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Lignin isolation during recycling of waste wood in an urban locale

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ABSTRACT

Waste wood (WW) was used as feed stock in an ethanol organosolv treatment to isolate lignin. The effects of treatment conditions (temperature, concentration of sulfuric acid and reaction time) on lignin yield were investigated using response surface methodology (RSM). Lignin yield was positively influenced by temperature and concentration of sulfuric acid but not by reaction time. The maximum lignin yield (12.46 g/100 g of dry wood with 44.25 % recovery) was achieved at 178.2ºC and 2.32 % H_2SO_4. Gel permeation chromatography showed that the isolated WW-lignin had low molecular weights. From the Fourier-transform infrared spectroscopy and proton nuclear magnetic resonance spectra, WEB-lignin was estimated to have more guaiacyl (G) units than syringyl (S) units, showing high purity. The ethanol organosolv treatment offers the possibility of using isolated WW as an untapped source of lignin.

Keywords: Waste wood; Lignin; Ethanol organosolv; Characterization

1. Introduction

Waste wood is generated in the order of 1.6–2.0 million tons per year in the Republic of Korea. Currently, large amounts of waste wood contaminated by paints, oils, preservatives, halogenated organic chemicals and heavy metals during processing and transport are improperly handled, producing environmental pollution via incineration and landfills. Nevertheless, waste wood, one component of lignocellulosic biomass, can be considered good feedstock, allowing available technologies to yield useful chemicals and fuels. Cellulose isolated from lignocellulosic biomass has been used primarily as raw material for the production of biofuels. Until recently, most lignin in lignocellulosic biomass was simply burned as a waste byproduct [1]. Lignin has several functional groups including aliphatic hydroxyl, carboxyl, and phenol groups which can be applied in various fields yielding products such as emulsifiers, dyes, flooring materials, adhesives, resins, dispersants, paints and fuels [2]. Using these functional groups, lignin can be used as a precursor of carbon fiber, vanilla, phenol, and ethylene [3,4] poly(ethylene terephthalate.

To extract lignin from lignocellulosic biomass, various methods such as acid hydrolysis, alkali hydrolysis and organosolv have been used [5,6]. Organosolv treatment is a chemical process, which fractionates biomass using an organic solvent such as methanol, ethanol, acetone, ethylene glycol or butanol at high temperatures [7,8]. Through several reactions such as hydrolysis of the lignin-hemicellulose bond in the organosolv treatment, cellulose remains as solid pulp and lignin is isolated into liquid fractions, achieving sulfur- free, high purity, high-quality lignin [9,10]. In this study, ethanol organosolv treatment of waste wood was carried out to extract lignin. The organosolv treatment was performed at a fixed concentration of ethanol, while reaction temperature, time of reaction and concentration of sulfuric acid (acid catalyst) were varied. The yield of lignin isolation was designed as the variable to determine the optimum conditions for lignin isolation from waste wood collected from Gwangju and Jeonnam areas. Experimental sets were designed using a rotatable, central composite design (CCD) and modeling for optimization of the variables maximizing

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lignin yield was performed using response surface methodology (RSM). The physiochemical properties of lignin isolated via the organosolv treatment were analyzed using comprehensive methods including elemental analysis, gel permeation chromatography (GPC), Fourier-transform infrared spectroscopy (FT-IR), thermogravimetric analyses (TGA) and proton nuclear magnetic resonance (^{1}H-NMR).

2. Materials and methods

2.1. Characterization of waste wood

Waste wood (WW) was sampled from a waste recycling company in Gwangju. Uncontaminated mixed wood (MW) as control material, was obtained from a sawmill in Gwangju. All samples were air-dried and milled by a disintegrator and then using sieves was separated into particles of 0.15–0.85 mm. The compositions of WW and MW were determined based on the type of analyzed material: (i) ash content (NREL/TP-510-42622); (ii) extractives (NREL/TP-510-42619); (iii) acid soluble and insoluble lignin (T222 Om-02); (iv) monosaccharide (NREL/TP-510-42618). All samples were analyzed in duplicate.

2.2. Ethanol organosolv treatment for extracting lignin

Ethanol organosolv treatment was performed in a 1 L batch reactor with a magnetic stirrer (CHEMRE SYSTEM Inc., Anyang, Republic of Korea). Biomass loading was 10% (30 g in 300 g total mass of the mixture). The treatment was performed by varying concentrations of sulfuric acid, reaction times and temperatures but with a fixed 65% (v/v) concentration of ethanol. After treatment, the mixture was filtered under a vacuum using What man grade 1 filter paper to separate solids (pulp) from the liquid. After washing the pulp with 600 ml of distilled water, the wash water was mixed with the separated liquid to precipitate lignin. The yield and recovery of obtained lignin were calculated by the following equations:

$$\textit{Lignin yield}\left(\frac{g}{100\,g}\textit{of dried wood}\right) = \frac{\textit{Extracted lignin}(g)}{\textit{Dried waste wood}(g)}\times 100 \tag{1}$$

$$\textit{Lignin yield Lignin recovery}(\%) = \frac{\textit{Extracted lignin}(g)}{\textit{Total lignin in dried waste wood}(g)}\times 100 \tag{2}$$

2.3. Experimental design and statistical analysis

Seventeen experimental sets were designed based on a rotatable CCD using three parameters (reaction temperature (150, 170, 190ºC), concentration of sulfuric acid (0.5, 1.25, 2.0 % w/w) and reaction time (40, 60, 80 min)) as independent variables and lignin yield as a dependent variable (Tables 1, 2). Statistical analysis for lignin yield was performed based on the experimental results using RSM. The general second order equation was expressed in Eq. (3)

$$y = \beta_0 + \sum_{i=1}^{n}\beta_i X_i + \sum_{i=1}^{n}\beta_{ii} X_i^2 + \Sigma \sum_{i<j-1}^{n}\beta_{ij} X_i X_j \tag{3}$$

where y is the dependent variable (lignin yield, wt %), β_0, β_i. β_{ii}, β_{ij} are the coefficients of Eq. (3), and X_i and X_j are independent variables.

RSM, analysis of variance (ANOVA), 2-D and 3-D graph creation were performed using Design-Expert (Version 7.0.0, Stat-Ease Inc., Minneapolis).

2.4. Lignin characterization

Elemental analyses of the lignin samples isolated from MW (MW-lignin) and WW (WW-lignin) were performed using a FLASH 2000 series elemental analyzer (Thermo Scientific, MA, US). Average molecular weight distributions of extracted lignin were determined by GPC analysis with an Ultimate 3000 gel permeation chromatography system (Thermo, MA, US) at 1 mL/min flow rate and 40ºC column temperature. The FT-IR spectra study was carried out in a Nicolet 6700 FT-IR spectrophotometer (Thermo, MA, US). The lignin samples were recorded with a resolution of 2 cm^{-1} in the region of 4000–400 cm^{-1}. The thermal properties of the lignin samples were determined by a Discovery TGA analyzer (TA Instruments, DE, US) making scans of temperatures from 25 to 800ºC with a heating rate of 10ºC/min. ^{1}H-NMR spectra were recorded using a AVANCE 600 MHz High Resolution NMR Spectrometer (Bruker, MA, US) with 128 scans and an acquisition time of 1.36 s. The chemical shifts of the ^{1}H-NMR spectrum were calibrated with reference to DMSO-d$_6$ at 2.49 ppm. All analyses were performed in duplicate.

Table 1
Levels of independent variables

Level		Independent variables		
		(X1) Temperature (ºC)	(X2) Concentration of sulfuric acid in mixture (% w/w)	(X3) Reaction time (min)
+ Alpha	+1.68179	203.6	2.5	93.64
Max	+1	190	2.0	80
Central level	0	170	1.25	60
Min	-1	150	0.5	40
– Alpha	-1.68179	136.4	0	26.36

Table 2
Experimental sets with three independent variables and results of lignin yield

Standard order	(X1) Temperature (°C)		(X2) Concentration of sulfuric acid in mixture (% w/w)		(X3) Reaction time (min)		(y) Lignin yield, % of dry wood	
	Coded value	Real value	Coded value	Real value	Coded value	Real value	Actual value	Predicted value
1	–1	150	–1	0.5	–1	40	1.117	3.364
2	+1	190	–1	0.5	–1	40	5.002	5.040
3	–1	150	+1	2	–1	40	9.499	10.159
4	+1	190	+1	2	–1	40	11.974	11.836
5	–1	150	–1	0.5	+1	80	2.127	3.364
6	+1	190	–1	0.5	+1	80	6.083	5.040
7	–1	150	+1	2	+1	80	9.185	10.159
8	+1	190	+1	2	+1	80	11.696	11.836
9	–1.68179	136.4	0	1.25	0	60	8.1745	5.634
10	+1.68179	203.6	0	1.25	0	60	7.355	8.451
11	0	170	–1.68179	0	0	60	1.8305	0.956
12	0	170	+1.68179	2.5	0	60	12.758	12.282
13	0	170	0	1.25	–1.68179	26.36	8.112	9.527
14	0	170	0	1.25	+1.68179	93.64	10.398	9.527
15	0	170	0	1.25	0	60	8.296	9.527
16	0	170	0	1.25	0	60	10.527	9.527
17	0	170	0	1.25	0	60	12.371	9.527

3. Results and discussion

3.1. Raw feedstock characterization

The main constituents of WW were ash (17.7%), total lignin (acid soluble and insoluble lignin, 28.16%) and glucose (29.44%) (Table 3). Xylose, mannose, galactose and arabinose represented minor constituents. The ash content (17.7%) of WW was higher than of MW (0.96%), while the glucose content (29.44%) in WW was lower than in MW (40.16%). Compared to other woods [11], WW is comprised of different fractions of ash and glucose. However, the total lignin content (28.16%) of WW was comparable to MW (27.17%) and other similar types of wood (around 32%) (Table 3). Considering its lignin content, the WW is seen as a valuable source of lignin for subsequent organosolv treatment.

3.2. The effects of treatment conditions on lignin yield from WW using organosolv

Based on the experimental results provided in Table 2, the relationship between reaction temperature (X_1), sulfuric acid concentration (X_2), reaction time (X_3) and lignin yield (y) was expressed by quadratic Eq. (4) using Design-Expert. The interaction terms (X_1X_2, X_2X_3, X_3X_1) and reaction times (X_3, X_3^2) were removed by the backward elimination method since they were not statistically significant. The ANOVA of quadratic Eq. (4) yields a p-value of < 0.001 confirming the statistical significance of this model. The probabilities of X_2 ($p < 0.0001$) and X_2^2 ($p < 0.05$) were found to have a significant effect on lignin yield (y).

$$y = -79.89 + 0.91X_1 + 9.8X_2 - 2.54\times10^{-3}X_1^2 - 2.11X_2^2 \tag{4}$$

Therefore, sulfuric acid concentration exhibited the most significant effect on promoting lignin isolation of WW. An increase in acid concentration improved recoveries of lignin in the liquid fraction. Acid treatment can increase solubilization of lignin into the aqueous phase through degradation of the linkage between lignin monomers [12] all v/v. Temperature also influenced lignin isolation, showing lignin yield increased as the process temperature was increased (Fig. 1). However, neither the lowest nor highest reaction times produced optimal lignin yields. The results indicate that temperature and sulfuric acid concentration exert independent, significant effects on lignin yield. The effects of the conditions selected for organosolv treatment on lignin yield from WW in the present study were similar to those of previous studies, which reported data obtained using poplar and lodgepole [13,14].

According to the plots (Fig. 1), the maximum lignin yield at 178.2°C and 2.32% H_2SO_4 was estimated to be 12.46 g/100 g of dry wood, while recovering 44.25% lignin. To validate our model, lignin extraction from WW was conducted under the optimal conditions derived from the 2-D contour graph. The WW-lignin yield was 13.57 ± 1.58 g/100 g of dry wood and recovery was 48.19%. These results revealed that the developed model could closely estimate the actual amounts of lignin extraction from WW by organosolv treatment. Also, for MW (control material) treated under the same conditions, lignin yield was 13.29 ± 0.32 g/100 g of dry wood and MW-lignin recovery was 48.91%. These results from the control material suggest that lignin recovery from WW via organosolv treatment can be comparable to that from other wood biomass, raising the possibility that WW represents an untapped source of lignin.

Table 3
Chemical constituents of WW, MW and other woods

Components (wt % dry basis)	WW	MW	Athel pine [11]	Eucalyptus [11]
Ash	17.70 ± 1.30	0.96 ± 0.10	5.43	2.14
ASLa	1.57 ± 0.03	0.97 ± 0.01	4.45	2.45
AILb	26.59 ± 0.26	26.20 ± 0.14	25.97	32.73
Glucose	29.44 ± 1.98	40.16 ± 0.55	49.34	44.45
Xylose	6.25 ± 0.28	6.34 ± 0.17	11.82	10.53
Mannose	3.41 ± 0.33	7.11 ± 0.08	0.27	0.28
Galactose	0.94 ± 0.003	1.73 ± 0.01	0.46	2.24
Arabinose	0.47 ± 0.0005	0.81 ± 0.01	0.68	0.82

[a]acid soluble lignin; [b]acid insoluble lignin

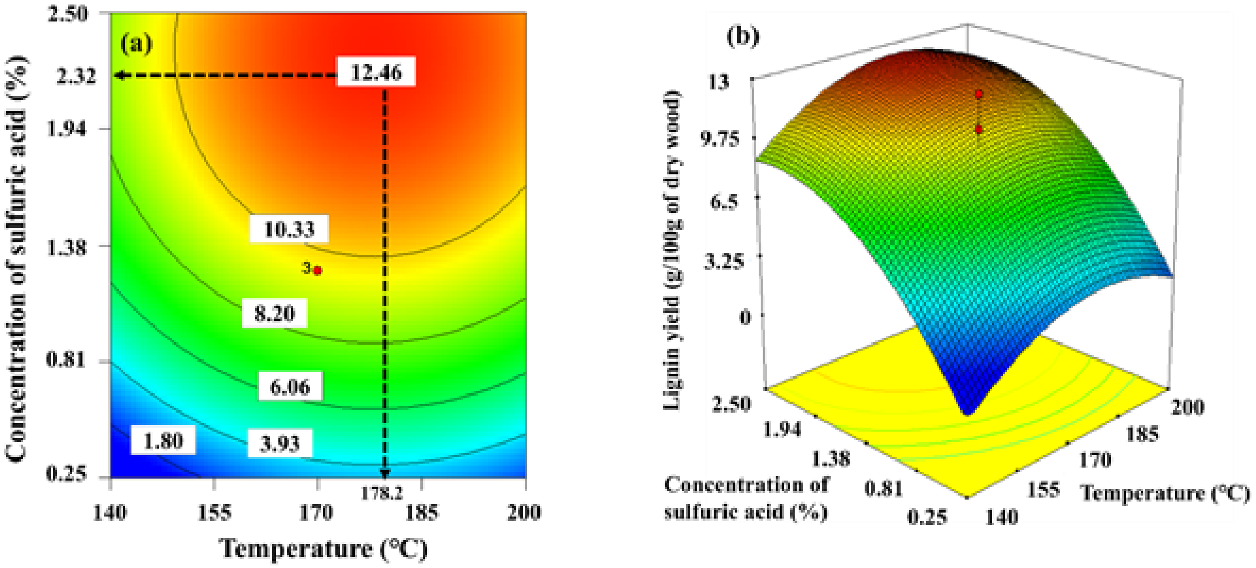

Fig. 1. (a) 2-D contour and (b) 3-D graph describing the effects of concentration of sulfuric acid and temperature on lignin yield from waste wood via organosolv treatment.

3.3. Characterization of isolated lignin

Comparing the elemental composition of the original biomass (WW) and organosolv lignin isolated from it, carbon and oxygen values show successful lignin isolation, reflecting an increase in carbon content from WW to WW-lignin, in addition to a decrease in oxygen content (Table 4). Carbon, hydrogen and oxygen contents and low amounts of contaminated elements (nitrogen and sulfur) confirm clear similarities between lignin samples tested from biomass (WW and MW) and supplied from Sigma-Aldrich. These results demonstrate that high quality lignin can be recovered from WW by organosolv treatment, even comparable to organosolv lignin from different sources [15]. The value of the double bond equivalent (DBE) of WW-lignin might indicate that the structure of lignin monomer comprising WW-lignin contained one or two alkene substituents in the aromatic ring.

Based on TGA analysis used to study how organic polymers decompose (Fig. 2), the weight loss of WW-lignin and MW-lignin at temperatures in the range of 120–230°C was observed with relatively stable thermal degradation of 4.5%, perhaps resulting from degradation of co-precipitated protein and hemicellulose [16]. The results are consistent with a previous report about characterization of lignin by glycerol organosolv treatment of Eucalyptus wood [17]. In our study, maximum degradation temperatures of WW-lignin and MW-lignin were 373°C and 388°C. The maximum decomposition temperature of lignin is often observed at 300–450°C, where cleavage of the β–β and C–C bonds occurs in the lignin polymer [18]. Based on both TGA and the first derivative of the TGA curve (DTG) curves (Fig. 2), the thermal properties of WW-lignin and MW-lignin was almost identical.

The FT-IR spectra of WW-lignin and MW-lignin in Fig. 3 show that the absorbance at 3440 cm^{-1} is assigned to aromatic and aliphatic O-H stretching (Table 5). The peak at 1373 cm^{-1} represents the characteristics of aliphatic C-H stretching. Peaks from 1328 cm^{-1} and 1267 cm^{-1} correspond to C-O stretching of the syringyl (S) and guaiacyl (G) units, respectively (Table 5). A previous study reported that the

Table 4
Elemental composition of WW, MW and organosolv lignin

	C (%)	H (%)	O (%)	N (%)	S (%)	C/O ratio	MMFa	DBEb
WW	42.14	5.86	40.35	2.23	0.18	1.044	$C_6H_{10.01}O_{4.3}$	2.131
WW-lignin	63.86	5.81	25.05	1.47	0.44	2.505	$C_9H_{9.83O}O_{2.70}$	5.173
MW	45.16	6.50	43.45	1.44	–	1.039	$C_6H_{10.37}O_{4.33}$	1.897
MW-lignin	65.08	5.63	23.79	1.12	0.30	2.742	$C_9H_{9.35}O_{2.46}$	5.394
OL[c]	67.20	5.68	26.92	0.20	–	2.50	$C_9H_{9.11}O_{2.69}$	5.455

[a]monomer molecular formula

[b]double bond equivalent; DBE = (2C+2-H+N-S)/2 (C, H, N, S: the number of atoms in the MMF)

[c]organosolv lignin supplied by Sigma Aldrich (Wang et al., 2009)

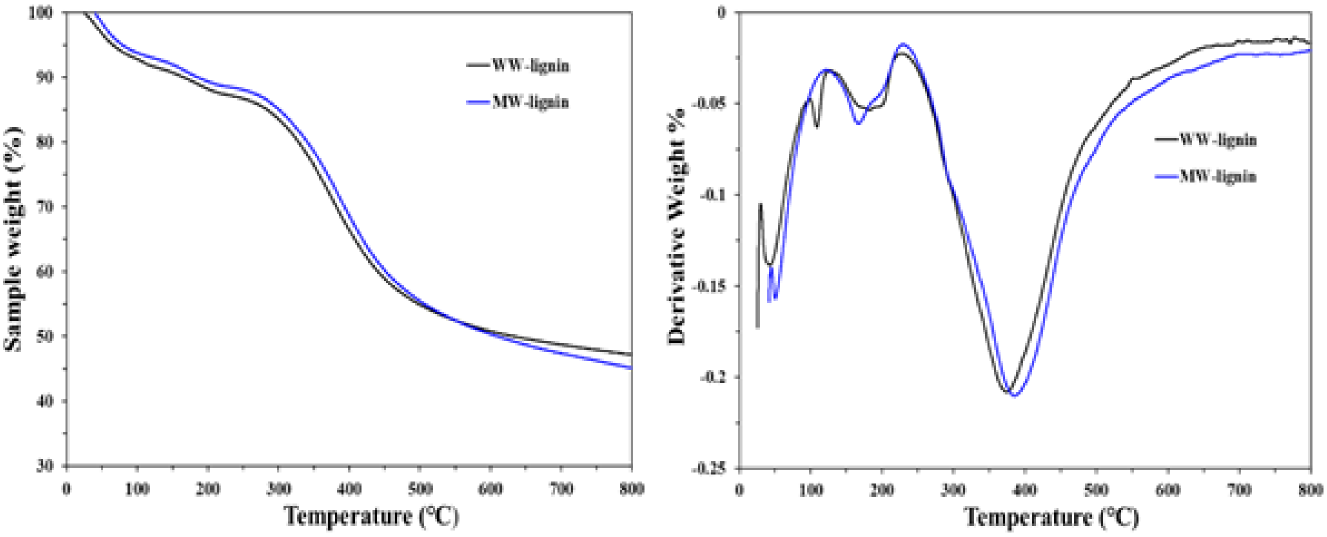

Fig. 2. TGA and DTG curves of WW-lignin and MW-lignin.

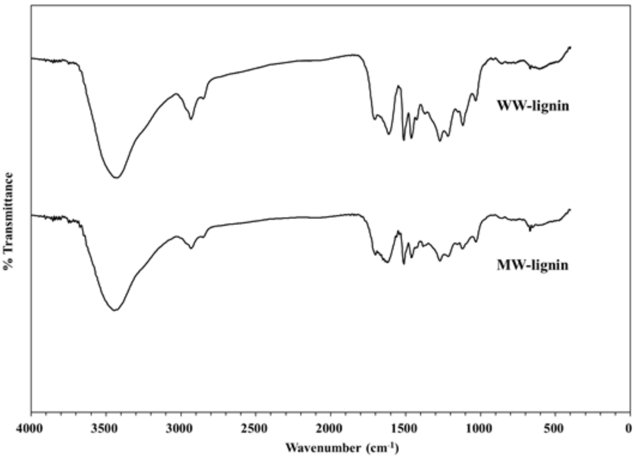

Fig. 3. FT-IR spectra of WW-lignin and MW-lignin.

lignin isolated from softwood has a low content of S units and is mainly composed of G units [19]. In both lignin samples, higher intensity of G units occurred at the peak of 1267 cm^{-1} than S units (peak at 1328 cm^{-1}). It can be estimated that WW and MW used in the present study had a more similar chemical composition of extracted lignin from softwood than hardwood.

The average molecular weight (M_w), average molecular number (M_n) and polydispersity (PDI) of WW-lignin and MW-lignin analyzed by GPC are presented in Table 6. Our results showed lower M_w and PDI than values obtained by lignin isolated from hybrid poplar [20]. The relatively low PDI indicates a high fraction of low M_w possibly forming C-C bonds related to the structures involving C5 in the aromatic ring [21]. Under severe conditions (higher temperatures and higher concentrations of sulfuric acid), the ether linkages in the lignin polymer are well cleaved, resulting in lower M_w and PDI [20]. The WW- and MW-lignin produced under our optimal conditions might result from the acid-catalyzed cleavage of the ether bond by high concentrations of sulfuric acid.

The ^{1}H-NMR spectra of WW- and MW-lignin are shown in Fig. 4. Both spectra were recorded in almost the same form, showing alkyl groups, carbonyl groups (RCO-C$\underline{H}_3$), methoxyl groups (R-O-C$\underline{H}_3$) and aromatic (G, S units) protons in signals at 0.8–1.5 ppm, 2–2.3 ppm, 3.8 ppm and 6.0–8.5 ppm, respectively (Fig. 4). A NMR spectrum of organosolv lignin from Sigma-Aldrich [22] showed band regions similar to WW-lignin at 0.7–1.5 ppm (aliphatic protons), 3.5–4.0 ppm (methoxyl group) and 6.0–8.0 ppm (aromatic

Table 5
Assignment of FT-IR spectra of WW-lignin, organosolv lignin from Sigma-Aldrich(OL-Sigma) and isolated from Miscanthus, respectively

WW-lignin (cm^{-1})	OL-Sigma (cm^{-1}) [24]	Miscanthus (cm^{-1}) [9]	Assignment
3440	3440–3200	3435	Phenolic and aliphatic O–H stretching
2933	2936–2938	2918	C–H stretching in methyl and methylene groups
2850	2842–2849	Exist[a]	C–H stretching in methoxy groups
–	–	1759	Aromatic acetate
–	–	1731	Aliphatic acetate
1705	1701–1703	1709	Unconjugated C=O stretching
–	–	1660	Conjugated C=O stretching
1612	1606–1610	1603	Aromatic skeleton C–C stretching
1512	1515–1516	1508	Aromatic skeleton C–C stretching
1460	1460–1461	1463	Asymmetric C–H deformation of methyl and methylene groups / aromatic ring vibrations
1423	1425–1426	1422	Aromatic skeleton C–C stretching
1373	–	1366	Aliphatic C–H stretching in CH_3
–	1328–1329	1328	C–O stretching of syringyl groups
1267	1270–1271	1267	C–O stretching of guaiacyl groups
–	–	1230	C–O stretching
1213	1216–1219	Exist[a]	Aromatic C–H deformation of guaiacyl groups
1155	–	1162	C–O stretch in ester group
1119	–	1126	Syringyl ring breathing
1032	1031–1034	1033	C–O(H) and C–O(C) stretching of first order aliphatic OH and ether groups
855	–	–	Aromatic C–H out of plane bending (G unit)
–	830–834	833	Aromatic C–H out of plane bending (S unit)

[a] peak existed, but the exact location is not revealed in the literature.

protons) (Fig. 4). This similarity of bands suggests that the WW-, MW-lignin and organosolv lignin from Sigma-Aldrich possess a similar chemical structure, also showing high purity of WW-lignin. Comparing signals of lignin from different biomass [15,21,23], the core of lignin was similar, indicating lignin was successfully isolated from WW.

Table 6
Molecular weight and polydispersity of WW-lignin and MW-lignin

Sample	M_w (g mol^{-1})	M_n (g mol^{-1})	PDI (M_w/M_n)
WW-lignin	983 ± 15	767 ± 12	1.28
MW-lignin	998 ± 61	779 ± 27	1.29

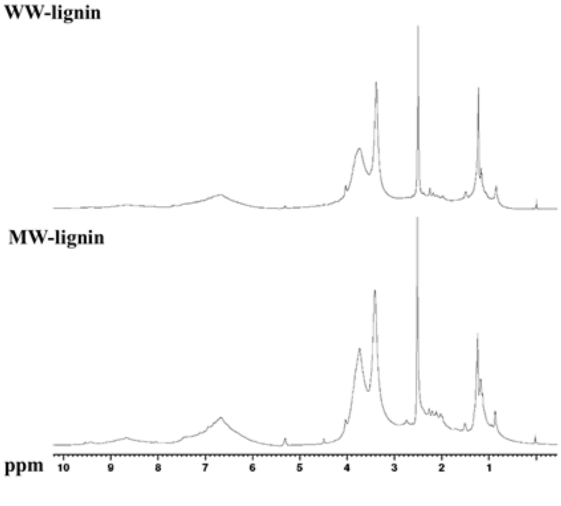

Fig. 4. ^{1}H-NMR spectra of WW-lignin and MW-lignin.

4. Conclusions

Ethanol organosolv treatment of WW was effective for lignin isolation, recovering 44.25 % lignin at 178.2ºC and 2.32 % H_2SO_4. The physiochemical characterization of WW-lignin was performed by elemental analysis, FT-IR, TGA, GPC, and ^{1}H-NMR. In all analyses, the characteristics of WW- and MW-lignin appeared similar. These results support organosolv extraction of lignin with high purity without interference from existing pollutants in WW. This study demonstrates the possibility of using WW for lignin valorization in biorefineries.

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