STRUCTURAL CHARACTERIZATION OF LIGNIN EXTRACTED WITH ALKALINE HYDROGEN PEROXIDE FROM FURFURAL RESIDUE

CHANG-ZHOU CHEN,[*] MING-FEI LI,[*] YU-YING WU[*] and RUN-CANG SUN[*,**]

[*]*Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing 100083, China*
[**]*State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China*
✉ *Corresponding author: Run-Cang Sun, rcsun3@bjfu.edu.cn*

Received August 6, 2013

Lignin from furfural residue was extracted with alkaline hydrogen peroxide at different temperatures and times. The structural features of lignins were characterized by elemental analysis, GPC, FT-IR, ^{1}H NMR, ^{13}C NMR and Py-GC/MS. Results showed that the yield of lignin increased with the increase of reaction time and temperature. The maximum lignin yield of 41.4% (corresponding to the original lignin) was achieved by extraction at 80 ºC for 3 h. The average-molecular weight (M_w) of the extracted lignins (780-850) was about 1/4 of that of the MWL (milled wood lignin) of furfural residue (2890), which indicated a severe degradation of furfural residue lignin under the treatment. Py-GC/MS analysis indicated that the major unit in lignins was *p*-hydroxycinnamyl (H), together with lower amounts of syringyl (S) and guaiacyl (G) units. The relative molar content of the H unit in the extracted lignins increased, as compared to MWL.

Keywords: furfural residue, lignin, alkaline hydrogen peroxide, Py-GC/MS

INTRODUCTION

Furfural residue (FR) is a byproduct rich in lignin and cellulose in the production of furfural. However, it is mainly burned to provide heat in the current industrial production.[1] It is estimated that about 23 million tons of furfural residues were available annually for alternative use between 2006 and 2009 in China,[2] which means that a great amount of lignin in FR has not been exploited. In recent decades, FR has been utilized as fertilizer, activated carbon, bio-ethanol feedstock, and adsorbent, etc.[3-5] However, investigation on the applications of lignin from FR is scarce.

Lignin, the third most abundant organic compound[6] in the world after cellulose and hemicelluloses, is an irregular and complex polymer in woody plants. It is estimated that there are about 300 billion tons of lignin on the earth and its annual biosynthetic production is of 20 billion tons. Thus, lignin is expected to play an important role as a potential raw material in the bio-based economy for the production of chemicals, materials and biofuels.[7] It is formed by oxidative coupling of three major monolignols, namely, *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, through an enzyme-initiated dehydrogenative polymerization.[8,9] These units are connected by various bonds. The relative abundance of the different linkages largely depends on the contribution of a particular monomer to the polymerization process, which makes the lignin form a network structure.[10] The predominant chemical inter-unit linkage is *β-O*-4′, which is also easily cleaved by chemical

treatment, providing a basis for industrial processes, for example, chemical pulping. The other linkages are *β*-5′, *β*-*β*′, 5-5′, 5-*O*-4′, and *β*-1′, etc., which are more stable than *β*-*O*-4′ in chemical degradation.[11] As a natural polymer rich in aromatic ring, lignin has significant potential applications in the fields of fuel and chemical materials, such as bio-oil, polymeric materials, antioxidants, green diesel, auxiliaries of building materials,[12] and carbon fibers.[13-16]

A cost-effective and eco-friendly separation method of lignin is the basis of commercial utilization of biomass feedstock. Many methods have been proven to be efficient and environmentally friendly for delignification of biomass feedstock. Among them, the oxygen-based methods involving the use of molecular oxygen, ozone, or peroxide as delignifying agent attract much attention.[17] Hydrogen peroxide, the most promising oxidants for green chemistry, is well known as an oxidant that reacts with lignin under alkaline conditions. Hydrogen peroxide is unstable under alkaline conditions and easily decomposes to more active radicals, such as hydroxyl radicals (OH•) and superoxide anion radicals (OO•-), which participate in the delignification. Alkaline hydrogen peroxide treatment has been widely used as pretreatment[18,19] and posttreatment[20,21] under mild temperatures and pressures (optimally at pH 11.5).[22] The previous study found that delignification with alkaline hydrogen peroxide is a promising treatment to achieve complete utilization of lignocelluloses without impact on environment.

In this study, a series of experiments were conducted to investigate the effects of the pretreatment time and temperature on the yield of lignin isolated with weakly alkaline hydrogen peroxide from FR. Furthermore, the isolated lignins were characterized as compared to milled wood lignin (MWL) from furfural residue by elemental analysis, GPC, FT-IR, ^{1}H NMR, ^{13}C NMR and Py-GC/MS.

EXPERIMENTAL

Materials

FR produced from corncob was obtained from Chunlei Furfural Corporation Hebei, China. After it was smashed, the FR was passed through a 40-mesh screen, dried in an oven at 60 ºC overnight. All materials were stored in sealed bags at room temperature until further processing. The chemical composition of the FR was cellulose 41.9%, lignin 34.6%, xylan 1.3% and ash 8.6%, determined according to the National Renewable Energy Laboratory method.[23]

Methods

Extraction of lignin

The samples were treated with alkaline hydrogen peroxide (pH = 11.9) containing 1.0% H_2O_2 (w/w) and 1.0% NaOH (w/w) under various times (0.5-3.0 h) and temperatures (30-80 ºC). All the treatments were conducted in water bath with stirring and reflux at a given temperature for a certain time. The insoluble solids were separated from the liquor fractions by centrifugation at 3800 rpm for 5 min, and the precipitations were washed several times by distilled water until neutral. Then the precipitations were dried in an oven at 60 ºC overnight. The supernatant was collected and evaporated in a vacuum rotary evaporator under reduced pressure to 20 mL, and the dissolved lignin was precipitated by adding 6 M HCl to the filter until pH 2. The lignin was recovered by centrifugation and washed with acidified water (pH 2). Then it was dried in an oven at 60 ºC overnight before analysis.

Preparation of milled wood lignin

After the FR sample was immersed in water, NaOH was slowly added to the mixture until neutral and the mixture was allowed to stand for 1 h. Then the mixture was filtered and washed twice with deionized water. The filter residue was dried in an oven at 60 ºC. The dried sample was extracted with toluene/ethanol (2:1, v/v) in a Soxhlet extractor for 6 h. Then the sample was milled for 48 h in a vibratory ball mill. The ball-milled sample was extracted with dioxane/water (9:1, v/v) for 48 h at room temperature. The dioxane/water soluble liquor was condensed to dryness under reduced pressure to obtain crude lignin. The crude lignin was dissolved in acetic acid/water (9:1, v/v), and it was dropped into water and centrifuged to obtain precipitation. The precipitation was dried and further dissolved into dichloromethane/ethanol (2:1, v/v), precipitated in diethyl ether, centrifuged, washed with ether, and then dried to obtain MWL.

Structural characterization of lignins

The FT-IR spectra of the lignin fractions were recorded in a Thermo Scientific Nicolet iN10 FT-IR Microscope (Thermo Nicolet Corporation, Madison, WI, USA) equipped with an MCT detector cooled by liquid nitrogen. The spectra were collected in the range

of 4000-650 cm^{-1} at 4 cm^{-1} resolution.

The molecular weight of the lignin samples was determined by gel permeation chromatography (GPC) after acetylation. The acetylation was performed as follows: the dried lignin fraction (20 mg) was dissolved in 2 mL of pyridine/acetic anhydride (1/2, v/v) mixture and the reaction flask was filled with nitrogen to prevent oxidation, and then was placed in darkness at room temperature for 48 h. After the reaction, the mixture was added dropwise to diethyl ether to precipitate the acetylated lignin, and then separated by centrifugation. The precipitation was repeatedly washed with diethyl ether for 3 times to obtain acetylated lignin. The acetylated lignin sample was then dissolved in tetrahydrofuran (2 mg/mL). Then the solution was analyzed on a high performance liquid chromatography system (Agilent 1200 series, Agilent technologies, USA) with a DAD detector and an auto-sampler under the following conditions: PL-gel 10 mm Mixed-B 7.5 mm ID column, injection volume 20 µL, eluent tetrahydrofuran, flow rate 1 mL /min, ambient temperature. The molecular weights were calibrated via monodisperse polystyrene standards.

Elemental analysis was performed using a Vario EL III Elemental analyzer instrument (Elementar, Germany) according to the literature.[24] The effective hydrogen-to-carbon ratio (H/Ceff) of lignin was calculated using the following equation (1):

$$\frac{H}{C_{\text{eff}}} = \frac{(\text{H} - 2\text{O})}{\text{C}} \quad (1)$$

where H, C, and O correspond to the moles of hydrogen, carbon, and oxygen in the sample, respectively.[25]

NMR spectra were recorded on a Bruker AVIII 400 MHz spectrometer at 25 ºC. For ^{1}H NMR examination, 20 mg acetylated lignin samples were dissolved in 1 mL $CDCl_3$, and the spectra were recorded at 100 MHz. For ^{13}C NMR spectra and heteronuclear single quantum correlation (HSQC) determination, 80 mg lignin samples were dissolved in 1 mL of DMSO-d_6. The quantitative ^{13}C NMR spectra were acquired with the following parameters: 30^{o} pulse flipping angle; 9.2 µs pulse width; 1.36 s acquisition time, 2 s delay time, 400 MHz with 30000 scans. The spectral widths for HSQC spectra were 2200 Hz and 15400 Hz for the ^{1}H and ^{13}C dimensions, respectively. The number of collected complex points was 1024 for the ^{1}H-dimension with a recycle delay of 1.5 s. The number of scan was 128, and 256 time increments were recorded in the ^{13}C-dimension. The $^{1}J_{CH}$ used was 146 Hz. Prior to Fourier transform spectroscopy, the data matrices were zero filled up to 1024 points in the ^{13}C-dimension.

Py-GC-MS measurements were conducted with a multi-shot pyrolyzer (EGA/PY-3030D, Frontier Laboratories, Japan) coupled to a GC-MS system (QP2010 Ultra, Shimadzu, Japan) equipped with an Ultra ALLOY+-5 (30 m × 0.25 mm × 0.25 µm) column. About 250 µg of the crushed lignin sample was loaded in a small platinum cup and then inserted into a quartz tube placed in the pyrolysis chamber. Detection conditions were as follows: the pyrolysis chamber was kept at 500 ºC for 10 s, the chromatography oven was initially kept at 50 ºC for 1 min and raised to 280 ºC at a rate of 3 ºC/min, and then ramped to 300 ºC at a heating rate of 30 ºC/min. The final temperature was held for 3 min. The temperatures of pyrolysis interface, detector and the GC-MS interface were set at 320, 200 and 280 ºC, respectively. Peak identification of the pyrolysis products was carried out by comparison of their mass spectra with the GC-MS library and data from literature.

RESULTS AND DISCUSSION

Yield of lignins

Generally, the delignification of lignocellulosics is largely dependent on the reaction time and temperature in the extraction process with chemicals. Koullas *et al*.[26] reported that wheat straw can be extensively delignified by the alkali treatment either at high temperatures and short times or at ambient temperatures and long times. However, as compared to the alkali pretreatment, alkaline peroxide treatment is more effective in lignin solubilization.[27] As expected, in this study, the yields of the dissolved lignins from FR increased with the increase of both treatment time and temperature. The yield profile of the lignins and residues at different times and temperatures are shown in Figure 1. The extraction of FR at 80 ºC for 0.5, 1.0, 1.5, 2.0 and 3.0 h, resulted in lignin fraction yields of 10.9, 11.5, 12.2, 12.8 and 14.3%, corresponding to 31.5, 33.3, 35.1, 37.0 and 41.4% of the original lignin, respectively. Accordingly, the yields of the residue based on raw material were 68.3, 68.2, 67.8, 66.3 and 64.9%, respectively. The yields of lignin at 30, 40, 50, 60, 70 and 80 ºC for 1.5 h were 8.9, 11.0, 11.2, 11.6, 11.9 and 12.2%, corresponding to the isolation of 25.7 31.8, 32.3, 33.6, 34.4 and 35.1% of the original lignin, respectively. Accordingly, the yields of the recovered residue from the treatment were 71.4, 69.5, 68.9, 68.0, 68.8 and 67.8%, respectively. Evidently, an increment in treatment time from 0.5 to 3.0 h led to an increase of the yield of the extracted lignin from 10.9 to 14.3%. An increment in temperature from 30 to

40 ºC led to an increase of the yield of the extracted lignin from 8.9 to 11.0%. However, a relatively small increase of the lignin yield resulted from a further increase in temperature from 40 to 80 ºC. The results indicated that alkaline hydrogen peroxide decomposition is strongly dependent on temperature. The extraction at a high temperature favored the generation of more active radicals, such as hydroxyl radicals (OH•) and superoxide anion radicals (OO•-), participating in the degradation reactions of FR lignin. Furthermore, the oxidation of lignin with alkaline peroxide at high temperature caused the rapid formation of carboxyl groups, which enhanced the solubility of the lignin in water.[17] Thus, the highest lignin yield of 14.3% was obtained at 80 ºC for 3.0 h.

Molecular weight and elemental analysis

The weight-average (Mw) and number-average (Mn) molecular weights of lignin fractions are presented in Table 1. As can be seen, the weight-average molecular weight of the extracted lignins ranged from 780 to 850 g mol^{-1}, which was about 1/4 of that of MWL (2890 g mol^{-1}). This suggested that the lignin fractions were seriously depolymerized during alkaline hydrogen peroxide treatment. The Mw of both MWL and extracted lignins were lower than that of corncob MWL (3464 g mol^{-1}).[2] All the facts demonstrate that the degradation of lignin in the corncob took place during furfural manufacture, and a further degradation of the FR lignin occurred during the extraction with alkaline hydrogen peroxide. A side chain displacement was caused by a Dakin-like reaction mechanism with the hydrogen peroxide, leading to the depolymerization of lignin.[28] The oxidation reaction caused the formation of a benzylic carbocation followed by nucleophilic addition of hydrogen peroxide. The nucleophilic group (hydroxy) attacked the benzylic carbocation, which led to the formation of diphenols and carboxylic acid. Additionally, the oxidative degradation of quinone structure or conjugated double bond with benzene ring under alkaline hydrogen peroxide was another reason for the depolymerization of lignin.

The results from elemental analysis are listed in Table 1. The chemical formulas were $C_9H_{8.96}O_{3.35}$, $C_9H_{9.65}O_{3.83}$, $C_9H_{9.50}O_{3.74}$, and $C_9H_{9.44}O_{3.77}$ for MWL, AL1 AL2, and AL3, respectively. As compared to MWL, the oxygen content in the extracted lignin fractions slightly increased resulting from the formation of oxygen-containing groups with the oxidation of hydrogen peroxide. The hydrogen-to-carbon effective (H/C_{eff}) ratio is a measure of how easily a feedstock can be converted into hydrocarbons, and the higher ratio means easier conversion. The H/C_{eff} ratios of petroleum-derived compounds were between 1 and 2, while for lignocellulosic biomass below 0.3.[29] From the data in Table 1, the H/C_{eff} ratio of MWL, AL1, AL2 and AL3 were 0.25, 0.22, 0.22 and 0.21, respectively. It is clear that the extracted lignins had a lower H/C_{eff} ratio than MWL, resulting from the oxidation of hydrogen peroxide.

FT-IR spectra analysis

The FT-IR spectra of the lignin samples are shown in Figure 2. A comparison between MWL and the extracted lignins revealed that all these lignin fractions showed similar spectral features, apart from slight changes in the intensities of the absorption bands, indicating that all the fractions had similar chemical structure. The characteristic bands of the lignin were assigned according to published data.[2,30,31] The broad band at 3410-3460 cm^{-1} corresponds to the hydroxyl groups in phenolic and aliphatic structures. The bands around 2940-2930 and 1451-1457 cm^{-1} represent C-H stretching vibration in the methyl of aromatic methoxy groups and the methyl and methylene groups of the side chains. The absorption at 1697 cm^{-1} is assigned to carbonyl/carboxyl stretching in unconjugated ketones, carbonyl and ester groups. The signals around 1601, 1511 and 1425 cm^{-1} are attributed to the skeletal and stretching vibrations of benzene rings, as a characteristic absorption of lignin. Oxidation by hydrogen peroxide led to the following observations: the absorption intensities of the peaks centered on 834, 1029, 1510 and 1600 cm^{-1} slightly decreased, while the intensities at 1698 cm^{-1} slightly increased. The low absorptions at 1329 and 1125 cm^{-1} manifest a low content of syringyl units in

all the lignin fractions, suggesting that syringyl units had a strong degradation reaction under the high temperature and acidic conditions during the production of furfural, and this may be a major cause of lignin degradation. The strong and broad bands in the spectra at 1258-1268 cm^{-1} originate from guaiacyl (G) rings breathing vibration, indicating an important structure in the FR lignin and the extracted lignins. The bands at 1000-1170 cm^{-1} correspond to polyxylose characteristic absorption. The bands at 1028-1031 cm^{-1} and 1121-1124 cm^{-1} (both from the ether bond of the C-*O*-C stretching vibration) in AL1, AL2 and AL3 spectra are relatively strong comparing with MWL, which indicated that the extracted lignin contained a little amount of xylan, in accordance with the result of ^{13}C NMR spectra.

The demethoxyl reactions of syringyl units in acidic media can be elucidated by Scheme 1. When the hydrion attacked the oxygen in a methoxy group bound to C3 of the benzene ring, the inductive effect caused a weakening of the carbon-oxygen bond energy between the C5 and methoxy group. A carbocation (III) was formed resulting from the cleavage of the linkage between the methoxy and the C5 of the aromatic ring. In acidic media, the structure with nucleophilic groups attacked the carbocation, which caused the formation of stable structures. This is one of the reasons for the condensation reaction of corncob lignin during the production of furfural.

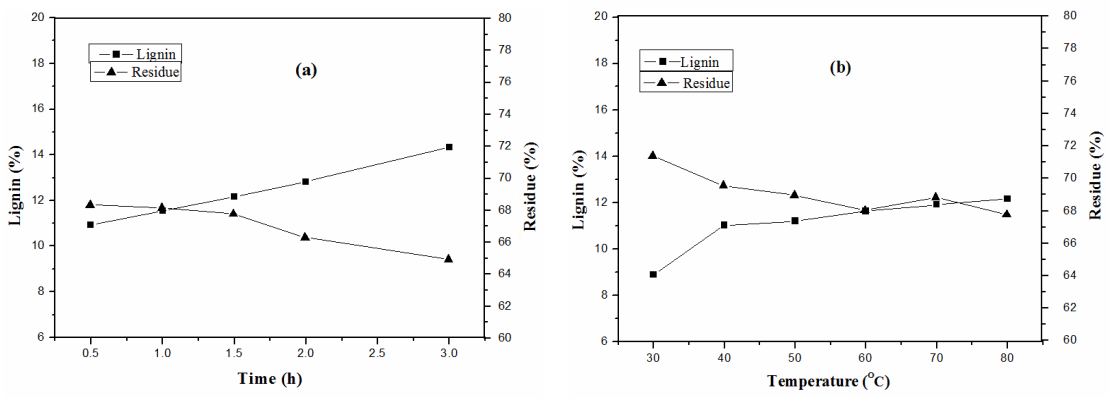


Figure 1: Effect of treatment time (a) and temperature (b) on the yields of extracted lignin and residue during extraction with alkaline hydrogen peroxide

Table 1
Elemental analysis, hydrogen-to-carbon effective (H/C_{eff}) ratio, weight-average (Mw) and number-average (Mn) molecular weight of lignin fractions

Sample[a]	Elemental analysis (%)			H/C_{eff}	Mw	Mn	Mw/Mn
	C	H	O		(g mol^{-1})	(g mol^{-1})	
MWL	63.33	5.25	31.42	0.25	2890	1290	2.25
AL_1	60.33	5.39	34.28	0.22	830	650	1.29
AL_2	60.88	5.35	33.77	0.22	780	640	1.22
AL_3	60.76	5.31	33.93	0.21	850	680	1.25

[a] MWL, milled wood lignin from FR; AL_1, AL_2 and AL_3 lignin fractions obtained by treatment in 1% H_2O_2 (w/w) and 1% NaOH (w/w) solution from FR at 30, 50 and 80 ºC for 1.5 h, respectively

^{1}H NMR spectra analysis

As can be seen in Figure 3, there was no great difference between these four ^{1}H NMR spectra of the lignin fractions. The signals between 0.8 and 1.6 ppm correspond to the protons in aliphatic moiety. All the extracted lignins showed a higher intensity in phenolic hydroxyl groups (2.22 ppm) than aliphatic hydroxyl (2.07 ppm), which indicated the cleavage of *β-O*-4′ bond during furfural production. The signal at 3.77 ppm corresponds to the protons of methoxy groups (−OCH_3). The signals between at 6.25 and 6.80 ppm attributed to the aromatic proton in syringyl units[32] were not observed in the spectrum, suggesting a trace of syringyl units in the lignin fractions. The signals at 6.99 and 7.26 ppm are originated from guaiacyl protons. The strong signals between 8.00 and 8.41 ppm are assigned to the protons of benzene rings in *p*-hydroxyphenyl, which indicated that the H unit is the major monomer of FR lignin. Moreover, the signal at 10.16 ppm is due to the carbonyl protons of aliphatic acid.

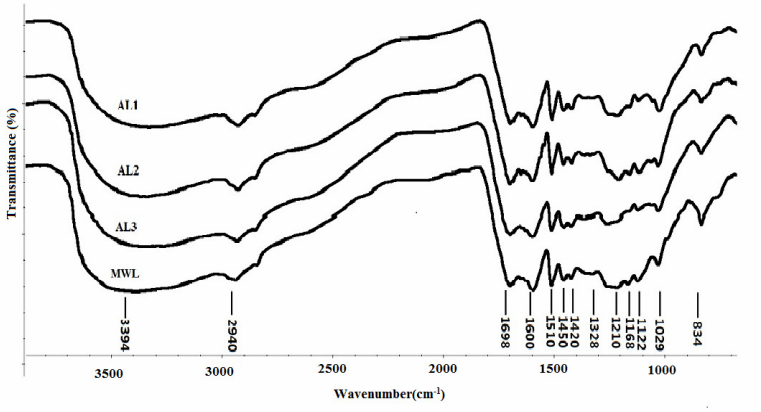


Figure 2: FT-IR spectra of extracted lignins (AL1, AL2 and AL3) as compared to MWL

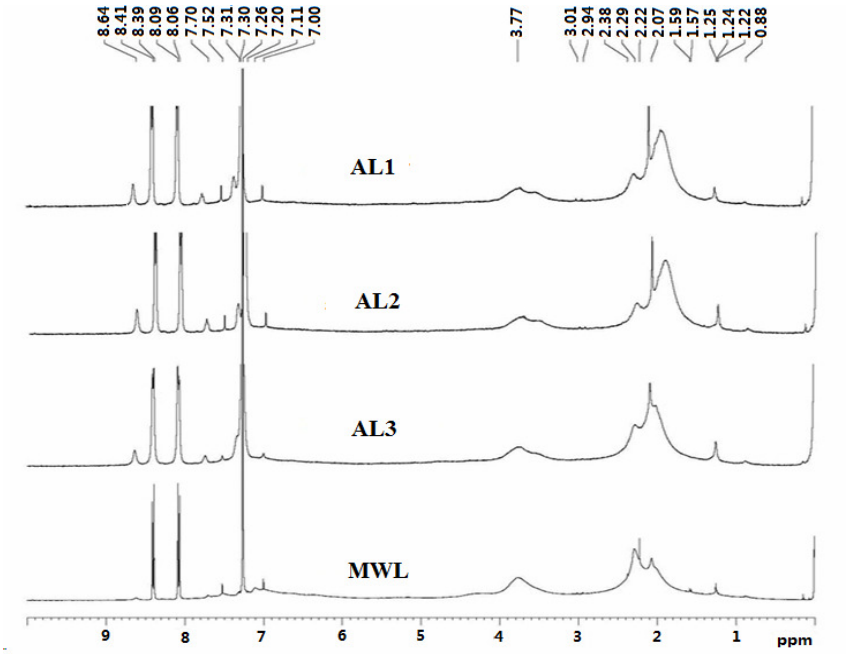


Figure 3: ^{1}H-NMR spectra of extracted lignins (AL1, AL2 and AL3) as compared to MWL

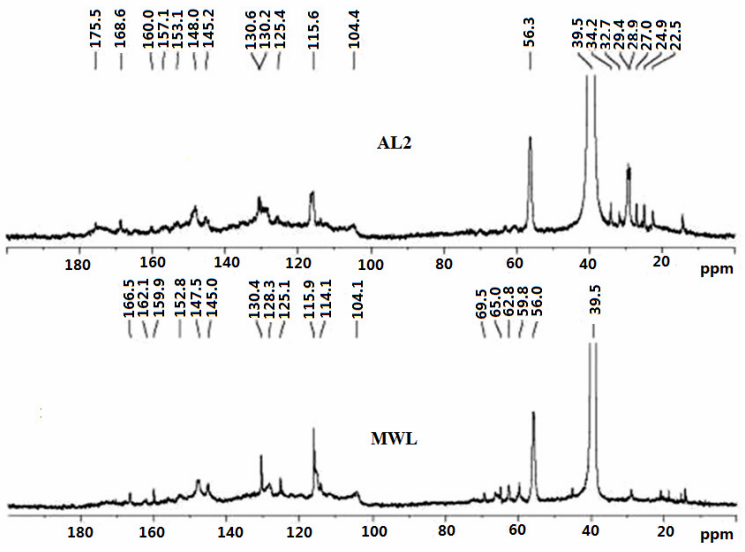
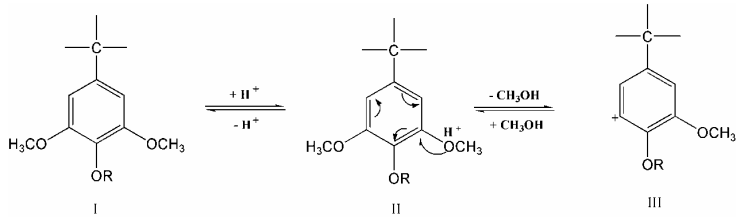


Figure 4: ^{13}C-NMR spectra of the lignin fraction (AL2) as compared to MWL



Scheme 1: Reaction of methoxyl under acidic conditions[2]

^{13}C NMR spectra analysis

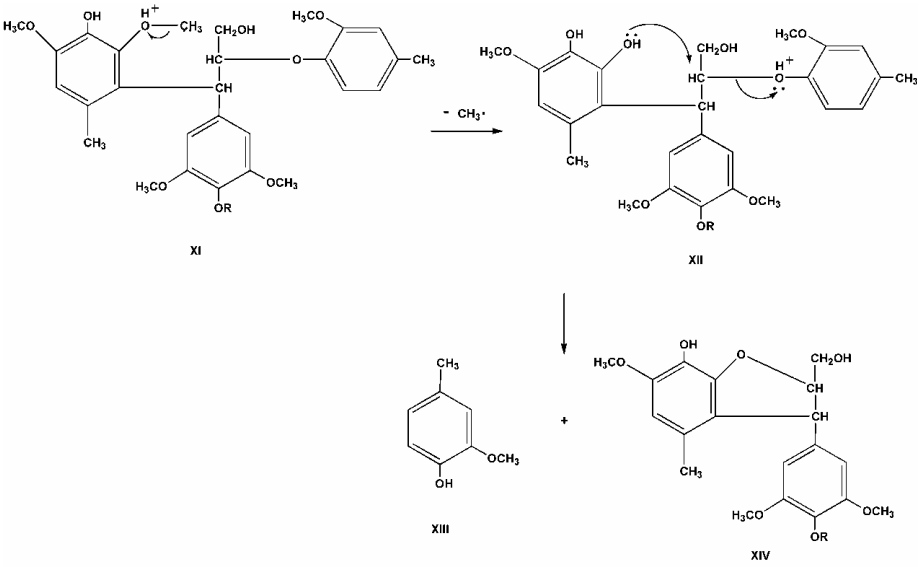
^{13}C NMR spectra of the lignin samples are presented in Figure 4. As can be seen, the main signal at 56.0 ppm is assigned to methoxy groups. The signals between 59.8 and 65.0 ppm correspond to C_γ. The peaks at 86.0 and 73.0 ppm are derived from carbon atoms C_β and C_α, respectively. However, these signals were not observed in the spectrum of MWL, indicating that a large amount of *β-O*-4′ structural units was split in the production of furfural. Saturated aliphatic carbons were observed in the region between 29.4 and 14.5 ppm, demonstrating that the extracted lignins contained a small amount of aliphatic compounds. This is consistent with the result of Py-GC/MS analysis afterwards. The signal at 125.1 ppm corresponds to *α*-carbonyl group in guaiacyl units. The C_3/C_5 signal of *p*-hydroxyphenyl units at 116.2 ppm is relatively strong in the spectra of MWL and the extracted lignins, indicating that the *p*-hydroxyphenyl unit is the major structure of FR lignin. The signal at 160.3 ppm is assigned to C-4 of *p*-hydroxyphenyl units. The signal at 166.9 ppm is derived from carboxyl groups (COOH and Ar-COOH), and guaiacyl units produce signals at 145.0 ppm (C-3 non-etherified) and 148.0 ppm (C-4 etherified). Furthermore, the syringyl units were detected by the signals at 154.0-152.0 ppm (C-3/C-5 etherified), 148.0 ppm (C-3/C-5 non-etherified), 137.9 ppm (C-4), 134.0 ppm (C-1), and 108.0-103.5 ppm (C-2/C-6). These signals are relatively weak, suggesting that large amounts of syringyl units were converted into G and H units and other degradation products in the furfural production by de-methylation and rearrangement. The relatively weak signal corresponding to xylose units in xylan was observed at 69.5 ppm in the MWL spectrum, which indicated that MWL

contained a small amount of xylan resulting from the condensation reaction of lignin with xylose and xylan in concentrated sulfuric acid.[33] No signal at 69.5 ppm was observed in the spectrum of AL2, indicating that the xylan was released from lignin during the extraction with alkaline hydrogen peroxide.

A catechol unit was formed by a possible hydrolysis of sterically hindered methoxy groups in syringyl to free phenolic hydroxyl group in acidic media, followed by the cleavage of syringyl ether bond (Scheme 2). This can be converted into a *β*-carbocation and a syringyl monomer structure (XII). The nucleophilic oxygen of the neighboring hydroxyl group attacked the *β*-carbocation, thus forming a new ether bond. A product (XIII) was obtained by the formation of the new bond. This is another reason for the demethoxylation and degradation of corncob lignin during the production of furfural. Additionally, phenolic compounds with a catechol unit were easily oxidized to give colored material, such as ortho-quinone,[34] resulting in the black appearance of the furfural residue lignin. The ortho-quinone was destroyed by the oxidation of hydrogen peroxide, which caused the further degradation of FR lignin during the extraction with alkaline hydrogen peroxide.

Py-GC/MS analysis

Py-GC/MS is a rapid and sensitive technique for analyzing the composition of lignin.[35,36] The pyrograms of MWL and the extracted lignin (AL2) are shown in Figure 5, and the identifications and relative molar abundances of the released compounds are listed in Table 2. As can be seen, guaiacol, phenol and syringol-type phenols, derived from the guaiacyl (G), *p*-hydroxycinnamyl (H) and syringyl (S) lignin units, respectively, were identified. From these data, the most important compounds (≥6.00%) of MWL identified were phenol (9.78%), 2-methoxy-phenol (9.45%), 2-methoxy-4-methyl-phenol (7.11%), 4-ethoxy-styrene (30.27%) and 2-methoxy-4-vinyl-phenol (14.78%). Those of AL2 lignin were phenol (12.26%), 4-methyl-phenol (11.42%), 4-ethyl-phenol (7.28%), 2-methoxy-4-methyl-phenol (8.67%) and 4-vinyl-phenol (20.60%).



Scheme 2: Degradation of lignin structure (XI) under acidic conditions

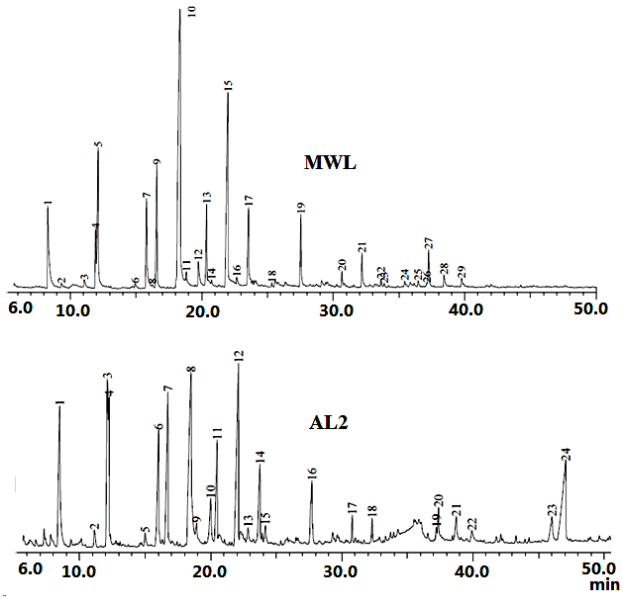


Figure 5: Py–GC/MS chromatograms of MWL and extracted lignin (AL_2)
(The identities and relative molar abundances of the numbered compounds are listed in Table 2)

Table 2
Identities and relative molar abundances of the compounds released after Py–GC/MS of MWL and extracted lignin (AL_2)

NO	Compound	R.T. (min)	Formula	MW (g mol^{-1})	Group	Molar abundances (%)
1[a]	Phenol	8.30	C_6H_6O	94	Phenyl	9.78
2[a]	Benzene, 1-methoxy-4-methyl-	9.32	$C_8H_{10}O$	122	Phenyl	0.27
3[a]	Phenol, 2-methyl-	11.07	C_7H_8O	108	Phenyl	0.56
4[a]	Phenol, 3- methyl-	11.92	C_7H_8O	108	Phenyl	3.91
5[a]	Phenol, 2-methoxy-	12.12	$C_7H_8O_2$	124	Guaiacyl	9.45
6[a]	Phenol, 2,6-dimethyl-	14.93	$C_8H_{10}O$	122	Phenyl	0.25
7[a]	Phenol, 4-ethyl-	15.80	$C_8H_{10}O$	122	Phenyl	5.85
8[a]	Phenol, 2-methoxy-4-methyl-	16.25	$C_8H_{10}O_2$	138	Guaiacyl	0.06
9[a]	Phenol, 2-methoxy-4-methyl-	16.59	$C_8H_{10}O_2$	138	Guaiacyl	7.11
10[a]	4-Ethoxystyrene	18.34	$C_{10}H_{12}O$	148	Phenyl	30.27
11[a]	Phenol, 2-ethyl-6-methyl-	18.83	$C_9H_{12}O$	136	Phenyl	0.41
12[a]	1,2-Benzenediol, 3-methoxy-	19.74	$C_7H_8O_3$	140	Syringyl	1.67
13[a]	Phenol, 4-ethyl-2-methoxy-	20.37	$C_9H_{12}O_2$	152	Guaiacyl	3.63
14[a]	Benzofuran, 2,3-dihydro-	20.70	C_8H_8O	120	Benzene	0.19
15[a]	2-Methoxy-4-vinylphenol	21.99	$C_9H_{10}O_2$	150	Guaiacyl	14.78
16[a]	3-Methoxybenzyl alcohol	22.65	$C_8H_{10}O_2$	138	Alcohol	0.37
17[a]	Phenol, 2,6-dimethoxy-	23.56	$C_8H_{10}O_3$	154	Syringyl	3.83
18[a]	Phenol, 2-methoxy-4-(1-propenyl)-,	25.33	$C_{10}H_{12}O_2$	164	Guaiacyl	0.15
19[a]	1,2,3-Trimethoxybenzene	27.53	$C_9H_{12}O_3$	168	Syringyl	3.31
20[a]	Benzene, 1,2,3-trimethoxy-5-methyl-	30.66	$C_{10}H_{14}O_3$	182	Syringyl	0.47
21[a]	3',5'-Dimethoxyacetophenone	32.19	$C_{10}H_{12}O_3$	180	Benzene	1.24
22[a]	Syringol, 4-(1-propenyl)-(cis)	33.63	$C_{11}H_{14}O_3$	194	Syringyl	0.23
23[a]	Benzofuran, 2,3-dihydro-	33.88	$C_{12}H_{18}O_4$	226	Benzene	0.05
24[a]	3-Hydroxy-4-methoxycinnamic acid	35.43	$C_{11}H_{14}O_3$	194	Guaiacyl	0.13
25[a]	Ethyl, 3-(4-hydroxy-3-methoxyphenyl)	36.45	$C_{12}H_{16}O_4$	224	Guaiacyl	0.14
26[a]	Ethanone, 1-(4-cyclohexylphenyl)-	37.13	$C_{14}H_{18}O$	202	Benzene	0.04
27[a]	Methyleugenol	37.25	$C_{11}H_{14}O_3$	194	Syringyl	1.20

28[a]	Acetophenone, 4'-hydroxy-3',5'-dimethoxy-	38.42	$C_{10}H_{12}O_4$	196	Syringyl	0.41
29[a]	Homosyringic acid	39.76	$C_{10}H_{12}O_5$	212	Syringyl	0.24
1[b]	Phenol	8.49	C_6H_6O	94	Phenyl	12.26
2[b]	Phenol, 2-methyl-	11.13	C_7H_8O	108	Phenyl	1.16
3[b]	Phenol, 4-methyl-	12.12	C_7H_8O	108	Phenyl	11.42
4[b]	Phenol, 2-methoxy-	12.25	$C_7H_8O_2$	124	Phenyl	5.44
5[b]	Phenol, 2,6-dimethyl-	15.00	$C_8H_{10}O$	122	Benzene	0.58
6[b]	Phenol, 4-ethyl-	16.03	$C_8H_{10}O$	122	Phenyl	7.28
7[b]	Phenol, 2-methoxy-4-methyl-	16.73	$C_8H_{10}O_2$	138	Guaiacyl	8.67
8[b]	4-Vinylphenol	18.50	C_8H8O	120	Phenyl	20.60
9[b]	Phenol, 4-ethyl-2-methyl-	18.92	$C_9H_{12}O$	136	Benzene	0.55
10[b]	1,4-Benzenediol, 2-methoxy-	20.00	C_7H_8O3	140	Guaiacyl	2.96
11[b]	Phenol, 4-ethyl-2-methoxy-	20.49	$C_9H_{12}O_2$	152	Guaiacyl	4.52
12[b]	2-Methoxy-4-vinylphenol	22.11	$C_9H_{10}O_2$	150	Guaiacyl	12.40
13[b]	3-Methoxybenzyl alcohol	22.85	$C_8H_{10}O_2$	138	Alcohol	0.72
14[b]	Phenol, 2,6-dimethoxy-	23.76	$C_8H_{10}O_3$	154	Syringyl	4.09
15[b]	4-Hydroxy-3-methoxybenzyl	24.17	$C_8H_{10}O_3$	154	Guaiacyl	0.55
16[b]	1,2,3-Trimethoxybenzene	27.71	$C_9H_{12}O_3$	168	Syringyl	3.53
17[b]	Benzene, 1,2,3-trimethoxy-5-methyl-	30.79	$C_{10}H_{14}O_3$	182	Syringyl	0.68
18[b]	3',5'-Dimethoxyacetophenone	32.31	$C_{10}H_{12}O_3$	180	Benzene	0.56
19[b]	1(2H)-Naphthalenone	37.20	$C_{14}H_{18}O$	202	Benzene	0.33
20[b]	Syringol, 4-(1-propenyl)-(cis)	37.37	$C_{11}H_{14}O_3$	194	Syringyl	0.70
21[b]	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	38.72	$C_{10}H_{12}O_4$	196	Syringyl	1.00

Superscripts a and b represent the pyrolysis products of MWL and extracted lignin (AL_2), respectively)

Table 3
Relative molar content of total H-, G- and S-type substituted compounds

Lignin samples[a] (%)	H	G	S	S/G
MWL	51.00	35.00	11.00	0.33
AL_2	58.00	29.00	10.00	0.34

[a] Corresponding to the lignin samples in Table 1

As can be seen from Table 3, the total relative percentages of G and S units in the furfural residue lignin after pretreatment showed a decrease from 35 to 23%, and 11 to 10%, respectively. The H units had an increase from 51 to 58%. Obviously, the major monomer was the H unit in the two lignin samples. The relatively small content of G and S units compared to H units in MWL indicated that the lignin of corncob had a serious de-methoxylation during the production of furfural. After the treatment with alkaline hydrogen peroxide, a certain amount of G and S units was converted into other substances, which is consistent with the results of FT-IR and[13] C NMR spectra analyses aforementioned. Furthermore, the oxidation of G and S units may be another major reason for lignin degradation during the treatment with alkaline hydrogen peroxide. It is worth noting that the extracted lignin was not pure, as evidenced by the identification of unsaturated fatty acids. Previous studies showed that the structure of lignin, particularly syringyl to guaiacyl (S/G) ratio, influences the delignification rate of the wood or nonwood materials.[37-39] S/G ratio can be obtained via using the molar areas of the peaks corresponding to syringyl and guaiacyl derivatives. The variation of S/G ratio of FR lignin after the treatment with alkaline hydrogen peroxide was rather small, changing from 0.33 in the control to 0.34 in AL2.

CONCLUSION

Lignins from furfural residue were successfully extracted by alkaline hydrogen peroxide treatment and were comprehensively characterized as compared to MWL. The yield of the extracted lignin increased with the increase in reaction temperature and time. The highest lignin yield of 41.40% (corresponding to the original lignin) was obtained by the extraction at 80 ºC for

3.0 h. Py/GC-MS analysis indicated that the total relative percentages of H, G and S units of MWL were 51, 35 and 11%, and those of the extracted lignin (AL2) were 58, 29 and 10%, respectively. The S/G ratios of MWL and the extracted lignin (AL2) were 0.33 and 0.34, respectively. De-methoxylation and degradation reactions of G- and S-type lignin structure of the furfural residue lignin occurred during alkaline hydrogen peroxide extraction process.

ACKNOWLEDGMENTS: The authors wish to express their gratitude for the financial support from the National Natural Science Foundation of China (31110103902) and Major State Basic Research Projects of China (973-2010CB732204).

REFERENCES

[1] Y. Xing, L. X. Bu, K. Wang and J. X. Jiang, *Cellulose Chem. Technol.*, **46**, 249 (2011).
[2] L. X. Bu, Y. Tang, Y. X. Gao, H. L. Jian and J. X. Jiang, *Chem. Eng. J.*, **175**, 176 (2011).
[3] Y. Tang, D. Q. Zhao, L. W. Zhu and J. X. Jiang, *Eur. Food. Res. Technol.*, **233**, 489 (2011).
[4] Y. J. Feng, F. Li, X. L.Wang, X. M. Liu and L. N. Zhang, *Pedosphere*, **16**, 668 (2006).
[5] G. Ren and K. Sheng, *Procs. Electric Technology and Civil Engineering (ICETCE), 2011 International Conference on. IEEE*, 2011, pp. 3846-3849.
[6] C. Vanderghem, A. Richel, N. Jacquet, C. Blecker and M. Paquot, *Polym. Degrad. Stabil.*, **96**, 1761 (2011).
[7] A. U. Buranov and G. Mazza, *Ind. Crop. Prod.*, **28**, 237 (2008).
[8] R. El Hage, N. Brosse, L. Chrusciel, C. Sanchez, P. Sannigrahi *et al.*, *Polym. Degrad. Stabil.*, **94**, 1632 (2009).
[9] R. B. Santos, E. A. Capanema, M. Y. Balakshin, H. M. Chang and H. Jameel, *J. Agr. Food. Chem.*, **60**, 4923 (2012).
[10] M. Sette, R. Wechselberger and C. Crestini, *Chem-Eur. J.*, **17**, 9529 (2011).
[11] W. Boerjan, J. Ralph and M. Baucher, Lignin biosynthesis, *Annu. Rev. Plant. Biol.*, **54**, 519 (2003).
[12] D. Stewart, *Ind. Crop. Prod.*, **27**, 202 (2008).
[13] J. F. Kadla, S. Kubo, R. A. Venditti, R. D. Gilbert, A. L. Compere *et al.*, *Carbon*, **40**, 2913 (2002).
[14] J. L. Braun, K. M. Holtman and J. F. Kadla, *Carbon*, **43**, 385 (2005).
[15] R. Ruiz-Rosas, J. Bedia, M. Lallave, I. G. Loscertales, A. Barrero, *et al.*, *Carbon*, **48**, 696 (2010).
[16] S. P. Maradur, C. H. Kim, S. Y. Kim, B. H. Kim, W. C. Kim *et al.*, *Synthetic. Met.*, **162**, 453 (2012).
[17] R. C. Sun, X. F. Sun, P. Fowler and J. Tomkinson, *Eur. Polym. J.*, **38**, 1399 (2006).
[18] B. C. Saha, M. A. Cotta, *Bioresource Technol.*, **104**, 349 (2006).
[19] P. Karagöz, I. V. Rocha, M. Özkan and I. Angelidaki, *Bioresource Technol.*, **104**, 349 (2012).
[20] B. Yang, A. Boussaid, S. D. Mansfield, D. J. Gregg and J. N. Saddler, *Biotechnol. Bioeng.*, **77**, 678 (2002).
[21] L. Kumar, R. Chandra and J. Saddler, *Biotechnol. Bioeng.*, **108**, 2300 (2011).
[22] J. M. Gould, *Biotechnol. Bioeng.*, **26**, 46 (1984).
[23] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, *et al.*, *Laboratory Analytical Procedure*, (2008).
[24] M. F. Li, S. N. Sun, F. Xu and R. C. Sun, *Chem. Eng. J.*, **179**, 80 (2012).
[25] Y. Zhao, Y. Fu and Q. X. Guo, *Bioresource Technol.*, **114**, 740 (2012).
[26] D. P. Koullas, P. F. Christakopoulos, D. Kekos, E. G. Koukios and B. J. Macris, *Biomass Bioenerg.*, **4**, 9 (1993).
[27] H. Z. Chen, Y. J. Han and J. Xu, *Process Biochem.*, **43**, 1462 (2008).
[28] A. Mancera, V. Fierro, A. Pizzi, S. Dumarçay, P. Gérardin, *et al.*, *Polym. Degrad. Stabil.*, **95**, 470 (2010).
[29] M. Zhang, F. L. Resende, A. Moutsoglou and D. E. Raynie, *J. Anal. Appl. Pyrol.*, **98**, 65 (2012).
[30] Q. L. Yang, J. B. Shi, Lu Lin, J. P. Zhuang, C. S. Pang *et al.*, *J. Agr. Food. Chem.*, **60**, 4656 (2012).
[31] X. Yang, F. Ma, Y. Zeng, H. Yu, C. Xu *et al.*, *Int. Biodeter. Biodegr.*, **64**, 119 (2010).
[32] M. S. Jahan, D. A. Chowdhury, M. K. Islam and S. M. Moeiz, *Bioresource Technol.*, **98**, 465 (2007).
[33] Y. Matsushita, A. Kakehi, S. Miyawaki and S. Yasuda, *J. Wood. Sci.*, **50**, 136 (2004).
[34] F. J. González-Vila, G. Almendros, J. C. Del Río, F. Martın, A. Gutiérrez *et al.*, *J. Anal. Appl. Pyrol.*, **49**, 295 (1999).
[35] J. Ralph and R. D. Hatfield, *J. Agr. Food. Chem.*, **39**, 1426 (1991).
[36] J. Rencoret, G. Marques, A. Gutiérrez, L. Nieto, J. Jiménez-Barbero, *et al.*, *Ind. Crop. Prod.*, **30**, 137 (2009).
[37] E. Ribechini, M. Zanaboni, A. M. Raspolli Galletti, C. Antonetti, N. Nassi o Di Nasso, *et al.*, *J. Anal. Appl. Pyrol.*, **94**, 223 (2012).
[38] J. C. del Rıo, A. Gutiérrez, J. Romero, M. J. Martınez and A. T. Martınez, *J. Anal. Appl. Pyrol.*, **58–59**, 425 (2001).
[39] S. Bauer, H. Sorek, V. D. Mitchell, A. B. Ibanez and D. E. Wemmer, *J. Agr. Food. Chem.*, **60**, 8203 (2012).