Characterisation of Sequential Solvent Fractionation and Base-catalysed Depolymerisation of Treated Alkali Lignin

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An alkali lignin (OL) with a weight-average molecular weight (M_w) of 11646 g/mol was used to prepare low-molecular weight lignin for resin synthesis. The low-molecular weight lignin feedstock was obtained *via* base-catalysed depolymerisation (BCD) treatments at different combined severity factors. Sequential fractionation of the OL and BCD-treated lignins using organic solvents with different Hildebrand solubility parameters were used to alter the homogeneity of the OL. The yield and properties of OL itself and OL and BCD-treated OL dissolved in propan-1-ol (F1), ethanol (F2), and methanol (F3) were determined. Regardless of the treatment applied, a small amount of OL was dissolved in F1 and F2. The BCD treatment did not increase the yield of F1 but did increase the yields of F2 and F3. Gel permeation chromatography (GPC) showed that the repolymerization reaction occurred in F3 for all BCD-treated OL, so these lignins were not suitable for use as feedstocks for resin production. The GPC, ^{13}Carbon-nuclear magnetic resonance, and Fourier transform infrared spectroscopy analyses confirmed that the F3 in OL exhibited the optimum yield, molecular weight distribution, and chemical structure suitable for use as feedstocks for resin synthesis.

Keywords: Lignin; Organic solvent fractionation; Alkaline hydrolysis; Molecular weight distribution; Functional groups

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INTRODUCTION

Lignin is a potential natural, renewable feedstock for conversion into phenolic compounds because it is polyphenolic in nature. Lignin makes up about 28% of the total mass of softwood and is a by-product generated by the chemical pulping process. Approximately 50 x 10^6 metric tons of lignin is produced by the pulp and paper industry annually (Mai *et al*. 2000). Given the vast quantity available from pulp and paper mills, lignin is a readily-available, cheap feedstock to produce phenolic compounds for the chemical industry. One potential application is in the synthesis of resin as a substitute for petroleum-based phenol compounds.

The heterogeneous structure and chemical reactivity of lignin are obstacles to its use in many applications. Due to its highly heterogeneous structure, lignin often reacts in unexpected ways. To process lignin into various end products, it is advantageous to increase its degree of homogeneity and purity (Stewart 2008). In one study, direct use of unmodified lignin as a feedstock for the synthesis of phenol formaldehyde (PF) resin, in which lignin served both as filler and as a phenol substitute, required long pressing times and high pressing temperatures because unmodified lignin has very low reactivity (Hu *et* *al.* 2011). The reactivity of unmodified lignin is low because of lesser ortho- and para-reactive sites and steric hindrance due to its polyphenolic macromolecular structures (Alonso *et al.* 2004; Effendi *et al.* 2008).

One method used to increase the reactivity of lignin is depolymerisation into lower-molecular weight fragments *via* hydrolysis (Hu *et al.* 2011). Hydrolysis depolymerises or degrades the lignin macromolecule into lower-molecular weight fragments by cleaving the ether bonds, aryl-alkyl bonds, aryl-aryl bonds, and alkyl-alkyl bonds that bind the phenylpropane units of lignin together, liberating phenolic compounds (Roberts *et al.* 2011; Toledano *et al.* 2012). Hydrolysis of lignin in an alkaline medium has been shown to increase the reactivity of lignin (Thring 1994; El Mansouri *et al.* 2006; Cheng *et al.* 2013).

Chemical bonds in lignin molecule can be cleaved when sufficient amount of heat and pressure are applied as in the lignin treated in supercritical water condition (Roberts *et al.* 2010a; 2010b). Among the bonds within a typical lignin molecule, the aryl-alkyl ether bond (the primary bond) can be cleaved at temperatures above 270 °C, while C-C bonds (aryl-aryl bonds and methylene bridging bonds) are more stable and can only be cleaved below 400 °C when an appropriate catalyst is applied (Roberts *et al.* 2010a,b). The depolymerisation of lignin can be executed at lower temperature (180 to 340 °C) if an appropriate catalyst such as NaOH is added (Thring 1994; Nenkova *et al.* 2008; Roberts *et al.* 2010a). During the hydrolysis of lignin in an alkaline medium, also known as base catalysed depolymerisation (BCD), hydrolytic reactions cleave lignin bonds to yield lower-molecular weight fragments. Nenkova *et al.* (2008) revealed that the degradation of lignin occurred at 180 °C when 5% of NaOH was used and treated for 6 h. The severity of BCD treatment can be represented by the severity factor, log R_0 (Zabaleta 2012). The author reported that the highest oil yield (22.5%) was obtained when the lignin was treated most severely (log R_0 7.7). Thring (1994) reported that the production of low molecular weight components *i.e.* phenols as the result from the depolymerisation of ALCELL® lignin began at log $R_0 = 4.45$. The conversion of ALCELL® lignin to liquid and volatile products increased steadily up to log $R_0 = 7.5$, after which the increase is very dramatic, possibly due to increasing cleavage of methylene linkages. Alkaline hydrolysis, compared to other lignin depolymerisation methods, has certain advantages. The required catalysts are cheap and commercially available.

The homogeneity of lignin can be enhanced by sequential fractionation in different organic solvents (Wang *et al.* 2010; Li *et al.* 2012). The heterogeneity of lignin can be reduced because different parts of the lignin molecule have different hydrogen-bonding capacity (Hildebrand solubility parameter) in different organic solvents. Low-molecular weight lignin fragments are dissolved in organic solvents with weak or moderate hydrogen-bonding capacities with a wider range of Hildebrand solubility parameters than the higher-molecular weight lignin fragments (Schuerch 1952). Wang *et al.* (2010) reported that anthraquinone lignin fractionated with hexane, diethyl ether, methylene chloride, methanol, and dioxane has a distinct average molecular weight and polydispersity distribution. The average molecular weight and polydispersity distribution for each fraction, extracted from each solvent, increased with their hydrogen-bonding capacity (Hildebrand solubility parameter). Li *et al.* (2012) revealed that sequential solvent fractionation effectively prepared lignin with a homogeneous structure and good functional properties for potential further application.

The aims of the present study were to investigate the effects of BCD treatments at different severity factors on the yield and properties of the treated lignins and to determine the appropriate treatment method to obtain the optimum yield of lignin with lower-molecular weight and higher reactivity for resin synthesis.

EXPERIMENTAL

Materials

The lignin used in this study was a low sulfonate content alkali lignin (96%) with weight-average molecular weight (M_w) of approximately 11646 g/mol. This lignin was labelled original lignin (OL). The other reagents used were NaOH solution (50% in H_2O), analytical grade propan-1-ol, denatured ethanol (95%) and methanol, and HPLC-grade acetonitrile. The lignin and NaOH solution was supplied by Sigma-Aldrich (M) Sdn. Bhd. and was used without further purification. All the solvents were supplied by Fisher Scientific (M) Sdn. Bhd. and were used as received.

Methods

Severity Factor, R_0

The severity of a treatment can be modelled mathematically (treatment severity parameter) using a model developed by Abatzoglou *et al*. (1992). This model was used to model lignocellulosic fractionation assuming that homogeneous models and laws were applicable, that the different lignocellulosic components (cellulose, hemicellulose, and lignin) did not interact during hydrolysis, and that each of these components was predominantly characterized by a distinct chemical bond, typically an ether bond. The authors concluded that a kinetic formalism for a complex reacting system can be developed based on a limited number of parameters grouped within a single severity factor. The severity factor, log R_0, is calculated using Eqs. 1 and 2,

$$R_0 = \int_o^t \exp\left(\frac{T_{exp} - T_b}{14.75}\right) dt \tag{1}$$

$$\log R_0 = \log\left(t\left(\frac{T_{exp} - T_b}{14.75}\right)\right) \tag{2}$$

where T_{exp} is the experimental temperature in °C, T_b is the boiling temperature of water (100 °C), and t is the reaction time in minutes (Kadam *et al.* 2009).

Base Catalysed Depolymerisation (BCD) Treatment of Alkali Lignin

Ten parts by weight of alkali lignin (OL) was mixed with 100 parts by weight of 0.76-M NaOH. A glass tube full of the liquid mixture was placed in a reactor. The mixture was exposed to BCD treatments at different treatment severity factors, as presented in Table 1. The mixture was first treated in an autoclave at 127 °C and 0.1379 MPa for 4 h. Then the mixture was taken out of the autoclave and placed in a pre-heated oven at various temperatures (170, 190, or 210 °C) for 30 min. Next, the whole reactor was removed from the oven and immersed in cold water to drastically reduce the reactor temperature. The reactor was then opened and the samples were removed. The solution was neutralized to pH 7 through titration with hydrochloric acid (HCl) and was evaporated in a rotary evaporator at 60 °C under vacuum before being further dried in an oven at 60 °C until a constant weight was achieved.

Table 1. Severity Factor, log R_0, for Base-catalysed Depolymerisation Treatment of OL

First BCD Treatment			Second BCD Treatment			Combined log R_0
Temperature (°C)	Time (min)	log R_0	Temperature (°C)	Time (min)	log R_0	
127	240	3.18	170	30	3.54	6.72
127	240	3.18	190	30	4.13	7.31
127	240	3.18	210	30	4.72	7.90

Sequential Fractionation with Organic Solvents

In the first stage of fractionation, OL and BCD-treated lignins were suspended in 150 mL of propan-1-ol, and the suspension was stirred with a magnetic stirrer at room temperature for 10 min. The mixture was then allowed to settle for 10 min before being filtered. The undissolved lignin residue was filtered off. This process was repeated with the same solvent until the resulting filtrate was colourless. The lignin dissolved in propan-1-ol was labelled F1. The undissolved lignin residue was allowed to dry completely prior to the following fractionation stages with ethanol (the second stage) and methanol (the third stage). The lignins dissolved in ethanol and methanol were labelled F2 and F3, respectively. The solvent was evaporated from the filtrate under a vacuum and the dissolved lignin from each extraction stage was dried in an oven at 105 °C for 2 h. Finally, the dried lignin was removed from the round bottom flask, powdered, and stored in a desiccator at room temperature before analysis. The yield of dissolved lignin in the filtrate for each solvent was calculated according to Eq. 3,

$$\boldsymbol{Yield}\ (\%) = \mathbf{100}\left(\frac{W_f}{W_i}\right) \tag{3}$$

where W_f is the oven-dried weight of the lignin recovered from each filtrate (g), and W_i is the initial oven-dried weight of the lignin in each fractionation stage (g).

Gel Permeation Chromatography (GPC)

The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (M_w/M_n) of OL, F1, F2, and F3 in OL and BCD-treated lignins were determined by gel permeation chromatography (GPC) using a Waters Ultrahydrogel 250 PKGD column (USA). The apparatus was operated at 50 °C and the mobile phase (80/20 water/acetonitrile with 0.1-M sodium nitrate buffer adjusted to pH 11.0 or higher with 50% sodium hydroxide) eluted at a flow rate of 0.3 mL/min. The injection volume was 20 µL. The standard samples used for calibration were narrow polyethylene oxide (PEO; molecular weights 5200, 11600, 24000, 48600, 79000, 148000, 273000, 410000, and 668000). The number-average (M_n) and weight-average (M_w) molecular weights of the lignin fractions were computed from their respective chromatograms. All results were reported as the mean of triplicate samples.

^{13}C Nuclear Magnetic Resonance (NMR) Spectroscopy

The structural characteristics of OL, F1, F2, and F3 in OL and BCD-treated lignins were determined using a Varian Unity Inova spectrometer (USA) operated at 500 MHz at ambient temperature. The chemical shifts of the respective compounds were reported in ppm. For each trial, 400 mg of sample was dissolved in 2 mL of deuterated dimethyl sulfoxide (DMSO-d_6). The concentration of each sample was kept consistent throughout the analysis. Three replicates were prepared for each material. For each sample, 30000 scans were recorded and the spectra were referenced to TMS at 0.00 ppm. The chemical shifts were assigned as suggested by Drumond *et al.* (1989), Robert (1992), Pan *et al.* (1994), and Holtman *et al.* (2006).

Fourier Transform Infra-Red (FT-IR) Spectroscopy

A FT-IR spectrophotometer was used to determine the functional groups present in OL, F1, F2, and F3 in OL and BCD-treated lignins. The FT-IR spectra tests were run at ambient temperature using pure samples across a wave number range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. The infrared spectra of the samples were generated using a Perkin-Elmer FT-IR apparatus (model spectrum 100 series; USA). All results represent the mean of triplicate samples. The absorption bands were assigned as suggested by Tejado *et al.* (2007).

RESULTS AND DISCUSSION

Yield and Molecular Weight Distributions of Lignin

The mean yield, M_n, M_w, and polydispersity index (M_w/M_n) values for OL, F1, F2, and F3 in OL and BCD-treated OL are presented in Table 2. From GPC analysis, the result shows that the average M_n and M_w values for OL were 2691 and 11646 g/mol, respectively while the M_w/M_n for OL was 4.33. The GPC chromatogram for OL is shown in Fig. 1. It was found that only a small amount of OL (0.40%) dissolved in F1 (propan-1-ol, δ: 24.9 $MPa^{1/2}$). For BCD-treated OL (combined log R_0 6.72, log R_0 7.31, and log R_0 7.90), 0.55, 0.46, and 0.36% of the starting lignin dissolved. The average values of M_n and M_w for F1 in OL and BCD-treated lignins were 1191 and 1428, 922 and 1046, 1062 and 1203, and 1043 and 1209 g/mol, respectively. The mean values of M_w/M_n for F1 in OL and BCD-treated lignins were 1.20, 1.13, 1.13, and 1.16, respectively. This shows that the structure of lignin dissolved in propan-1-ol was more uniform and smaller than that of undissolved lignin. The mean yield values for F1 in OL and BCD-treated lignins were not significantly different. This indicates that the different severity factors used in this study did not increase the yield of lignin with average M_w between 1046 and 1428 g/mol.

The yield for F2 (ethanol, δ: 26.2 $MPa^{1/2}$) in OL was 0.57% of the starting lignin. The yields for F2 in BCD-treated lignins were 4.34, 3.53, and 3.94% of the starting lignin, respectively. It was found that the M_n and M_w for F2 in OL and BCD-treated lignins were higher than those in F1. The M_n values for F2 in OL and BCD-treated lignins were 1179, 1065, 1421, and 1337 g/mol, respectively, while the M_w they were 1518, 1292, 1680, and 1639 g/mol, respectively. The yields for F2 in BCD-treated lignins were significantly higher than the yield for F2 in OL, whereas the yields for F2 among the BCD-treated lignins were not significantly different. The polydispersity index for F2 in OL (1.29), combined log R_0 6.72- (1.21), combined log R_0 7.31- (1.18), and combined log R_0 7.90- (1.23) treated lignins were higher than in F1, indicating that the structure of lignin dissolved in ethanol is less uniform and larger than that of the lignin structure in F1. The BCD treatment increased the yield of lignin molecules with average M_w of 1292 to 1680 g/mol, but more severe treatment conditions did not produce any more lignin with average M_w of 1292 to 1680 g/mol.

Regardless of treatment, it was also found that more lignin was dissolved in F3 (methanol, δ: 29.7 MPa$^{1/2}$) than in F1 or F2. The yield for F3 in OL was 38.01% of the starting lignin, while the yields for F3 in BCD-treated lignins were 74.03, 68.12, and 72.25%, respectively. The M_n and M_w for F3 in OL were 2205 and 4179 g/mol, respectively, and the M_n and M_w for F3 in BCD-treated lignins were 2684 and 4806, 3496 and 7629, and 3963 and 10634 g/mol, respectively. The M_n and M_w for F3 in OL and BCD-treated lignins were higher than those in F1 and F2. Yuan *et al.* (2009) obtained similar results in which the molecular weights and polydispersity indices of degraded *Eucalyptus pellita* lignin were higher in the methanol-soluble fraction than in the ethanol- and propan-1-ol-soluble fractions.

The BCD treatment had a significant effect on the yield for F3 in OL and BCD-treated lignins. However, higher severity factors did not significantly affect the yield. This suggests that BCD treatment at combined log R_0 6.72 increased the yield of OL with average M_w of 4800 g/mol. More severe treatment conditions (combined log R_0 7.31 and log R_0 7.90) did not further increase the yield of lignin with lower M_w but increased the M_n and M_w, increasing M_w/M_n. The M_w/M_n values for F3 in OL and BCD-treated lignins were 1.90, 1.78, 2.17, and 2.68, respectively. The increase in M_w/M_n with increasing treatment severity indicates that the lignin was repolymerized when treated under the most severe conditions. This can be attributed to repolymerization of lignin molecules through the formation of unstable carbanion species. The phenolic and catecholic monomers are negatively charged and exist in equilibrium with their corresponding phenolate and carbanion species under BCD conditions. The latter have a negative charge in ortho or para position to the phenolic hydroxyl group (McDonough 1993). According to Roberts *et al.* (2011), the carbanion generated during the BCD treatment forms C-C bond with carbonyl group (ketone) *i.e.* 3,5-dimethoxy-4-hydroxyacetophenone through aldol addition. As there is no carbonyl group in the lignin molecules of OL used in this study, the generated carbanion could not participate in the repolymerization of OL. The repolymerization reaction occurred in OL when treated at combined log R_0 7.31 and 7.90 could be attributed to crosslinking of phenolate units similarly to reactions during phenolic curing reactions (Chakar and Ragauskas 2004; Wang *et al.* 2009). According to Olarte (2011), formaldehyde may form as a by-product from the degraded side chain of phenyl-propane units (Cγ) and may be involved in this repolymerization reaction.

The average M_w of OL was 11646 g/mol, and it was totally soluble in water. This indicates that the OL used in this study consisted of high-molecular weight lignin fraction, and the polarity of this lignin was high. As the water and methanol are strong hydrogen-bonding solvents, the solubility parameter of the solvents would affect the solubility and molecular weight of lignin (Schuerch 1952). The cited author reported that high-molecular weight lignin fraction tends to dissolve in solvents with higher solubility parameter. Since the solubility of methanol (δ: 29.7 MPa$^{1/2}$) was lower than water (δ: 48.0 MPa$^{1/}$2), therefore, a lesser amount of the high-molecular weight OL was dissolved in methanol. Hence, the yield for F3 in OL was low and the M_w of this lignin fraction was lower than the OL which was 4179 g/mol.

The high-molecular weight OL also did not dissolve in propan-1-ol or ethanol because the solubility parameter of these solvents (δ: 24.9 MPa$^{1/2}$ for propan-1-ol and δ: 26.2 MPa$^{1/2}$ for ethanol) was lower than methanol. Hence, the yields and M_w for F1 and F2 in OL were lower than the yield and M_w for F3 in OL. The increasing of yield for F3 in combined log R_0 6.72 is because this treatment had successfully degraded the OL. Hence, increasing the amount of lower-molecular weight fraction and the average of M_w

of this lower-molecular weight fraction was approximately 4800 g/mol. Since methanol dissolves the OL with average M_w in the range of 4200 g/mol (as found in the average M_w for F3 in OL), the increasing of the amount of lignin fraction with average M_w of 4800 g/mol due to the degradation of OL when treated at combined log R_0 6.72 thus will increases the yield for F3 at this severity factor.

As discussed above, the solubility parameter of methanol limits its ability to dissolve high-molecular weight lignin fraction from the OL, but there is increased amount of lignin fraction with high-molecular weight after treatment at combined log R_0 7.90 dissolved in methanol. This may be attributed to degradation of aliphatic hydroxyl group on the side chain of lignin molecule (Pouteau *et al.* 2005). The authors reported that the reduction of the aliphatic hydroxyl group decreases the polarity of the lignin molecules.

Table 2. Yield, Number-average Molecular Weight (M_n), Weight-average Molecular Weight (M_w), and Polydispersity Index (M_w/M_n) for F1, F2, and F3 in OL and Base-catalysed Depolymerisation-treated OL

Treatments		Lignin Fractions			
		Without Fractionation	F1	F2	F3
OL	Yield (%)	-	-	-	-
	M_w (g/mol)	11646 ± 1972.93	-	-	-
	M_n (g/mol)	2691 ± 276.27	-	-	-
	M_w/M_n	4.33 ± 0.54	-	-	-
OL	Yield (%)	-	0.40 ± 0.003	0.57 ± 0.001	38.01 ± 0.02
	M_w (g/mol)	-	1428 ± 24.44	1518 ± 19.7	4179 ± 762.94
	M_n (g/mol)	-	1191 ± 21.28	1179 ± 17.04	2205 ± 232.11
	M_w/M_n	-	1.20 ± 0.02	1.29 ± 0.01	1.90 ± 0.18
Combined log R_0 6.72	Yield (%)	-	0.55 ± 0.001	4.34 ± 0.01	74.03 ± 0.02
	M_w (g/mol)	-	1046 ± 6.66	1292 ± 61.61	4806 ± 793.02
	M_n (g/mol)	-	922 ± 9.85	1065 ± 24.34	2684 ± 182.66
	M_w/M_n	-	1.13 ± 0.01	1.21 ± 0.03	1.78 ± 0.18
Combined log R_0 7.31	Yield (%)	-	0.46 ± 0.003	3.53 ± 0.006	68.12 ± 0.02
	M_w (g/mol)	-	1203 ± 1.15	1680 ± 19.50	7629 ± 1538.69
	M_n (g/mol)	-	1062 ± 1	1421 ± 12	3496 ± 286.37
	M_w/M_n	-	1.13 ± 0.0006	1.18 ± 0.02	2.17 ± 0.27
Combined log R_0 7.90	Yield (%)	-	0.36 ± 0.002	3.94 ± 0.006	72.25 ± 0.07
	M_w (g/mol)	-	1209 ± 42.1	1639 ± 7.37	10634 ± 440.02
	M_n (g/mol)	-	1043 ± 24.33	1337 ± 2.31	3963 ± 57.83
	M_w/M_n	-	1.16 ± 0.01	1.23 ± 0.005	2.68 ± 0.07

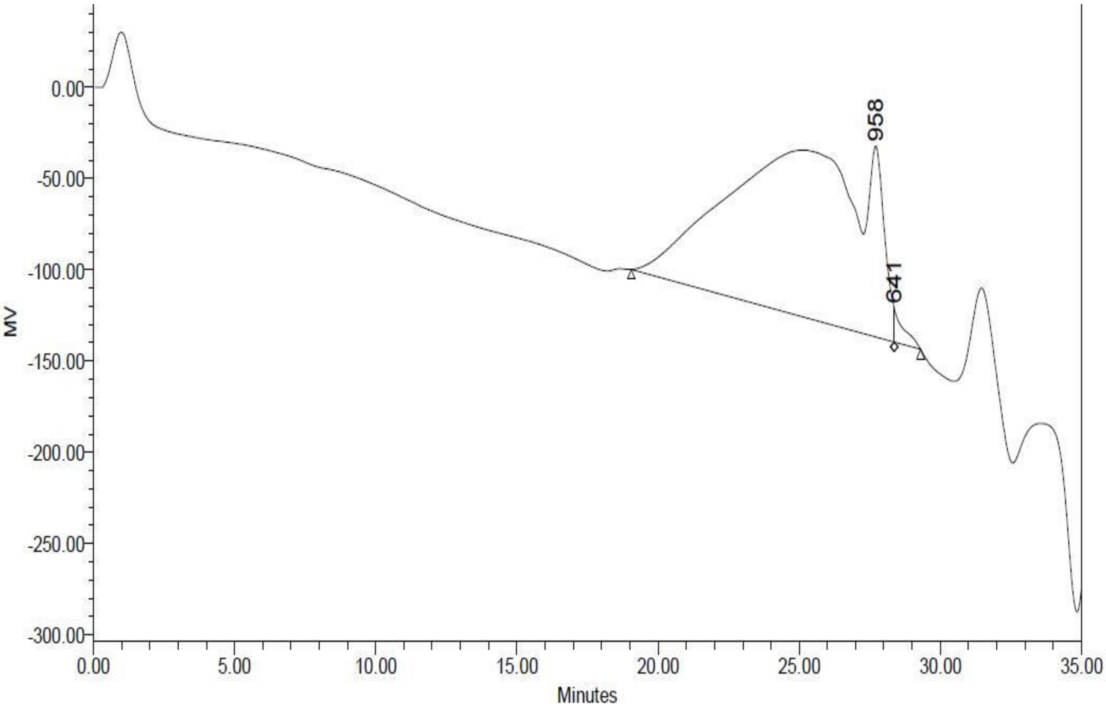

Fig. 1. GPC chromatogram of OL (without base-catalysed depolymerization and solvents fractionation treatments)

Semi-Quantitative ^{13}C Nuclear Magnetic Resonance (NMR) Spectra

In this study, the absorption intensities of each peak for the alkali lignin (OL), F3 in OL, and combined log R_0 6.72-treated OL were normalised against an internal standard peak at 55.6 ppm (Table 3). The F1 and F2 in OL and combined log R_0 6.72-treated OL ^{13}C-NMR spectra are not discussed because their peak intensities were very low. The ^{13}C-NMR spectra for the rest of the lignin fractions are not discussed because their peak intensities were very low and their weight-average molecular weights (M_w) were high.

The chemical shift assignments for ^{13}C-NMR spectrum and the relative intensities of the peaks assigned to different chemical structures for OL, F3 in OL, and combined log R_0 6.72-treated OL are presented in Table 3. The results show that solvent fractionation and BCD treatment changed the chemical structure of the OL. The phenolic hydroxyl (168.9 ppm) was one of the chemical structures affected by the treatments. The F3 in OL had the most phenolic hydroxyl (0.36) as compared to the OL (0.10) and combined log R_0 6.72-treated OL (0.15). This may be because the F3 in OL had lower M_w than the OL because lignin molecules with more free phenolic hydroxyls were fractionated out and dissolved in the methanol. The low phenolic hydroxyl content in combined log R_0 6.72-treated OL may be attributed to free phenolic hydroxyls involved in crosslinking reactions during the BCD process in a manner similar to a phenolic curing reaction (Wang *et al.* 2009). According to Malutan *et al.* (2008), free phenolic hydroxyl is important in the chemical modification of lignin (*i.e.*, the glyoxalation reaction) because it forms quinone methide intermediates in an alkaline medium.

The low phenolic hydroxyl content in combined log R_0 6.72-treated OL can also be detected through the C-4 in non-etherified G units (145.8 ppm). The lower relative intensities of the peak 145.8 ppm (0.18) for combined log R_0 6.72-treated OL indicate that free C-4 positions without ether bonds were less available. This was also supported by the peak attributed to C-4 in etherified G units (146.8 ppm), the relative intensities of which the combined log R_0 6.72-treated OL was higher (0.26). This suggests that an ether bond occupied the C-4 position of combined log R_0 6.72-treated OL.

Other changes in the chemical structures of the lignins occurred in the C-β in alkyl-alkyl bond and aryl-alkyl bond for β-β units (53.8 ppm) and β-5 units (53.4 ppm). The relative intensities of these two peaks for combined log R_0 6.72-treated OL were 0.22 and 0.19, respectively, lower than in OL (0.25 and 0.22, respectively) and F3 in OL (0.30 and 0.26, respectively). This suggests that dealkylation of the side chains of lignin phenyl-propane units occurred during the BCD treatment process (Roberts *et al.* 2011). This finding was in agreement with results reported earlier in the previous section (*i.e.*, yield and molecular weight distributions of lignin) in which the yield for F3 in combined log R_0 6.72-treated OL was higher than that for F3 in OL. This indicates that the BCD treatments successfully cleaved lignin phenyl-propane side chains in β-β units and β-5 units, yielding more lignin with average M_w of 4800 g/mol.

Table 3. Chemical Shift Assignments for ^{13}C-NMR Spectra and Relative Intensities of Peaks for different Chemical Structures for OL, F3 in OL, and Combined log R_0 6.72-treated OL

δ ^{13}C-NMR (ppm)	Structure	Lignin Fractions		
		OL	F3 in OL	F3 in Combined log R_0 6.72-treated OL
170.8	Primary aliphatic hydroxyl	0.09	0	0
168.9	Phenolic hydroxyl	0.10	0.36	0.15
149.4	C-3 in etherified G units	0.26	0.23	0.21
146.8	C-4 in etherified G units	0.28	0.29	0.26
145.8	C-4 in non-etherified G units	0.22	0.23	0.18
145.0	C-4/C-4’ of etherified 5-5 units	0.21	0.21	0.21
143.3	C-4 in ring B of β-5 units, C-4/C-4’ of non-etherified 5-5 units	0.21	0.22	0.20
132.4	C-5/C-5’ in etherified 5-5 units	0.20	0.18	0.18
129.3	C-β in φ-CH=CH-CHO	0.27	0.27	0.23
125.9	C-5/C-5’ in non-etherified 5-5 units	0.21	0.23	0.22
118.4	C-6 in G units	0.24	0.23	0.22
115.1	C-5 in G units	0.29	0.31	0.27
111.1	C-2 in G units	0.26	0.28	0.23
71.2	C-α in G type β-O-4 units (threo), C-γ in G type β-β	0.11	0	0
62.8	C-γ in G type β-5, β-1 units	0.09	0	0
60.2	C-γ in G type β-O-4 units	0.30	0.32	0.21
55.6	C in φ-OCH3	1.00	1.00	1.00
53.8	C-β in β-β units	0.25	0.30	0.22
53.4	C-β in β-5 units	0.22	0.26	0.19

Quantitative FT-IR Spectra

The lignin content can be determined with FT-IR spectroscopy by performing univariate analysis. In univariate analysis, the intensity of one lignin band is used to calculate the lignin concentration. This is possible because the observed IR band intensity is usually a linear function of the lignin concentration. The absorption intensities for each band were normalised based on the vibration of the aromatic ring appearing at 1600 cm^{-1}. The quantitative analysis based on FT-IR spectra was referred to previous studies as reported by Malutan *et al.* (2008), El Mansouri *et al.* (2011), and Mancera *et al.* (2011). Table 4 shows the band assignments for FT-IR spectrum and the relative absorbance bands for each functional group for OL and F3 in OL. The FT-IR spectra of OL and F3 in OL are shown in Figs. 2 and 3. The chemical structure of OL used in this study is illustrated in Fig. 4.

The average relative absorbance of hydroxyl (OH) bands for F3 in OL were higher than for OL. The OL dissolved in methanol possessed more phenolic OH group than the OL. This was confirmed by the increase in the relative absorbance bands of phenolic OH at 1375 and 1325 cm^{-1} for F3 in OL lignin. The increase in phenolic OH groups for F3 in OL lignin likely corresponds to its lower molecular weight or the fact that it is more highly branched than OL (Saito *et al.* 2014).

The average relative methoxyl group absorptions for F3 in OL were higher than for OL. Previous studies have also reported that lignin dissolved in methanol possesses more methoxyl groups than unfractionated lignin (Li *et al.* 2012; Arshanitsa *et al.* 2013). The relative absorbance of ether bonds at 1120 cm^{-1} remained nearly the same for OL and F3 in OL, indicating that solvent fractionation did not cleave ether bonds within the lignin molecule.

Table 4. Band Assignments for FT-IR Spectra and Relative Absorbance of Bands for each Functional Group for OL and F3 in OL

Band (cm^{-1})	Group	Lignin Fractions	
		OL	F3 in OL
3420 to 3405	Phenolic OH and aliphatic OH	0.34	0.43
1365	Phenolic OH	0.50	0.66
1220	Phenolic OH and ether	0.99	1.15
Mean Value		0.61	0.75
2960 to 2925	CH_3 and CH_2	0.11	0.24
1460		0.60	0.71
Mean Value		0.36	0.48
1270	C-O in Guaiacyl units	0.69	0.75
1030	Ether	1.19	1.19
Mean Value		0.94	0.97
2850 to 2840	Methoxyl-OCH_3	0.05	0.13
1600	C-C vibration of aromatic ring	1.00	1.00
1515		0.60	0.70
Mean Value		0.80	0.85

The average relative absorbances of the aromatic ring C-H vibration bands at 1600 and 1500 cm^{-1} for F3 in lignin were higher than for OL. The greater the absorption intensity of this band, the greater is the likelihood of formaldehyde or glyoxal to react and be incorporated into the aromatic ring during later hydroxymethylation or glyoxalation reactions or in resin formulation reactions (Mancera *et al.* 2011). The results of the semi-quantitative FT-IR analysis agree with those obtained using ^{13}C-NMR.

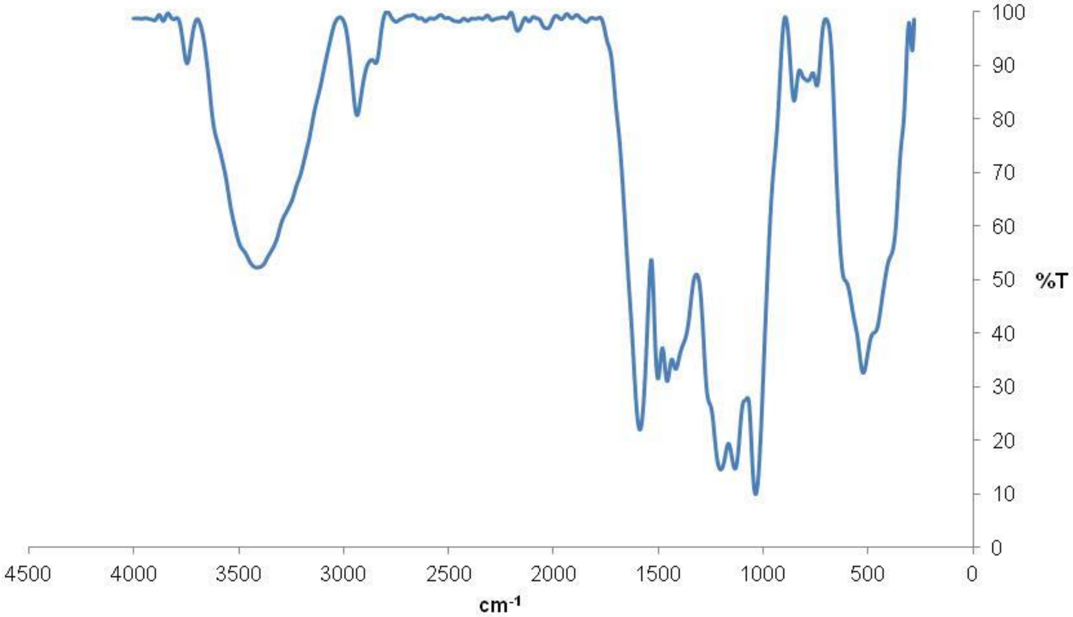

Fig. 2. FT-IR spectrum of OL (without base-catalysed depolymerization and solvents fractionation treatments)

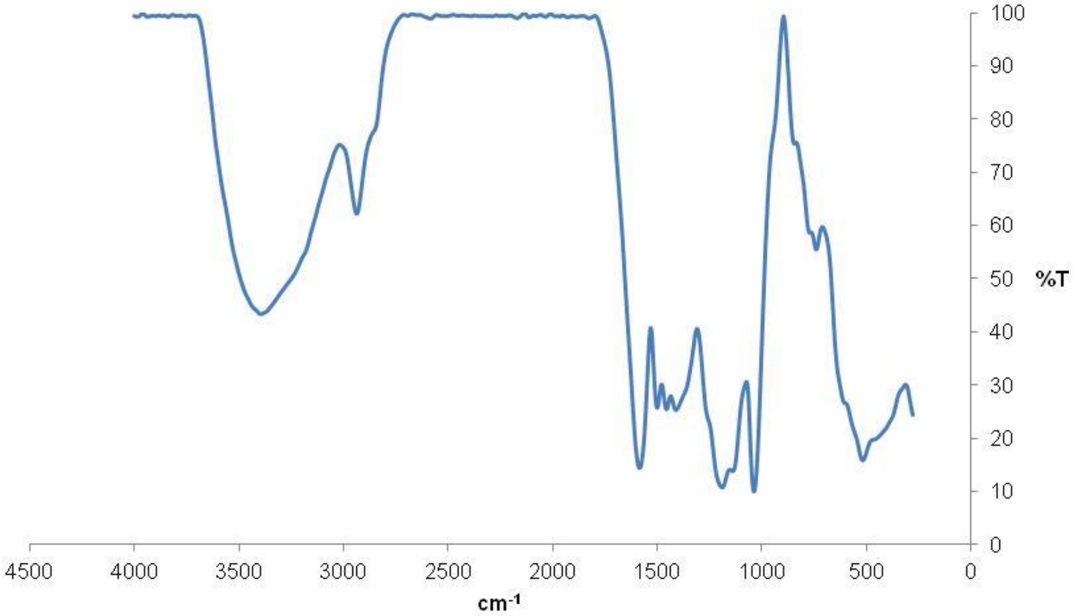

Fig. 3. FT-IR spectrum of F3 in OL (OL without base-catalysed depolymerization treatment but fractionated with methanol)

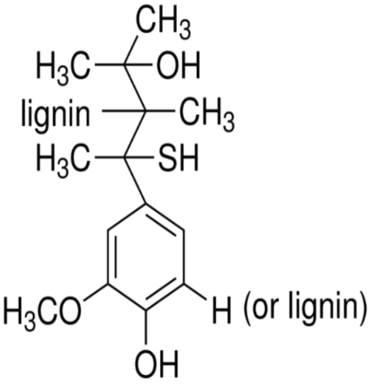

Fig. 4. Chemical structure of softwood alkali lignin used in this study

CONCLUSIONS

1. Base-catalysed depolymerisation (BCD) treatment did not increase the yield of an alkali lignin (OL) dissolved in propan-1-ol or ethanol but did increase the yield of OL dissolved in methanol.
2. Repolymerisation of OL occurred in BCD-treated OL, reducing the phenolic hydroxyl group content.
3. Lower-molecular weight, more homogeneous OL tended to dissolve in propan-1-ol and ethanol, but their overall soluble lignin yields were low.
4. The yield of OL dissolved in methanol was higher than OL dissolved in propan-1-ol of ethanol due to dealkylation of phenyl-propane side chains.
5. The OL dissolved in methanol had higher molecular weight, was less homogeneous, and had a bulkier structure than OL dissolved in propan-1-ol or ethanol.
6. ^{13}Carbon-NMR and FT-IR spectroscopy analyses confirmed that the original lignin (OL) dissolved in methanol (F3 in OL) exhibited the optimum yield, molecular weight distribution, and chemical structures for use as a feedstock for resin synthesis.

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