

# Supercritical Water-induced Lignin Decomposition Reactions: A Structural and Quantitative Study

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The use of supercritical water for the decomposition of lignin and evaluation of its influence on lignin decomposition and conversion to various products was the thrust of the current study. Poplar alkali lignin (AL), corncob-to-xylitol residue lignin (XRL), and cornstalk-to-ethanol residue lignin (ERL) were the lignin species studied because they constitute the main residual lignins available in the biomass refinery industry. The lignins were characterized by elementary analysis, Fourier transform infrared spectrometry (FT-IR), phosphorus nuclear magnetic resonance (<sup>31</sup>P-NMR), and X-ray diffraction (XRD), and their hydrothermal depolymerization products were analyzed by gas chromatography-mass spectrometer (GC-MS). The results showed that the residual lignin is a potential source for valuable aromatics. The XRL had the best total phenolics yield, 140 mg/g, while AL had the lowest, 90 mg/g. The maximum yields of phenol (28.94 mg/g) and 4-ethylphenol (36.21 mg/g) were obtained from XRL depolymerization at 375 °C for 30 min, and the optimal yields of guaiacol (14.34 mg/g) and 2,6-dimethoxyphenol (15.67 mg/g) were achieved by AL at 375 °C for 30 min. The information here provides some insights toward developing selective biorefinery methods for lignin-to-organic products conversion processes.

*Keywords:* Supercritical water; Lignin; Phenolics; Quantitative analysis

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## INTRODUCTION

Biomass is a vital feedstock for sustainable production of fuels, chemicals, and energy. It consists of three major biopolymers that are ubiquitous in the biosphere. Among those biopolymers, cellulose is the dominant component; after cellulose (including chitin), lignin is the most abundant natural organic biopolymer on earth. It is a major component of lignocellulosic biomass (15% to 30% by weight, 40% by energy) (Pandey and Kim 2011). The demand for alternative renewable energy sources has catapulted a carbon-based energy and material platform into prominence for the production of transportation biofuels and bulk “green” chemicals (Morais *et al.* 2015). With respect to aromatic-based chemicals, the most accessible bio-based feedstock is lignin (Pińkowska *et al.* 2012).

Traditionally, alkali lignin in black liquor has been used as a combustion fuel in pulp mills, a binder/adhesive, a dispersant, or an additive in cement. In pulp mills, black

liquor is concentrated by evaporation and has been used to supply over 50% of a mill's energy demands. Annually, over 50 million tons of lignin worldwide is burned in the recovery boilers of pulp mills (Farag *et al.* 2014). In general, although high-quality alkali lignin can be produced by acidification of black liquor, it should be noted that there are many higher-value applications. However, only a small proportion of lignin (~1%) has been used as a raw material for chemicals with a higher value than fuel. Corncoobs, a ubiquitous agricultural waste, have been the main feedstock used for ethanol and xylitol production *via* acid hydrolysis. The main by-product of these reactions, corncob acid hydrolysis residue (CAHR), is produced from the corncob-to-xylitol/ethanol pre-treatment process. The lignin contents (w/w on a dry CAHR basis) vary from approximately 20% to 60%. Until now, most commercial lignin has been supplied from the papermaking industry (*i.e.*, sulfite pulping and kraft pulping processes) as by-products, and the potential amount of residual lignin produced from the cellulosic ethanol or xylitol industry has been increasing (Ragauskas *et al.* 2014). Because of the large amount of aromatic structures present in lignin, the main high added-value applications are aromatic chemicals (Stewart 2008). Aromatic commodities that are derived from lignin include BTX (benzene, toluene, and xylene), phenol, and vanillin, which offer a significant market potential having an estimated market value.

Diverse technologies have been investigated for producing value-added products from lignin, such as pyrolysis, gasification, hydrogenolysis, oxidation, and liquefaction in different solvent systems (Morais *et al.* 2016). Among these, the hydrothermal process is one of the most effective approaches, because water at high temperatures and high pressures behaves as an environmentally benign solvent, and it has remarkable properties as a reaction medium. For example, water near the critical point ( $T_c = 374.2$  °C and  $P_c = 22.1$  MPa) has a lower dielectric constant, fewer and weaker hydrogen bonds, and a higher isothermal compressibility than ambient liquid water. Moreover, it also has higher  $H^+$  and  $OH^-$  ion concentrations than liquid water under certain conditions, which will be a benefit for biomass processing and conversion even in the absence of an added catalyst (Jin and Enomoto 2008; Wahyudiono *et al.* 2011). Ye *et al.* (2012) studied the effect of hydrothermal reaction conditions on the degradation of corn stalk lignin and obtained optimized yields of 8% and 27% (relative peak areas) for phenol and 4-ethylphenol, respectively. Gosselink *et al.* (2012) used supercritical fluid (300 to 370 °C) to convert organosolv hardwood and wheat straw lignins to obtain 10% to 12% phenolic oil and monomeric aromatic compounds. Song *et al.* (2013) investigated the conversion of native birch wood lignin to monomeric phenols with a total selectivity of > 90% at a lignin conversion of approximately 50%. Several authors (Karagöz *et al.* 2004; Lavoie *et al.* 2011; Nguyen *et al.* 2014; Zhang *et al.* 2014) have also used a lignin hydrothermal conversion process in near-critical water with strong bases as catalysts. The aforementioned investigations reported the potential utilization of lignin and focused mostly on improving the yield of phenolic compounds or exploring the mechanism of the process using lignin model compounds. The potential obstacles to the development of a lignin-based industry have not garnered much attention. Farag and Chaouki (2015) made an economic evaluation for converting lignin into chemicals, and the result indicated the estimated selling price would not compete with that of fossil fuel based chemicals, which was primarily due to the high cost of the lignin feedstock. So, looking for a potential resource of lignin as well as an improved process is important in promoting the valorization of lignin into aromatics.

The present investigation therefore focused on the hydrothermal conversion of three representative residual lignin samples, carried out using supercritical water (375 °C, 22.07 MPa) at various residence times (0 to 60 min). The characterization of lignin samples and quantitative analysis of the aromatic products from hydrothermal conversion were performed to ascertain the differences in the behavior of lignin from different sources.

## EXPERIMENTAL

### Lignin Isolation and Purification

The lignin sample AL was obtained from in-house poplar sulfate pulping black liquor. The chemical composition of poplar biomass, the pulping method employed, and the chemical properties of the black liquor have been previously reported (Zhang and Liu 2012). The isolation and purification processes for AL were also previously reported (Sun *et al.* 2002). Corn cob acid hydrolysis residue (CAHR) was collected from a continuous acid hydrolysis process to convert corn cob to xylitol. The lignin content in CAHR was 18.4%, as has been reported (Wang *et al.* 2014). The sample XRL was isolated from CAHR using a modified enzymatic/mild acidolysis method previously reported (Lou and Wu 2011). The third lignin residue sample was obtained from Longlive International Trade Co., Ltd. (Shandong, China), precipitated from the process residues of cornstalk to ethanol, in which the lignin content was 31.2%. The lignin was further extracted using benzene-ethanol mixture to remove impurities and was identified as cornstalk-to-ethanol residual lignin (ERL).

### Hydrothermal Conversion

The hydrothermal conversion experiments were conducted in a high-pressure autoclave with a 4848 reactor controller (Parr Instrument Company, USA). The 250-mL batch reactor was equipped with a pressure gauge (0 to 35 MPa), a pressure relief valve, and a thermocouple. The lignin samples (2 g) were loaded into the reactor with 80 mL of deionized water and purged with nitrogen three times. The reactor was heated to a desired temperature (375 °C) at a heating rate of 10 °C/min over 30 min, after which the reaction temperature was held at a desired reaction time ranging from 0 to 60 min. The pressure at 375 °C was found to be approximately 22.07 MPa. After the reaction, the reactor was cooled to room temperature by immersing the reactor in cold water. Each run was repeated in triplicate.

### Products Separation

Gas products were collected by a latex rubber inflatable device for GC analysis. The instrument was equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) that consisted of mainly CO<sub>2</sub>, CH<sub>4</sub>, CO, and H<sub>2</sub> gases. The gas compositions after the hydrothermal conversion process were similar in all three cases, while the yields (< 5%) were negligible. The liquid fractions after the reaction were collected by washing with ethyl acetate and filtering with a pre-weighed G3 funnel fitted with a polytetrafluoroethylene (PTFE) membrane to separate solid residues. This water-ethyl acetate liquid fraction was then subjected to an extraction process. Anhydrous sodium sulfate was added to the obtained liquid fraction to remove water. The solid residue (SR) was oven-dried at 105 °C overnight before weighing. The yield of hydrothermal conversion of solid residues (YSR) was calculated using the following equation:

$$\text{YSR} = m_{\text{SR}} / \text{mL} \quad (1)$$

where  $m_{\text{SR}}$  is the mass of over dried solid residue (mg) and mL is the mass of the lignin initially used (g).

### Lignin and Solid Residue Analysis

The ash and moisture contents were determined by ASTM D 1102 (1984) and ASTM D 4442 (2007) methods, respectively. Elemental analyses of the lignin and solid residues were performed on a Vario Micro analyser (EL III, Germany). The elemental composition of C, H, N, and S contents were measured and the O content was calculated by difference. Fourier transform infrared spectroscopy of the lignin samples were recorded on a Shimadzu FTIR spectrophotometer (IR Prestige-21, Japan) using a KBr pellet containing ~1% sample over a range of 4000 to 500  $\text{cm}^{-1}$ . The characteristic bonds and functional groups of lignin were analyzed with an NMR spectrometer (Bruker Avance II 400 MHz, Germany). The NMR used an inverse gated decoupling pulse sequence. The presence of aliphatic hydroxyl groups, phenolic hydroxyl groups, and carboxyl functional groups in the lignin were determined using  $^{31}\text{P}$ -NMR spectra (Crestini and Argyropoulos 1997). The crystal structure analysis by XRD was performed in a D/max 2500 VL/PC X-ray diffractometer (Bruker D8-Advance, Germany) using Cu  $K\alpha$  radiation (40 kV, 200 mA) from 5° to 85° with a step size of 0.01 °/s.

### Qualitative and Quantitative Analyses of the Liquid Products

Qualitative examination of the liquid products was performed on a GC-MS (Shimadzu QP 2010, Shimadzu, Japan) equipped with a SHRXI-5 MS capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ). Helium was used as the carrier gas at a flow rate of 1 mL/min. The GC oven temperature for analysis was set as follows: initiated at 50 °C; held for 2 min, increased at a rate of 10 °C/min to 160 °C; held for 2 min; raised to 250 °C at a rate of 10 °C/min; and held at this final temperature for 2 min. The injector temperature was 250 °C with a split ratio of 50:1. The mass selective detector was operated with an electron impact (EI) ionization mode. The data was analyzed with a NIST library.

The main phenolic compounds with high yields (based on peak area percentage) in the liquid products were identified. They were phenol, 4-methylphenol, guaiacol, 4-ethylphenol, 4-methylguaiacol, 3-methoxycatechol, 4-ethylguaiacol, catechol, 4-methylcatechol, 2,6-dimethoxyphenol, 1,2,3-trimethoxybenzene, and 1,2,4-trimethoxybenzene. The standard compounds were purchased from Sigma-Aldrich (USA). The major constituents were quantified by an external standard method. Total phenolic compounds (TPC) were calculated as follows: the sum of main phenolic compounds accurately quantified using an external standard and the other phenolic compounds quantified assuming a response factor (1.0) compared with guaiacol.

## RESULTS AND DISCUSSION

### Lignin Characterization

The elemental analysis (based on dry lignin weight) and properties of lignin samples are shown in Table 1. Clearly, the sample AL contained more oxygen and sulfur content but less carbon, hydrogen, and nitrogen than XRL and ERL samples. The extremely high content of sulfur in the AL is likely a consequence of kraft cooking.

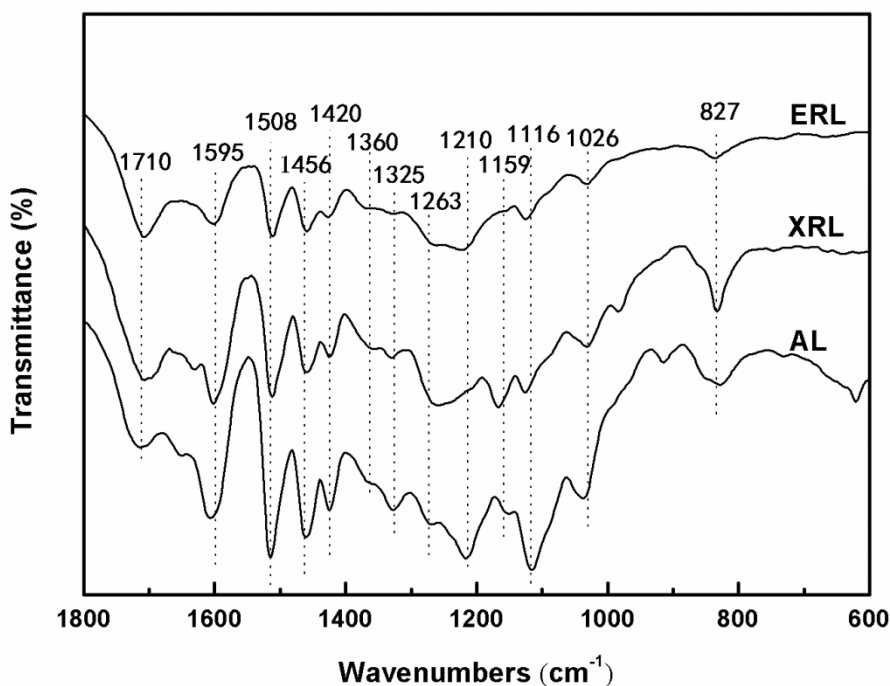
Moreover, the energy contents of the raw lignin materials and the solid residues were calculated and are listed in Table 1.

**Table 1.** Chemical Analysis of Lignin and SR

Sample	Proximate analysis (wt.%)		Elemental composition (wt.%)					HHV (MJ/kg) <sup>a</sup>
	Ash	Moisture	C	H	O	N	S	
AL	2.9	1.6	55.9	3.6	36.7	0.6	3.2	17.51
AL SR (30 min)	--	--	78.8	3.4	17.0	0.4	0.4	28.47
AL SR (60 min)	--	--	76.2	3.6	19.3	0.4	0.5	27.47
XRL	8.1	1.5	58.7	5.2	34.9	0.7	0.5	21.05
XRL SR (30 min)	--	--	77.7	3.4	17.8	0.8	0.3	27.96
XRL SR (60 min)	--	--	76.3	4.0	18.3	1.3	0.1	28.25
ERL	6.5	1.6	64.9	5.7	27.7	1.6	0.1	25.14
ERL SR (30 min)	--	--	79.0	3.5	16.3	1.0	0.2	28.81
ERL SR (60 min)	--	--	77.1	3.7	18.3	0.8	0.1	28.09

<sup>a</sup>HHV, higher heating value. Evaluated using Dulong's formula:  
 $HHV = 0.3383 \cdot C + 1.422 \cdot (H - O/8)$ .

Figure 1 displays the normalized FTIR spectra of AL, XRL, and ERL samples, whose peak assignments were completed according to previous publications (Pandey 1999; Xiao *et al.* 2013; Sammons *et al.* 2013).



**Fig. 1.** FTIR spectra of the obtained residual lignins

Typical absorption peaks and lignin absorption intensity at 1595, 1456, and 1420  $\text{cm}^{-1}$  were observed in all three samples indicating an analogous initial structure; the absorbance at 1710  $\text{cm}^{-1}$  implies the existence of carboxyl which may originate during

biomass processing. However, the key differences observed were the presence of peaks at 1325, 1263, 1209, 1159, 1116, 1026, and 827  $\text{cm}^{-1}$ . The AL had strong intensities at the critical peaks belonging to syringyl (S-unit) units (1325 and 1116  $\text{cm}^{-1}$ ), whereas XRL demonstrated sharp peaks at 1157  $\text{cm}^{-1}$  for the ester group of the hydroxylphenyl propane (H-unit) units.

To further quantify and compare the functional groups of the three residual lignins, quantitative  $^{31}\text{P}$  NMR was carried out and the content of different hydroxyl groups of the three lignins is presented in Table 2. It was expected that the AL would contain more condensed structures (1.0 mmol/g) because of alkali-induced condensation reactions. However, the lignin isolation and purification processes accounted for the differences in the aliphatic hydroxyls.

The isolation method of XRL was not so severe, yielding a maximum aliphatic OH group content (3.857 mmol/g), while AL had the least (0.750 mmol/g) because of the hydrolytic alkali reactions occurring during the pulping process. The distribution of phenolic groups in the three lignins differed extensively between the biomasses both in relative content and the type of OH in each group. The XRL and ERL samples were rather similar in terms of G/H/S proportions having values  $\sim 1.52/2.14/1$  and  $1.82/1.30/1$ , respectively. It differed appreciably from the AL sample, which contained the lowest proportion of H-phenolic groups (G/H/S = 2.23/0.2/1).

**Table 2.** Quantitative  $^{31}\text{P}$ -NMR analysis of AL, XRL, and ERL Samples

Types of functional groups	Chemical shift (ppm)	AL (mmol/g)	XRL (mmol/g)	ERL (mmol/g)
Aliphatic OH	150.0–145.0	0.750	3.857	1.149
Guaiacol OH (G)	143.6–142.6	0.580	1.436	1.170
<i>p</i> -Hydroxy OH (H)	138.6–137.0	0.050	2.027	0.835
Syringyl OH (S)	140.2–138.6	0.250	0.947	0.642
G:H:S	-	2.23:0.2:1	1.52:2.14:1	1.82:1.30:1
Condensed phenol OH	145.5–143.5 and 142.4–140.2	1.000	0.228	0.409
Total phenol OH	-	0.880	4.410	3.056
Total OH	-	2.630	8.841	4.205
Carboxyl group	136.0–134.0	0.340	0.777	1.703

## Liquid Product Analysis

### *Qualitative analyses of phenolic compounds*

The qualitative analyses from GC-MS spectra results are shown in Table 3. It should be noted that the bio-oil compounds contained phenolic compounds, aliphatic hydrocarbons, esters, alcohols, *etc.*

The phenolic compounds were formed by the cleavage of  $\text{C}\alpha/\text{C}\beta$ ,  $\text{C}\beta/\text{C}\gamma$ , or reductive cleavage of  $\alpha\text{-O-4}$  and  $\beta\text{-O-4}$  linkages in lignin. The aliphatic side-chain containing phenylpropane units in lignin was relatively plasma insensitive, but easily cleaved when treated under supercritical water conditions as observed by Tang *et al.* (2010). Thus, alcohols could be generated by the cleavage of both ether linkages and lignin side chains (Cheng *et al.* 2012).

**Table 3.** Qualitative Analyses (Based on the Peak Area-%) of Phenolic Compounds from Lignin Hydrothermal Degradation in Supercritical Water

RT (min)	Compounds	Lignin:	AL		XRL		ERL	
		Minutes:	10	60	10	60	10	60
5.700	Ethylbenzene		1.1	1.5	0.9	0.6	1.1	0.2
5.717	1,3-Dimethyl-benzene		2.7	1.2	2.5	0.5	2.9	0.7
6.292	<i>o</i> -Xylene		0.9	-	0.8	-	1.0	-
8.767	Phenol		5.3	9.9	27.8	21.6	15.7	14.8
11.100	<i>o</i> -Cresol		2.4	2.5	1.3	1.5	1.3	1.7
11.767	4-Methylphenol		0.3	3.8	4.2	4.3	3.5	4.3
12.158	Guaiacol		16.5	16.3	10.9	6.5	13.0	6.8
13.700	2-Ethylphenol		-	0.4	0.5	0.6	0.7	1.0
13.758	2-Methoxyguaiacol		1.1	2.0	0.3	0.3	0.6	0.4
14.067	2,4-Dimethylphenol		-	0.8	0.3	0.3	0.3	0.5
14.075	2,3-Dimethylphenol		0.3	0.7	-	-	0.4	0.4
14.617	4-Ethylphenol		0.5	2.1	26.3	25.4	18.7	23.5
15.417	4-Methylguaiacol		12.8	0.8	5.2	-	6.9	0.3
15.442	Catechol		-	-	0.3	10.1	-	8.8
16.458	3-Methoxyphenol		0.3	0.9	-	-	-	-
16.792	2-Ethyl-6-methylphenol		-	-	-	0.9	0.8	0.4
16.800	3-Isopropylphenol		0.4	0.9	0.8	1.7	1.4	1.6
17.367	3-Methoxycatechol		11.0	11.9	2.7	4.8	3.7	4.6
17.758	2,6-Dimethoxytoluene		0.4	0.6	-	-	-	-
17.967	4-Ethylguaiacol		4.7	4.4	6.9	3.9	8.4	5.9
18.267	4-Methylcatechol		2.1	4.5	0.5	2.2	0.9	2.6
18.933	2,5-Diethylphenol		-	2.4	-	0.6	1.0	0.5
18.942	6-Ethyl-3,4-dimethylphenol		-	-	0.4	0.4	0.6	1.2
19.05	1-Phenylethanol		-	-	0.2	0.4	-	0.5
19.258	1,4-Dimethoxy-benzene,		1.0	-	0.4	-	0.8	0.8
19.275	2,3-Dimethylhydroquinone		-	1.9	-	0.6	-	-
19.408	4-Ethyl-1,2-dimethoxybenzene		0.5	1.6	-	0.3	0.6	1.6
19.417	Vanillin		-	-	0.2	-	0.7	2.7
19.733	4-Ethylresorcinol		-	-	-	0.3	-	0.5
19.867	4-(2-Propenyl)-phenol		-	-	-	0.5	-	-
19.925	2-Methoxy-4-(2-propenyl)-phenol		-	-	-	-	1.1	-
20.058	2,6-Dimethoxyphenol		18.0	12.0	3.1	2.4	5.4	2.9
20.267	3,4-Dimethoxyphenol		-	3.7	0.9	0.6	0.7	0.5
20.375	4-Butyl-phenol		-	-	-	0.7	-	-
20.525	1,2,3-Trimethoxybenzene		5.6	-	1.5	0.5	2.7	2.8
20.542	4-Propylguaiacol		1.6	1.9	0.6	0.4	0.7	0.6
20.958	4-Ethylcatechol		-	-	-	2.3	1.2	3.6
21.208	4-(1-Methylethyl)-benzaldehyde		-	1.3	-	1.3	-	1.8
22.500	2,3,5-Trimethyl-1,4-benzenediol		0.3	-	-	0.5	0.4	-
22.675	1,2,4-Trimethoxybenzene		5.6	6.4	-	1.9	-	0.2
23.817	4-Hydroxy-3-methoxyacetophenone		1.1	-	-	0.3	0.7	-
24.275	Methyl eugenol		-	-	-	0.8	0.6	-
24.667	1,2,3-Trimethoxy-5-methylbenzene		2.7	2.0	0.6	0.5	1.3	0.6
24.858	1-(4-Hydroxy-3-methoxyphenyl)-2-propanone		0.7	1.6	-	-	0.5	0.6

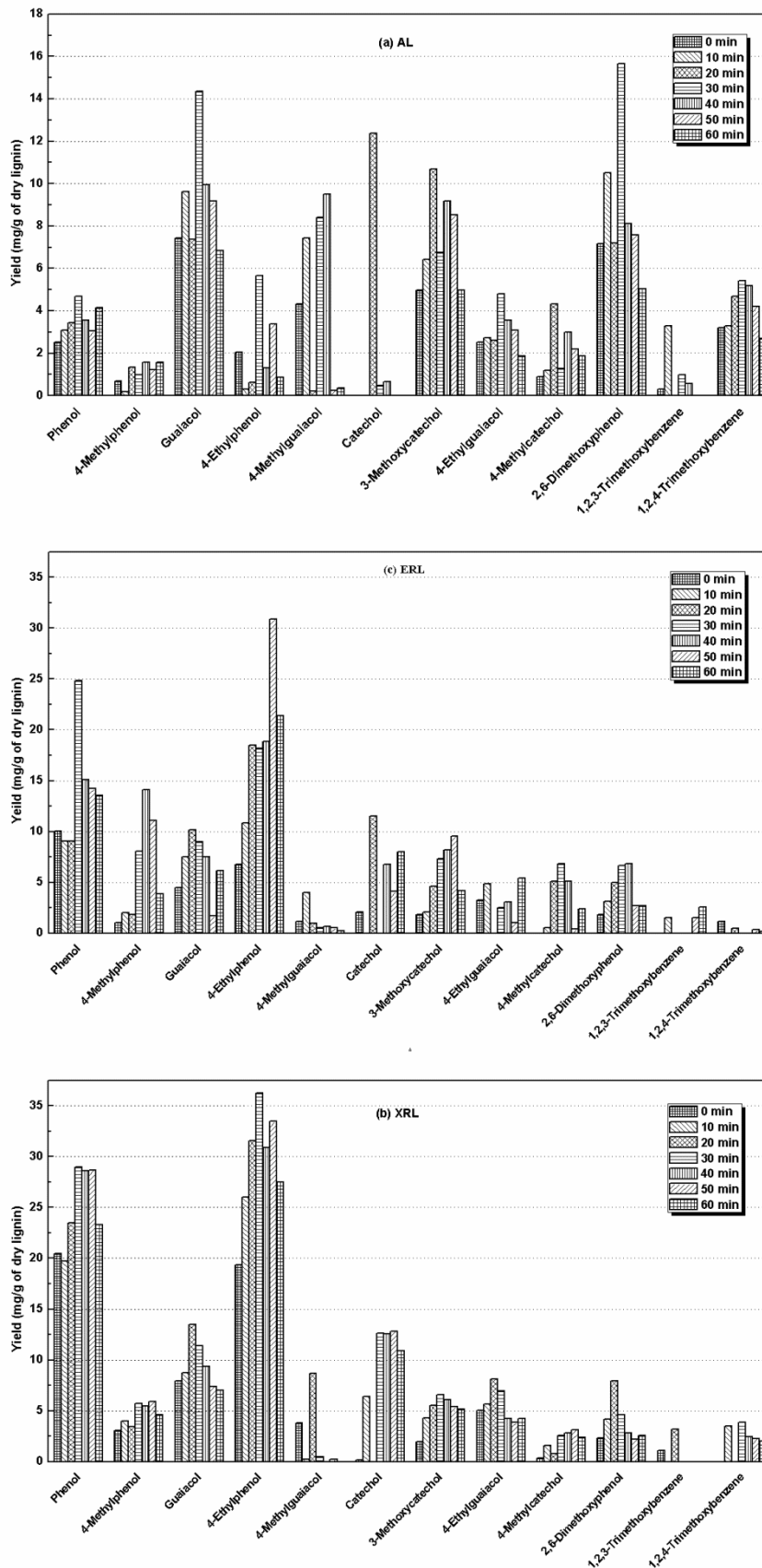


Fig. 2. Quantitative analyses of main phenolic compounds



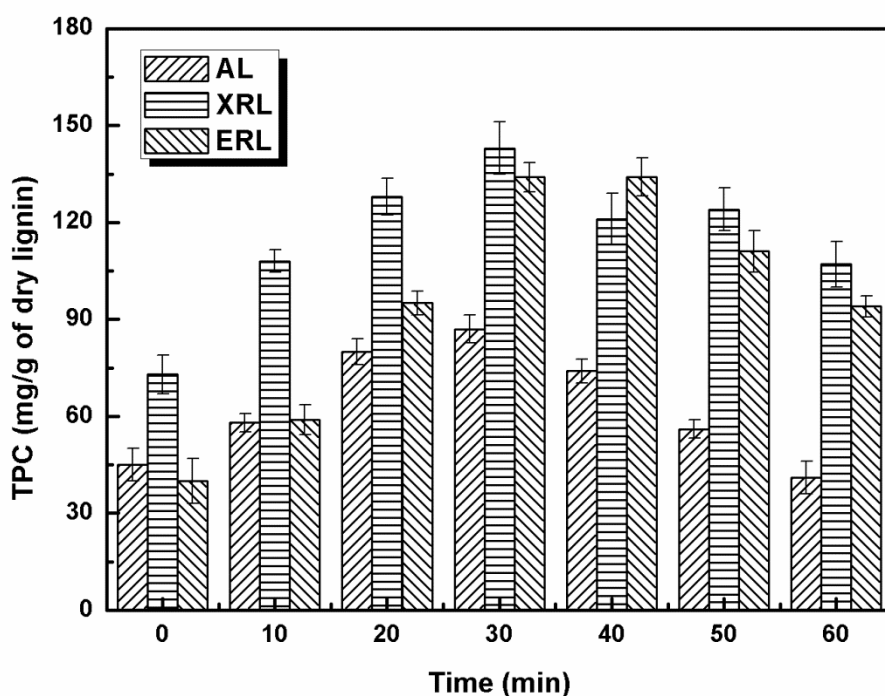
The AL sample had a smaller percentage of detectable phenolic compounds because it was composed of simpler structural units or smaller molecules due to the alkali hydrolysis in the cooking process (Table 2). GPC results from past studies (Cheng *et al.* 2012) also supported this observation. Additionally, the following trends were observed: The guaiacol and 2,6-dimethoxyphenol from AL sample accounted for 16.52% and 18.01% of the total peak area over 10 min, respectively. For XRL and ERL, the phenol and 4-ethylphenol were the two most abundant compounds; the products of XRL and ERL had more H-type compounds than AL. However, the products of AL had more S-type compounds than XRL and ERL, whereas the differences in G-type products were not noticeable. Most of the aromatic compounds with larger peak areas were derived from the phenylpropane building blocks, such as guaiacyl (G), syringyl (S), and hydroxyphenolic (H) units of lignin; Meanwhile, the major compounds and the relative area (%) of each of the lignin samples varied because of the different ratios of the phenylpropane building blocks and the various mechanisms of structural rearrangement and cleavage (Sun *et al.* 2002; Buranov and Mazza 2008; Asmadi *et al.* 2011).

#### *Quantitative analysis of predominant phenolic compounds*

The yields of the predominant phenolic compounds for all three residual samples depended on the holding time, as demonstrated in Fig. 2. For the products from hydrothermal decomposition of AL in Fig. 2(a), the largest yield of G-type aromatic products (guaiacol) and S-type aromatic products (2, 6-dimethoxyphenol) were obtained at 30 min at yields of 14.34 and 15.67 mg/g, respectively. On the other hand, the XRL was converted into phenol (28.94 mg/g), guaiacol (13.48 mg/g), and 4-ethylphenol (36.21 mg/g) at 30 min, but contained more H-type aromatic products in comparison to AL. Despite the fact that the XRL has a structurally similar composition to corn biomass, ERL products had a lower proportion of phenol (24.81mg/g), guaiacol (10.15 mg/g), and 4-ethylphenol (30.90 mg/g), but more of H-type compounds (such as 4-methylphenol 14.14 mg/g) at different reaction times. The acid pre-treatment during bioethanol process lead therefore to the degradation of the  $\beta$ -O-4 linkages to release a large proportion of syringyl and guaiacyl units (Yasuda *et al.* 1999).

Additionally, the holding time affects the products of hydrothermal decomposition of lignin during the reaction. For example, the yield of phenol from AL was 2.51 mg/g at the beginning, much lower than that after 30 min (4.69 mg/g). Under the same conditions (0 to 30 min), the yield of guaiacol increased from 7.42 mg/g to 14.34 mg/g. Over the holding time range of 30 to 60 min, the yield of guaiacol decreased as the reaction time increased and the yield of phenol did not show any decreasing trend. The phenolic products primarily contained G-, H-, or S-type products and derivatives. The main products (phenol, guaiacol, and 2, 6-dimethoxyphenol) primarily formed through the O-CH<sub>3</sub> bond homolysis in H-, G- and S-type lignins, respectively. Additionally, phenol and guaiacol can also be produced through demethoxylation of the G- and S- units. Because the compounds is influenced by a series of reactions, such as cleavage of building block linkages, radical-induced rearrangements, demethoxylation, and radical coupling reactions (Asmadi *et al.* 2011), *etc.*, products also contained a few other phenolic derivatives. For example, 4-methylguaiacol (9.51 mg/g) and 3-methoxycatechol (10.68 mg/g) from AL may be formed through the coupling of O-CH<sub>3</sub> homolysis products, carbon-centered radicals, and methyl radicals (Asmadi *et al.* 2012). The substantial presence of 4-methylphenol and 4-ethylphenol in the XRL could also be caused by a higher probability for the formation and coupling of methyl- radicals and phenyl radicals from H-type units. Additionally, a lower

level of G-type compounds formed from lignin ether-bond hydrolysis can easily lead to polyhydroxy phenol by dealkylation reactions, as shown in past work (Kanetake *et al.* 2007; Toor *et al.* 2011). Thus, catechol compounds can be obtained from guaiacol. In a similar manner, 3-methoxycatechol should also be observed from 2,6-dimethoxyphenol, in which the demethoxylation reaction occur rapidly with complete depolymerization within a short residence time (Tau and Yukihiro 2012). When the water reached supercritical temperature, condensation reactions involving reactive low-molecular-weight fragments (such as phenols and catechols) are believed to have occurred and resulted in a decrease of phenolic hydroxyls (Matsushita *et al.* 2013). In the existing reaction conditions, the yields of phenolic compounds did not directly correspond to the time changes, and thus a detailed mechanism of hydrothermal decomposition of lignin is particularly difficult to postulate because the raw material can be degraded into a huge number of compounds.



**Fig. 3.** Yields of total phenolic compounds (TPC) as a function of holding time

It is clear that the largest yields of phenol (28.94 mg/g) and 4-ethylphenol (36.21 mg/g) were obtained from XRL at 30 min. Optimal yields of guaiacol and 2,6-dimethoxyphenol obtained were 14.34 mg/g and 15.67 mg/g from AL after 30 min. Hence, the types of lignin and the reaction conditions are key factors to obtain the required phenolic products in high purity.

Figure 3 presents the yields of the total phenolic compounds (TPC) obtained after hydrothermal conversion (at 375 °C of different lignins). At least 40 mg and at the most 140 mg phenolic compounds were obtained from 1 g lignin under supercritical conditions. The sample XRL had the best total phenolics yield (70 to 140 mg/g), while AL had the lowest (40 to 90 mg/g). The TPC of all lignin samples was significantly influenced by reaction time. For example, in the case of XRL, after 30 min, the TPC increased from 74

mg to 140 mg, although it decreased after longer times. When AL or ERL was used, the trend was found to be the same.

It was also found that the TPC tended to increase when the lignin contained a higher amount of functional groups, such as methoxyl, hydroxyl, and carboxyl groups. Again, from the spectroscopic data ( $^{31}\text{P}$ -NMR and FTIR), it appeared that a large difference in TPC was associated with the structural differences among AL, XRL, and ERL. For example, AL possessed lower phenolic hydroxyl content than either XRL or ERL, a fact that could lead to a lower proportion of phenolic compounds in the bio-oils. Also, AL had an extremely high content of sulfur (3.2%), which dropped to 0.4% to 0.5% (Table 1) after hydrothermal degradation. Such a finding indicated that a part of the produced fractions was sulfur-containing compounds (such as methylthio-cyclohexane, 1-methyl-4-(methylthio)-benzene, 1-methyl-4-(methylthio)-benzene, 1, 2-benzenedithiol, 1-[4-(methylthio)-phenyl]-ethanone, 1-methoxy-2-methyl-4-(methylthio)-benzene, *etc.*), as confirmed by GC-MS analysis.

### Solid Residues Analysis

#### *Yields of lignin degradation residues*

Figure 4 shows the yields of lignin degradation of solid residues (YSR) as a function of residence time. The solid residues had around 20% to 30% yield with respect to lignin. The YSR for the three lignin samples decreased initially, and then it increased over the hold time. The relative high solid residue yield after 0 min of reaction time was attributed to incompletely degraded lignin. With increasing time, the lignin was further degraded and a lower amount of solid residues were collected after 30 min.

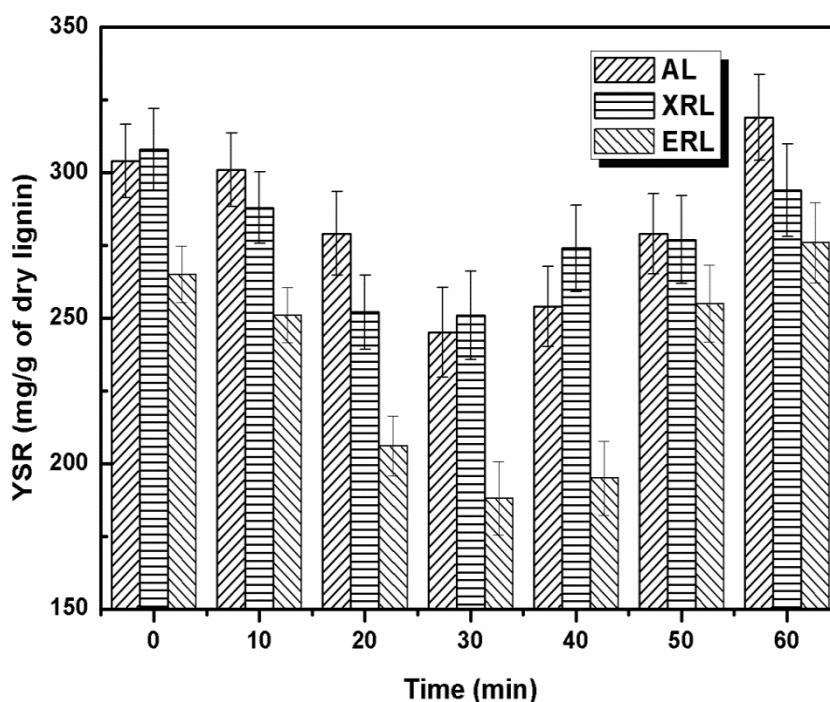


Fig. 4. Yields of lignin solid residues (YSR) with residence time

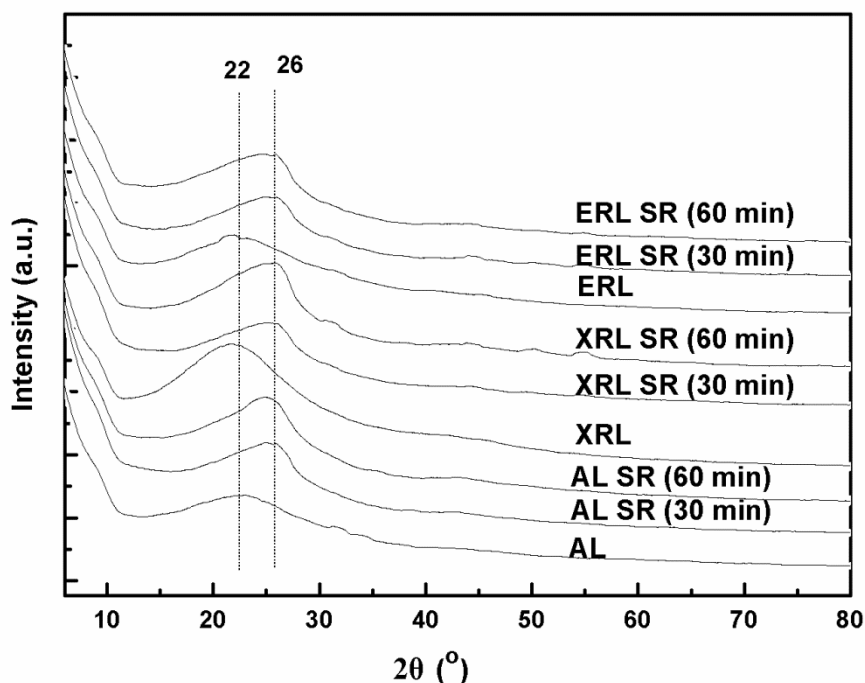
Repolymerization was promoted along with degradation. Over a short time, degradation could play a leading role and lead to lower solid residues. After longer times, the reaction rate of repolymerization exceeded that of degradation, leading to higher solid residues.

#### *Chemical characterization of solid residues*

Table 1 also shows the results of chemical analysis for solid residues from different lignin depolymerization reactions. The SR composition had a marked change when compared with the three lignin samples. At a hold time of 30 min for AL, the carbon showed a clear increase from 55.9% to 78.8%, while the oxygen content decreased from 36.7% to 17.0%. As the hold time increased to 60 min, a slightly decrease in the carbon content (from 78.8% to 76.2%), together with a slight increase in oxygen (from 17.0% to 19.3%), and hydrogen content (from 3.4% to 3.6%) were observed. The solid residues of XRL and ERL indicated the same trend.

The energy content of the solid residues (HHV) is shown in Table 1. The hydrothermal conversion led to an increase in the HHV of the solid residues. For example, the energy content of the starting dry AL feedstock was 17.51 MJ/kg. At a reaction time of 30 min, the SR had an HHV of 28.47 MJ/kg, *i.e.*, an increase of 63% compared to the AL. Also, a similar result was found for XRL and ERL samples, an increase of 33% and 15%, respectively. These increases in char energy density compared to different raw biomass feedstock are in agreement with the literature (Hoekman *et al.* 2011; Mumme *et al.* 2011). Additionally, the energy contents of solid residues showed no substantial difference as the reaction time ranged from 30 to 60 min.

#### *XRD analyses of solid residues*



**Fig. 5.** XRD curves of lignin and SR

The XRD curves of lignin and solid residues are shown in Fig. 5. The only peak ranging from 20° to 26° corresponded to a stacking of aromatic layers (Lu *et al.* 2002). It is evident from Fig. 5 that the XRD peaks at 30 min and 60 min showed a distinct difference, which again indicates that the residues reacted under supercritical conditions. As hydrothermal conversion reaction time increased, the side chains were eliminated and the aromatics depolymerized to form a cross-linked microcrystalline structure. The peak moved from 22° to 26°, which became much sharper and was closer to that of graphite (26.6°). These results indicated that the solid residues at supercritical water had a highly crystalline structure with a high degree of long range order. A similar result was obtained in a previous study by Hu *et al.* (2014).

## CONCLUSIONS

1. Residual lignin can be utilized as an abundant source for aromatics production. Under supercritical water conditions, the three residual lignin samples were nearly completely depolymerized, and the solid residues had a significant increase in the HHV.
2. The XRL is composed of more H-type units in comparison to the wood-based AL, which is a mixture of predominately G- and S-type units. Thus, XRL is a promising candidate for H-type phenolic products. The largest yields of phenol (28.94 mg/g) and 4-ethylphenol (36.21 mg/g) were obtained from XRL after 30 min of reaction. AL has high potential to produce value-added G- and S-type compounds. The optimal yields of guaiacol and 2,6-dimethoxyphenol from AL were 14.34 mg/g and 15.67 mg/g, respectively, after 30 min.
3. Selective production of phenolic compounds from specific lignin species can contribute to the development of a lignin-based biorefinery platform.

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## REFERENCES CITED

- Asmadi, M., Kawamoto, H., and Saka, S. (2011). "Thermal reactions of guaiacol and syringol as lignin model aromatic nuclei," *J. Anal. Appl. Pyrolysis*. 92(1), 88-98. DOI: 10.1016/j.jaap.2011.04.011
- Asmadi, M., Kawamoto, H., and Saka, S. (2012). "The effects of combining guaiacol and syringol on their pyrolysis," *Holzforschung* 66(3), 323-330. DOI: 10.1515/HF.2011.165
- ASTM D 1102 (1984). "Standard test method for ash in wood," American Society Testing and Materials, American.

- ASTM D 4442 (2007). "Standard test methods for direct moisture content measurement of wood and wood-base materials," American Society Testing and Materials, American.
- Buranov, A. U., and Mazza, G. (2008). "Lignin in straw of herbaceous crops," *Ind. Crops Prod.* 28(3), 237-259. DOI: 10.1016/j.indcrop.2008.03.008
- Cheng, S., Wilks, C., Yuan, Z., Leitch, M., and Xu, C. C. (2012). "Hydrothermal degradation of alkali lignin to bio-phenolic compounds in sub/supercritical ethanol and water-ethanol co-solvent," *Polym. Degrad. Stab.* 97, 839-848. DOI: 10.1016/j.polymdegradstab.2012.03.044
- Crestini, C., and Argyropoulos, D. S. (1997). "Structural analysis of wheat straw lignin by quantitative <sup>31</sup>P and 2D NMR spectroscopy," *J. Agric. Food Chem.* 45(4), 1212-1219. DOI: 10.1021/jf960568k
- Farag, S., and Chaouki, J. (2015). "Economics evaluation for on-site pyrolysis of kraft lignin to value-added chemicals," *Bioresour. Technol.* 175, 254-261. DOI: 10.1016/j.biortech.2014.10.096
- Farag, S., Kouisni, L., and Chaouki, J. (2014). "Lumped approach in kinetic modeling of microwave pyrolysis of kraft lignin," *Energy Fuels* 28(2), 1406-1417. DOI: 10.1021/ef4023493
- Gosselink, R. J. A., Wouter, T., van Dam, J. E. G., de Jong, Ed., Göran G., Scott, E. L., and Sanders, J. P. M. (2012). "Lignin depolymerisation in supercritical carbon dioxide/acetone/water fluid for the production of aromatic chemicals," *Bioresour. Technol.* 106, 173-177. DOI: 10.1016/j.biortech.2011.11.121
- Hoekman, S. K., Broch, A., and Robbins, C. (2011). "Hydrothermal carbonization (HTC) of lignocellulosic biomass," *Energy Fuels* 25(4), 1802-1810. DOI: 10.1021/ef101745n
- Hu, J., Shen, D., Wu, S., Zhang, H., and Xiao, R. (2014). "Effect of temperature on structure evolution in char from hydrothermal degradation of lignin," *J. Anal. Appl. Pyrolysis.* 106, 118-124. DOI: 10.1016/j.jaap.2014.01.008
- Jin, F., and Enomoto, H. (2008). "Application of hydrothermal reaction to conversion of plant-origin biomasses into acetic and lactic acids," *J. Mater. Sci.* 43(7), 2463-2471. DOI 10.1007/s10853-007-2013-z
- Kanetake, T., Sasaki, M., and Goto, M. (2007). "Decomposition of a lignin model compound under hydrothermal conditions," *Chem. Eng. Technol.* 30(8), 1113-1122. DOI: 10.1002/ceat.200700066
- Karagöz, S., Bhaskar, T., Muto, A., and Sakata, Y. (2004). "Effect of Rb and Cs carbonates for production of phenols from liquefaction of wood biomass," *Fuel* 83(17), 2293-2299. DOI: 10.1016/j.fuel.2004.06.023
- Lavoie, J. M., Baré, W., and Bilodeau, M. (2011). "Depolymerization of steam-treated lignin for the production of green chemicals," *Bioresour. Technol.* 102(7), 4917-4920. DOI: 10.1016/j.biortech.2011.01.010
- Lou, R., and Wu, S. B. (2011). "Products properties from fast pyrolysis of enzymatic/mild acidolysis lignin," *Appl. Energy.* 88(1), 316-322. DOI: 10.1016/j.apenergy.2010.06.028
- Lu, L., Kong, C., Sahajwalla, V., and Harris, D. (2002). "Char structural ordering during pyrolysis and combustion and its influence on char reactivity," *Fuel* 81(9), 1215-1225. DOI: 10.1016/S0016-2361(02)00035-2
- Matsushita, Y., Jo, E. K., Inakoshi, R., Yagami, S., Takamoto, N., Fukushima, K., and Lee, S. C. (2013). "Hydrothermal reaction of sulfuric acid lignin generated as a by-

- product during bioethanol production using lignocellulosic materials to convert bioactive agents,” *Ind. Crops Prod.* 42, 181-188. DOI: 10.1016/j.indcrop.2012.05.030
- Morais, A. R. C., Pinto, J. V., Nunes, D., Roseiro, L. B., Oliveira, M. C., Fortunato, E., and Bogel-Lukasik, R. (2016). “Imidazole: Prospect solvent for lignocellulosic biomass fractionation and delignification,” *ACS Sustain. Chem. Eng.* 4(3), 1643-1652. DOI: 10.1021/acssuschemeng.5b01600
- Morais, A. R., da Costa Lopes, A. M., and Bogel-Lukasik, R. (2015). “Carbon dioxide in biomass processing: Contributions to the green biorefinery concept,” *Chem Rev.* 115(1), 3-27. DOI: 10.1021/cr500330z
- Mumme, J., Eckervogt, L., Pielert, J., Diakité, M., Rupp, F., and Kern, J. (2011). “Hydrothermal carbonization of anaerobically digested maize silage,” *Bioresour. Technol.* 102(19), 9255-9260. DOI: 10.1016/j.biortech.2011.06.099
- Nguyen, T. D. H., Maschietti, M., Belkheiri, T., Åmand, L. E., Theliander, H., Vamling, L., and Andersson, S. I. (2014). “Catalytic depolymerisation and conversion of kraft lignin into liquid products using near-critical water,” *J. Supercrit. Fluids.* 86(1), 67-75. DOI: 10.1016/j.supflu.2013.11.022
- Pandey, K. (1999). “A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy,” *J. Appl. Polym. Sci.* 71(12), 1969-1975. DOI: 10.1002/(SICI)1097-4628(19990321)71:12<1969::AID-APP6>3.3.CO;2-4
- Pandey, M. P., and Kim, C. S. (2011). “Lignin depolymerization and conversion: A review of thermochemical methods,” *Chem. Eng. Technol.* 34(1), 29-41. DOI: 10.1002/ceat.201000270
- Piñkowska, H., Wolak, P., and Złocińska, A. (2012). “Hydrothermal decomposition of alkali lignin in sub- and supercritical water,” *Chem. Eng. J.* 187, 410-414. DOI: 10.1016/j.cej.2012.01.092
- Ragauskas, A. J., Beckham, G. T., Biddy, M. J., Chandra, R., Chen, F., Davis, M. F., and Wyman, C. E. (2014). “Lignin valorization: Improving lignin processing in the biorefinery,” *Science* 344(6185), 709-719. DOI: 10.1126/science.1246843
- Sammons, R. J., Harper, D. P., Labbé, N., Bozell, J. J., Elder, T., and Rials, T. G. (2013). “Characterization of organosolv lignins using thermal and FT-IR spectroscopic analysis,” *BioResources* 8(2), 2752-2767. DOI: 10.15376/biores.8.2.2752-2767
- Song, Q., Wang, F., Cai, J., Wang, Y., Zhang, J., Yu, W., and Xu, J. (2013). “Lignin depolymerization (LDP) in alcohol over nickel-based catalysts via a fragmentation–hydrogenolysis process,” *Energ. Environ. Sci.* 6(3), 994-1007. DOI: 10.1039/c2ee23741e
- Stewart, D. (2008). “Lignin as a base material for materials applications: Chemistry, application and economics,” *Ind. Crops Prod.* 27(2), 202-207. DOI: 10.1016/j.indcrop.2007.07.008
- Sun, R., Sun, X. F., Wang, S. Q., Zhu, W., and Wang, X. Y. (2002). “Ester and ether linkages between hydroxycinnamic acids and lignins from wheat, rice, rye, and barley straws, maize stems, and fast-growing poplar wood,” *Ind. Crops Prod.* 15(3), 179-188. DOI: 10.1016/S0926-6690(01)00112-1
- Tang, Z., Zhang, Y., and Guo, Q. (2010). “Catalytic hydrocracking of pyrolytic lignin to liquid fuel in supercritical ethanol,” *Ind. Eng. Chem. Res.* 49(5), 2040-2046. DOI: 10.1021/ie9015842
- Tau, L. K., and Yukihiko, K. (2012). “Reaction kinetics of the lignin conversion in supercritical water,” *Ind. Eng. Chem. Res.* 51(37), 11975-11988. DOI: 10.1021/ie300921d

- Toor, S. S., Rosendahl, L., and Rudolf, A. (2011). "Hydrothermal liquefaction of biomass: a review of subcritical water technologies," *Energy* 36(5), 2328-2342. DOI: 10.1016/j.energy.2011.03.013
- Wahyudiono, Sasaki, M., and Goto, M. (2011). "Thermal decomposition of guaiacol in sub- and supercritical water and its kinetic analysis," *J. Mater. Cycles. Waste.* 13(1), 68-79. DOI 10.1007/s10163-010-0309-6
- Wang, C., Lyu, G., Yang, G., Chen, J., and Jiang, W. (2014). "Characterization and hydrothermal conversion of lignin produced from corncob acid hydrolysis residue," *BioResources* 9(3), 4596-4607. DOI: 10.15376/biores.9.3.4596-4607
- Xiao, L. P., Shi, Z. J., Xu, F., and Sun, R. C. (2013). "Characterization of lignins isolated with alkaline ethanol from the hydrothermal pretreated *Tamarix ramosissima*," *Bioenerg. Res.* 6(2), 519-532. DOI: 10.1007/s12155-012-9266-3
- Yasuda, S., Hamaguchi, E., and Asano, K. (1999). "Ready chemical conversion of acid hydrolysis lignin into water-soluble lignosulfonate III: Successive treatment of acid hydrolysis lignin and a lignin model compound by phenolation and arylsulfonation," *J. Wood Sci.* 45(3), 245-249. DOI: 10.1007/BF01177733
- Ye, Y., Fan, J., and Chang, J. (2012). "Effect of reaction conditions on hydrothermal degradation of cornstalk lignin," *J. Anal. Appl. Pyrolysis.* 94, 190-195. DOI: 10.1016/j.jaap.2011.12.005
- Zhang, C. J., and Liu, Y. (2012). "Componential analysis of black liquor and determining of dissolution lignin," *Paper Paper Making* 31(1), 63-64. DOI:10.13472/j.ppm.2012.01.040
- Zhang, Y. M., Peng, Y., Yin, X. L., Liu, Z. H., and Li, G. (2014). "Degradation of lignin to BHT by electrochemical catalysis on Pb/PbO<sub>2</sub> anode in alkaline solution," *J. Chem. Technol. Biotechnol.* 89(12), 1954-1960. DOI: 10.1002/jctb.4282

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