Oxidative Depolymerizaton of Kraft Lignin and its Application in the Synthesis of Lignin-phenol-formaldehyde Resin

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Kraft lignin (KL) was valorized by introducing phenolic hydroxyl groups and adjusting the molecular weight by oxidative depolymerization. Hydrogen peroxide with copper sulfate as a catalyst was employed in this process. The depolymerized lignin (DL) was characterized with differential ultraviolet spectrum (UV), Fourier transform infrared (FT-IR) spectrometry, gel permeation chromatography (GPC), and heteronuclear single quantum correlation (HSQC) spectra. Both the molecular weight (M_w and M_n) and the polydispersity of the depolymerized lignin decreased compared with default kraft lignin. The content of phenolic hydroxyl groups increased from 1.55 to 2.66 mmol/g. The depolymerized lignin was used in the synthesis of lignin-phenol-formaldehyde (LPF) resin as a substitution of phenol. The physical properties including viscosity, bonding strength, and free formaldehyde content of the adhesive met the GB/T 14704-2006 standard with the substitution of 50% phenol with DL.

Keywords: Kraft lignin; Oxidative depolymerization; Phenolic hydroxyl group; Lignin-phenol-formaldehyde resin

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INTRODUCTION

Due to concerns about the increasing depletion of fossil fuels and serious environmental problems (Long *et al*. 2015), a lot of attention has been brought to the utilization of lignocellulose biomass in the production of valuable materials, chemicals, and energy. The renewable lignocellulose material mainly consists of cellulose, hemicellulose, and lignin. Cellulose and hemicellulose have been used in the paper industry and other biorefinery processes, such as platform chemicals and biofuel preparation. However, there are still many challenges related to the efficient utilization of lignin (Ragauskas *et al*. 2014).

The output of lignin is high, and there are approximately 50 million tons of lignin (mostly Kraft lignin, KL) generated from the paper industry yearly. Most of it is burned to recover the heat energy and chemicals in the recovery plant of pulp mills. Lignin is a kind of amorphous substance randomly built with phenolic blocks of p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units (Erdocia *et al*. 2014), which are linked with ether bonds and carbon-carbon bonds. This natural and renewable multi-phenolic biopolymer can be potentially applied in the sustainable production of many high value-added products (Huang *et al*. 2014; Azadfar *et al*. 2015). As a natural multi-phenolic polymer, lignin has been regarded as a potential alternative of phenol in the production of phenol formaldehyde resins. The global demand of phenol, which is refined from fossil resources, for the production of phenol formaldehyde resin was 3.21 million tons, accounting for 34.8% of its total production in 2013 (Zhu 2015). Therefore, the substitution of phenol with KL to produce lignin-phenol-formaldehyde resin can help to reduce the consumption of fossil resources. However, KL from the paper industry is poorly suited for many down-stream applications because it has a high molecular weight and polydispersity, and it lacks reactivity for the chemical synthesis. Researches have been conducted to change the nature of KL through depolymerization (Dai *et al*. 2016; Servaes *et al*. 2016), phenolation (Naseem *et al*. 2016), demethylation (Gibson *et al*. 2014), catalytic reduction (Huang *et al*. 2014), hydrothermal treatment (Licursi *et al*. 2015), *etc*., to make KL suitable for utilization. While some problems are related to processing cost, the environmental effects and activation of the lignin molecules need to be further considered and overcome. In this study, a catalytic oxidative process was performed for the depolymerization of KL, aiming to introduce more phenolic hydroxyl groups into the lignin structure and lower the molecular weight and its polydispersity. The depolymerized lignin (DL) was characterized with the aid of differential ultraviolet spectra (UV), gel permeation chromatography (GPC), Fourier transform infrared (FT-IR), and heteronuclear single quantum correlation (HSQC) spectra. The depolymerized lignin was used in the synthesis of lignin-phenol-formaldehyde (LPF) resin as a substitution of phenol. The measurements of pH, solid content, viscosity, free formaldehyde, and bonding strength were also performed on the lignin-phenol-formaldehyde (LPF) resin (GB/T 147 32-2006).

EXPERIMENTAL

Materials

The kraft lignin used in this work was isolated from the black liquor of Asia Symbol (Shandong) Paper Mill China with acidic precipitation (Tejado *et al.* 2007). The raw material of the black liquor is mixed wood chips and the pulping conditions for soft wood is 170 °C, 4.5 h, active alkali of 25%, sulphidity of 25%, for hardwood material, 165 °C, 4.5 h, active alkali of 22%, sulphidity of 20%. The ratio of the black liquor from the two pulping process is 6:4.

The sediment was washed with distilled water to a neutral pH and vacuum-dried at room temperature. All the chemicals, sodium hydroxide, hydrogen peroxide, copper sulfate and hydrochloric acid, were analytical-grade and were purchased from Guangfu Chemicals Company (Tianjin, China) and were used without further purification.

Methods

Oxidative depolymerization of kraft lignin

The depolymerization process for the analysis was conducted in a 15-mL reactor lined with Teflon. In a typical process, 0.5 g of KL was dissolved in 5mL of 7 wt.% sodium hydroxide solution, then 0.02 g copper sulfate and 0.04 mL of 5 wt.% hydrogen peroxide solution were added to the solution. Then the reactor was heated in an oil bath at 100 °C for 2.5 h and stirred at 500 rpm. The reaction mixture was centrifuged to separate the char (around 0.01 g) (Toledano *et al*. 2014). The supernatant was acidified with 1 M HCl to pH 2~2.5 to make DL precipitated. DL was isolated by centrifugation and washed with distilled water to a pH 6 to 6.5 before it was vacuum-dried at room temperature for 72 h (Erdocia *et al*. 2014). Figure 1 shows the scheme for the preparation of DL.

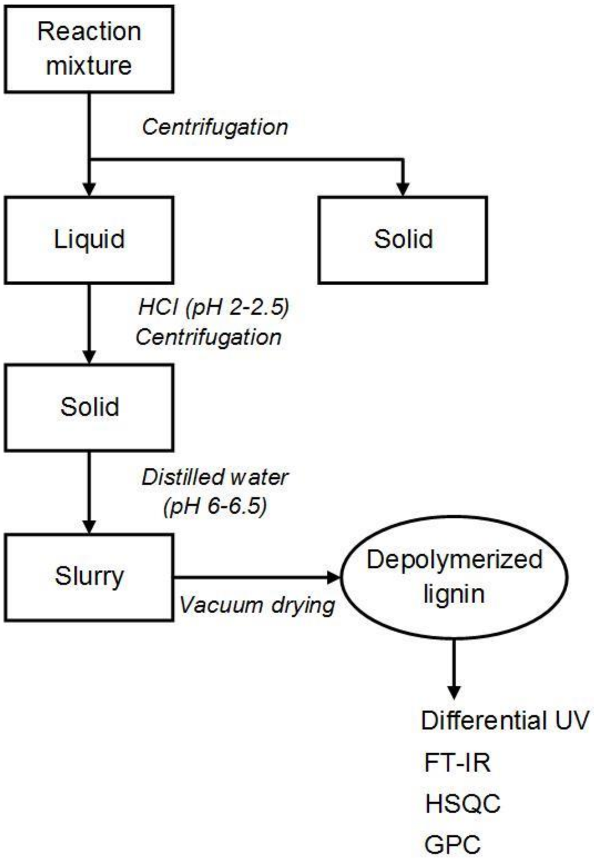

Fig. 1. Scheme for the preparation and characterization of depolymerized lignin

Characterization of kraft lignin and depolymerized lignin

The quantification of phenolic hydroxyl (mmol/g) of KL and DL was performed with a UV spectrophotometer (TU-1901, Puxi, Beijing, China) according to a published method (Wu 1993).

The FT-IR spectra were recorded with KBr discs on a Nicolet 6700 (Thermo Fisher, United States) in the region of 4000 cm^{-1} to 400 cm^{-1} with the ratio of lignin to KBr of 1:100.

The molecular weights (M_w and M_n) were measured with GPC on a Waters 1515 GPC (Waters, Singapore) equipped with the differential refraction detector and Styragel column (HT6E-HT5-HT3, Waters, Singapore) with tetrahydrofuran (THF) as the eluent under the flow rate of 1.0 mL/min. Polystyrene was used as the external standard (Long *et al*. 2015).

HSQC spectra were recorded at 25 °C on a Bruker AVIII 400 MHz (Bruker, Germany) using the z-gradient triple resonance probe. Lignin samples (60 mg) were dissolved in 0.50 mL of DMSO-d6, and spectra were recorded in heteronuclear single quantum correlation (HSQC) spectra. The spectral widths for the HSQC spectra were 5000 Hz and 20000 Hz for the ^1H and ^{13}C dimensions, respectively. The number of collected complex points was 1024 for the ^1H dimension with a recycle delay of 1.5 s. The number of transients was 64, and 256 time increments were recorded in the ^{13}C dimension. Prior to Fourier transformation, the data matrices were zero filled to 1024 points in the ^{13}C dimension (Yang *et al*. 2016).

Synthesis and characterization of lignin-phenol-formaldehyde resin

DL used in the synthesis of lignin-phenol-formaldehyde (LPF) resin was prepared in the same condition as that for analysis in a 500 mL vessel. LPF was synthesized with 50 wt.% substitution of phenol with DL. The total molar ratio of phenolic hydroxyl to formaldehyde was 1:1.8, and NaOH was 15% of the total weight of phenol and DL. In the first step, DL and 1/3 of the total formaldehyde (37 wt.%) and NaOH (8.5 wt.%) were added to a three-neck flask equipped with a mechanical stirrer. Then the flask was heated to 80 °C in an oil bath with a rate of 0.5 °C/min. After staying at 80 °C for 30 min, the mixture was cooled down to 60 °C. In the second step, phenol and another 2/3 part of formaldehyde were added. Then the temperature was raised to 80 °C with a rate of 0.5 °C /min, and maintained at 80 °C for 1.5 h. Next, the mixture was cooled to 40 °C and the lignin-phenol-formaldehyde resin was obtained. For comparison, the LPF from KL was synthesized in the same condition.

Preparation of plywood test sample and characterization of lignin-phenol-formaldehyde resin

The bonding strength of resin was measured according to the Chinese National Standard method (GB/T 147 32-2006). In this work, the poplar wood was employed in the preparation of plywood test samples (200 mm×200 mm× 2 mm) using the LPF resin (from both KL and DL). The middle layer of the plywood was coated with 140 to 160 g/m^2 adhesive on each side. The laminated samples were hot-pressed at 145 °C under 1.0 MPa for 7.0 min. Then the samples for the test were prepared according to the regulations in GB/T 147 32-2006, and the dimensions of the sample are shown as follows. The testing procedure and duplications for the measurement followed the regulation in Chinese National Standard (GB/T 147 32-2006). The detailed process is not presented in the manuscript.

RESULTS AND DISCUSSION

Phenolic Hydroxyl Content

The phenolic hydroxyl content was measured by differential UV according to the methods in published literature (Wu *et al.* 1993; Lupoi *et al.* 2015). The differential UV spectra of KL and DL are shown in Fig. 2. KL and DL showed similar curves within the range from 200 nm to 400 nm. However, it was clear that DL had a higher absorption coefficient ($\Delta\varepsilon$) than KL from 200 nm to 400 nm. The concentration of phenolic hydroxyl in DL and KL were 2.66 mmol/g and 1.55 mmol/g, respectively. Above all, the oxidative depolymerization process could effectively produce new phenolic hydroxyl groups in the lignin structure.

FT-IR Analysis

To better understand structural changes, the KL and DL were characterized by FT-IR spectroscopy, which is illustrated in Fig. 3. All spectra were normalized using the stable aromatic skeletal vibration peak at 1515 cm^{-1} (Popescu *et al.* 2006; Zhuang *et al.* 2012). The assignments of peaks according to literature published and the relative absorbance after normalization are listed in Table 1 (Bauer *et al*. 2012; Ghaffar and Fan 2013).

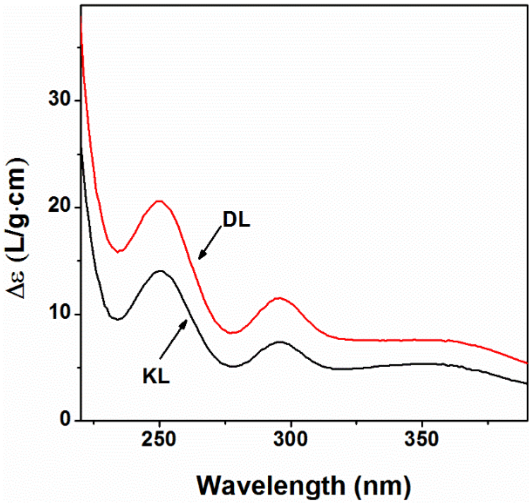

Fig. 2. Differential UV spectra of KL and DL

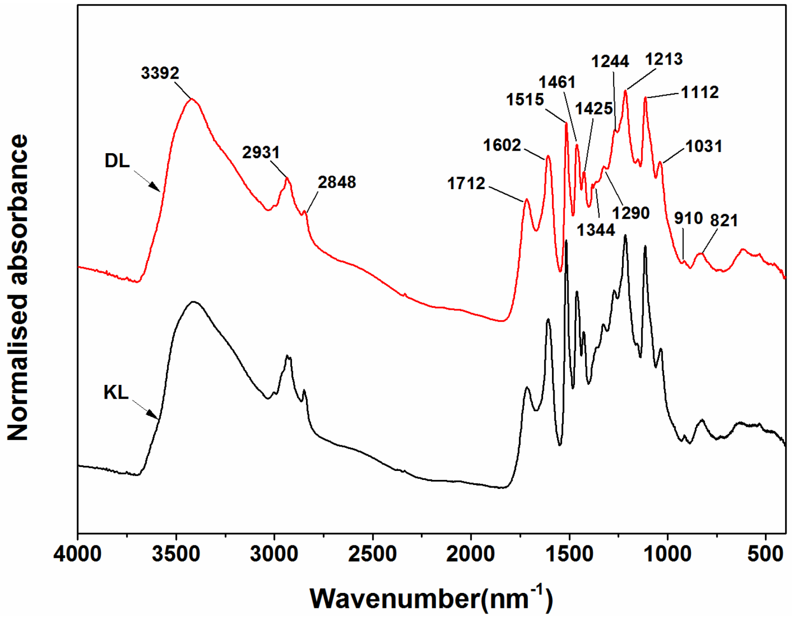

Fig. 3. FT-IR spectra of KL and DL

It can be observed from Fig. 3 that the FT-IR spectra of KL and DL were quite similar. The bands at 1602 cm^{-1} and 1515 cm^{-1} corresponding to the aromatic skeletal vibration that represented fundamental aromatic structure of lignin were similar between KL and DL, which implies that the basic structure of lignin did not change during the depolymerization process (Yang *et al.* 2016). The wide absorption band from 3500 cm^{-1} to 3200 cm^{-1} (around 3392 cm^{-1}) which corresponded to O-H stretching and hydrogen bonding increased obviously. It also can be found from Table 1 that the intensity of the signals for the side chains, such as 2931 cm^{-1} and 2848 cm^{-1} for the asymmetric and symmetrical stretching of CH_3 and CH_2, and 1461 cm^{-1} for the bending of CH_3, were reduced in DL compared with KL, which indicated that the breaking of the side chain occurred to some extent during the depolymerization process (Liu *et al.* 2016). The weakened C-O-C stretching signals at 1112 cm^{-1}, 1031 cm^{-1}, and 910 cm^{-1} suggested that the cleavage of C-O-C after depolymerization treatment. Combined with the analysis of UV spectra, the FT-IR spectra of KL and DL revealed that the original aromatic structure did not change much, and the side chains were broken, with the release of phenolic hydroxyl groups through oxidative depolymerization.

Table 1. Relative Changes of Chemical Structures through FT-IR Analysis

Peaks (cm^{-1})	Assignments	Relative peak intensity of KL	Relative peak intensity of DL
3392	O-H stretching vibration	0.2308	0.5081
2931	C-H stretching vibration of methyl, methylene	0.8078	0.6019
2848	C-H stretching vibration of methyl, methylene	0.7002	0.4904
1602	Aromatic skeletal vibration	0.8827	0.7225
1515	Aromatic skeletal vibration	1	1
1461	C-H bending vibration in CH_3	0.9252	0.8264
1344	C-O stretching vibration of S and condensed G units	0.8076	0.6484
1290	C-O stretching vibration in G units	0.8839	0.7427
1244	C-O stretching vibration in G units	0.9905	0.8323
1213	C-O stretching vibration in G units	0.97323	0.945836
1112	C-O-C stretching vibration	1.0865	0.9746
1031	C-O-C stretching vibration	0.8529	0.6263
910	C-O-C stretching vibration	0.5256	0.3283

HSQC Analysis

To better understand the structural changes of lignin during the oxidative depolymerization treatment, 2D-HSQC NMR was performed, and the results are illustrated in Figs. 4 and 5. The assignments of cross-signals in the HSQC spectra of lignin are listed in Table 2, based on previous literature (Rencoret *et al.* 2008; Wen *et al*. 2013).

In the side-chain region, the cross-signal of methoxy groups (OCH_3, δC; δH 55.7; 3.70) was predominant for both KL and DL. The signal of β-O-4 aryl ether linkages (β-O-4，A) was pretty clear (Fernández-Costas *et al*. 2014). The cross-signal at δC; δH 71.6; 4.83 was assigned to C_α–H_α in β-O-4 substructure with a free OH at γ position. The signal attributed to the C_γ–H_γ in the β-O-4 substructure was distinguished at δC; δH 59.5; 3.69. The correlation signal of the structure of C_α–H_α, C_β–H_β, and C_γ–H_γ could be found at δC; δH 84.9; 4.70, 53.5; 3.05, 71.0; 4.16 to 3.82, respectively. The phenylcoumaran (β-5) substructures were observed (δC; δH 62.3; 3.70) in KL. In the aromatic region, correlated signals from guaiacyl (G) and syringyl (S) lignin units were observed. The S-type lignin unit exhibited a signal at δC; δH 104.0; 6.72 for the $C_{2,6}$-$H_{2,6}$ correlation, and signal that corresponded to the $C_{2,6}$-$H_{2,6}$ correlation in C_α-ketone S unit structure could not be observed at δC; δH 106.3; 7.31. The G unit showed different correlations for C_2-H_2 δC; δH 111.0; 6.99, C_6-H_6 δC; δH 119.0; 6.80. Nevertheless, C_5-H_5 δC; δH 114.0; 6.68 + 6.91 could not be observed from the KL and DL structure. It could be explained that C_5 in G-type was vulnerable to the condensation reaction that resulted in stable C_{aryl}-C_{aryl} linkages.

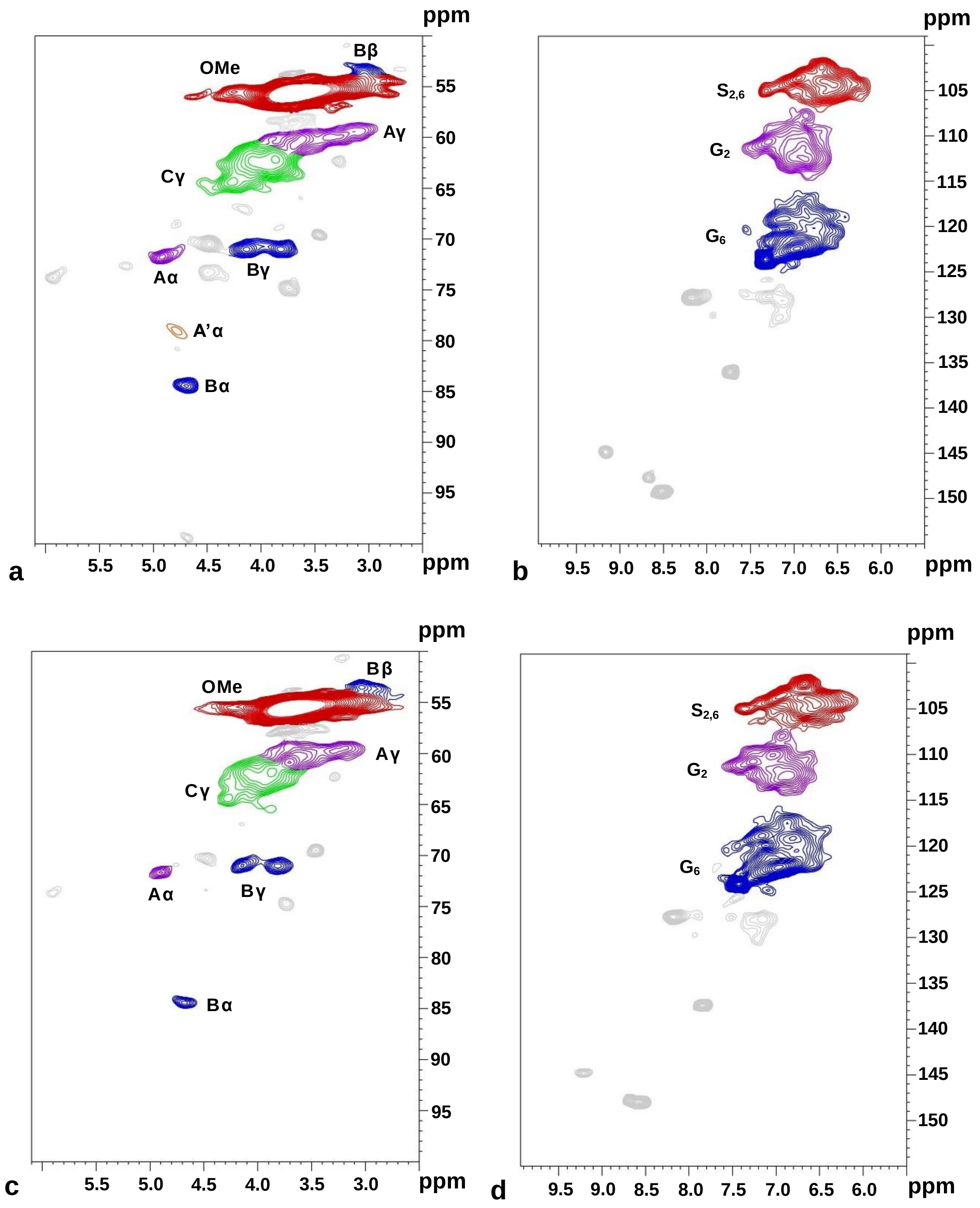

Fig. 4. Side-chain region (a, c) and aromatic regions (b, d) in the HSQC spectra of KL (a, b) and DL (c, d)

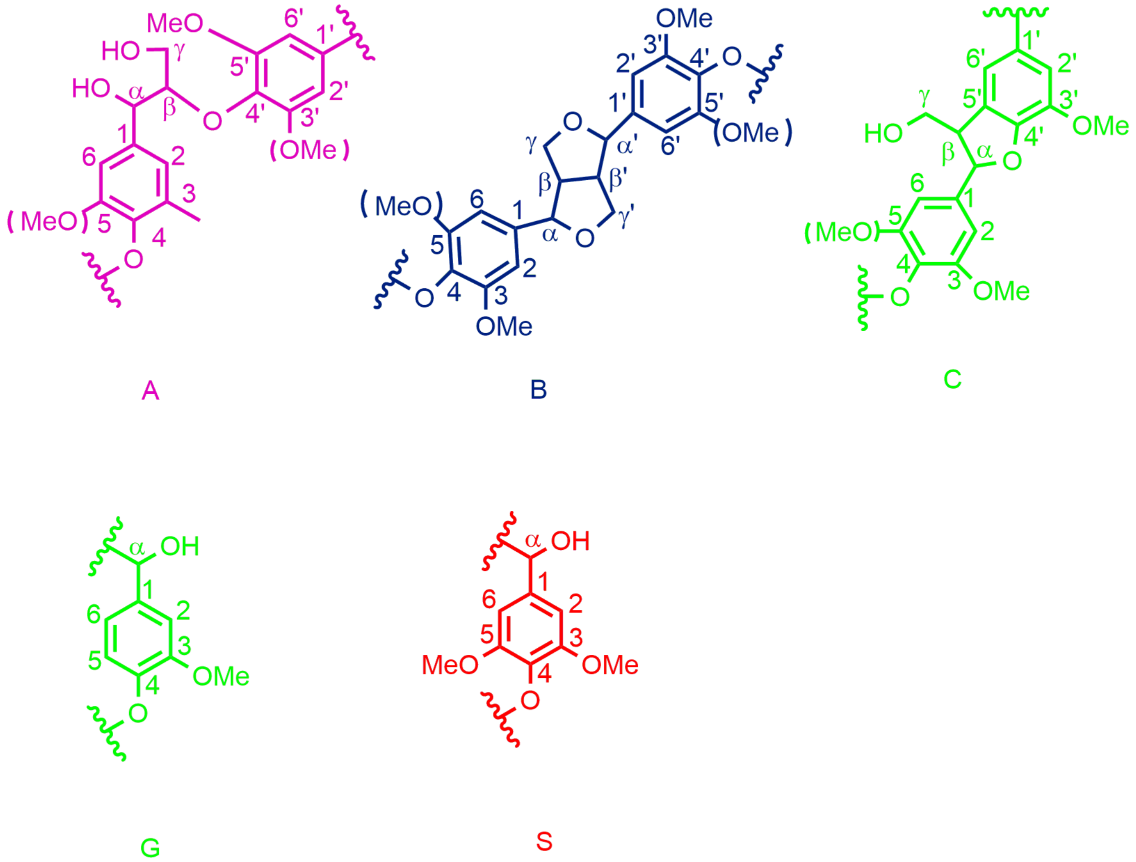

Fig. 5. Main classical substructures involving different side-chain linkages and aromatic units identified by HSQC of DL and KL: (A) β-*O*-4 aryl ether linkages with a free-OH at the γ-carbon; (B) resinol substructures formed by β-β, α-*O*-γ, and γ-*O*-α linkages; (C) phenycoumarane substructures formed by β-5 and α-*O*-4 linkages; (G) guaiacyl units; and (S) syringyl units

Table 2. NMR Assignments of Major Components in the HSQC Spectra of KL and DL

Label	δ_C; δ_H (ppm)	Assignments
B_{β}	53.5; 3.05	$C_{\beta}-H_{\beta}$ in β-β (resinol) substructures (B)
$-OCH_3$	55.7; 3.70	C−H in methoxyls
A_{γ}	59.5; 3.69	$C_{\gamma}-H_{\gamma}$ in β-*O*-4 substructures (A)
C_{γ}	62.3; 3.70	$C_{\gamma}-H_{\gamma}$ in phenylcoumaran substructures (C)
B_{γ}	71.0; 3.79 to 4.16	$C_{\gamma}-H_{\gamma}$ in β-β resinol substructures (B)
A_{α}	71.6; 4.83	$C_{\alpha}-H_{\alpha}$ in β-*O*-4 linked to a S units (A)
B_{α}	84.9; 4.64	$C_{\alpha}-H_{\alpha}$ in β-β resinol substructures (B)
$S_{2,6}$	104.0; 6.72	$C_{2,6}-H_{2,6}$ in syringyl units (S)
G_2	111.0; 6.99	C_2-H_2 in guaiacyl units (G)
G_6	119.8; 6.80	C_6-H_6 in guaiacyl units (G)

Changes of Molecular Weight

The results for molecular weight (M_w, M_n) of KL and DL analyzed using GPC are given in Table 3. It was observed that M_n and Mw decreased from 3458 g/mol and 6748 g/mol of KL to 3191 g/mol and 4314 g/mol of DL, respectively. The results suggested that some of the chemical connections, such as ether bonds in the side chains and other bonds, were vulnerable to the oxidative depolymerization condition and were cleaved. This finding was in agreement with the results from the structure analysis of FT-IR and 2D-HSQC NMR. The polydispersity index (PDI) of molecular weight decreased from 1.95 of KL to 1.30 of DL, indicating that the distribution of the molecular weight became narrow and the heterogeneity of lignin was partly weakened. This result was positive for further application of KL.

Table 3. Molecular Weights (M_w and M_n), Polydispersity Index (PDI = M_w/M_n) and Changes of KL and DL

	M_n (g/mol)	M_w (g/mol)	PDI
KL	3458	6748	1.95
DL	3191	4314	1.30
Changes %	-7.7	-36.1	-33.3

Properties of Lignin-phenol-formaldehyde Resin

The properties of the synthesized lignin-phenol-formaldehyde resin are illustrated in Table 4. It can be seen that when DL accounted for 50% of the total weight of the phenolic substance, the viscosity, bonding strength, and free formaldehyde content of the resin fulfilled the GB/T 14704-2006 standard. The results showed that the DL obtained from the oxidative depolymerization of KL demonstrated a good performance in the production of lignin-phenol-formaldehyde resin.

Table 4. GB/T 14732-2006 Requirements and the Performance of Lignin-phenol-formaldehyde Resin from KL and DL

	pH	Solid Content (%)	Viscosity (mPa·s)	Free Formaldehyde (%)	Bonding Strength (MPa)
GB/T	≥7.0	≥35.0	≥60.0	≤0.3	≥0.7
LPF Resin from KL	10.54	36.0	61	0.20	0.81
LPF Resin from DL	11.41	55.1	68	0.28	1.21

CONCLUSIONS

In this work, an effective depolymerization method was applied to release etherified phenol groups in the structure of kraft lignin. After the depolymerization treatment, the phenolic hydroxyl content increased from 1.55 mmol/g to 2.66 mmol/g. The molecular weight of depolymerized kraft lignin is lower than kraft lignin and the polydispersity decreased from 1.95 to 1.3 due to cleavage between lignin units. The depolymerized lignin used in the synthesis of lignin-phenol-formaldehyde (LPF) resin with a substitution of 50% phenol displayed a good performance in the physical properties including viscosity, bonding strength, and free formaldehyde content.

ACKNOWLEDGEMENTS

This work was supported by the National Undergraduate Training Programs for Innovation and Entrepreneurship (201510022035), China.

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Article submitted: February 15, 2017; Peer review completed: May 2, 2017; Revisions accepted: October 23, 2017; Published: January 3, 2018.
DOI: 10.15376/biores.13.1.1223-1234