together with 200 mL of distilled water. The reactor was sealed and purged with nitrogen gas three times to remove air and for detecting possible leakages. Subsequently, reactions were carried out at 270, 290, 310, and 350 ˚C for 10, 20, 30, 60, and 120 min. Reactor contents were heated from room temperature to the desired temperature under constant stirring at 200 rpm. Upon reaching the reaction time, the reactor was cooled to room temperature by circulating water in the cooling tube inside of the reactor vessel, after which the pressure was released through the relief valve and the reactor was opened.

2.2.2. Bio-Oil Extraction

The separation procedure is schematically presented in Figure 1. The contents of the reactor were emptied and filtered to remove solids from the aqueous phase. The aqueous phase containing the degraded lignin compounds was solvent extracted by mixing 100 mL ethyl acetate to recover the bio-oil. Ethyl acetate was removed from the mixture with rotary evaporator and the bio-oil was recovered as a viscous liquid.

2.2.3. Solids Separation

The reactor was filled with 200 mL of 1 M NaOH and agitated under high speed (700 rpm) for 30 minutes to completely clean the reactor from char and residual lignin remaining on the reactor walls and the propeller. The caustic solution from the reactor was mixed with the filtered solids. Subsequently, the solution was filtered, separating the solid char from the dissolved lignin residue. 5 M H_2SO_4 was added to acidify the filtered caustic solution to a pH of 1.5 at which the residual lignin was precipitated and the solution was filtered to recover the residual lignin. After thoroughly washing with distilled water, the precipitated lignin was left for drying at room temperature overnight.

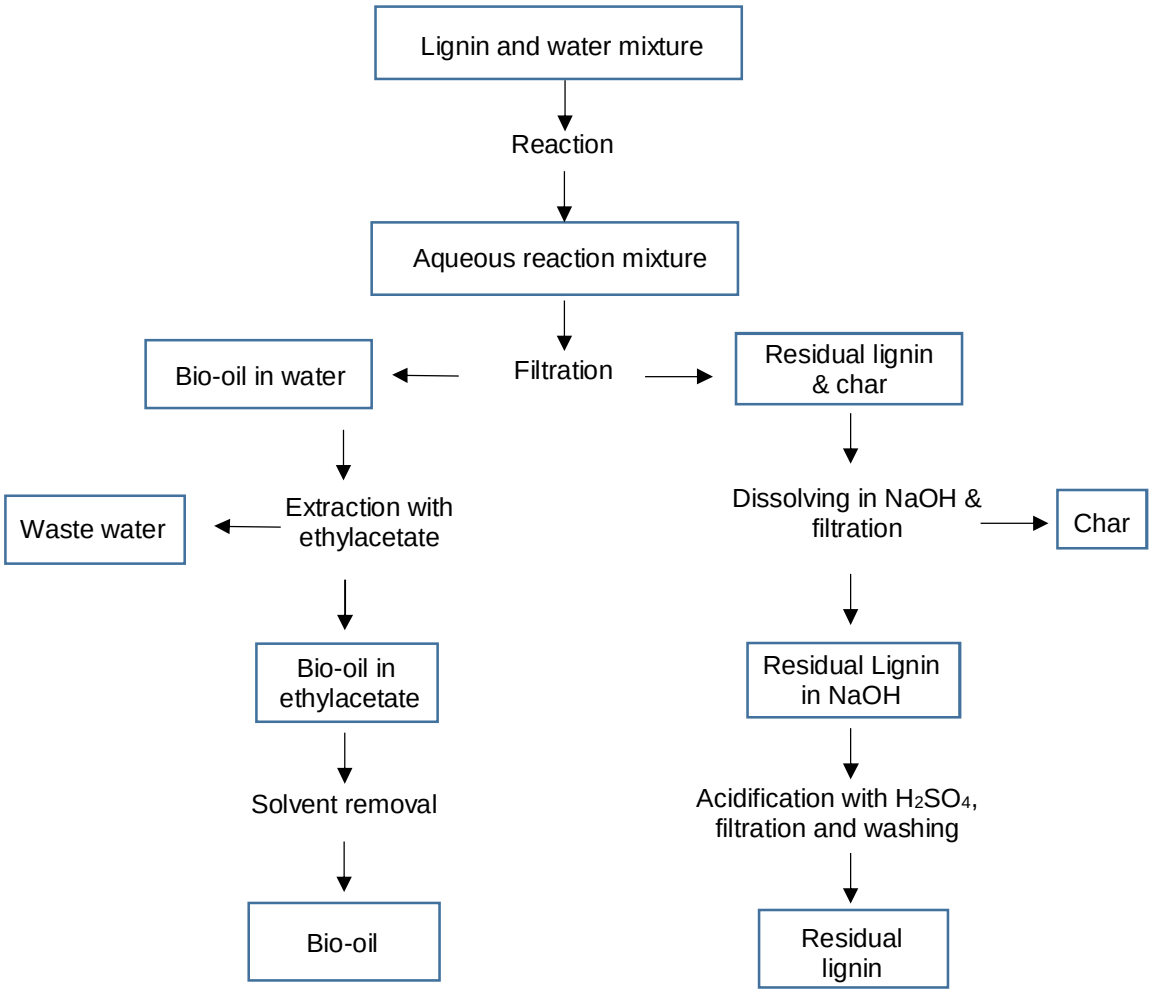


Fig 1. Procedure for products separation and recovery.

2.3. Analytical Methods

The molecular weight averages of the substrate lignin and the bio-oil were determined with Agilent HPLC-system by means of Phenogel (5 µm – 5 nm and 100 nm) columns and UV detector at 280 nm. THF was used as an eluent at a rate of 1.0 mL min^{-1} and the analysis was carried out at room temperature. Calibration was performed using syringol

and biphenyl together with polystyrene standards ranging from 76,600 g mol^{-1} to 208 g mol^{-1}. Lignin sample was acetylated prior to analysis to make it soluble in THF by a published method [27] with a slight modification: ethanol (instead of methanol) was added to and removed from the sample seven times to completely remove unreacted acetylation chemicals and evaporated to dryness. Bio-oil samples were analyzed without acetylation.

Phenolic products present in bio-oil were characterized using GC-MS (Thermo scientific trace 1300 ISQ and TG-200 MS capillary column with dimensions: 30 m, 0.25 mm, 0, 25 µm). 1 µL of bio-oil diluted in ethylacetate was injected at 280 ˚C into the column using splitless mode. Helium was utilized as a carrier gas at a rate of 1 mL min^{-1}. Temperature program for the analysis was as follows: After 2 min hold at 40 ˚C, oven was heated to 280 ˚C at 6 ˚C min^{-1} and hold for 2 min. MS detector was operated in an electron ionization mode at 70 eV.

Elemental analysis for lignin was performed using a Flash EA 1112 Elemental Analyzer Series CHNS/O with auto sampler MAS200R from Thermo Finnigan. For bio-oil, elemental analyses were carried out by PerkinElmer Model 2400 Series II CHNS Elemental Analyzer (230 V). The amount of oxygen in the samples was calculated by subtracting the sum of other elements from 100%.

The amount of water in THF and selected samples of bio-oil was determined by Karl Fischer titration. Bio-oil samples were dissolved in THF prior to analysis. The mixture was then titrated with solution of Hydranal Composit 5. Results for bio-oil water content were corrected by subtracting the water content of THF.

The amount of organic carbon originating from water solubles after hydrothermal treatment was determined by analyzing the aqueous phase obtained after solids separation from the reaction mixture. The aqueous phase was analyzed with total organic carbon (TOC) analyzer (TOC-V_{CPH}) by Shimadzu. The amount of TOC was then converted to the stoichiometric amount of lignin by using the C-9 formula for lignin which is $C_9H_{7.25}O_{2.28}(OCH3)_{1.54}$. The details for the determination of the C-9 formula are given elsewhere [28].

The moisture content of the substrate lignin was determined by drying to constant weight at 105 ˚C.

3. RESULTS AND DISCUSSION

3.1. Mass Balances

The basic characteristics of the used organosolv lignin are summarized in Table 1. It can be observed from Table 1 that used lignin sample is sulfur free, having high purity (low

ash and carbohydrate content) and narrow molar mass distribution in comparison to the alkali lignins used in earlier studies [22, 23, 26, 29].

At any reaction condition, lignin degradation products were classified in four categories, namely: bio-oil, residual lignin (RL), char, and water solubles. It is important to mention that monoaromatic phenolic compounds were recovered as a part of the bio-oil and not included in the water solubles. The solid residue which was insoluble in NaOH was defined as char whereas the solid residue which was soluble in NaOH and recovered after acidification was named as residual lignin (see Figure 1). Besides the mentioned products, gases were also produced during the reactions, particularly at 350 °C. The gaseous phase was not recovered and analyzed, instead the gases were released to the atmosphere through the reactor's relief valve. The amount of gases formed was determined by calculation: subtracting the weights of the other degradation products from the original lignin dry weight. Figure 2 (a – d) represents the mass balances of the different products obtained after hydrothermal degradation of lignin at reaction times ranging from 10 min to 120 min and at temperatures ranging from 270 °C to 350 °C.

Table 1.

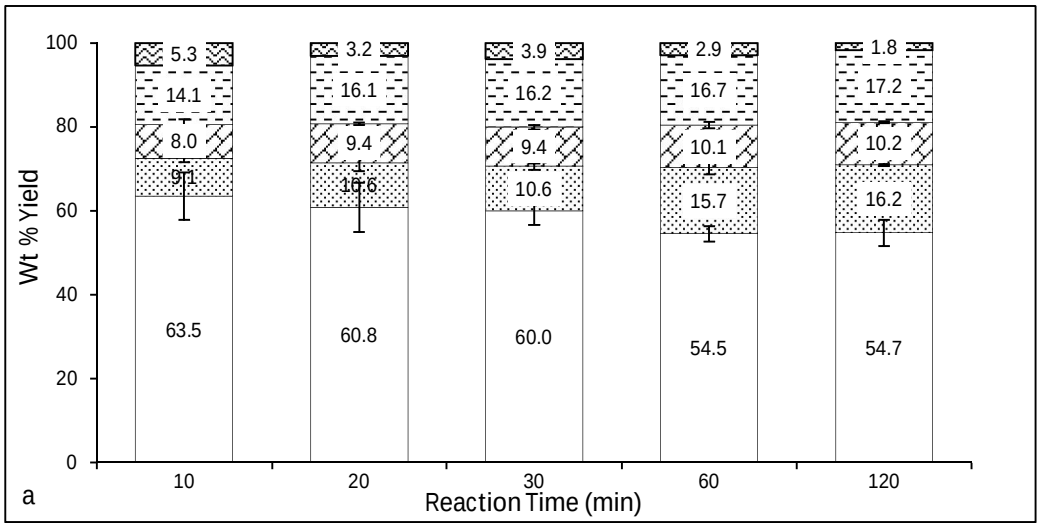
Properties of substrate beech organosolv lignin. The elemental composition as wt.% of dry lignin was: 62.54% C, 5.91% H, 0.25% N, 30.85% O, 0.00% S

Ash	Sugars	Mw[a]	Mn[a]	PD[b]	Moisture	Heating Value (Absolute dry lignin)	S / G Ratio[c]	Amount of β-O-4 linkages
wt.%	wt.%	g mol^{-1}	g mol^{-1}		wt.%	kJ g^{-1}		Moieties per aromatic ring
0.05	2.4	3428	606	5.66	4.39	24.12	1.29	0.27

a. Number-average (Mn) and Weight-average (Mw) molecular weights b. Polydispersity (PD) c. Syringyl to guaicyl units

A significant degradation of lignin ranging between 36 and 54 wt.% was observed during the first 10 min at all temperatures. The exact scheme of lignin degradation is unclear because of its complicated network structure with different types of bonds connecting the phenolic and non-phenolic groups; still, based on the abundance and low bond dissociation energies of ether linkages, it can be assumed that the decomposition starts with the breakdown of ether bonds. After the initial 10 min, the degradation of lignin progressed slowly even at elongated reaction times for 270, 290 and 310 °C which could be related to the presence of high-energy bonds in the lignin structure. The lignin degradation rate was very high at 350 °C. The yield of residual lignin obtained at 350 °C and 10 min was 45.7 wt.% which further decreased to 12.6 wt.% at 120 min. The rapid lignin conversion at all reaction times of 350 °C could be attributed to the further decomposition of some strong C-C bonds under high thermal stress in addition to the ether linkages [30]. However, the increased degradation of lignin did not significantly

273 increase the bio-oil yield but contributed mostly to the formation of water solubles, char,
274 and gas.



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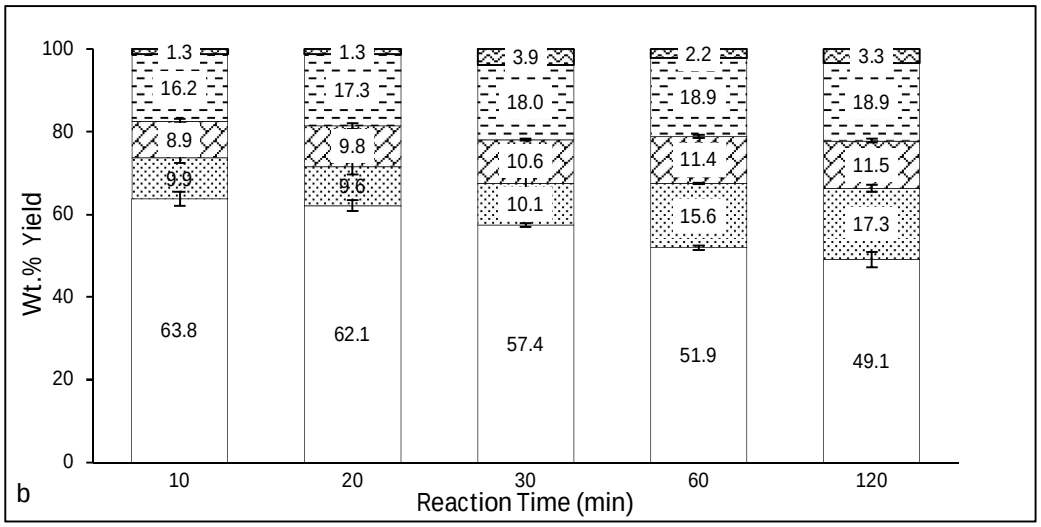

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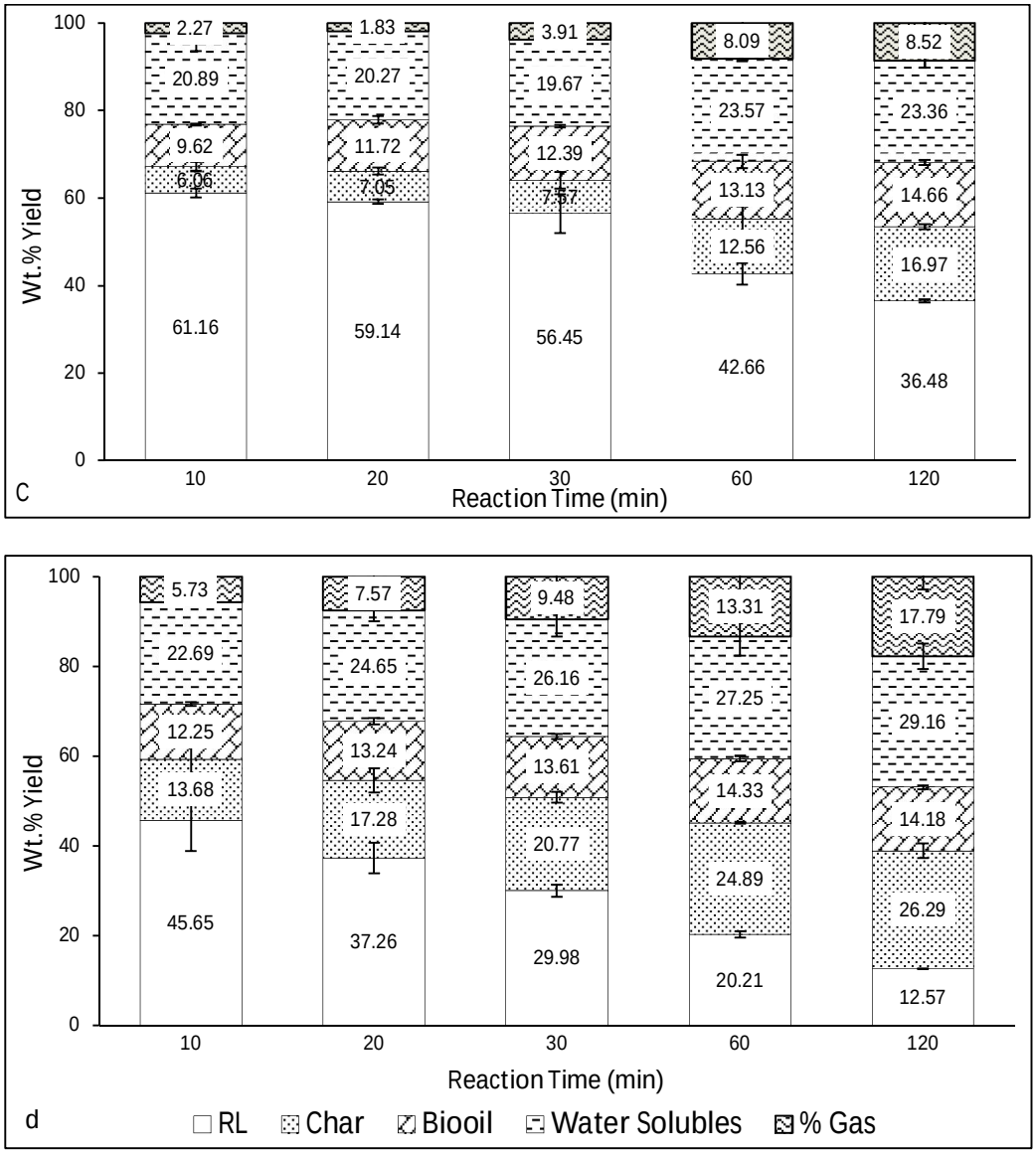


Fig 2. The yields of hydrothermal degradation products obtained at (a) 270 ˚C (b) 290 ˚C (c) 310 ˚C and (d) 350 ˚C at different reaction times, wt.% of original lignin. The gas yield was determined by calculation.

The yield of char increased along with the increase in reaction time at all tested temperatures. However, the yield of char decreased from 9.1 wt.% at 270 °C and 10 min to 6.1 wt.% at 310 °C and 10 min followed by an increase to 13.7 wt.% at 350 °C and 10 min. A similar trend was reported in an earlier study carried out by Hu *et al*. [31]. The reason for the higher char yield at 270 °C may be the incomplete degradation of lignin which then transforms to char. When temperature was raised to 310 °C, the char yield decreased due to increased lignin degradation. Enhanced dealkylation and hydrolysis of lignin at 350 °C could have increased the formation of reactive small molecular weight compounds, which then repolymerize by radical coupling and condense with each other

causing increased char yield at 350 °C. It can be seen from Figure 2d that the char yield at 350 °C and 10 min was 13.7 wt.%, prominently increasing to 26.3 wt % at 120 min. Similar results have been reported earlier [20, 21].

The yield of the formed gas is lower than the char yield under all reaction conditions. It is observed that the gas formation also increased significantly at 350 °C from 5.6 wt.% at 10 min to 17.7 wt.% at 120 min. These results are comparable to results obtained from the hydrothermal treatment of aspen wood lignin at 350 °C and 10 min [20]. Our results suggest that the change in the yield of gases is higher than the changes in the yields of water solubles and bio-oil at 350 °C. Similar increase in gas formation at higher temperatures was also observed in the study carried out by Daniel *et al.* [32]. H_2, CO_2, and CH_4 have been identified as the main gaseous components forming during lignin hydrothermolysis [22].

The yield of bio-oil generally increased along with increasing reaction time at each temperature except for 350 °C and 120 min where a slight decrease in the bio-oil yield was observed. The highest yield of bio-oil was 14.7 wt.% achieved at 310 °C and 120 min whereas the minimum oil yield of 8.0 wt.% was obtained at 270 °C and 10 min. The increase in the bio-oil yield is due to further degradation of lignin and reaction intermediates either by hydrolysis or by the fragmentation of C-C bonds through radical cleavage [21, 33]. The decrease in the yield of bio-oil at 350 °C and 120 min might be caused by repolymerization of reaction intermediates to form char or by degradation into smaller molecular components and formation of gases [21, 32].

The water solubles represent the soluble lignin fractions as determined by total organic carbon (TOC) measurement. The yield of water solubles obtained at 270, 290, 310 and 350 °C with 10 min reaction time were 14.1 wt.%, 16.2 wt.%, 20.9 wt.% and 22.7 wt.%, respectively, which increased to only 17.2 wt.%, 18.9 wt.%, 23.4 wt.% and 29.2 wt.%, respectively, at reaction time of 120 min indicating an overall increase in the yield of water solubles along with increasing temperature. It is important to mention that under all reaction conditions, the yield of water solubles is higher than the yield of char. This increase in the water solubles might be caused by the formation of alcohols, such as methanol, due to hydrolysis of methoxy groups, and ethanol by hydrolysis of alkyl side chains. Another reason could be the presence of acetic acid which could result from the reactions of carbohydrates present as an impurity in the feed lignin. The presence of aromatic compounds in water solubles in our study is unclear as the individual chemical compounds in this fraction were not characterized.

3.2. Bio-oil Characterization

A GC-MS chromatogram of a selected bio-oil sample after hydrothermolysis at 350 °C and 60 min is shown in Figure 3 with the list of identified monoaromatic phenolic

compounds given in Table 2. Compounds 1 – 5, 7, 8, 10, 11 were identified and quantified using model compounds while 6, 9, 12, 13 and 14 were identified based on literature [34] and not quantified. GC-MS chromatograms at all temperatures are presented as Figures A1, A2, A3 and A4 and in additional information.

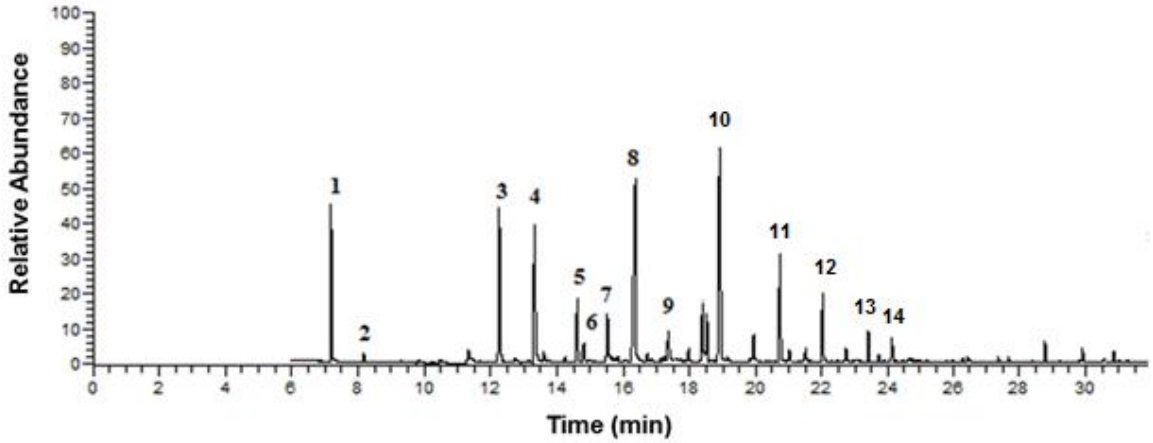
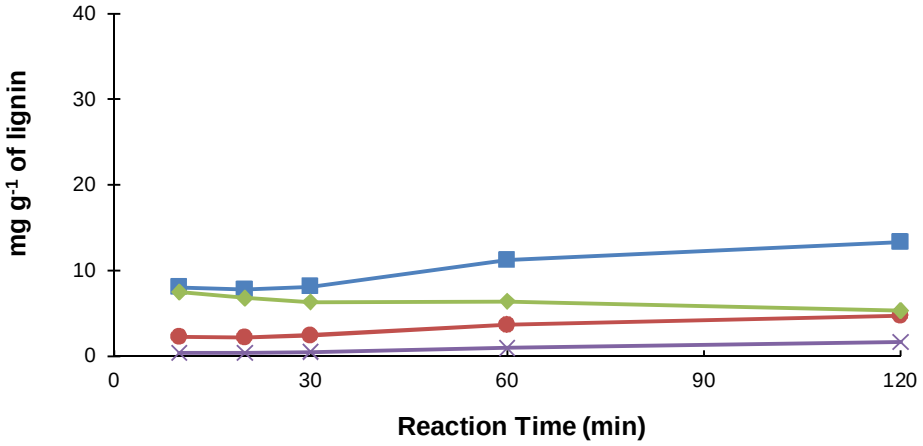


Figure 3. GC-MS chromatogram of selected bio-oil sample after hydrothermolysis of lignin at 350 °C and 60 min.

Table 2. List of identified monomeric compounds.

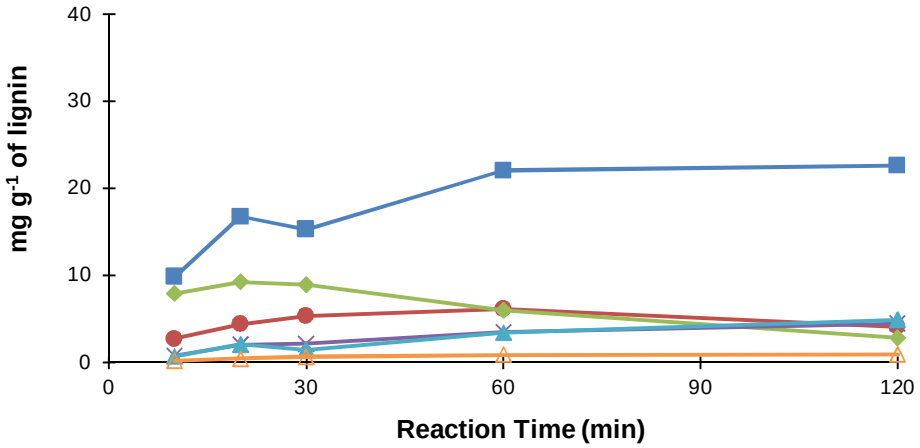
	Compounds	Main Fragments	RT (min)
1	Anisole	108, 78	7.18
2	Phenol	94, 66, 65	8.18
3	Guaiacol	109,124, 81	12.28
4	Pyrocatechol	110, 81, 92	13.33
5	4-Methylguaiacol	138, 123, 95	14.62
6	3-Methylcatechol	124, 78, 123	14.81
7	4-Methylcatechol	124, 123, 78	15.52
8	3-Methoxycatechol	140, 125, 97	16.36
9	3-Methylguaiacol	123, 138, 139	17.37
10	Syringol	154, 139, 93	18.92
11	4-Methylsyringol	168, 153, 125	20.73
12	4-Ethylsyringol	167, 182	22.02
13	4-Propylsyringol	167, 196	23.41
14	Guaiacylacetone	137, 180, 122	24.16

Figure 4 (a – d) reveals the change in the yield of selected individual monoaromatic phenolic compounds over time and Figure 4 (e) represents the change in the yield of total monoaromatic phenolic compounds in bio-oil samples obtained at various reaction conditions.


40
30
20
10
0
mg g-1 of lignin
0
30
60
90
120
Reaction Time (min)

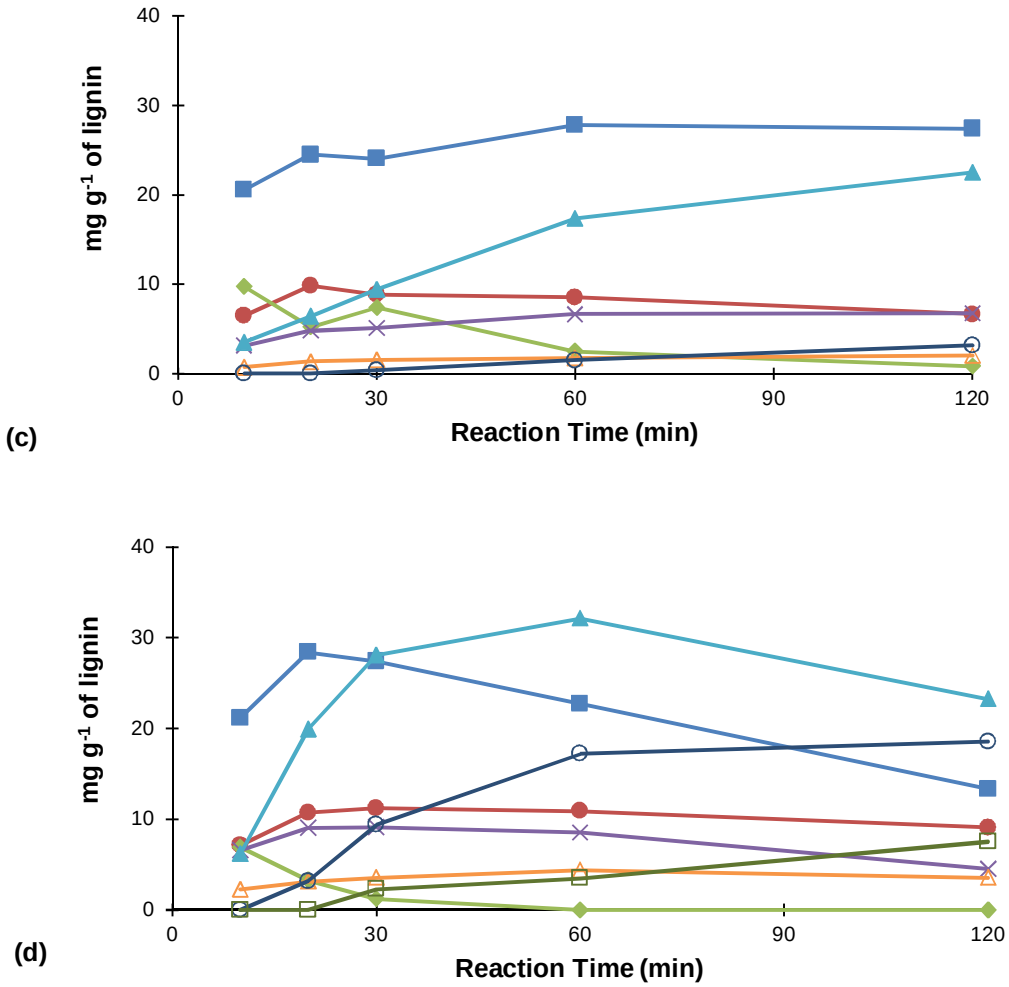
(a)

342


40
30
20
10
0
mg g-1 of lignin
0
30
60
90
120
Reaction Time (min)

(b)

343


40
30
20
10
0
mg g-1 of lignin
0
30
60
90
120
Reaction Time (min)
(c)
40
30
20
10
0
mg g-1 of lignin
0
30
60
90
120
Reaction Time (min)
(d)
Syringol
Guaiacol
Syringaldehyde
4-Methyl Syringol
3-Methoxycatechol
4-Methylguaiacol
Pyrocatechol
4-Methylcatechol

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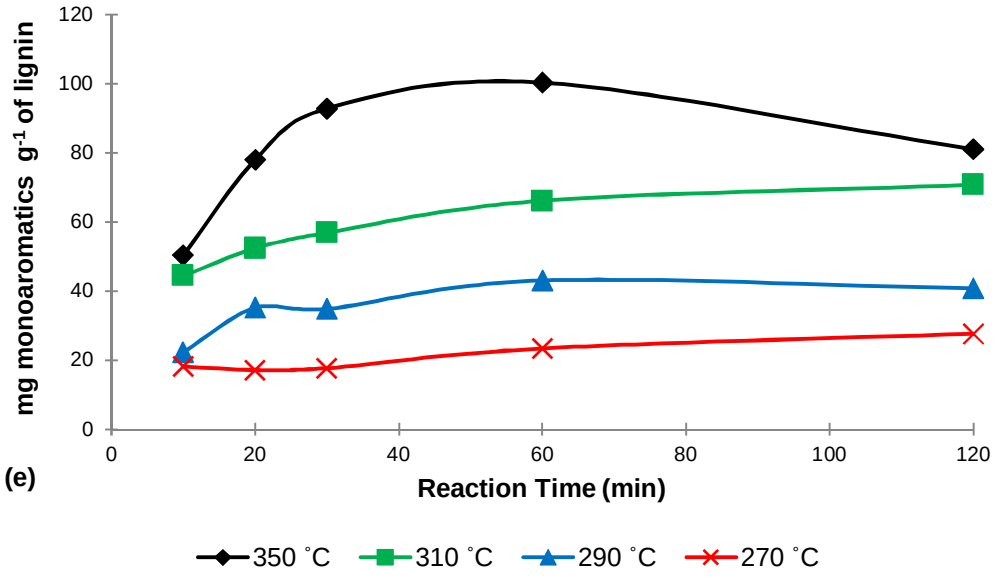

Fig 4. Quantification of identified monoaromatic phenolic compounds present in bio-oil samples obtained at (a) 270 ˚C (b) 290 ˚C (c) 310 ˚C and (d) 350 ˚C at different reaction times. (e) Yield of total monoaromatics at all reaction conditions.

The hydrolysis of low energy ether linkages gives rise to the formation of phenoxy and alkyl aromatic radicals, which transform to different phenolic products. At higher temperatures weak acids are also produced from degradation of lignin side chains and as degradation products of carbohydrate contamination in the substrate lignin. This assumption is well supported by the measured pH (~ 4.0 – 4.5) of selected water phases obtained after hydrothermolysis. Under severe reaction conditions, these acids can further catalyze the hydrolysis process causing an increase in the formation of smaller phenolic compounds such as catechol and methoxycatechols.

The minimum yield of monoaromatic compounds achieved at 270 °C and 10 min was 1.8 wt.% of initial amount of lignin (21.6 wt.% of bio-oil) which contained 0.8 wt.% syringol, 0.7 wt.% syringaldehyde, and 0.2 wt.% guaiacol. On the contrary, the maximum yield of monoaromatic compounds achieved at 350 °C and 60 min was 10.1 wt.% (65.6 wt.% of bio-oil) which contained 3.2 wt.% 3-methoxycatechol, 2.3 wt.% syringol, 1.7 wt.% pyrocatechol, 1.1 wt.% guaiacol, and less than 1 wt.% of each 4-methylsyringol, 4-methylguaiacol, 4-methylcatechol, and phenol. This trend of increasing total yield of monoaromatics with increasing temperature in subcritical water has been observed also in other studies [22, 23].

Syringol and guaiacol are the basic hydrolysis products of lignin and their yields increased with time. The yield of syringol reached 1.3 and 2.3 wt.% after 120 min at 270 and 290 °C, respectively. The guaiacol yield was comparatively lower than the syringol yield. This

is due to the fact that more syringyl than guaiacyl units are present in the substrate lignin, which originates from hardwood. Moreover, the two methoxyl groups present in the syringyl units, compared to only one in guaiacyl units, could kinetically favor the formation of more syringyl than guaiacyl derivatives [35]. The yield of guaiacol reached 0.5 and 0.4 wt.% after 120 min at 270 and 290 °C, respectively. The yield of syringaldehyde is observed to be at its highest at the shortest reaction time (10 min) in all reaction temperatures. It can be seen from Figure 3d that syringaldehyde vanishes at 350 °C and 60 min possibly to char by etherification and esterification reactions. At 350 °C syringol yield started to decrease after 30 min; guaiacol seemed to have a stable behaviour at both 310 and 350 °C.

The impact of increasing temperature was higher compared to the reaction time on the formation of monoaromatics. Pyrocatechol started to be produced at 310 °C and 60 min but the yield was less than 1 wt.%. 3-methoxycatechol was formed at 290 °C but the yield was below 1 wt.%. The yield of pyrocatechol increased rapidly at 350 °C whereas the yield of 3-methoxycatechol increased at both 310 and 350 °C. As seen (Figure 3 d), at 350 °C and 10 min the formation of pyrocatechol and 3-methoxycatechol were 0 wt.% and 0.6 wt.%, respectively. These values increased to 1.7 wt.% and 3.2 wt.% at 60 min. The yield of 3-methoxycatechol was higher than pyrocatechol under all reaction conditions. Pyrocatechol has been reported to be formed due to cleavage of a methyl group from guaiacol under severe hydrothermal conditions [22, 30]. Our results show, however, an increase in the yield of pyrocatechol along with increasing time at 350 °C without any significant decrease in the yield of guaiacol. This may be due to a constant formation of guaiacol along with a concomitant transformation of the compound to pyrocatechol. Another explanation mentioned in an earlier work [32] is that catechols could be generated from the bulk reactive intermediate phase through a parallel reaction path which is still unknown.

The production of 4-methylcatechol was also observed in the reactions at 350 °C above 30 min of residence time. The observed 4-methylcatechol possibly resulted as a product of 4-methyl guaiacol dealkylation. The yield of 4-methylcatechol reached only 0.8 wt.% at 350 °C and 120 min. Phenol was only detected in extreme conditions of 350 °C above 60 min in negligible amounts. Phenol is reported [30] to originate from guaiacol via catechol as an intermediate product. For syringol an analogous degradation route with guaiacol can be suggested: under severe hydrothermal conditions syringol is hydrolyzed to 3-methoxycatechol with simultaneous production of methanol. A decrease in the yield of abundant monoaromatics such as syringol and 3 -methoxycatechol at longer reaction times was seen, caused either by their reaction to form other monomers or by their repolymerization to dimers, trimers, and oligomers leading eventually to formation of char. Due to the limitations of our current analytical methods we were only able to identify

monoaromatics from the bio-oil samples but based on the GPC results (discussed below) we speculate that the bio-oil contains also phenolic dimers, trimers, and oligomers.

Table 3 presents the results of bio-oil elemental analysis. Minor changes in the elemental composition of the bio-oil samples along with the reaction conditions are observed. The slight decrease in the oxygen content of bio-oils compared to the feed lignin indicates the formation of volatiles by decarbonylation (loss of CO), decarboxylation (loss of CO_2), or dehydration (loss of H_2O). The high heating values (HHV) of the samples slightly increased at longer reaction times at 350 °C, which is in line with the results of the elemental analysis. The water content of bio-oil samples was taken into account in order to calculate the elemental analysis on dry basis. Water content of bio-oil samples was in the range of 2 – 6 wt.%. Water content in bio-oil samples at all reaction conditions are presented in table B of additional information.

Table 3.

Elemental analysis of bio-oil samples obtained at 270, 290, 310 and 350 °C at different reaction times on wt % dry basis.

Temp (˚C)				**270**						**290**		
Time (min)	**% N**	**% C**	**% H**	**% O**	**Sum**	**HHV[a] by Dulong (kJ g^{-1})**	**% N**	**% C**	**% H**	**% O**	**Sum**	**HHV[a] by Dulong (kJ g^{-1})**
Lignin	0.25	62.6	6.0	30.8	99.6	24.12						
10	0.2	63.4	6.5	30.0	100.0	25.3	0.3	63.9	6.6	29.3	100.0	25.8
20	0.2	63.5	6.3	30.0	100.0	25.1	0.1	64.3	6.3	29.3	100.0	25.5
30	0.3	63.9	6.8	29.0	100.0	26.2	0.3	63.8	6.4	29.5	100.0	25.5
60	0.2	63.5	6.0	30.3	100.0	24.7	0.2	64.6	6.0	29.3	100.0	25.1
120	0.2	63.9	6.0	29.9	100.0	24.9	0.2	64.8	6.1	28.9	100.0	25.6
Temp (˚C)				**310**						**350**		
Time (min)	**% N**	**% C**	**% H**	**% O**	**Sum**	**HHV[a] by Dulong (kJ g^{-1})**	**% N**	**% C**	**% H**	**% O**	**Sum**	**HHV[a] by Dulong (kJ g^{-1})**
10	0.2	62.7	6.4	30.7	100.0	24.9	0.2	63.8	6.1	29.9	100.0	25.0
20	0.1	64.7	6.2	29.0	100.0	25.6	0.2	64.9	5.9	29.0	100.0	25.3
30	0.2	64.8	6.6	28.5	100.0	26.2	0.1	65.3	6.0	28.6	100.0	25.6
60	0.1	65.3	6.2	28.4	100.0	25.9	0.1	64.7	6.3	28.8	100.0	25.8
120	0.1	66.5	6.0	27.4	100.0	26.2	0.1	66.0	6.1	27.8	100.0	26.1

a. High heating values (HHV) are calculated for water free samples.

Results of molecular weight distribution of bio-oil samples are presented in Table 4. A small decrease in the molar mass at 270 °C with time was observed but no notable change was seen at 350 °C. The polydispersity (PD) of all samples are below 1.4 suggesting that the degraded lignin monoaromatics and oligomers have much narrower molecular weight distribution than the original lignin (with a PD of around 5.5). The deviation from 1 in PD of bio-oil samples is indicating presence of di and tri-aromatic compounds.

Table 4. Weight-average (Mw) and number-average (Mn) molecular weights and poly dispersity (PD) of bio-oil samples at 270, 290, 310 and 350 °C at different reaction times.

Temp (˚C)	270			290			310			350		
Time (min)	Mw (g mol^{-1})	Mn (g mol^{-1})	PD	Mw (g mol^{-1})	Mn (g mol^{-1})	PD	Mw (g mol^{-1})	Mn (g mol^{-1})	PD	Mw (g mol^{-1})	Mn (g mol^{-1})	PD
Lignin	3428	606	5.5									
10	291	218	1.3	288	218	1.3	261	209	1.2	242	201	1.2
20	289	218	1.3	305	222	1.4	263	209	1.3	264	206	1.3
30	273	215	1.3	269	214	1.3	254	207	1.2	239	206	1.2
60	257	210	1.2	244	202	1.2	256	258	1.0	253	218	1.2
120	250	207	1.2	241	204	1.2	212	251	0.8	261	224	1.2

Figure 5 represents molecular weight distribution of bio-oil samples obtained at different temperatures after 120 min of reaction. It can be seen that peaks in the monomeric region (molecular weight less than 200 g mol^{-1}) are shifting towards low molecular weight region with increasing temperature. This may be caused by the subsequent degradation of larger monomers to smaller monomers with longer reaction times (e.g. syringol degrading to 3-methoxycatechol). Nevertheless, it is interesting to note that in dimer and trimer region (200 g mol^{-1} < M_w < 300 g mol^{-1}), peaks first shift from high to low molecular weights at reaction temperatures 270 – 310 °C, but at 350 °C are shifted towards higher molecular weights. This indicates that repolymerization reactions take place at 350 °C. Similar trend can be seen for the oligomeric compounds (molecular weight higher than 300 g mol-^{1}).

In the GPC experiments, UV detection was used. This explains why peak intensities in the monomeric region decrease along with increasing reaction temperature even though the relative amount of monomeric compounds in the bio-oils is increasing: the monomeric compounds formed at lower temperatures are probably powerful UV chromophores, causing a strong absorbance. For example, as observed in the GC-MS results, the yield of syringaldehyde (incorporating a carbonyl group which is a strong UV chromophore) decreased from 0.5 wt.% at 270 °C to 0 wt.% at 350 °C after 120 min of reaction time. Analogously, the increasing peak intensities in the di,- tri, and oligomeric region does not necessarily indicate increasing overall yield of compounds in these areas, but only formation of one or more structures with strong UV absorbance, such as stilbenes [36].

These structures could not be identified by GC-MS because the dimers are impossible to ionize in the MS detector.

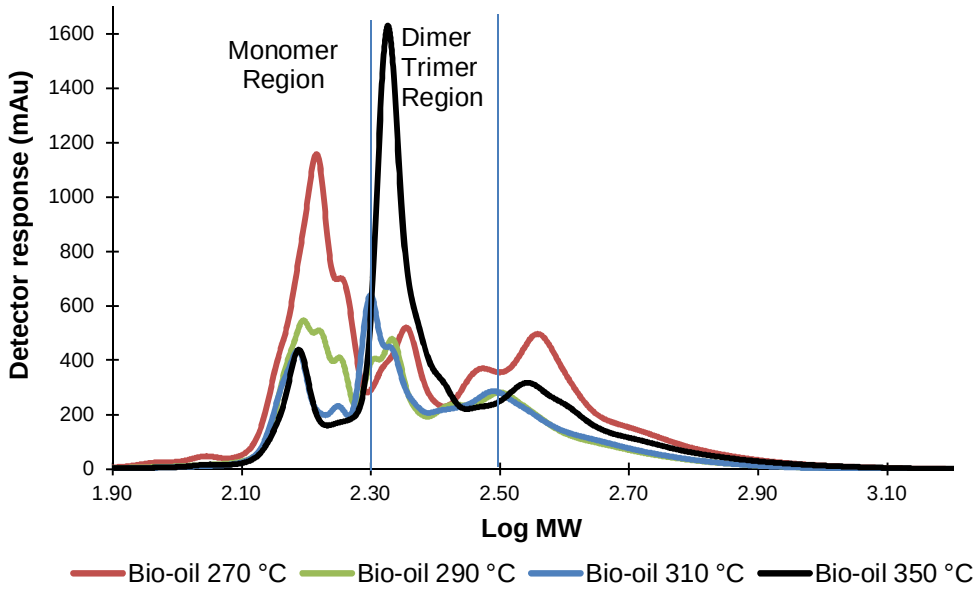

Figure 5. Molecular weight distribution of bio-oil samples at different reaction temperatures after 120 min.

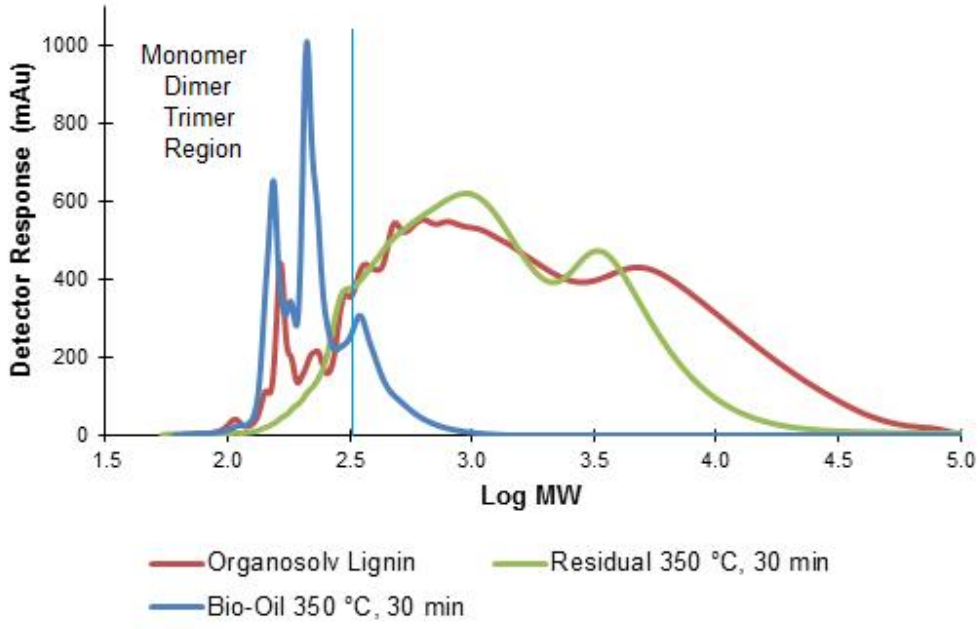

Figure 6. Comparison of molecular weight distribution of selected bio-oil sample, residual lignin and feed organosolv lignin.

The comparison of molecular weight distributions of a selected bio-oil sample, residual lignin, and feed organosolv lignin is shown in Figure 6, strongly indicating successful

degradation of the lignin, as well as efficient isolation of the formed small molecular weight compounds. The peaks for monomers, dimers and trimers present in the feed lignin are completely lost and are not present in the residual lignin; nevertheless, bio-oil sample's GPC results show clear peaks for monomers, dimers, and trimers, confirming their presence.

4. REACTION PATHWAYS

It is challenging to describe the reaction pathways for the decomposition of lignin because of the formation of a large number of different intermediates and products through a multitude of reaction steps. However, based on the obtained results and the discussion above, a simplified network of reaction pathways is proposed in Figure 7 considering the major products (*e.g.* residual lignin, char, water solubles, gas, as well as the most important monoaromatic compounds present in bio-oil). At temperatures of 270 and 290 °C, lignin was converted mainly to water solubles and residual lignin with low char yields, especially after 10 min – with longer times char yield increased but stayed lower than the yield of water solubles. A noteworthy increase in the formation of gas was observed at 310 °C and 60 min together with an increase in the yield of water solubles, char, and bio-oil. The formation of char and gas phase components was substantial at 350 °C, resulting in high conversions of lignin.

Our reaction pathway describing lignin degradation contains a bulk reactive phase, which contains the reaction intermediates. These reaction intermediates are considered to behave in two different ways: firstly they may convert into smaller molecular weight compounds through hydrolysis; secondly, repolymerization – especially at higher temperature and longer residence times – to dimers, trimers, oligomers, and finally to char is also possible. After the reactions are stopped, the formed phenolic monomeric compounds – together with dimers, trimers, and oligomers – are extracted with ethylacetate and collected as bio-oil.

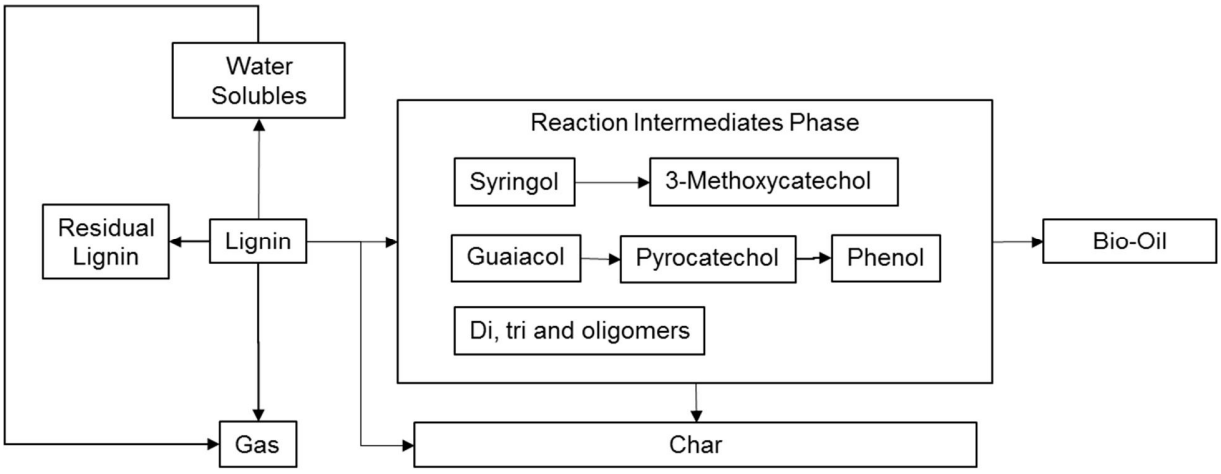

Figure 7. Proposed network of reaction pathways for lignin degradation under hydrothermolysis.

5. CONCLUSIONS

Sulfur-free lignin was depolymerized in an environmentally friendly process using water as a solvent. The results indicate that lignin can be effectively degraded into phenolic compounds using non-catalytic hydrothermolysis. Bio-oil was recovered as a viscous liquid, containing a substantial amount of monoaromatic compounds (the maximum yield of monoaromatics was 10.1 wt.%, at 350 °C and 60 min). Reaction temperature proved to be highly influential on the spectrum of the products. Syringol, guaiacol, and syringaldehyde were the most abundant monoaromatics at 270 and 290 °C, whereas 3-methoxycatechol, pyrocatechol, 4-methylsyringol together with syringol and guaiacol were the dominant monoaromatics at 310 and 350 °C. The molecular weight of the feedstock, organosolv lignin, was 3,428 g mol^{-1} while the respective value for the bio-oil samples was 200 – 310 g mol^{-1} (Mw 212-305; Mn = 202-258) indicating a substantial degradation and a dominance of mono- and di-aromatic constituents in the bio-oil. Suppressing the repolymerization of the reaction products leading to char formation is highly challenging during non-catalytic hydrothermal reactions, particularly at higher reaction temperatures. Maximizing the bio-oil yield through inhibiting the formation of char calls for further research with catalysts and co-solvents, for example alcohols, which is a part of our future plans.

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