

Pyrolysis Properties of Lignins Extracted from Different Biorefinery Processes¹

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ABSTRACT

The non-isothermal and isothermal pyrolysis properties of H lignin and P lignin extracted from different biorefinery processes (such as supercritical water hydrolysis and fast pyrolysis) were studied using thermogravimetry analysis (TGA) and pyrolyzer-gas chromatography/mass spectrometry (Py-GC/MS). The lignins were characterized by ultimate/proximate analysis, FT-IR and GPC. Based on the thermogravimetry (TG) and derivative thermogravimetry (DTG) curves, the thermal decomposition stages were obtained and the pyrolysis products were analyzed at each thermal decomposition stage of non-isothermal pyrolysis. The isothermal pyrolysis of lignins was also carried out at 400, 500, and 600 °C to investigate the pyrolysis product distribution at each temperature. In non-isothermal pyrolysis, P lignin recovered from a fast pyrolysis process started to decompose and produced pyrolysis products at a lower temperature than H lignin recovered from a supercritical water hydrolysis process. In isothermal pyrolysis, guaiacyl and syringyl type were the major pyrolysis products at every temperature, while the amounts of p-hydroxyphenyl type and aromatic hydrocarbons increased with the pyrolysis temperature.

Keywords: pyrolysis, lignin, pyrolytic lignin, supercritical water hydrolysis

1. INTRODUCTION

The rapid increase in the number and severity of the problems associated with the use of fossil fuels and the emission of greenhouse gas pollutants has led to demands for the development of renewable and clean sources of energy (Lee *et al.*, 2016b). Lignocellulosic biomass is one important resource that could be used for the production of energy and valuable chemicals using an environmentally friendly process (Min and Um, 2017; Ryu *et al.*, 2016). Lignocellulosic biomass

is abundant and carbon neutral and, therefore, has been receiving considerable attention as a renewable energy source (Mu *et al.*, 2013; Collard and Blin, 2014; Gong *et al.*, 2016).

Pyrolysis, a thermochemical biomass conversion method, is a thermal decomposition reaction that produces liquid, gas, and solid products under an oxygen-free atmosphere at a temperature of 400 - 600 °C. Compared to other thermochemical conversion methods such as gasification, combustion and torrefaction, pyrolysis produces a liquid product, known as “bio-oil,”

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which could be to use as an industrial fuel and as a raw material for the chemical industry (Hwang *et al.*, 2012; Kim *et al.*, 2013; Moon *et al.*, 2016). In recent decades, many studies addressing the pyrolysis of biomass and biomass components have been reported, with all of these producing a liquid product (Burhenne *et al.*, 2013; Dabros *et al.*, 2018). Lignocellulosic biomass is consisted of three components, including cellulose, hemicellulose, and lignin. Cellulose and hemicellulose could be efficiently converted to bio-alcohols and bio-gasoline via biochemical, catalytic and thermochemical reactions (Kang and Lee, 2015; Hwang and Choi, 2018). Compared to cellulose and hemicellulose, lignin has attracted little attention as a biofuel feedstock because of its complex three-dimensional polymeric structure, high molecular weight, and thermal resistance (Lee *et al.*, 2016a; Kawamoto, 2017). Lignin, however, being a biopolymer consisting of phenylpropane units such as p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, offers the greater potential for renewable energy and chemical applications due to its being abundant in nature (De Wild *et al.*, 2014; Kim *et al.*, 2012).

Research into the pyrolysis of lignin has increased steadily with the goal of producing phenolic compounds from various lignins, while a lignin pyrolysis mechanism has also been suggested. Since the 1970s, the pyrolysis of lignin has been studied using various types of lignin such as Kraft lignin, Milled wood lignin, Alcell lignin, and Asian lignin (Amen-Chen *et al.*, 2001; Zhou *et al.*, 2013). A study of the lignin pyrolysis mechanism was also performed using model compounds with β -O-4 linkages or extracted lignin (Drage *et al.*, 2002; Chu *et al.*, 2013) however, the details of the mechanism remain unclear because of the complicated network structure and pyrolysis reaction pathways of lignin (Kim *et al.*, 2017).

In the case of lignin, the extraction methods and source species could lead to differences in the lignin

pyrolysis properties. Zhang *et al.* (Zhang *et al.*, 2017) compared the fast pyrolysis behavior of three kinds of corn stover lignins acquired using different isolation methods. Corn stover lignins were produced using three methods, namely, Bjorkman milling, organosolv extraction, and gamma-valerolactone (GVL) extraction. Wang *et al.* (Wang *et al.*, 2015) reported on the pyrolysis behaviors of four lignins isolated from pine wood. They isolated Alkali lignin, Klason lignin, Organosolv lignin, and milled-wood lignin from the same pine wood and compared their pyrolysis behaviors using thermogravimetric analysis coupled with Fourier-transform infrared analysis (TG-FTIR), as well as pyrolyzer-gas chromatography/mass spectrometry (Py-GC/MS). Compared to the Klason and Organosolv lignins, the alkali and milled-wood lignins produced more phenols at low temperatures due to the breakage of the abundant and weak ether linkages in their structures. The pyrolysis behavior of lignins sourced from different tree species was reported by other researchers. Wang *et al.* (Wang *et al.*, 2009) compared two milled-wood lignins from Manchurian ash hardwood (MA) and Mongolian Scots pine softwood (MSP) using TG-FTIR. Relative to the hardwood lignin, the softwood lignin exhibited a higher thermal stability. Zhou *et al.* (Zhou *et al.*, 2016) compared hardwood, softwood, and herbaceous lignins in terms of their thermochemical conversion. The pyrolysis of the Herbaceous lignin produced the largest amount of phenolic monomers, while softwood lignin produced more phenolic monomers than the hardwood lignin.

There have been very few studies that have compared the pyrolysis properties of lignin obtained from biorefinery processes such as pyrolysis and hydrolysis. Especially, as novel technique, supercritical water was used in hydrolysis process with advantages such as shorter reaction time, low toxicity and without pre-treatment. Therefore, in the present study, lignins obtained from supercritical water hydrolysis and fast pyrolysis were evaluated in terms of their pyrolysis

properties. The ultimate, proximate analysis, FT-IR and GPC were used to characterize properties of lignins. The non-isothermal and isothermal pyrolysis of lignins were analyzed by thermogravimetry analysis (TGA) and Py-GC/MS.

2. MATERIALS and METHODS

2.1. Sample

Quercus mongolica was subjected to supercritical water hydrolysis and fast pyrolysis processes, to acquire the residual hydrolysis lignin (H lignin) and pyrolytic lignin (P lignin), respectively. H lignin was obtained from the solid (about 10.5 wt%) produced by a supercritical water hydrolysis pilot plant (Jeong *et al.*, 2017; Jang *et al.*, 2018). This solid was freeze-dried and then dissolved in a 0.5 M NaOH solution. Then, a precipitate was obtained by acidifying the solution to pH 2–3 using HCl. Then, the H lignin was collected by filtration with deionized water, after which it was freeze-dried. P lignin was prepared using a cold water separation method, as described in the literature (Scholze and Meier, 2001; Kim *et al.*, 2016; Kim *et al.*, 2011). Pyrolytic lignin, that is, the water-insoluble fraction of the pyrolysis oil, was obtained about 11 wt% from *Quercus mongolica* pyrolysis oil produced at 550 °C in a fluidized-bed pyrolysis reactor. These lignin samples were dried at 80 °C for 6 h prior to the start of the experiments. Ultimate and proximate analysis of samples of H lignin and P lignin were carried out using elemental analysis (Elementar, vario Macro

cube) and thermogravimetric analysis (TGA, Pyris 8000, Perkin Elmer Co.) according to the analysis procedure described in the literature (Lee *et al.*, 2016a). The results of the ultimate and proximate analysis are listed in Table 1. For the characterization of lignin properties such as molecular weight and functional groups, Gel-Permeation Chromatography (GPC, Viscotek, USA) and Fourier-transform Infrared spectroscopy (FT-IR) analysis were also performed. FT-IR analysis was carried out using a Nicolet iS10 (Thermo Fisher Scientific, USA) equipped with an attenuated total reflectance (ATR). A total 32 scans per sample were analyzed at 4cm⁻¹ spectral resolution, with in the range of 4000-600cm⁻¹. GPC was used for molecular mass and polydispersity analysis of lignins. Lignin samples were dissolved in tetrahydrofuran (1mg/ml) and the injection volume was 100μ l.

2.2. Thermogravimetric analysis

A thermogravimetric analysis (TGA, Pyris 8000, Perkin Elmer Co.) was carried out to determine the thermal decomposition characteristics. A lignin sample (about 5 mg) was pyrolyzed using a heat profile with a range of 40–700 °C and a heating rate of 20 °C/min under a helium flow.

2.3. Analytical pyrolysis using Py-GC/MS

Two analytical pyrolysis methods, namely, single-shot (isothermal pyrolysis) and multi-shot (non-isothermal pyrolysis) Py-GC/MS, were conducted using a pyrolyzer

Table 1. Ultimate and proximate analysis of H lignin and P lignin

wt%	Ultimate analysis					Proximate analysis			
	C	H	N	S	O	Moisture	Volatiles	Fixed carbon	Ash
H lignin	65.46	5.40	0.34	0.21	28.59	2.6	56.8	40.5	0.2
P lignin	72.22	6.71	0.38	0.00	20.69	2.8	68.9	27.3	1.0

(Py-2020iD, Frontier Laboratories Ltd.) and a gas chromatograph combined with a mass spectrometer (GC/MS, 7890A/5975C inert, Agilent Technologies). For each run, 1 mg of lignin was placed in a sample cup. For the non-isothermal pyrolysis of lignin, the sample cup was placed in the furnace and then heated to the pyrolysis end temperature at a heating rate of 20 °C/min under an He atmosphere in each pyrolysis zone, as obtained from the DTG curves. The pyrolysis vapor was transferred to the MS detector via a MicroJet Cryo-Trap (MJT-1030E, Frontier Laboratories Ltd.) and GC separation column (DB-5MS, 30 m length × 0.25 mm inner diameter × 0.25 μm film thickness) under a 50-mL/min helium flow. For the GC separation, the oven temperature was programmed to increase from 40 °C (10 min) to 310 °C (7 min) at a heating rate of 10 °C/min. The column flow was 0.7 mL/min. For the isothermal pyrolysis experiments, the sample cup was dropped into the preheated furnace at 400, 500, and 600 °C, and allowed to pyrolyze for 2 min. After the sample was pyrolyzed, the sample was analyzed under the same conditions as those of the non-isothermal pyrolysis experiments (separation column, oven temperature program). Non-isothermal and isothermal pyrolysis products were identified using the Nist 5th library.

3. RESULTS and DISCUSSION

3.1. Characterization of lignins

The GPC analysis results, mass average molecular weight (Mw), number average molecular weight (Mn) and poly dispersity (Mw/Mn), are shown in Table 2. The average molecular weight of H lignin was higher than P lignin, suggesting that higher degree of depolymerization was occurred by pyrolysis than by supercritical water hydrolysis. The molecular weight of H lignin and P lignin showed lower than that of

Table 2. Molecular weight and poly dispersity of lignins.

	Mw	Mn	Poly dispersity (Mw/Mn)
H lignin	2516	1617	1.239
P lignin	1390	1123	1.556

milled wood lignin (Mw: about 6,700-12,000 Mn: about 2,000-5,500) reported previous literature because of depolymerization by pyrolysis and hydrolysis (Kim *et al.*, 2011; Zhang *et al.*, 2017; Wang *et al.*, 2014). The value of poly dispersity, width of the molecular weight distribution, showed that poly dispersity of H lignin was lower than that of P lignin, indicating narrower molecular weight distribution of H lignin (Wang *et al.*, 2014; Seo *et al.*, 2019).

Fig. 1 showed FT-IR spectra of H lignin and P lignin. The similar FT-IR spectra presented due to same raw biomass indicating that extracted lignin structure did not change significantly depending on thermochemical process condition. The broad band at 3600-3000 cm⁻¹, hydroxyl groups of the aliphatic and phenolics, was presented by both lignin spectra. Phenolic hydroxyl group and C-O deformation in the methoxyl group were presented in the wavelength range 1120-1110 and 1030-1020 cm⁻¹, respectively. The aromatic ring band (1510-1500 cm⁻¹) of P lignin showed higher intensity

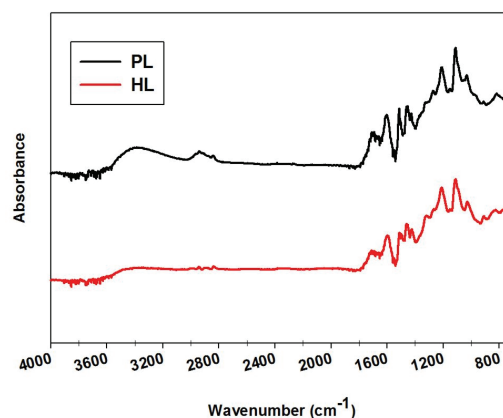


Fig. 1. FT-IR spectra of lignins.

than H lignin. The peaks of P lignin at 1700 cm^{-1} , unconjugated ketone and carboxyl group stretching, was higher than that of HL because pyrolytic lignin extracted from pyrolysis oil could contain some hemicellulose pyrolysis compounds (Wang *et al.*, 2014; Zhang *et al.*, 2017; Seo *et al.*, 2019; Kim *et al.*, 2011).

3.2. Thermogravimetry analysis

The thermogravimetry (TG) and differential thermogravimetry (DTG) curves for the H lignin and P lignin under an He atmosphere, obtained at a heating rate of 20 °C/min up to a final temperature of 700 °C , are shown in Fig. 2. Compared to the H lignin (45.5 wt.%), the P lignin produced less solid residue (31.4 wt.%) at the final temperature of 700 °C (Table 3). This result was consistent with that of a proximate analysis that found that the P lignin produced more volatile matter and a smaller amount of solids (fixed carbon + ash) than the H lignin (Table 1). Both the H and P lignins exhibited a wide decomposition temperature range because of there being many aromatic rings with various branches, the activity of the chemical bonds, and the functional groups (Wang *et al.*, 2009). The P lignin decomposed with a weight loss at $120\text{--}600\text{ °C}$, while the H lignin decomposed with a weight loss

Table 3. Thermal decomposition stages and pyrolysis char yield

	H lignin	P lignin
Thermal decomposition stage	120–200 °C	120–250 °C (Zone D)
	200–400 °C (Zone A)	250–600 °C (Zone E)
	400–500 °C (Zone B)	-
	500–600 °C (Zone C)	-
Pyrolysis char at 700 °C	45.5 wt.%	31.4 wt.%

at $200\text{--}600\text{ °C}$. The different thermal decomposition properties, including the decomposition temperature range and amount of solid residue at the final temperature, were derived from differences in the chemical structure and the processes. The P lignin, which has poor thermal stability, started to decompose at a lower temperature than the H lignin due to the different process conditions of fast pyrolysis and supercritical water hydrolysis. Lin *et al.* (Lin *et al.*, 2015) reported on the pyrolysis of lignin obtained from different isolation processes such as milled Amur linden wood lignin (MWL), enzymatic hydrolysis corn stover lignin (EHL), wheat straw Alkali lignin (AL), and wheat straw

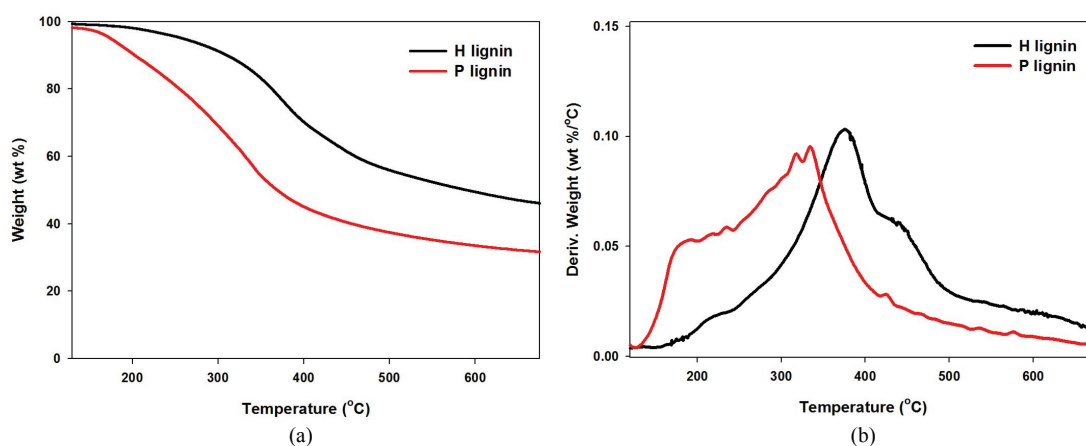


Fig. 2. (a) TG and (b) DTG curves of H lignin and P lignin.

Sulfonate lignin (SL). The four kinds of lignin produced different DTG curves including the maximum decomposition temperature and rate as a result of the different structures and compositions caused by the different isolation processes. Wang *et al.* (Wang *et al.*, 2014) reported on the pyrolysis behavior of pyrolytic lignin and milled wood lignin. Compared to milled wood lignin, pyrolytic lignin decomposed at a lower temperature due to its poor thermal stability, while its char yield was lower at the final temperature. In the DTG curves for the lignins, the distinct weight loss stages obtained by dividing the decomposition temperature range of 120–600 °C are listed in Table 3. From these decomposition stages, multi-shot non-isothermal pyrolysis-GC/MS were used to understand formation of pyrolysis product in respect stages.

3.3. Non-isothermal pyrolysis of lignins

Fig. 3 shows the chromatograms of lignin pyrolysis for each temperature range, based upon a distinct weight loss in thermogravimetry analysis: 200–400 °C (Zone A), 400–500 °C (Zone B), and 500–600 °C (Zone C) for H lignin and 120–250 °C (Zone D), and 250–600 °C (Zone E) for P lignin. Fig. 3 (a), H lignin chromatograms, shows 24 representative pyrolysis peaks. The major large pyrolysis product peaks were dimethoxy phenol, hydroxy-methoxybenzoic acid, and methoxy-methyl phenol in Zone A; methoxy benzenediol, methoxy phenol, and dimethoxy phenol in Zone B; and phenol, methyl phenol, and toluene in Zone C. For the P lignin, 21 predominant pyrolysis peaks are presented in Fig. 3 (b). In this case, dimethoxy propenyl phenol, methoxy prophenyl phenol, and hydroxy dimethoxy benzaldehyde were the main pyrolysis products in Zone D, while those in Zone E were hydroxy methoxy benzoic acid, dimethoxy phenol, and methoxy benzenediol. The main pyrolysis peaks of the H lignin and P lignin are listed in Table 4. The identified peaks

were categorized into eight groups, namely, acids, ketones, furans, p-hydroxyphenyl type (H-unit), guaiacyl type (G-unit), syringyl type (S-unit), Catechol, and aromatic hydrocarbons (benzene, toluene, naphthalene). The peak areas and peak area % are listed in Table 5. Both the H lignin and P lignin started to decompose at 120 °C. In the case of the P lignin, the pyrolysis products were produced in the first temperature zone (120–250 °C) while for the H lignin, moisture volatilization occurred at 120–200 °C and pyrolysis products began to be produced at 200 °C. The P lignin decomposed and produced pyrolysis products at a lower temperature than the H lignin. This result was consistent with the results of the thermogravimetry analysis. Wang *et al.* (Wang *et al.*, 2014) reported similar results in that the pyrolytic lignin obtained from lauan pyrolysis oil decomposed at a lower temperature than milled-wood lignin isolated from the same lauan. This was caused by the pyrolytic lignin being more sensitive to temperature than the milled-wood lignin. Chang *et al.* (Chang *et al.*, 2011) also compared pyrolytic lignin with Alkali lignin. Compared to Alkali lignin, pyrolytic lignin decomposed at a lower temperature due to its lower thermal stability.

The major pyrolysis products of H lignin in Zone A were G and S units and a small amount of acids and catechol were also obtained (Table 5). In Zone B for the H lignin, relatively small amounts of acids, H unit, G unit, S unit, and catechol were produced, while a few H unit and aromatic hydrocarbons were obtained in Zone C for the H lignin. In the case of the P lignin, both Zones D and E exhibited similar pyrolysis product trends in that G and S units were mainly produced, while acids, ketones, furans, H unit, catechol, and aromatic hydrocarbons were produced in relatively small amounts. The major pyrolysis products, G and S units, were produced at 200–400 °C for H lignin, and at 120–600 °C for P lignin. Although the P lignin decomposed at a lower temperature, the

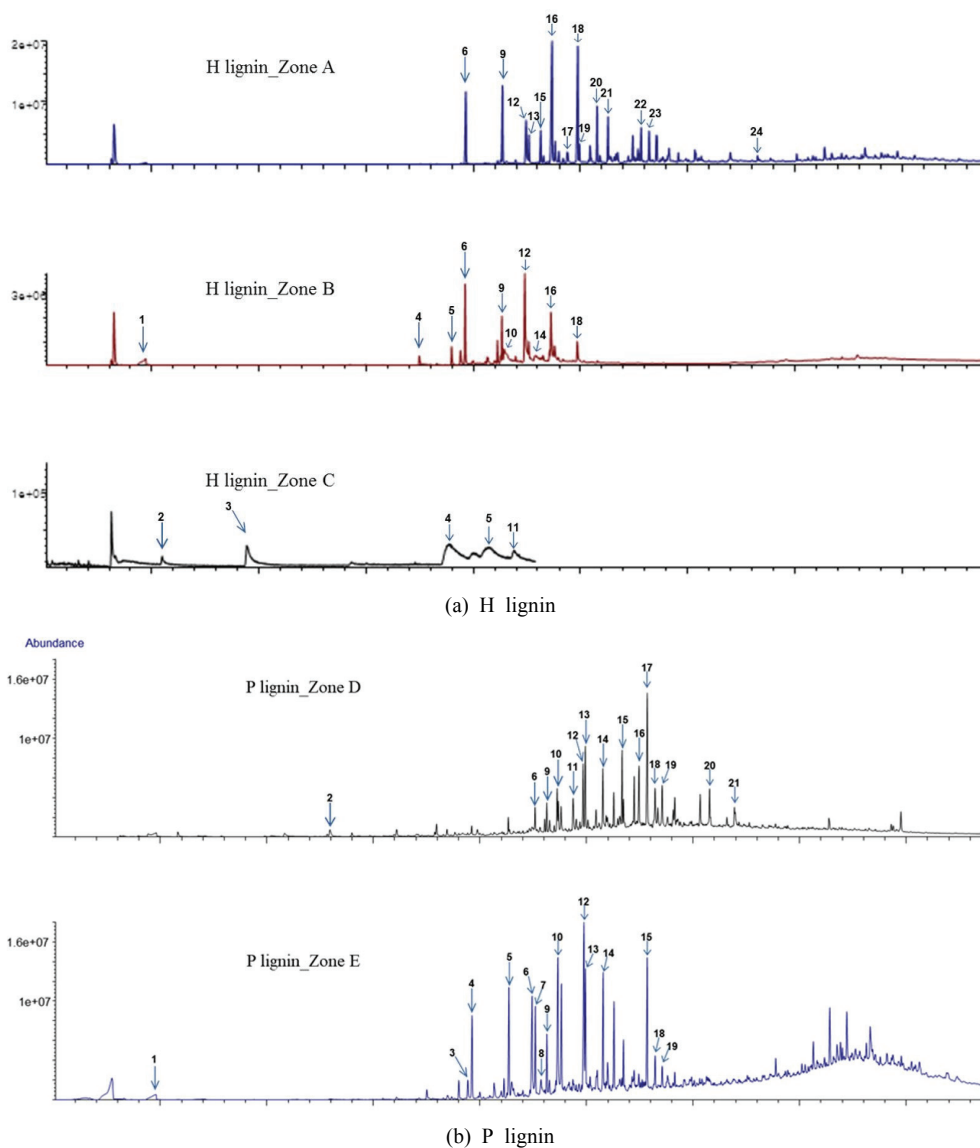


Fig. 3. Chromatograms of non-isothermal pyrolysis of lignins.

pyrolysis products were obtained over a wide temperature range of 120–600 °C. In the case of the H lignin, which started to decompose at 200 °C, the decomposition reaction almost ended in Zone A (200–400 °C). The minor pyrolysis products included ketones and furans that were obtained as a result of the non-isothermal pyrolysis of P lignin. Typically, ketones

and furans were produced from the pyrolysis of carbohydrates such as xylan (Lv and Wu, 2012). This result implies that the P lignin obtained from *Quercus mongolica* pyrolysis bio-oil contained some hemicellulose pyrolysis compounds such as ketones and furans as shown in FT-IR result (Fig. 1). Fortin *et al.* (Fortin *et al.*, 2015) investigated the structural properties

Table 4. Pyrolysis products of H lignin and P lignin (H: p-hydroxyphenyl type, G: guaiacyl type, S: syringyl type, C: catechol)

Peak no.	H lignin		P lignin	
	R.T.	Compounds	R.T.	Compounds
1	4.8	Acetic acid	4.8	Acetic acid
2	5.4	Benzene	12.9	Furfural
3	9.4	Toluene	19	Phenol, -methyl- (H)
4	18.8	Phenol (H)	19.6	Phenol, -methoxy- (G)
5	19	Phenol, -methyl- (H)	21.3	Phenol, -methoxy-methyl- (G)
6	19.6	Phenol, -methoxy- (G)	22.4	Benzenediol, -methoxy- (C)
7	20.6	Phenol, -dimethyl- (H)	22.6	Phenol, -ethyl-methoxy- (G)
8	21.1	Phenol, -methoxy-methyl- (G)	22.9	Benzenediol, -methyl- (C)
9	21.3	Phenol, -methoxy-methyl- (G)	23.2	Methoxy-vinylphenol (G)
10	21.5	Benzenediol (C)	23.8	Phenol, -dimethoxy- (S)
11	21.9	Naphthalene	24.3	Phenol, -methoxy-(propenyl)- (G)
12	22.4	Benzenediol, -methoxy- (C)	24.8	Benzoic acid, -hydroxy-methoxy- (G)
13	22.6	Phenol, -ethyl-methoxy- (G)	25	Phenol, -methoxy-(propenyl)- (G)
14	22.9	Benzenediol, -methyl- (C)	25.8	Benzene, -trimethoxy-methyl-
15	23.2	Methoxy-vinylphenol (G)	26.6	Phenol, -dimethoxy-(propenyl)- (S)
16	23.8	Phenol, -dimethoxy- (S)	27.4	Benzaldehyde, -hydroxy-dimethoxy- (S)
17	24.8	Benzaldehyde, -hydroxy-methoxy- (G)	27.8	Phenol, -dimethoxy-(propenyl)- (S)
18	24.9	Hydroxy-methoxybenzoic acid (G)	28.2	Ethanone, -(hydroxy-dimethoxyphenyl)- (S)
19	25	Phenol, -methoxy-(propenyl)- (G)	28.6	Butanone, -(trihydroxy-methylphenyl)- (S)
20	25.8	Ethanone, -(dihydroxy-methoxyphenyl)- (G)	30.3	Hexadecanoic acid
21	26.3	Methyl-dimethoxybenzaldehyde (S)	30.8	Dimethoxy-hydroxycinnamaldehyde (S)
22	26.6	Phenol, -dimethoxy-(propenyl)- (S)	31.9	Octadecadienoic acid
23	28.2	Ethanone, -(hydroxy-dimethoxyphenyl)- (S)		
24	31.9	Octadecenoic acid		

Table 5. Product distribution of non-isothermal pyrolysis of lignins

Peak area(counts x10 ⁻⁶) [Peak area %]	H lignin			P lignin	
	Zone A 200–400 °C	Zone B 400–500 °C	Zone C 500–600 °C	Zone D 120–250 °C	Zone E 250–600 °C
Acids	16.58 [2.95]	3.55 [4.65]	-	19.56 [5.46]	8.92 [1.43]
Ketones	-	-	-	7.8 [2.18]	4.04 [0.65]
Furans	-	-	-	4.36 [1.22]	-
P-hydroxyphenyl type (H-unit)	-	7.42 [9.73]	1.20 [49.93]	1.36 [0.38]	18.58 [2.99]
Guaiacyl type (G-unit)	197.43 [35.17]	18.87 [24.74]	-	79.52 [22.21]	183.91 [29.58]
Syringyl type (S-unit)	168.67 [30.05]	9.59 [12.57]	-	142.67 [39.85]	171.15 [27.52]
Catechol	30.25 [5.39]	23.26 [30.48]	-	-	47.46 [7.63]
Aromatic hydrocarbons	-	-	0.62 [30.49]	2.56 [0.71]	-

Table 6. Product distribution of isothermal pyrolysis of lignins

Peak area(counts × 10 ⁻⁶) [Peak area %]	H lignin			P lignin		
	400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
Acids	17.34 [3.04]	22.66 [3.42]	14.24 [3.22]	17.17 [2.32]	17.05 [1.99]	14.63 [2.42]
Ketones	-	-	-	-	-	1.25 [0.21]
Furans	-	-	-	8.87 [1.2]	11.62 [1.36]	10.61 [1.76]
P-hydroxyphenyl type (H-unit)	-	7.99 [1.21]	10.82 [2.45]	4.42 [0.6]	11.79 [1.38]	13.83 [2.29]
Guaiacyl type (G-unit)	170.90 [29.96]	191.11 [28.82]	119.34 [26.97]	191.29 [25.82]	223.00 [26.03]	159.21 [26.35]
Syringyl type (S-unit)	135.50 [23.76]	149.06 [22.48]	102.11 [23.08]	112.93 [15.24]	130.42 [15.22]	92.38 [15.29]
Catechol	36.45 [6.39]	43.77 [6.6]	34.53 [7.81]	21.66 [2.92]	24.59 [2.87]	18.00 [2.98]
Aromatic hydrocarbons	-	1.53 [0.23]	4.35 [0.98]	-	1.23 [0.14]	4.01 [0.66]

of the pyrolytic lignins obtained from switchgrass fast pyrolysis oil. They reported that the hemicellulose xylan backbone remained intact and connected to the lignin through ferulate ester linkages.

3.4. Isothermal pyrolysis of lignins

The isothermal pyrolysis of lignins obtained from supercritical water hydrolysis and fast pyrolysis processes was carried out to investigate the distribution of pyrolysis products such as phenolics and aromatic hydrocarbons at different pyrolysis reaction temperatures (400, 500, and 600 °C). Table 6 lists the MS peak areas and peak area % for the isothermal pyrolysis of H and P lignin. The phenolics were divided into p-hydroxyphenyl type (H-unit), guaiacyl type (G-unit), syringyl type (S-unit), and catechol. Among them, guaiacyl and syringyl types, especially hydroxy-methoxy benzoic acid and dimethoxy phenol, were the major pyrolysis products for both lignins. The guaiacyl and syringyl types were produced in large amounts at

500 °C while the guaiacyl type were the predominant compound group. As minor pyrolysis products, p-hydroxyphenyl type, catechol, and aromatic hydrocarbons were also obtained. The amounts of p-hydroxyphenyl type and aromatic hydrocarbons produced increased with the pyrolysis reaction temperature for both lignins. P-hydroxyphenyl type was newly detected at 500 °C in the H lignin, while the aromatic hydrocarbons were newly produced at 500 °C for both lignins. This is because the guaiacyl and syringyl types were converted to p-hydroxyphenyl type, while further reaction led to the production of aromatic hydrocarbons via cracking reactions such as demethoxylation, dealkylation, and dehydroxylation. Kim *et al.* (Kim *et al.*, 2016) reported on the lignin decomposition mechanism after studying the pyrolysis of *pinus radiata*. They suggested reaction pathways in which p-hydroxyphenyl type were produced by the demethoxylation and dealkylation reactions of the guaiacyl and syringyl types, with aromatic hydrocarbons being produced from the dehydroxylation of p-hydroxyphenyl type. The

production of the p-hydroxyphenyl type and aromatic hydrocarbons was enhanced as the reaction temperature increased. Shen *et al.* (Shen *et al.*, 2015) reported similar results for the thermochemical conversion of maple, rice straw, and rice husk lignins. The pyrolysis of the three lignin samples mainly produced guaiacyl and syringyl types, while the formation of p-hydroxyphenyl type and aromatic hydrocarbons was promoted as the temperature increased, due to the enhancement of the demethoxylation and dehydroxylation reactions.

4. CONCLUSION

A comparison of the lignins recovered from the *Quercus mongolica* biorefinery processes was conducted to determine the pyrolysis properties such as the molecular weight, thermal decomposition behavior and pyrolysis product distribution. P lignin had lower molecular weight than H lignin and is partly composed of hemicellulose component. The H lignin and P lignin exhibited different thermal decomposition behaviors in that the P lignin began to decompose and produce pyrolysis products at a lower temperature than the H lignin due to its lower thermal stability. The P lignin produced not only phenolics but also ketones and furans, given that it has a hemicellulose component. Both the H lignin and P lignin produced guaiacyl and syringyl types as major products as well as relatively small amounts of p-hydroxyphenyl type, catechols, and aromatic hydrocarbons. The production of p-hydroxyphenyl type and aromatic hydrocarbons could be promoted by increasing the temperature, as this enhanced the demethoxylation and dehydroxylation reactions.

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REFERENCES

- Amen-Chen, C., Pakdel, H., Roy, C. 2001. Production of monomeric phenols by thermochemical conversion of biomass: a review. *Bioresource Technology* 79: 277-299.
- Burhenne, L., Messmer, J., Aicher, T., Laborie, M.P. 2013. The effect of the biomass components lignin, cellulose and hemicellulose on TGA and fixed bed pyrolysis. *Journal of Analytical and Applied Pyrolysis* 101: 177-184.
- Chang, S., Zhao, Z., Zheng, A., Zhang, W., Li, H. 2011. Properties of pyrolytic lignin from bio-oil. *Transactions of the Chinese Society of Agricultural Machinery* 42: 99-105.
- Chu, S., Subrahmanyam, A.V., Huber, G.W. 2013. The pyrolysis chemistry of a B-O-4 type oligomeric lignin model compound. *Green Chemistry* 15: 125-136.
- Collard, F., Blin, J. 2014. A review on pyrolysis of biomass constituents: mechanisms and composition of the products obtained from the conversion of cellulose, hemicellulose and lignin. *Renewable and Sustainable Energy Reviews* 38: 594-608.
- Dabros, T.M.H., Stummann, M.Z., Hoj, M., Jensen, P.A., Grunwaldt, J.D., Gabrielsen, J., Mortensen, P.M., Jensen, A.D. 2018. Transportation fuels from biomass fast pyrolysis, catalytic hydrodeoxygenation, and catalytic fast hydrolysis, *Progress in Energy and Combustion Science* 68: 268-308.
- De Wild, P.J., Huijgen, W.J.J., Gosselink, R.J.A. 2014. Lignin pyrolysis for profitable lignocellulosic biorefineries. *Biofuels, Bioproducts and Biorefining* 8: 645-657.
- Drage, T.C., Vane, C.H., Abbott, G.D. 2002. The closed system pyrolysis of B-O-4 lignin substructure model compounds. *Organic Geochemistry* 33: 1523-1531.
- Fortin, M., Beromi, M.M., Lai, A., Tarves, P.C., Mullen,

- C.A., Boateng, A.A., West, N.M. 2015. Structural analysis of pyrolytic lignins isolated from Switch-grass fast-pyrolysis oil. *Energy and Fuels* 29: 8017-8026.
- Gong, S.H., Ahn, B.J., Lee, S.M., Lee, J.J., Lee, Y.K., Lee, J.W. 2016. Thermal degradation behavior of biomass depending on torrefaction temperatures and heating rates. *Journal of the Korean Wood Science and Technology* 44(5): 685-694.
- Hwang, H., Choi, J.W. 2018. Preparation of nanoporous activated carbon with sulfuric acid lignin and its application as a biosorbent. *Journal of the Korean Wood Science and Technology* 46(1): 17- 28.
- Hwang, H., Oh, S., Kim, J.Y., Lee, S., Cho, T., Choi, J.W. 2012. Effect of particle size and moisture content of woody biomass on the feature of pyrolytic products. *Journal of the Korean Wood Science and Technology* 40(6): 445-453.
- Jang, S.K., Kim, J.H., Jeong, H., Choi, J.H., Lee, S.M., Choi, I.G. 2018. Investigation of conditions for dilute acid pretreatment for improving xylose solubilization and glucose production by supercritical water hydrolysis from *Quercus mongolica*. *Renewable Energy* 117: 150-156.
- Jeong, H., Park, Y.C., Seong, Y.J., Lee, S.M. 2017. Sugar and ethanol production from woody biomass via supercritical water hydrolysis in a continuous pilot-scale system using acid catalyst. *Bioresource Technology* 245: 351-357.
- Kang, A., Lee, T.S. 2015. Converting sugars to biofuels: ethanol and beyond. *Bioengineering* 2: 184-203.
- Kawamoto, H. 2017. Lignin pyrolysis reaction. *Journal of Wood Science* 63: 117-132.
- Kim, J.Y., Heo, S., Park, S.Y., Choi, I.G., Choi, J.W. 2017. Selective production of monomeric phenols from lignin via two-step catalytic cracking process. *Journal of the Korean Wood Science and Technology* 45(3): 278-287.
- Kim, J.Y., Kim, T.S., Hwang, H., Oh, S., Choi, J.W. 2012. Chemical structural characterization of lignin extracted from pitch pine with ionic liquid (1-ethyl-3-methylimidazolium acetate). *Journal of the Korean Wood Science and Technology* 40(3): 194-203.
- Kim, J.Y., Oh, S., Hwang, H., Moon, Y., Choi, J.W. 2013. Evaluation of primary thermal degradation feature of *M. Sacchariflorus* after removing inorganic compounds using distilled water. *Journal of the Korean Wood Science and Technology* 41(4): 276-286.
- Kim, K.H., Moon, S.J., Kim, T.S., Lee, S.M., Yeo, H., Choi, I.G., Choi, J.W. 2011. Characterization of pyrolytic lignin in biooil produced with yellow poplar (*Liriodendron tulipifera*). *Journal of the Korean Wood Science and Technology* 39(1): 86-94.
- Kim, Y.M., Jae, J., Myung, S., Sung, B.H., Dong, J.I., Park, Y.K. 2016. Investigation into the lignin decomposition mechanism by analysis of the pyrolysis product of *Pinus radiata*. *Bioresource Technology* 219: 371-377.
- Lee, H.W., Kim, Y.M., Jae, J., Sung, B.H., Jung, S.C., Kim, S.C., Park, Y.K. 2016a. Catalytic pyrolysis of lignin using a two-stage fixed bed reactor comprised of in-situ natural zeolite and ex-situ HZSM-5. *Journal of Analytical and Applied Pyrolysis* 122: 282-288.
- Lee, J.H., Moon, J.G., Choi, I.G., Choi J.W. 2016b. Study on the thermochemical degradation features of empty fruit bunch on the function of pyrolysis temperature. *Journal of the Korean Wood Science and Technology* 44(3): 350-359.
- Lin, X., Sui, S., Tan, S., Pittman Jr, C.U., Sun, J., Zhang, Z. 2015. Fast pyrolysis of four lignins from different isolation processes using Py-GC/MS. *Energies* 8: 5107-5121.
- Lv, G., Wu, S. 2012. Analytical pyrolysis studies of corn stalk and its three main components by TG-

- MS and Py-GC/MS. *Journal of Analytical and Applied Pyrolysis* 97: 11-18.
- Min, C.H., Um, B.H. 2017. Effect of process parameters and kraft lignin additive on the mechanical properties of miscanthus pellets. *Journal of the Korean Wood Science and Technology* 45(6): 703-719.
- Moon, J., Lee, J.H., Hwang, H., Choi, I.G., Choi, J.W. 2016. Effect of inorganic constituents existing in Empty Fruit Bunch (EFB) on features of pyrolysis products. *Journal of the Korean Wood Science and Technology* 44(5): 629-638.
- Mu, W., Ben, H., Ragauskas, A., Deng, Y. 2013. Lignin pyrolysis components and upgrading-technology review. *Bioenergy Research* 6: 1183-1204.
- Ryu, G.H., Jeong, H.S., Jang, S.K., Hong, C.Y., Choi, J.W., Choi, I.G. 2016. Investigation of furfural yields of liquid hydrolyzate during dilute acid pretreatment process on quercus mongolica using response surface methodology. *Journal of the Korean Wood Science and Technology* 44(1): 85-95.
- Scholze, B., Meier, D. 2001. Characterization of the water-insoluble fraction from pyrolysis oil (pyrolytic lignin). Part 1. Py-GC/MS, FTIR, and functional groups. *Journal of Analytical and Applied Pyrolysis* 60: 41-54.
- Seo, J.H., Jeong, H., Lee, H.W., Choi, C.S., Bae, J.H., Lee, S.M., Kim, Y.S. 2019. Characterization of solvent-fractionated lignins from woody biomass treated via supercritical water oxidation. *Bioresource Technology* 275: 368-374.
- Shen, D., Liu, G., Zhao, J., Xue, J., Guan, S., Xiao, R. 2015. Thermo-chemical conversion of lignin to aromatic compounds: effect of lignin source and reaction temperature. *Journal of Analytical and Applied Pyrolysis* 112: 56-65.
- Wang, S., Wang, K., Liu, Q., Gu, Y., Luo, Z., Cen, K., Fransson, T. 2009. Comparison of the pyrolysis behavior of lignins from different tree species. *Bio-technology Advances* 27: 562-567.
- Wang, S., Lin, H., Ru, B., Sun, W., Wang, Y., Luo, Z. 2014. Comparison of the pyrolysis behavior of pyrolytic lignin and milled wood lignin by using TG-FTIR analysis. *Journal of Analytical and Applied Pyrolysis* 108: 78-85.
- Wang, S., Ru, B., Lin, H., Sun, W., Luo, Z. 2015. Pyrolysis behaviors of four lignin polymers isolated from the same pine wood. *Bioresource Technology* 182: 120-127.
- Zhang, H., Wu, S., Xie, J. 2017. Evaluation of the effects of isolated lignin on enzymatic hydrolysis of cellulose. *Enzyme and Microbial Technology* 101: 44-50.
- Zhang, J., Kim, K.H., Choi, Y.S., Motagamwala, A.H., Dumesic, J.A., Brown, R.C., Shanks, B.H. 2017. Comparison of fast pyrolysis behavior of cornstover lignins isolated by different methods. *ACS Sustainable Chemistry and Engineering* 5: 5657-5661.
- Zhou, S., Garcia-Perez, M., Pecha, B., Kersten, S.R.A., McDonald, A.G., Westerhof, R.J.M. 2013. Effect of the fast pyrolysis temperature on the primary and secondary products of lignin. *Energy and Fuels* 27: 5867-5877.
- Zhou, S., Xue, Y., Sharma, A., Bai, X. 2016. Lignin valorization through thermochemical conversion: comparison of hardwood, softwood and herbaceous lignin. *ACS Sustainable Chemistry and Engineering* 4: 6608-6617.