

Chemical Structure and Pyrolysis Characteristics of the Soda-Alkali Lignin Fractions

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In the present work, three different kinds of lignin fractions (L1, L2, and L3) were isolated from the alkali black liquor of *Cunninghamia lanceolata* by selective precipitation at the pH values of 8 (fraction L1), 5 (fraction L2), and 2 (fraction L3). Elemental analysis, gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FT-IR), ³¹P nuclear magnetic resonance (³¹P-NMR), thermal gravimetric analysis (TG), and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) were used to characterize the chemical structure and thermochemical properties of the three lignin fractions. The results showed that L1 presented higher heating value (HHV) and molecular weight compared with L2 and L3. The structures and functional group types were similar for the three lignin grades. However, there was more hydroxyl group in L1 than that in L2 and L3, and the L3 contained a higher amount of carboxylic hydroxyl. L1 exhibited the lowest weight loss value (47.8%) at 200 to 600 °C and the highest amount of charred residue (45.1%), which was exactly the opposite for L3. Phenols, the dominant pyrolysis products, constituted 92.17% of all the pyrolysis products for L1, 93.93% for L2, and 88.09% for L3.

Keywords: Lignin; Elemental analysis; GPC; FT-IR; ³¹P-NMR; TG; Py-GC/MS

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INTRODUCTION

With the progress of society and the ever-shrinking fossil fuel reserves, people are beginning to pay more attention to the efficient utilization of biomass resources. Lignocellulose produced by photosynthesis is the most abundant renewable biomass resource with a supply of approximately 200 billion metric tons every year in the world (García *et al.* 2009). As with cellulose and hemicellulose, lignin is one of the main components of lignocellulose (Toledano *et al.* 2010). Lignin is a random, amorphous, three-dimensional phenolic polymeric network that does not have a uniform, homogeneous, well-defined chemical structure with well-established repeating units (Cateto *et al.* 2008). As the by-product in paper pulp, as well as the bioethanol industries, most lignin is burned as low-grade fuel, and only a small amount is isolated (Sahoo *et al.* 2011) and commercialized (*ca.* 2%) (Cateto *et al.* 2008; Pińkowska *et al.* 2012). Compared with the cellulose and hemicellulose, the development and utilization of the lignin on a large scale has not been achieved yet. Furthermore, the prospective utilization lignin for energy and bio-fuels valorization is regarded as the field with the most reliability for commercial application. Also, advanced thermochemical technologies (*e.g.* decomposition, gasification, and upgrading) can be applied for the conversion of lignin to high-value compounds such as liquid fuels, hydrogen, and aromatic monomers (Manara *et al.* 2014).

There are mainly three approaches to the fractionation of lignin. The first method is selective precipitation, which has been achieved by gradually decreasing black liquor's pH by adding mineral acid (Sun and Tomkinson 2001; Mussatto *et al.* 2007). This method is simple and low-cost, but it has the disadvantage of a relatively low purity of the lignin precipitated. Another approach to fractionate lignin is to utilize selective solvents (enzymes, biomimetic catalysts, ionic liquids, *etc.*) for the lignin extraction; such an approach is used in the synthesis of high-value products with high production costs at the same time (Kilpeläinen *et al.* 2007). Membrane technology is the third way to fractionate lignin, and this approach makes it possible to obtain lignin fractions with defined molecular weight distributions by reagent-free treatment. The effectiveness of the fractionating process depends on the selection of the proper cut-off when using the membrane technology (Colyar *et al.* 2008; Jönsson *et al.* 2008). But when it comes to the utilization of industrial lignins, there are still many problems to be resolved, such as the heterogeneity of the lignin and the lack of effective methods for separation of the lignin with high purity and low cost. Therefore, further study is required to separate and characterize the lignins with the purpose of optimal use (García *et al.* 2009).

In this paper, three different lignin fractions (L1, L2, and L3) were obtained by selective precipitation from the black liquor. Their chemical structure and pyrolysis properties were researched by elemental analysis, gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FT-IR), ³¹P nuclear magnetic resonance (³¹P-NMR), thermal gravimetric analysis (TG), and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Though similar studies have been carried out dealing with lignin isolation by acid precipitation (Sun *et al.* 2001; García *et al.* 2009; Toledano *et al.* 2010), this research combined the different selective precipitation and the analysis of the obtained lignin fractions with different detection means. These could provide information about the chemical structure and thermochemical property, which was very helpful for the optimal utilization of the lignin.

EXPERIMENTAL

Materials

Black liquor sourcing

Cunninghamia lanceolata was acquired from Guangdong Province (P. R. China). The raw material was pulped in a batch reactor, at 170 °C for 2 h, with a 7.7% sodium hydroxide solution (w/v), solid/liquid ratio of 1/4 (w/w), and continuous stirring. After the reaction, the black liquid was separated from the pulp, and then subjected to filtration with a screen of 38 micron size.

Lignin isolation

The obtained black liquor was dropwise acidized with sulfuric acid solution (10%, w/w) to a pH value of 8 at 60 °C. Stirring was maintained throughout the acidification process. After the acid addition, the liquor was centrifuged at 5000 rpm for 5 min. The precipitated lignin was separated, washed more than twice with acidified water at pH 2 to remove contamination like inorganic salt, and then freeze-dried for 24 h. This brown powder was designated as L1. The remaining supernatant was stirred and acidized once again to the pH value of 5. After the process of centrifugal separation, washing more than twice with acidified water at pH 2 and freeze-drying, another lignin fraction was obtained,

named L2. At last, the pH value of the rest supernatant was adjusted to 2. The same subsequent steps such as separation, washing, and drying were carried out to get the third lignin fraction, which was called L3.

Instrumental Methods

The elementary compositions of the three lignin fractions were determined with a Vario-EL CUBE elemental analyzer (Elementar, Germany).

Prior to molecular weight determination, the samples were acetylated as follows: the freeze-dried lignin (300 mg) placed in an Erlenmeyer flask was dried under vacuum at 40 °C. Then, anhydrous pyridine (16 mL) and acetic anhydride (8 mL) were successively added, and kept at room temperature for 72 h in the dark. Diethyl ether (200 mL) was then added to precipitate lignin. The acetylated lignin was collected after centrifugal separation and vacuum drying and then was dissolved in THF (1 mg/mL) for GPC study with an Agilent 1200 series liquid chromatograph equipping a differential refractive index detector. Polystyrene standards were used to make calibration.

Fourier transform infrared spectroscopy (FTIR) spectra were acquired using a Nexus 670 spectrophotometer (Thermo Nicolet, USA). The samples were pressed into a KBr pellet (1:100). Spectra were obtained in the range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} , and 64 scans for each sample.

Quantitative ^{31}P -NMR experiments were performed on a Bruker 400 MHz spectrometer. The lignin sample (40 mg) was dissolved in pyridine- d_5 /CDCl $_3$ (1.6:1 v/v, 800 μL) acting as the solvent. The cholesterol (4 mg) was used as the internal standard, chromium acetylacetonate (0.55 mg) as the relaxation reagent and 2-chloro-4,4,5,5-tetramethyl-1,3,2-ioxapholane (TMDP) (130 μL) as the phosphitylating agents. The reaction was carried out for 2 h (Wu *et al.* 2006).

The thermo-stability properties of the samples were studied with a thermal gravimetric analyzer (NETZSCH Corporation, Germany). High-purity nitrogen was used as the carrier gas with a flow velocity of 25 mL/min. The samples of 5 to 10 mg were heated at a rate of 20 °C/min and from 25 °C up to 700 °C.

Fast pyrolysis experiments were carried out by Py-GC/MS with the carrier gas high-purity helium. Pyrolysis of the samples was studied with the CDS5150 (Chemical Data System, USA) analytical pyrolyzer. Each sample of about 0.1 mg was pyrolyzed to 600 °C at 10 °C/ms, and kept at the final temperature for 15 s. The flow velocity of the carrier gas was 50 mL/min with split ratio of 50/1. The temperatures of injector and ion source were both 250 °C. The temperature of the column was programmed from 50 to 250 °C and at 10 °C/min after an initial retention time of 1 min and kept at the final temperature for 2 min. The semipolar column (DB1701, 30 m x 0.25 mm, 0.25 μm film thickness) was used to separate the pyrolysis products. The mass spectrometer was set at an ionizing voltage of 70 eV with mass range m/z 42 to 450. The identification of lignin products was accomplished by the comparison of mass fragment with the National Institute of Standards and Technology (NIST) Mass Spectral library.

RESULTS AND DISCUSSION

Elemental Composition Analysis

The organic element (C, H, N, and S) contents of the three lignin fraction were measured with the elemental analyzer. The O content was calculated by differences.

Table 1 shows the results of the elemental composition. It can be seen that the C and H contents decreased gradually in L1, L2, and L3, while the O and N contents increased. There was no S element detected in L1, L2, or L3.

The empirical formula and high heating value (HHV) of the L1, L2, and L3 are also listed in Table 1. These quantities were calculated by the elemental composition and the Dulong formula (Yuan *et al.* 2009), respectively. HHV depends on the percentage of C, H, O, and S, especially the C content. It can be observed that L1 had the largest HHV and the lowest O/C ratio among the three lignin fractions, which was beneficial for energy-oriented utilization.

Table 1. Elemental Analysis of the Three Lignin Fractions

| Component | N% | C% | H% | S% | O% | Empirical formula | HHV (MJ/kg) |
|-----------|------|-------|------|------|-------|--|-------------|
| L1 | 0.08 | 65.66 | 6.12 | 0.00 | 27.78 | [C ₁₀ H _{11.19} O _{3.17} N _{0.01}] _n | 25.99 |
| L2 | 0.09 | 62.86 | 6.00 | 0.00 | 30.76 | [C ₁₀ H _{11.46} O _{3.67} N _{0.01}] _n | 24.34 |
| L3 | 0.15 | 62.74 | 5.95 | 0.00 | 30.80 | [C ₁₀ H _{11.37} O _{3.68} N _{0.02}] _n | 24.21 |

Molecular Weight Distribution Analysis

The GPC is a fast, simple and reliable detection method used to measure the molecular weight distribution, which involves the chromatographic fractionation of macromolecules according to molecular size (Zhou *et al.* 2007; Ghaffar and Fan 2013). The weight-average molecular weight (M_w), the numerical-average molecular weight (M_n), and the polydispersity (M_w/M_n) of the obtained three fractions from black liquor were measured using GPC, and the results are given in Table 2.

From Table 2, the M_w and M_n of L1, L2, and L3 were both gradually decreasing. That was to say, the cross-linking degree of L1 among the three fractions was becoming larger and that lignin with larger molecular weight would be precipitated earlier in the selective precipitation process. That is because lignin macromolecule is fully dissolved in the form of lignin sodium salt and hydrophilic colloid in the black liquor. When the black liquor is neutralized with the acid and its pH value is gradually decreased, the electronic substitution reaction occurs and the alkali lignin colloid is damaged at the same time, which results in generating insoluble lignin. Then lignin with larger molecular weight may possess more complex spatial structure and worse hydrophilicity, which leads to its precipitation at a relative higher pH value.

In addition, the polydispersities of the three lignin fractions made very little difference. The empirical formulas of L1, L2, and L3 could also be established as C_{881.76}H_{986.72}O_{279.77}N_{0.92}, C_{744.79}H_{853.65}O_{273.31}N_{0.91}, and C_{575.17}H_{654.01}O_{211.73}N_{1.18}, respectively, which were calculated by the elemental compositions shown in Table 1 and the mass-average molecular weight.

Table 2. Molecular Weights of the Three Acetylated Lignin Fractions

| Component | Mw(g/mol) | Mn(g/mol) | Mw/Mn |
|-----------|-----------|-----------|-------|
| L1 | 16115 | 8780 | 1.84 |
| L2 | 14218 | 7679 | 1.85 |
| L3 | 11001 | 5934 | 1.85 |

FT-IR Spectroscopy Analysis

In order to reveal the functional groups and chemical bonds present in the lignin fractions, such as carbonyl, hydroxyl, methoxy, C–H bond, and C=C bond, FT-IR analyses of the three lignin fractions were carried out. FT-IR spectra and assignments of FT-IR absorption bands of L1, L2, and L3 are shown in Fig. 1 and Table 3, respectively. It can be observed that compared with L1 and L2, the absorption signal of L3 at wavenumber 1654 cm^{-1} almost disappeared, which indicated that there were less conjugated carbonyl groups in L3. The conjugated carbonyl reduction was associated with the occurring of the acetal reaction under the catalysis of acid (Zhang 2012).

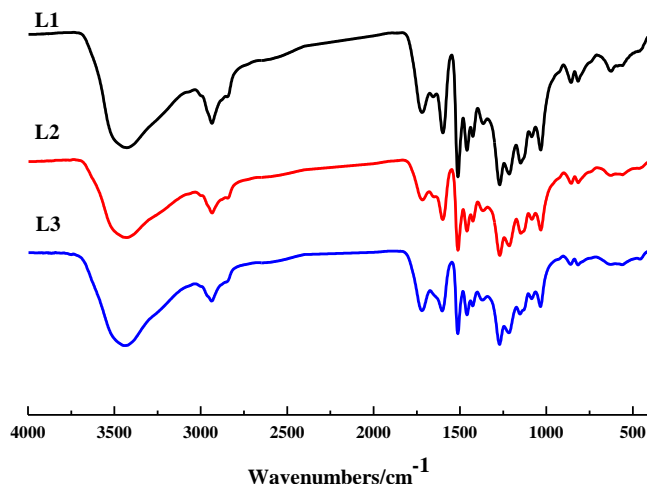


Fig. 1. FT-IR spectra of the three lignin fractions

Table 3. Assignments of FT-IR Absorption Bands

| Wavenumber (cm^{-1}) | | | Functional groups | Origin |
|---------------------------------|-------------|-------------|--------------------------|--|
| L1 | L2 | L3 | | |
| 3428 | 3428 | 3433 | O-H stretching | Phenolic and alcoholic groups |
| 2935, 2844 | 2935, 2846 | 2936, 2846 | C-H stretching | -CH ₃ , -CH ₂ , -CH |
| 1716 | 1719 | 1720 | C=O stretching | Non-conjugated carbonyl |
| 1649 | 1654 | — | C=O stretching | Conjugated carbonyl |
| 1599, 1511, | 1599, 1512, | 1603, 1512, | C=C stretching | Aromatic ring |
| 1425 | 1425 | 1426 | C-H in-plane bending, | |
| 1459 | 1459 | 1459 | C-H bending | Asymmetric -CH ₃ , -CH ₂ |
| 1365 | 1365 | 1370 | C-H bending | Condensed Syringyl or Guaiacyl unit |
| 1269 | 1270 | 1271 | =C-O-R stretching | -OCH ₃ and -OH at Guaiacyl unit |
| 1147 | 1149 | 1152 | C-H in-plane bending | Guaiacyl unit |
| 1083 | 1085 | 1085 | C-O bending | primary alcohol, aliphatic ether |
| 1032 | 1033 | 1034 | C-H bending, C-O bending | Aromatic ring, -OCH ₃ , primary alcohol |
| 856 | 857 | 859 | C-H out-of-plane bending | Guaiacyl unit |

The rest of the FT-IR bands of the three lignin fractions were roughly the same, except for different absorption intensities. The absorption signals of L1 were stronger than L2 and L3 at wavenumber 3428, 1512, 1270, and 1033 cm^{-1} , respectively, corresponding to a O-H stretching, a benzene ring stretching, a =C-O-R stretching, and an aromatic ring C-H bending or C-O bending, which suggested that the concentration of guaiacyl-type units in L1 was higher.

Lignin Structural Analysis Using Quantitative ^{31}P -NMR

The ^{31}P -NMR spectroscopy technique was developed in the 1990s and is identified as a very powerful tool for lignin structure characterization (Cateto *et al.* 2008). It makes it possible to discriminate between the three forms of phenolic hydroxyl groups existing in the lignin (*p*-hydroxyphenyl, guaiacyl, and syringyl units), as well as condensed phenolic hydroxyl groups, aliphatic hydroxyl groups, and carboxylic acid protons. Quantitative ^{31}P -NMR spectroscopy is presented in Fig. 2. With the integral areas of each type of hydroxyl group (Fig. 2) and internal standard mass added, corresponding hydroxyl group contents could be calculated, which are summarized in Table 4.

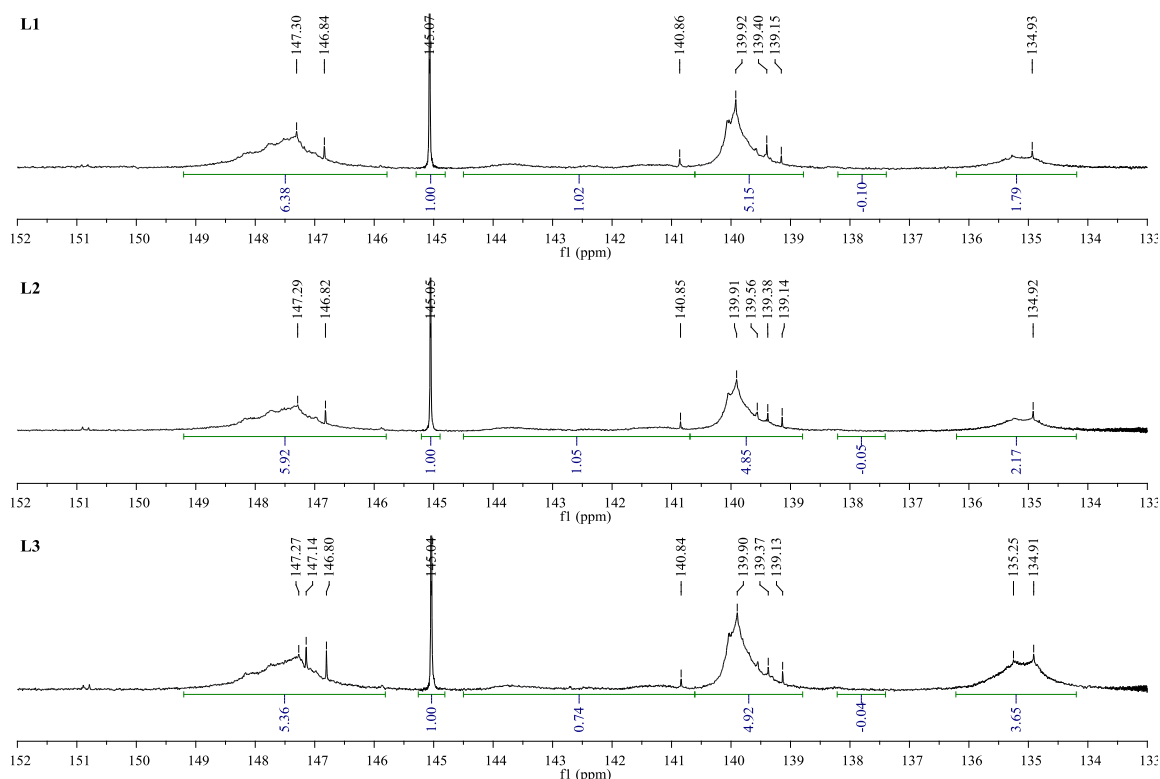


Fig. 2. Quantitative ^{31}P -NMR spectra of the three lignin fractions

Clearly, it can be seen that the aliphatic hydroxyl group was the dominant hydroxyl type in these three lignin samples. This finding was consistent with previous study for milled wood lignin (Huang *et al.* 2011). Among them, L1 had the highest content of aliphatic hydroxyl groups, followed by L2, and finally L3. The amount of C5 condensed phenolic hydroxyl group in L1 (0.26 mmol/g) and L2 (0.27 mmol/g) was slightly higher than that in L3 (0.20 mmol/g). Another significant result was that L1 (1.35

mmol/g) contained the most guaiacyl hydroxyl group, which was in accordance with the FT-IR observations already shown. In addition, L3 had approximately two times the amount of carboxylic hydroxyl than that in L1 and L2. This could be explained because carboxyl is hydrophilic, and this would make it difficult for the lignin sample with more carboxylic hydroxyl to precipitate at a certain pH. Regarding the content of total hydroxyl groups, L1 ranked the first, followed by L2 and L3. This result was in consistent with that of the FT-IR analysis.

Table 4. Functional Groups Content of the Three Lignin Fractions by Quantitative ^{31}P -NMR

| Chemical shift (ppm) | Hydroxyl type | Hydroxyl content (mmol/g) | | |
|----------------------|-------------------------|---------------------------|------|------|
| | | L1 | L2 | L3 |
| 149.2~145.8 | Aliphatic - OH | 1.67 | 1.48 | 1.43 |
| 144.8~140.6 | Condensed phenolic - OH | 0.26 | 0.27 | 0.20 |
| 140.6~138.8 | Guaiacyl - OH | 1.35 | 1.21 | 1.31 |
| 138.2~137.4 | p-Hydroxyphenyl I - OH | 0.03 | 0.01 | 0.01 |
| 136.2~134.2 | Carboxylic - OH | 0.47 | 0.54 | 0.97 |
| — | Total - OH | 3.31 | 2.95 | 2.95 |

Thermogravimetric (TG) Analysis

Thermogravimetric analysis is widely used to study how organic polymers decompose (Toledano *et al.* 2010). TG curves display the weight loss of samples in relation to the temperature of thermal degradation, while the first derivative of the TG curve (DTG) reveals the corresponding rate of weight loss. The TG and DTG curves of the three lignin fractions obtained under nitrogen at the heating rates of 20 °C/min are shown in Figs. 3 and 4, respectively. Thermal degradation onset temperature, major degradation temperatures, and percentage of charred residue are given in Table 5.

The onset temperatures observed for L1, L2, and L3 were 117.4 °C, 109.1 °C, and 104.3 °C, respectively. Weight loss within 100 °C can be attributed to the loss of moisture from lignin (Jakab *et al.* 1995; Xiao *et al.* 2001). The peak at 379 °C to 383 °C was attributed to lignin degradation. Fraction L1 obtained the highest temperature of maximum weight loss peak, followed by L2 and finally L3. The percentage of degradation in the range of 200 °C to 600 °C was used to exhibit their degradation behavior at this major degradation temperature range. Fraction L3 obtained the highest percentage weight loss (55.1%) and L1 the lowest weight loss (47.8%). The lignin degradation at the temperature below 300 °C occurs primarily by cleavage of the bonds which have low activation energy; further heating above 400 °C gives rise to stable bonds cleavage (Manara *et al.* 2014). A great amount of lignin is still residual after 700 °C due to its condensation or relocation (Sun *et al.* 2000). And that makes residual lignin more thermally stable with a slower decomposition rate and higher activation energy. There were about 45.1% of charred residue in L1, 36.1% in L2, and 35.5% in L3. The higher char content of lignin suggests that it could be used as a fire retardant in composite products (Sahoo *et al.* 2011).

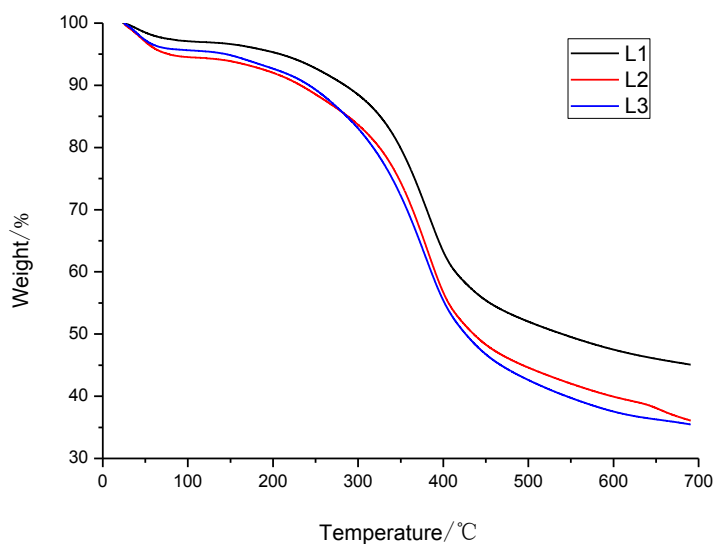


Fig. 3. TG curves of the three lignin fractions at 20 °C/min

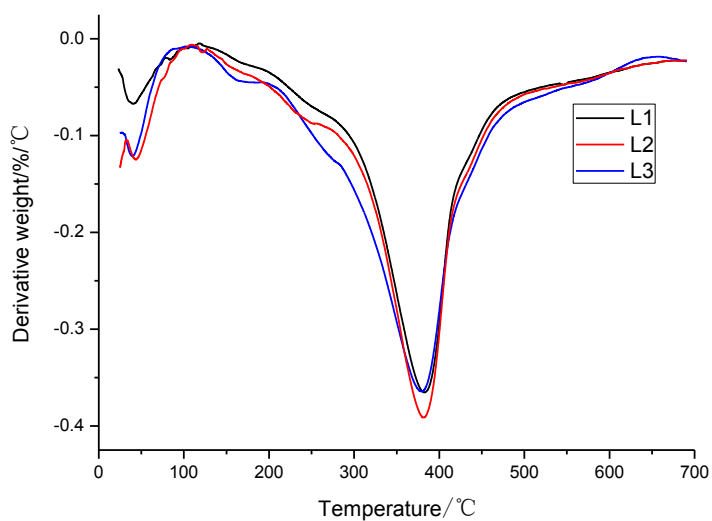


Fig. 4. DTG curves of the three lignin fractions at 20 °C/min

Table 5. Thermogravimetric Analysis of the Three Lignin Fractions

| Component | Onset temperature (°C) | Major degradation temperatures (°C) | Degradation at 200 °C-600 °C (%) | Charred residue (%) |
|-----------|------------------------|-------------------------------------|----------------------------------|---------------------|
| L1 | 117.4 | 382.6 | 47.8 | 45.1 |
| L2 | 109.1 | 381.7 | 52.1 | 36.1 |
| L3 | 104.3 | 379.1 | 55.1 | 35.5 |

Py-GC/MS Analysis

Py-GC/MS is widely used to provide detailed structural information (Lou *et al.* 2010) and pyrolysis characteristics for a polymer that degrades into low molecular weight

compounds by pyrolysis. The total ion chromatogram of the three lignin fractions is shown in Fig. 5. Table 6 illustrates the pyrolysis products at 600 °C. The unlikeness of the species and contents of the pyrolysis products suggests that there were differences in chemical structure and pyrolysis properties for L1, L2, and L3. All of the products from the three lignin fractions pyrolysis can be placed in the classifications of furans, phenols, non-phenolic monocycle arenes, and non-phenolic polycycle arenes. Furans were derived from the degradation of hemicellulose, and others stemmed from the degradation of lignin. Of all the pyrolysis products, more phenols but less non-phenolic monocycle arenes and non-phenolic polycycle arenes were produced in L1 and L2 than those in L3. This indicated that the lignin precipitated in a lower pH tended to produce more of the non-phenolic monocyclic and polycyclic arenes in the pyrolysis process. Among these products, phenols occupied the maximum proportion (L1 92.17%, L2 93.93%, and L3 88.09%). In the 36 kinds of phenolic pyrolysis products, the dominant substances were guaiacol, 2-methoxy-4-methylphenol, 2-methoxy-4-ethylphenol, 2-methoxy-4-vinylphenol, and some others, as illustrated in Fig. 5. β -O-4, α -O-4, and 4-O-5 bonds were the main types of ether bond in the lignin structure. All of them could produce guaiacol in the lignin degradation process. This was the reason why relative content of guaiacol was high in lignin degradation products. Catechol and 4-methycatechol were the main secondary reaction products of demethoxylation or demethylation of guaiacol (Feng *et al.* 2009).

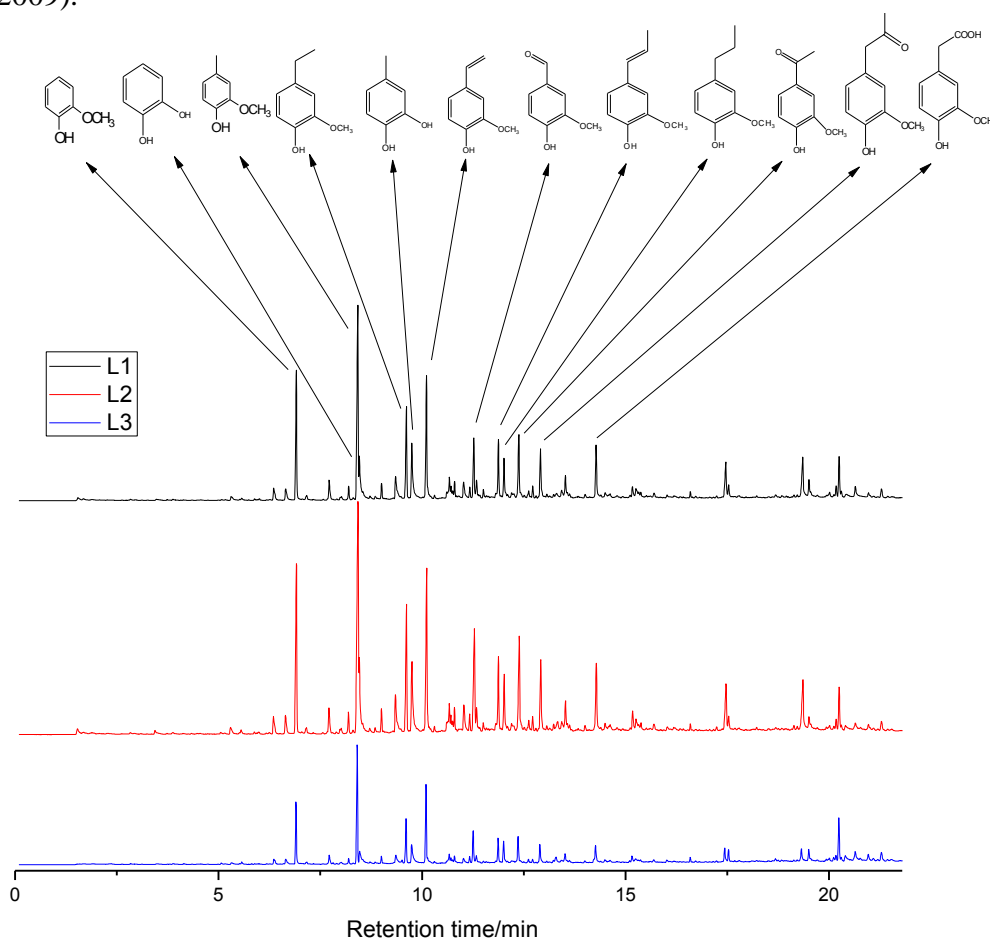


Fig. 5. Total ion chromatogram of the three lignin fractions at 600 °C

Table 6. Pyrolysis Products Analysis of the Three Lignin Fractions at 600 °C

| Groups | Library/ID | Area Pct/% | | |
|--------------|--|------------|-------|-------|
| | | L1 | L2 | L3 |
| Furans (1) | Furfural | — | 0.19 | — |
| | Phenol | 0.52 | 0.54 | 0.49 |
| Phenols (36) | Phenol, 2-methyl- | 1.09 | 1.06 | 1.01 |
| | Phenol, 4-methyl- | 1.19 | 1.10 | 0.98 |
| | Guaiacol | 7.95 | 8.13 | 6.84 |
| | Phenol, 3,5-dimethyl- | 1.59 | 1.30 | 1.48 |
| | Phenol, 2-ethyl- | 0.37 | 0.40 | 0.40 |
| | Phenol, 2-methoxy-6-methyl- | 0.77 | 0.85 | 0.67 |
| | Phenol, 2-methoxy-4-methyl- | 13.71 | 14.16 | 13.89 |
| | Catechol | 4.62 | 3.74 | 3.85 |
| | Benzofuran, 2,3-dihydro- | 0.30 | 0.29 | — |
| | 1,2-Benzenediol, 3-methyl- | 2.38 | 2.54 | 2.28 |
| | Propanal, 2-methyl-3-phenyl- | — | — | 0.69 |
| | Phenol, 2-methoxy-4-ethyl- | 5.68 | 5.70 | 5.50 |
| | Catechol, 4-methyl- | 5.43 | 5.12 | 4.67 |
| | Phenol, 2-Methoxy-4-vinyl | 8.40 | 8.47 | 10.09 |
| | 1,3-Benzenediol, 4,5-dimethyl- | 0.42 | 0.47 | — |
| | Eugenol | 1.51 | 1.47 | 1.43 |
| | 1,2-Benzenediol, 4-(1,1-dimethylethyl)- | 0.70 | 0.69 | 0.58 |
| | Phenol, 2-methoxy-4-(1-propenyl)- | 0.46 | 0.46 | 0.34 |
| | 4-Ethylcatechol | 1.67 | 1.87 | 0.90 |
| | 3-Allyl-6-methoxyphenol | 0.67 | 0.75 | 0.69 |
| | Vanillin | 3.91 | 5.67 | 3.98 |
| | Phenol, 2-methoxy-4-(1-propenyl)-, (E)- | 4.94 | 4.43 | 3.95 |
| | Phenol, 2-methoxy-4-propyl- | 3.81 | 3.96 | 3.55 |
| | Ethanone, 1-(4-hydroxy-3-methoxyphenyl)- | 4.71 | 5.41 | 3.85 |
| | 2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)- | 3.43 | 3.88 | 2.72 |
| | Benzoic acid, 4-hydroxy-3-methoxy- | 0.42 | 0.96 | 1.35 |
| | Phenol, 4-(3-hydroxy-1-propenyl)-2-methoxy- | 0.52 | 0.81 | 0.63 |
| | 2,4'-Dihydroxy-3'-methoxyacetophenone | 1.32 | 1.57 | 1.73 |
| | Benzeneacetic acid, 4-hydroxy-3-methoxy- | 3.71 | 3.82 | 3.10 |
| | 2-Naphthalenol, 3-methoxy- | 0.51 | 0.65 | 0.56 |
| | .Beta.-(4-hydroxy-3-methoxyphenyl)propionic acid | 1.04 | 1.10 | 1.27 |
| | 2-Propenal, 3-(4-hydroxy-3-methoxyphenyl)- | 0.95 | 0.85 | 1.02 |
| | 4H-1-Benzopyran-4-one, 3,5,7,8-tetrahydroxy-6-methyl-2-phenyl- | 2.02 | 0.81 | 1.75 |
| | Phenol, 4,4'-methylenebis[2,6-dimethyl- | 0.80 | 0.46 | 0.74 |
| | 1,1'-Biphenyl, 6-hydroxy-2',3',4'-trimethoxy- | 0.63 | 0.42 | 1.08 |
| | <i>Total</i> | 92.17 | 93.93 | 88.09 |

| | | | | |
|-----------------------------------|--|------|------|------|
| | 2,5-Dimethylanisole | 0.45 | 0.40 | 0.40 |
| | 3,4-Dimethoxytoluene | 0.80 | 0.80 | 0.72 |
| | Benzene, 1,2-dimethoxy-4-(2-propenyl)- | 0.41 | 0.39 | 0.33 |
| Non-phenolic monocycle arenes (7) | 1H-Indene-1,3(2H)-dione, 2-(2-ethylpropylidene)- | — | 0.42 | — |
| | 1,2-Benzenedicarboxylic acid, bis(2-Methylpropyl) ester | 0.29 | 0.25 | 0.47 |
| | Dibutyl phthalate | 0.79 | 0.59 | 1.48 |
| | 1H,12H-Furo[3',2':4,5]furo[2,3-h]pyrano[3,4-[1]benzopyran-,12-dione, 3,4,7a,9,10,10a-Hexahydro-5-methoxy-, (7a-cis)- | 1.79 | 0.53 | 2.05 |
| | <i>Total</i> | 4.53 | 3.38 | 5.46 |
| | Anthracene | — | 0.34 | 0.26 |
| | Pyrene, 1,6-bis(1,1-dimethylethyl)- | 0.65 | 0.33 | 0.60 |
| Non-phenolic polycycle arenes (4) | Benzo[c]phenanthrene, 4-methyl- | 2.65 | 1.84 | 5.27 |
| | Benz(a)anthracene, 3,9-dimethyl- | — | — | 0.31 |
| | <i>Total</i> | 3.29 | 2.50 | 6.44 |

CONCLUSIONS

In the present study, alkali lignin from *Cunninghamia lanceolata* was separated into three fractions by successive fractional precipitation at the pH values of 8 (fraction L1), 5 (fraction L2), and 2 (fraction L3). The results showed that L1 with the higher molecular weight had a larger high heating value (HHV) and lower O/C ratio when compared with L2 and L3. The dominant hydroxyl type in these three lignin samples was the aliphatic hydroxyl group, and L1 ranked the first, followed by L2 and finally L3. L3 had approximately two times higher amount of carboxylic hydroxyl than that in L1 and L2. L1 obtained more total hydroxyl group than L2 and L3. According to the TG and DTG information, L1 exhibited the lowest weight loss value (47.8%) at 200 to 600 °C and the highest amount of charred residue (45.1%), which was exactly the opposite for L3. The species and content of the fast pyrolysis products were different for the three fractions. Phenols occupied the maximum proportion of the pyrolysis products, and the relative content of phenols was 92.17% for L1, L2 93.93%, and L3 88.09%. Additionally, L3 produced more of the non-phenolic monocyclic and polycyclic arenes in the pyrolysis process. These results indicated that the lignin precipitated in a higher pH tended to possess a higher molecular weight and a higher HHV, and it would give rise to enhanced charred residue. These properties of the lignin provided some evidence for its potential utilization toward energy direction due to its higher energy content (lower O/C ratio) or via pyrolysis/carbonization applications for carbonaceous material purposes (e.g. activated carbon). On the contrary, gasification reactions could be proposed as more suitable for the lignin precipitated at a lower pH.

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