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Comparative Characterization of Degraded Lignin Polymer from the Organosolv Fractionation Process with Various Catalysts and Alcohols

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ABSTRACT: Triploid poplar was fractionated using mild organosolv process, and detailed characteristic elucidation of the lignin obtained was performed to determine the effects of various chemicals (sodium hydroxide, triethylamine, and formic acid) and solvents (methanol, ethanol, *n*-propanol, and *n*-butanol). Both nondestructive techniques (e.g., NMR technology) and degradation methods (e.g., alkaline nitrobenzene oxidation) were performed to comparatively evaluate the structural degradation of lignin molecules. The addition of acidic and basic catalysts improved the purity of lignin by acid hydrolysis and the cleavage of the ester groups and other types of lignin–carbohydrate interactions formed by polyoses and lignin under the basic conditions. A certain amount of aryl alkyl ether linkages (β-O-4) was cleaved during the fractionation process, whereas other carbon–carbon linkages were resistant to degradation. The formation of new carbon–carbon bonds led to the lignin fraction with obviously higher molecular weight and thermal stability, resulting from the induced carbon cation under the acidic condition. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39673.

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INTRODUCTION

Lignocellulosic biomass has recently become a high priority for many countries and will play a major role in the chemical industry in the near future. Production of bioethanol from renewable lignocellulosic materials has been successfully realized by enzymatically hydrolyzing the polysaccharides and microbially fermenting the C_5 and C_6 sugars in large scale. However, this bioconversion process fails to make use of the noncellulosic components, and then the utilization efficiency of bioresources is unequal to satisfy the industrialization production. It believes that the final replacement of fossil energy by bioenergy is based on the full utilization of all components of biomass for fuels, chemicals, and materials, known as biorefinery scenario.[1] Lignin is an essential wood component accounting from 10 to 30% of the organic carbon in the biosphere.[2] As the most complex and irregular heteropolymers present in the cell walls of vascular plants, lignin is built from three basic monolignols (*p*-coumaryl, coniferyl, and sinapyl alcohols) connected by various inter units bonds, such as several types of ether (e.g., β-*O*-4, α-*O*-4, 4-*O*-5) and carbon–carbon (e.g. β-β, β-5, 5-5) linkages mediated by laccases and peroxidases.[3–5] With the rapid spread of biomass utilization, lignin is considered as a potential starting material for the manufacture of adhesives, epoxi- and phenolic-resins, and polyolefins because of its polyphenolic chemical structure.[6,7] Therefore, more investigations devoted to the elucidation of its structure, purity, and properties are being under way.

Although ongoing EtOH-centric processes focused on cell wall deconstruction and biofuel production with lower cost, the breakthrough of fractionation technology will offer an additional financial upside to relax economic hurdles.[8] Organosolv process was firstly used to chemically fractionate lignocellulosic materials, then modified and assessed by the pulp and paper industry as an alternative to Kraft pulping of hardwoods. Recently, this process is extensively investigated in detail from the angles of the recovery of carbohydrate and lignin, and the enzymatic hydrolyzability. Historically, ethanol is the most common solvent in organosolv process, normally operating under high-temperatures (> 150°C) or high-pressures (> 15 bar) with or without the addition of catalysts. The hydrolyzed lignin

dissolves in the organophilic phase and is recovered as filtrate via precipitation reaction, and the organic solvents are easy to be recovered by distillation and recycled. Employment of organic acids as solvents in organosolv process has proved to be promising process to efficiently fractionate lignocelluloses into cellulose, hemicelluloses, and lignin under conventional condition.[9] Under alkaline conditions, extensive delignification and hemicelluloses preservation in solid fraction were observed.[10] With respect to the pretreatment chemicals, it may also be advantageous to utilize different alcohols rather than ethanol. To determine the advantages of these fractionation processes on the further utilization of lignin, evaluation of the characteristic changes in the lignin obtained is needed.

In the present work, lignin from triploid poplar was fractionated by different organosolv processes, which were varied in alcohols and catalysts. The lignin fractions obtained were characterized by subjecting to polysaccharides and phenolic acid/aldehyde components, gel permeation chromatography (GPC), Fourier transform infrared (FTIR) spectroscopy, Heteronculear Single Quantum Coherence Nuclear Magnetic Resonance (HSQC NMR) spectroscopy, and thermal analysis. We aimed to exploit the relationship between lignin structure and oragnosolv pretreatment conditions, thus enrich the knowledge of the structure and further improve the utilization of this most complicated lignocellulosic component—the lignin polymer.

EXPERIMENTAL

Raw Materials

Triploid Poplar (*Populus tomentosa* Carr.) of 4-year-old was cut from Shandong Province, China. After being debarked and air-dried, the tree trunks were chipped using a custom-designed chipper. The chips were ground, and the fraction passing 40-mesh was collected for chemical analysis. The main chemical compositions are: wax (4.2%), glucose (44.5%), xylose (19.8%), Klason lignin (21.4%), and ash (5.1%). The standard deviation was less than 5%.

Organosolv Fractionation

Prior to organosolv fractionation, the wood powder was first dewaxed with toluene–ethanol (2 : 1, vol/vol) in a Soxhlet extractor for 6 h. The extracted free sample (10.0 g) was then treated with 70% aqueous alcohol solution with or without catalyst, and fractionated by removing hemicelluloses and precipitating lignin in acidic solution as described in Figure 1.

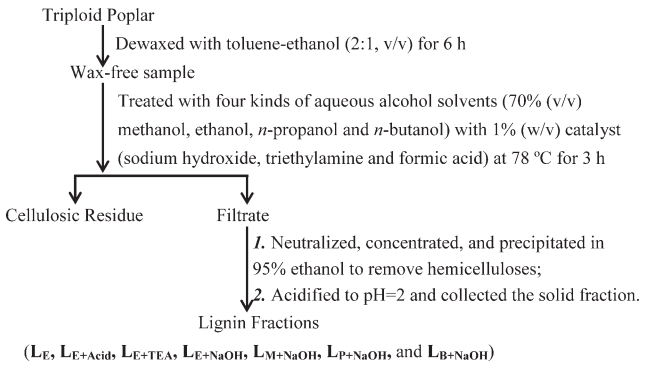


Figure 1. Scheme for separation of lignin fractions.

Four kinds of aqueous alcohol solvents (70% (vol/vol) methanol, ethanol, *n*-propanol, and *n*-butanol) and three catalysts (sodium hydroxide, triethylamine, and formic acid) with the fixed concentration of 1% (wt/vol) were employed in current study. According to the previous investigation,[11–13] the cooking runs were carried out in a round-bottom flask with external heater and condenser, and a wood to liquid ratio of 1 : 20 (g/mL) was employed. After reaching the designed temperature (80°C), the mixtures were cooled to room temperature and filtrated under vacuum. The hemicellulosic components were fractionated with alcohol precipitation, and the lignin macromolecules were obtained by acidification with HCl. All the lignin samples were freeze-dried and kept in a desiccator at room temperature for further analysis. To reduce errors and confirm the results, each experiment was repeated twice under the same condition. The yields of the lignin fractions were given on a dry weight basis related to the raw material as the average of the replicates.

Wet-chemical Analysis

The composition of neutral/acidic sugars and phenolic acids/aldehydes were determined by the high-performance anion-exchange chromatography (HPAEC) with pulsed amperometric detector (PAD) and an ion exchange Carbopac PA-1 column (Dionex ICS 3000, US) and a HPLC system (Agilent 1200 series, US) with a ZORBAX Eclipse XDB-C18 column, respectively, as described in previous articles.[7,14] All analyses were run at least twice, and the errors for the sugar and aromatic compounds analysis were less than 1% and 8%, respectively. The molecular weight distribution was determined by GPC on a PLgel 5 mm Mixed-D column, eluting with tetrahydrofuran (THF) at a flow rate of 0.5 mL/min.[15] To calibrate the column, monodisperse polystyrene of known molecular weights (1320, 9200, 16,000, 435,500 g/mol) (Polymer Laboratories Ltd., UK) were used as the standards.

Spectroscopic Characterization

FTIR spectra of the lignin fractions were recorded on a FTIR spectrophotometer (Tensor 27, Bruker, Germany) using a KBr disc containing 1% finely ground samples. Thirty-two scans were taken of each sample recorded from 3600 to 800 cm^{-1} at a resolution of 2 cm^{-1} in the transmission mode. The ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AV III NMR spectrometer at 400 MHz by dissolving 10 mg and 80 mg lignin in 0.5 mL DMSO-d_6, respectively. The chemical shifts were calibrated relative to the signals from DMSO-d_6, used as an internal standard at 2.49 ppm for the ^{1}H-NMR spectrum. A 30° pulse flipping angle, a 9.2 μs pulse width, 1.89 s delay time, and 1.36 s acquired time between scans were used. The spectral widths for the HSQC NMR were 5000 and 20,000 Hz for ^{1}H- and ^{13}C dimensions, respectively. Prior to Fourier transformation, the data matrixes were zero filled up to 1024 points in the ^{13}C dimension. Data processing was performed using standard Bruker Topspin-NMR software.

Thermal Analysis

A Shimadzu (Japan) DTG-60 simultaneous thermogravimeric/differential thermal analysis (TGA-DTA) apparatus was employed for thermal stability tests. This apparatus detects the mass loss

Table I. Yield (wt %, Related to the Starting Material) and Molecular Weight Related Information of Isolated Lignin Fractions

	L_E	L_{E+Acid}	L_{E+TEA}	L_{E+NaOH}	L_{M+NaOH}	L_{P+NaOH}	L_{B+NaOH}
Yield	0.4	1.1	0.7	3.4	4.5	4.1	3.2
$\overline{M}_w$	3214	19960	3462	3360	3347	1521	2023
$\overline{M}_n$	2080	5680	2164	1887	1785	664	807
$\overline{M}_w/\overline{M}_n$	1.5	3.5	1.6	1.8	1.9	2.3	2.5

with a resolution of 0.1 μg. Samples were heated at a constant rate of 10 °C/min from room temperature to 600°C, under a nitrogen flow of 20 mL/min. The thermal decomposition temperature was taken at the onset of significant (≥0.5%) weight loss, after the initial moisture loss.

RESULTS AND DISCUSSION

Fractional Yield and Purity

The effectiveness of organosolv process is based on its ability to progressively break down and modify the lignin macromolecule until the resulting molecular fragments become small enough to dissolve in the aqueous liquor. As can be seen, ethanol ogranosolv process without any catalyst under the condition given only yielded 0.4% lignin related to the starting material, amounting to 2% of total lignin in triploid poplar (Table I). Besides, about 13.0% polysaccharides were associated with lignin, deriving from what is called lignin–carbohydrate complex (LCC) (Table II). By adding 1% formic acid, the yield of lignin fraction was slightly increased to 1.1% and the content of polysaccharides was significantly decreased to 4.1%. This phenomenon was probably due to the partial hydrolysis of glycoside bonds in hemicelluloses and ether bonds in LCC surrounding cellulosic framework, which was of benefit for leasing lignin macromolecule from lignocellulosic matrix. In comparison, inorganic basic catalyst was more efficient than formic acid to fractionate lignin. As shown, 3.2–4.5% lignin (15–21% based on 21.4% Klason lignin in raw material) were isolated under such mild conditions in different alcohols containing 1% NaOH (Table I). As lignin fractionation is a combination of lignin degradation and dissolution of the degraded fragments, type and concentration of the aqueous alcohol solution can achieve a dramatic impact on the fractionation efficiency. Ni and Hu reported that lignin solubility in ethanol–water mixture increased as the ethanol concentration increased and reached a maximum at an ethanol concentration of ~70%.[16] Further increase in the ethanol concentration resulted in a slight decrease in the lignin solubility. According to the results of solubility tests conducted on ALCELL® lignin at room temperature, methanol and ethanol showed slightly higher solubility of lignin than *n*-propanol and *n*-butanol.[17] However, the yields of the isolated lignins in different alcohols were similar, probably due to the synergistic effect of water. It is also worthy to note that the content of polysaccharides was only 1.7% in L_{M+NaOH}, indicating the obvious cleavage of lignin–carbohydrate linkages. As we known, methanol cannot form azeotrope and exists in the form of gas at 78°C, generating higher hydroxide ion concentration at the same dosage of NaOH, and then promoting the base-catalyzed cleavage of ester linkages between hemicelluloses and lignin. Likewise, low sugar content was also observed in L_{P+NaOH} (1.4%) and the probable explanation was related to the physiochemical characteristics of *n*-propanol. It is surprising to note that the addition of 1% triethylamine neither increased the fractionation efficiency, nor significantly improved the purity of lignin fraction. The water–triethylamine system has been recognized to have a lower critical solution temperature, which means that they separate into two liquid phases at higher temperatures.[18] Under the given condition, most triethylamine was thereby located at the upper layer and did not act as catalyst. It is rational to observe that the yield and sugar content in L_{E+TEA} were similar to that in L_E.

Molecular Weight Distribution

Molecular weight distribution was determined to estimate the effects of different organosolv processes on the polymer molecular structures. As shown in Figure 2 (top), the polydispersity of lignin fractions was hardly affected by the basic catalysts (inorganic and organic); however, the organosolv process under acidic condition significantly changed the macromolecular structure. Obviously, the main peak of molecular weight was shifted to the higher molecular weight region and the diauxie distribution

Table II. Monosaccharide Components (wt %, Related to the Lignin Samples) of Isolated Lignin Fractions

	Rhamnose	Arabinose	Galactose	Glucose	Mannose	Xylose	Total
L_E	0.08	1.57	2.36	3.59	0.49	4.93	13.02
L_{E+Acid}	0.03	0.27	0.37	2.41	ND[a]	1.05	4.05
L_{E+TEA}	0.03	0.67	0.50	1.68	0.13	3.07	9.06
L_{E+NaOH}	0.67	0.95	1.39	2.46	0.52	1.48	4.56
L_{M+NaOH}	ND	ND	ND	1.01	ND	0.69	1.70
L_{P+NaOH}	ND	0.16	ND	0.91	0.05	0.31	1.43
L_{B+NaOH}	ND	0.19	0.42	1.37	0.42	0.66	3.05

[a] ND = not detectable.

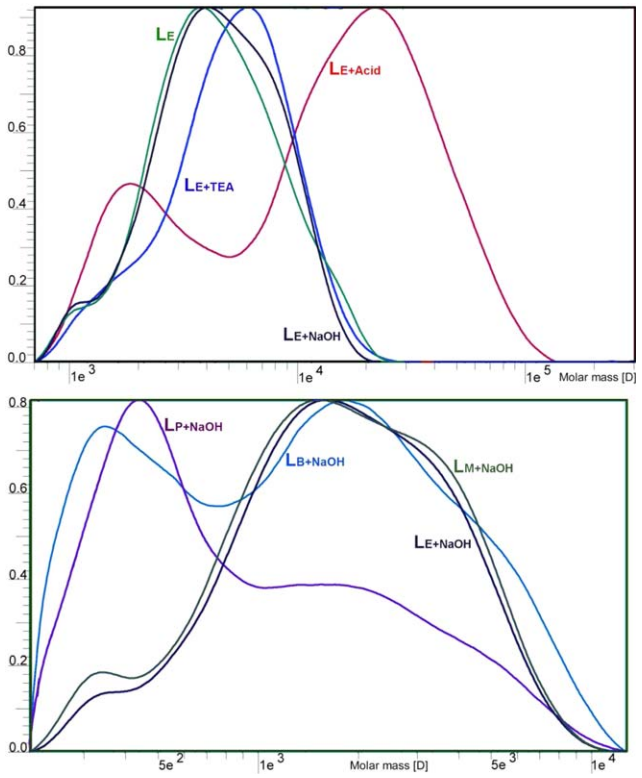


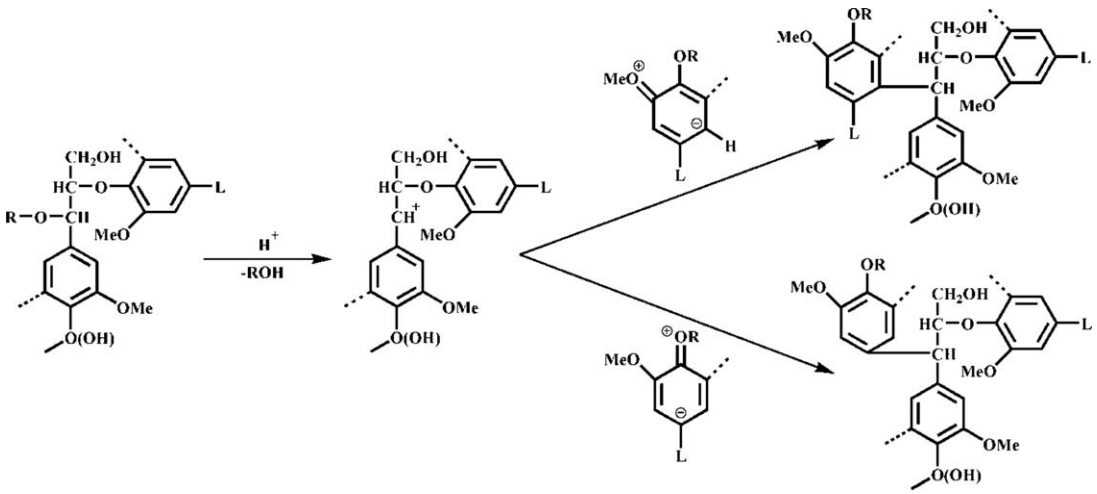
Figure 2. Molecular weight distributions of the separated lignin fractions. L_E, L_{E+NaOH}, L_{E+TEA} and L_{E+Acid} (top); L_{M+NaOH}, L_{E+NaOH}, L_{P+NaOH} and L_{B+NaOH} (bottom). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

pattern was clearly presented. The small peak in the low molecular region probably came from the lignin fragment resulted from the acid-catalyzed α/β ether cleavage. The notable increment of molecular weight was likely due to the condensation reactions resulted from the formation of carbon cation in the acid system (Scheme 1). The carbon cation could then readily bind with an electron-rich carbon atom in the aromatic ring of another lignin unit to form new C—C bond. Accordingly, the polydispersity was increased (Table II).

Comparison in the variation of molecular weight with different alcohols, methanol and ethanol similarly kept the original macromolecule of poplar lignin; however, *n*-propanol and *n*-butanol induced a partial fragment of the lignin macromolecule (Figure 2, bottom). All organosolv processes rely on chemical breakdown of the lignin prior to dissolving it. Thereby, the decrease of molecular weight was certainly helpful to improve the fractionation efficiency. *n*-Propanol exhibited better effect than *n*-butanol for breaking lignin macromolecule, probably due to the fact that *n*-propanol can fully miscible with water and the solubility of *n*-butanol in water is 7.7 g/100 mL.[19] Another probable speculation was the steric hindrance in lignin structure against alcohol with relatively longer chains.

Evaluation of Structural Characteristics of Lignin Fractions

Lignin characterization involves two aspects: the ratio of lignin precursors and the interunit linkages among them. Alkaline nitrobenzene oxidation has been widely used for identifying the structural units of lignin. In the case of oxidation, the main constitutive monomeric lignin units of guaiacyl and syringyl produced the corresponding vanillin and syringaldehyde, respectively. As shown in Table III, the *V/S* ratio (1.4) of the lignin fraction extracted with ethanol aqueous solution was very close to the data previously reported for wild-type poplar.[20] As observed above, triethylamine actually failed to promote delignification under the given condition, the same ratio of *V/S* as L_E was, thereby, not surprised to be identified in L_{E+TEA}. The addition of formic acid slightly decreased the *V/S* ratio (1.3), and totally opposite phenomena were observed under basic conditions (2.5–3.0). These results clearly revealed the different structural changes under acidic and basic circumstances. Condensation reactions occurred when the carbon cation was formed under acidic condition, which normally located at C_α of the side chain. The free C_5 position in G units was the most electron-rich carbon atom and easiest to form C—C bonds. Therefore, some part of the original G units was lost and could not be examined. Base not only breaks the ester and ether bond in lignin macromolecule, but also leads to the demethylation reactions to form new phenolic hydroxyl group and methanol.[21] In this process, syringyl nuclei



Scheme 1. Condensation reaction under acidic condition.

Table III. Yield of Phenolic Acids and Aldehydes (Relative % of Oxidation Products, wt/wt) Obtained by Alkaline Nitrobenzene Oxidation of Isolated Lignin Fractions

Phenolic acids and aldehydes	L_E	L_{E+Acid}	L_{E+TEA}	L_{E+NaOH}	L_{M+NaOH}	L_{P+NaOH}	L_{B+NaOH}
p-Hydrozybezonic acid	1.4%	0.0%	0.0%	0.0%	0.9%	0.0%	0.0%
p-Hydroxybenzaldehyde	6.8%	7.8%	7.9%	5.9%	6.0%	2.5%	10.1%
Vanillic acid	6.5%	6.2%	6.7%	7.9%	7.3%	5.3%	8.8%
Vanillin	45.4%	44.6%	47.6%	60.5%	59.1%	66.5%	53.4%
Acetovanillone	0.9%	1.2%	0.9%	2.2%	0.5%	0.4%	1.9%
Syringic acid	32.8%	35.4%	31.2%	19.8%	22.0%	22.3%	21.7%
Syringaldehyde	3.5%	3.8%	4.5%	2.3%	2.0%	1.7%	3.3%
Acetosyringone	1.1%	1.0%	1.2%	1.4%	1.1%	1.4%	0.8%
V/S[a]	1.4	1.3	1.5	3.0	2.7	2.8	2.5

[a] *V* represents the total amount of vanillin, vanillic acid and acetevanillone, S represents the total amount of syringaldehyde, syringic acid and acetosyringone.

proved to be less stable than guaiacyl nuclei. The significant increase of *V/S* ratio was consequently observed in the lignin fractions obtained from the basic organosolv process. The type of alcohols did not affect the demethylation to some extent.

FTIR technology has been widely employed to rapidly and simply examine lignin. The lignin fractions show typical FTIR spectra of lignin (Figure 3), although they were treated under different conditions. The absorptions around 1600, 1510, and 1425 cm^{-1} indicate the aromatic skeleton vibrations, while the band at 1460 cm^{-1} is assigned to the C—H asymmetric deformations. However, a slight difference can be clearly distinguished on the closer examination among the lignin fractions isolated with different alcohols. The adsorption at 1665 cm^{-1} is attributed to the C═O stretching in conjugated *p*-substituted aryl ketones,[22] which is the typical functional group in Hibbert's ketone resulting from acidolysis reactions.[23] On the other hand, a minor amount of acidolysis reactions still occurred, evidenced by the presence of this adsorption in all the spectra under such basic conditions. However, as illustrated in Figure 3, the intensity of this band was obviously weakened in the lignin fraction isolated in *n*-propanol, then in *n*-butanol. This phenomenon

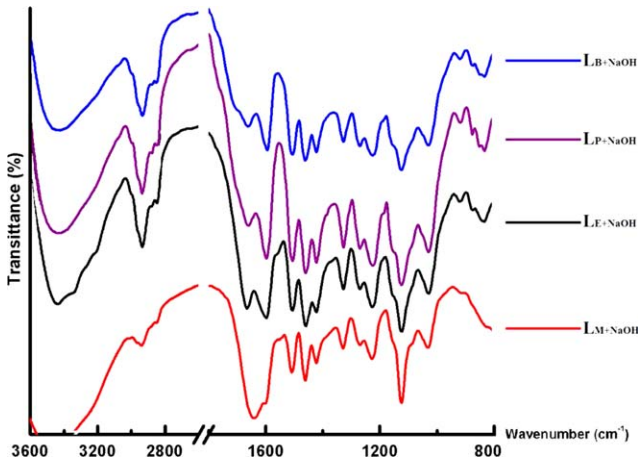


Figure 3. FTIR spectra of the lignin fractions L_{M+NaOH}, L_{E+NaOH}, L_{P+NaOH} and L_{B+NaOH}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

indicated that alcohols with longer chains were easier to form α-alcohol substructures, inhibiting the formation of Hibbert's ketone. This ether substructure has high activity, and is favorable for further degradation of lignin. This result confirmed the structure variety of the isolated lignin as illustrated in GPC analysis. For the similar explanation stated above, *n*-propanol is better than *n*-butanol to form ether bond at the C_α position.

NMR technology has been extensively used in the field of lignin structure analysis, revealing both the aromatic units and the different inter-unit linkages present in lignin macromolecule. In this study, ^1H- and ^{13}C-NMR spectra of L_{E+NaOH} were recorded, and the signal assignments were primarily in accordance with the previous literatures.[24–26] In the proton NMR spectrum (Figure 4), the intense peaks at 3.7 and 3.3 ppm are assigned to methoxyl group and hydrogen deuterium oxygen, respectively. The integral of all signals between 6.7 and 7.3 ppm belongs to aromatic protons, particularly for G (7.2–7.3 ppm) and S (6.6–7.0) units. The content of *β-O-4′* structure could be assessed by $C_\alpha H$ (4.8–5.3 ppm), $C_\beta H$ (4.6–4.3 ppm), and $C_\gamma H$ (4.1-4.2 ppm) signals presented in the side chain of such structural units. This indicated that *β-O-4′* linkage was the predominant interunit linkage in the native lignin, and the fractionation process under the given alkaline condition did not significantly attack this substructure. In terms of the ^{13}C spectrum (Figure 5), characteristic aromatic carbon signals of etherified and non-etherified syringyl (152.1–152.5 ppm, C3/C5, etherified; 147.6 ppm, C3/C5, non-etherified; 138.0 ppm, C4, etherified; 134.8 ppm, C1, etherified; 133.2 ppm, C1, non-etherified; and 104.3-107.9 ppm, C2/C6) and guaiacyl (149.1 ppm, C3, etherified; 145.8 ppm, C4, etherified; 145.3 ppm, C4, non-etherified; 134.8 ppm, C1, etherified; 133.2 ppm, C1, non-etherified; 119.2 ppm, C6; 114.9 ppm, C5; and 111.1 ppm, C2) residues were clearly identified. *p*-Coumarate ester has been demonstrated to be connected at γ-position of the lignin side chain in a previous literature,[27] thereby, it is not surprising to observe some weak signals attributing to this substituent. In addition, a small amount of ferulic acid, both etherified and esterified (131.2 ppm, C2/C6, *p*-coumarate ether; 128.5 ppm, C2/C6, *p*-coumarate ester; and 121.2 ppm, C6, ferulate ester), was also detected in the ^{13}C-NMR spectrum. These phenomena revealed that ferulic and *p*-coumaric acids were not completely saponified by 1% NaOH

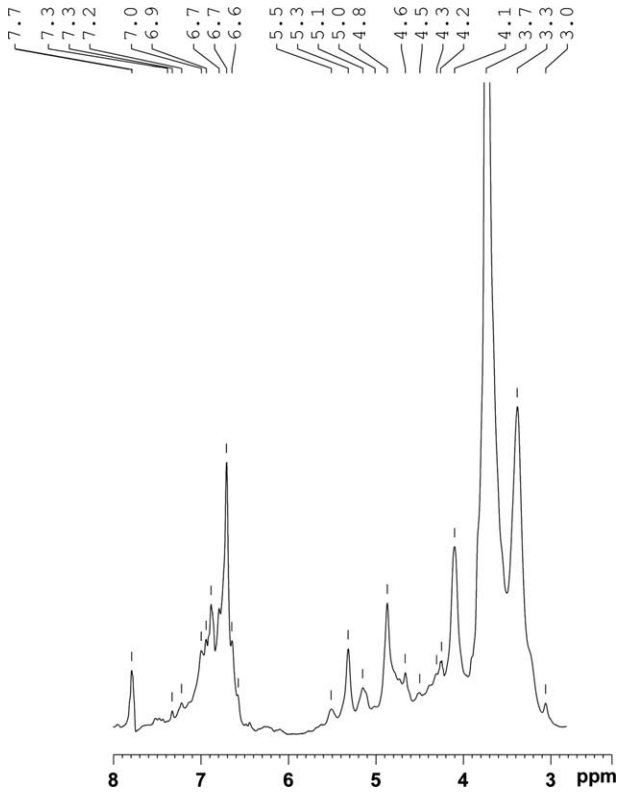


Figure 4. ^{1}H-NMR spectrum of L_{E+NaOH}.

and remained bound to the solubilized lignin. Additionally, the signals between 60 and 90 ppm came from the aliphatic carbons, where the strong resonances were assigned to α (71.2–72.1 ppm), *β* (85.0–87.0 ppm), and *γ* (60.0–61.5 ppm) positions in *β*-*O*-4′ or *γ*-acylated *β*-*O*-4′ substructures. The sharp peak at 56 ppm conclusively belongs to the —OCH_3 group in syringyl and guaiacyl units.

Two dimension ^{1}H- and ^{13}C-NMR have been widely employed to provide important structural information of lignin. The HSQC NMR spectrum of L_{E+Acid} is divided into the side aliphatic region (δ_C/δ_H 45–100/3.0–6.0) and aromatic region (δ_C/δ_H 95–135/6.4–8.0) (Figure 6). The *β*-*O*-4′ and *γ*-acylated *β*-*O*-4′ substructures were still dominant in the macromolecular structure, corresponding to the strong signals at δ_C/δ_H 60.4/3.4–4.0 (C_γ in I), 63.0/3.6–3.9 (C_γ in I′), 71.4/4.7 (C_α in I), 72.1/4.9 (C_α in I′), 80.9/4.5 (C_β in I′), 84.1/4.3 (C_β in I, G units), and 86.3/4.1 (C_β in I, S units). In addition, a certain amount of resinol subunits (*β*-*β*/α-*O*-*γ*′/*γ*-*O*-*α*′, II) (δ_C/δ_H 54.0/3.1, C_β in II; δ_C/δ_H 71.2/3.8 and 4.2, C_γ in II; δ_C/δ_H 85.3/4.7, C_α in II) and small amount of phenylcoumarans (*β*-5′, III) (δ_C/δ_H 53.5/3.5, C_β in III; δ_C/δ_H 60.4/3.2, C_γ in III; δ_C/δ_H 87.3/5.5, C_α in III) were also detected in the spectrum. These results indicated that the organosovl process under the present acidic condition could partially cleave the ether bond, and form a certain amount of C—C bonds. The main cross-signals in the aromatic region of the HSQC spectrum [Figure 6(b)] corresponded to the aromatic ring-based lignin units. By integrating the area of $C_{2,6}/H_{2,6}$ in S

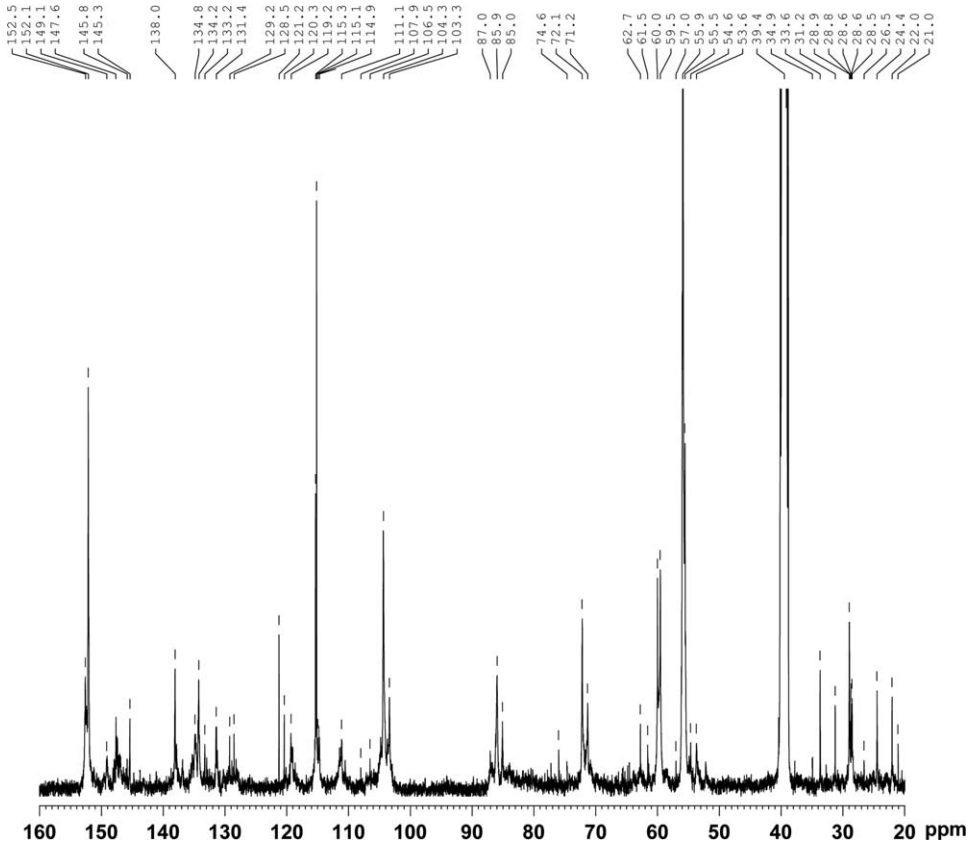


Figure 5. ^{13}C-NMR spectrum of L_{E+NaOH}.

and G unit, respectively, the S/G ratio (0.81) was in good agreement with the result of alkaline nitrobenzene oxidation (0.77).

Thermal Stability

Lignin is the most thermo-stable component among the lignocellulosic materials, mainly due to the inherent structure of aromatic rings with various branches.[28] Clearly, ethanol organolv process with basic catalysts improved the thermal stability of the isolated lignin, evidence by the relatively slower weight loss rate and higher non-volatile residues from L_{E+NaOH} and L_{B+NaOH} than L_E (Figure 7). Accordingly, the exothermic peaks in DTA curves shifted to higher temperature region and exhibited lower intensities. As we known, hemicelluloses are much easier to be pyrolyzed than lignin.[28] Thereby, the obvious cleavage of lignin–carbohydrate linkages under basic condition released part of hemicelluloses, which is the possible reason for the increasing thermal stability. Another possible explanation was the condensation reactions accompanied by the lignin fractionation. The phenolate anions could react with quinone methide under alkaline condition, resulting in the formation of a carbon–carbon bond between one of *o*- or *p*-ring position and the α-side chain position of another unit. The newly formed C—C bonds are more stable than the ether bonds. In terms of different alcohols, L_{B+NaOH} and L_{E+NaOH} exhibited the similar DTA curves before the temperature reached 500°C. The charring process occurred and a certain amount of CH_4 was released when the temperature was higher than 500°C, due to the cracking of methoxyl group (—OCH_3) in lignin.[28] Consequently, the increased degradation rate of L_{E+NaOH} than that of L_{B+NaOH} was probably attributed to the relatively lower content of S units in L_{E+NaOH}. The higher molecular weight of L_{E+NaOH} than L_{B+NaOH} was another potential reason for this phenomenon.

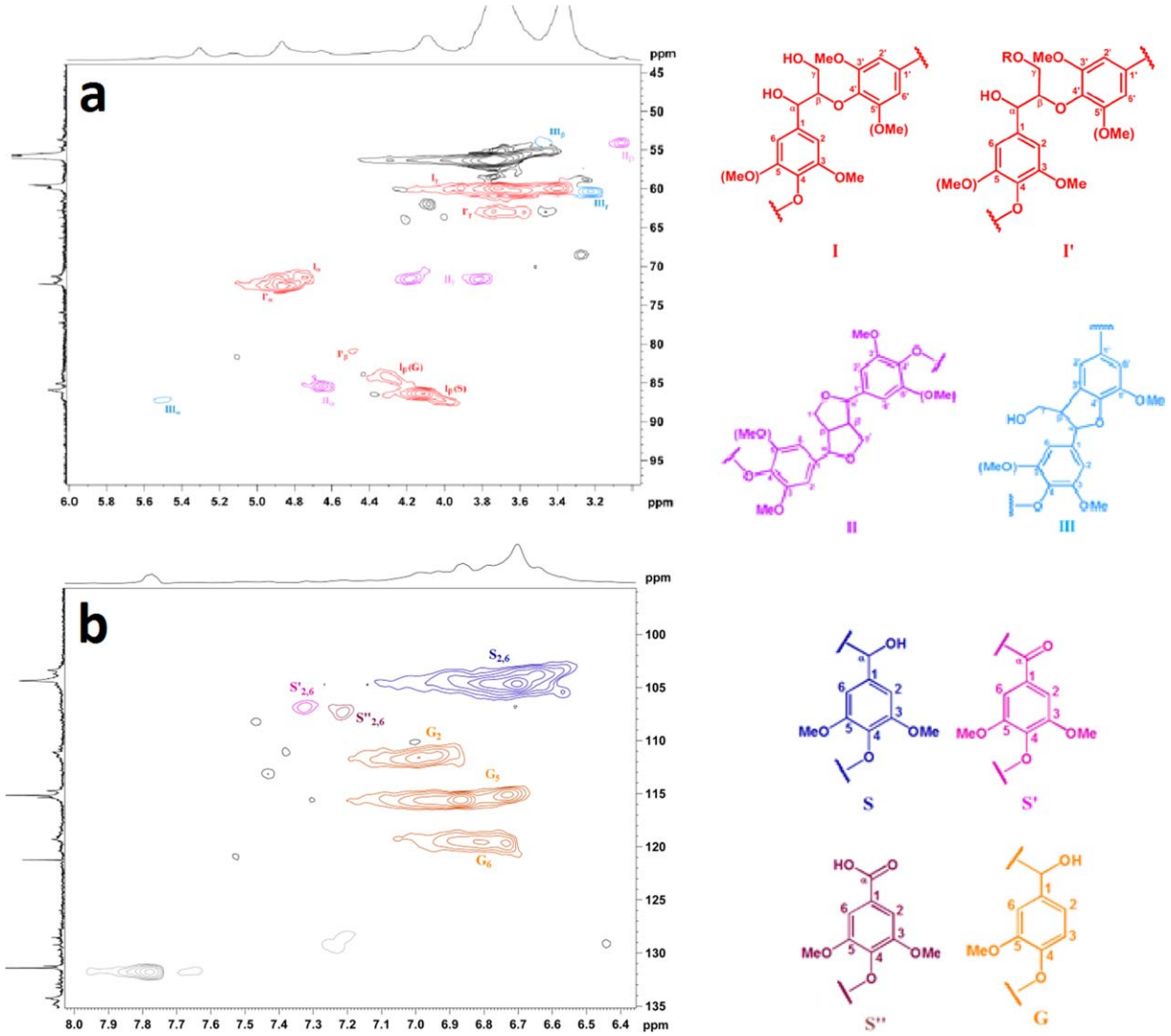


Figure 6. HSQC spectra of the lignin fraction L_{E+Acid} [(a) side aliphatic region; (b) aromatic region], and main classical substructure identified: (I) *β*-*O*-4′ substructure; (I′) *γ*-acylated *β*-*O*-4′ substructure; (II) resinol substructure, formed by *β*-*β*′ coupling and *α*-*O*-*γ*′ and *γ*-*O*-*α*′ bonding during quinine methide rearomatization; (III) phenylcoumaran, formed by *β*-5′ coupling and subsequent *α*-*O*-4′ bonding; (S) syringyl unit; (S′) oxidized syringyl units with a C_α ketone; (S′) oxidized syringyl units with a C_α carboxyl group; (G) guaiacyl unit. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

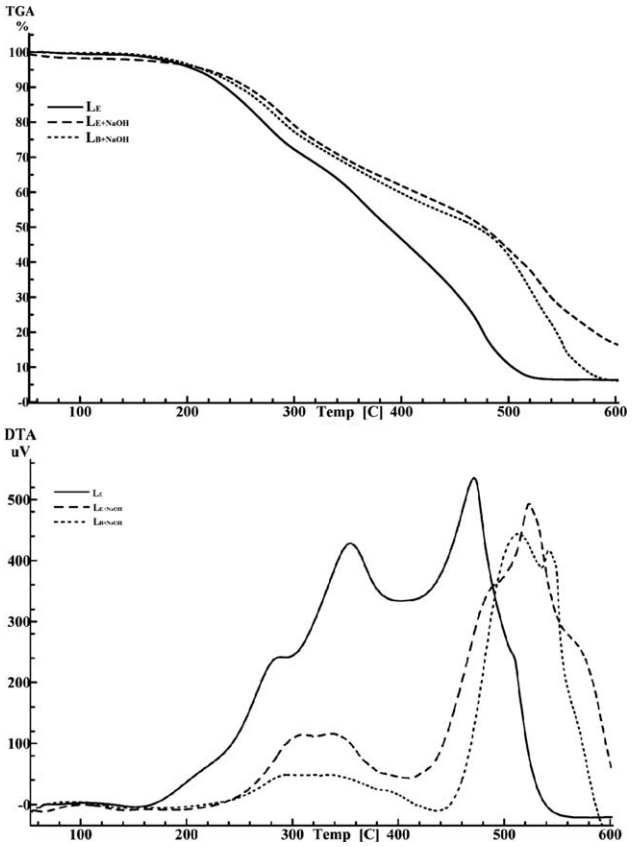


Figure 7. TGA/DTA curves of the lignin fractions L_E, L_{E+NaOH}, and L_{B+NaOH}.

CONCLUSIONS

In summary, triploid poplar lignin was fractionated in different alcohols with various catalysts. The analyses demonstrated that both the addition of acidic and basic catalysts improved the purity of lignin by hydrolysis and the cleavages of the ester groups and other types of lignin–carbohydrate interaction formed by polyoses and lignin. Some new carbon–carbon bonds were produced in the presence of acidic catalyst. The physicochemical characteristics of the different alcohols resulted in different catalytic capacities, in which *n*-propanol and *n*-butanol degraded lignin macromolecule more effectively.

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