

Structural Changes of Lignin after Ionic Liquid Pretreatment

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Changes of lignin's structure were investigated resulting from an ionic liquid ([Bmim]Cl, 1-butyl-3-methylimidazolium chloride salt) pretreatment. The purified lignin was pretreated by [Bmim]Cl under the following conditions: the ionic liquid to lignin mass ratio was 10:1, the temperature was 85 °C, and the processing time was 2 h and 4 h. The chemical structure of lignin was studied via Ultraviolet (UV) spectra, Fourier Transform infrared (FT-IR) spectra, Nuclear Magnetic Resonance Spectroscopy (¹³C-NMR), Gel Permeation Chromatography (GPC), X-ray photoelectron spectroscopy (XPS), and Thermogravimetric Analysis (TG). The total content of phenolic hydroxyl increased with increased time. Moreover, the contents of [OH_i] and [OH_{ii}] (types of phenolic hydroxyl groups) groups were disproportionately increased. The main structure of lignin still was present after the [Bmim]Cl pretreatment. The β-O-4 linkages were broken apart. The degree of lignin degeneration increased with increased time, after being pre-treated with [Bmim]Cl. Simultaneously, a condensation reaction also took place during the pretreatment. Understanding the chemical changes to wheat straw lignin during an ionic liquid pretreatment provides an important theoretical basis for its further industrial use.

Keywords: Ionic liquid; Lignin; Degradation

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INTRODUCTION

Lignin is one of the major components of plant structure. It is the second most abundant naturally occurring polymer next to cellulose. In the paper and pulp industries, lignin is extensively generated as a byproduct (Pan *et al.* 2004), and is mainly discharged in the form of waste. In the pulp and paper industries, kraft cooking is the main pulping process. Approximately 130 million tons of pulp is produced worldwide annually (Tran and Vakkilainen 2008). This has resulted in serious environmental pollution, such as water contamination, which has attracted the government and society's attention. The major chemical functional groups in lignin include hydroxyl, methoxyl, carbonyl, and carboxyl groups; however, these vary in amount and proportion depending on the type of industrial lignin. Lignin can be dissolved in many organic solutions, such as dimethyl formamide, dioxane, dimethyl sulfoxide, acetone, *etc.* Researchers have suggested that lignin could be used in many areas, such as adhesives (Ma *et al.* 2011; Hong *et al.* 2016), fertilizers (Kumar *et al.* 2009), reinforcement for polymeric systems (Cazacu *et al.* 2004), *etc.* Lignin has not been widely utilized in many industries due to its low vacancy on its aromatic ring and its considerably lower reactivity compared to phenol and related compounds. These characteristics limit the industrial use of lignin. In fact, lignin is considered the most difficult type of biomass to convert into valuable chemicals (Farrán

et al. 2015). Without modification to functional groups, lignin is still largely used as fuel in the pulp and paper industry. If suitable chemical methods could be developed, lignin could represent a new raw material (Binder *et al.* 2009).

Lignin is a highly branched, aromatic polymer of phenylpropanoid units and often serves as the glue that binds cellulose and hemicellulose by imparting rigidity, moisture, and microbial resistance to lignocellulose (Chandra *et al.* 2007). Lignin is a major component of cell wall, wherein it provides rigidity, internal transport of water and nutrients, and protection against attack by microorganisms (Buranov and Mazza 2008). The units of lignin are phenylpropane, which differ only with respect to the degree of substitution by methoxyl groups on the aromatic ring (Fig. 1). Depending on its composition of guaiacyl (G), syringyl (S) and *p*-hydroxyphenylpropane (H) units, wheat straw lignin has been classified as GSH-lignins, softwood lignin as G-lignins, and hardwood lignin as GS-lignins (Sun *et al.* 1997). During the lignification process, these lignin monomers connect with each other *via* a variety of inter linkages: β -O-4, α -O-4, β -5, β -1, 5-5, 4-O-5, and β - β (Boerjan *et al.* 2003).

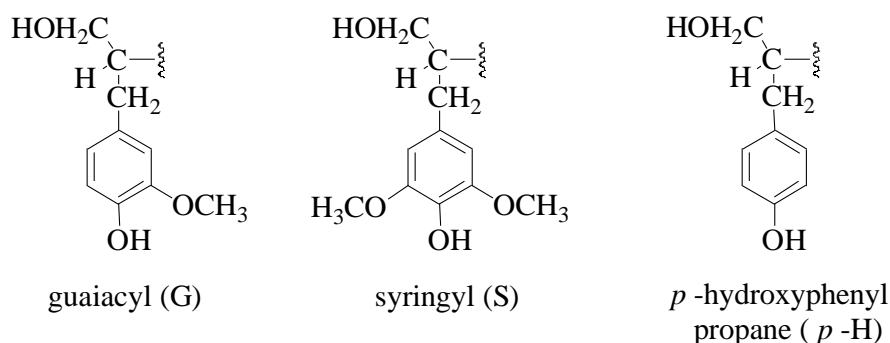


Fig. 1. Schematic representation of the structural units of lignin

Ionic liquids (ILs) are low-melting-point salts that are comprised entirely of cations and anions (Welton 1999; Earle and Seddon 2000). Ionic liquids have been successfully applied in organic synthesis, catalytic, electrochemical, and materials science on account of their tunable solvation properties (Crowhurst *et al.* 2003; Crowhurst *et al.* 2004). As environmentally-friendly solvents, ionic liquids have received increasing attention and exhibit a tremendous ability to dissolve cellulose (Zhu *et al.* 2006), hemicellulose (Sun *et al.* 2011), and lignin (Fu *et al.* 2010). The ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) was used as a solvent to extract the lignin from wood to aid in the hydrolysis of cellulose (Lee *et al.* 2009). More recently, this ionic liquid was used to extract lignin from lignocellulosic biomass (Kim *et al.* 2011). Pu *et al.* (2007) studied the solubility of residual softwood kraft pulp lignin in different ionic liquids. The solubility of residual softwood kraft pulp lignin is 13.9 g/L in [Bmim]Cl at 75 °C. Lignin extracted from IL (ILL) can be used as a raw material with high added value. All of these studies focused on the lignin that was extracted with an ionic liquid but ignored the effect on the structure of lignin during its dissolution with an IL. Understanding the structural features of lignin after pretreatment with an IL is very important.

In this study, the authors characterized the changes in lignin after being processed by [Bmim]Cl. Relatively low temperatures were used in this study. The effect of different processing times on the structure of lignin at a fixed temperature was investigated. A

combination of techniques, such as UV, thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), gel permeation chromatography (GPC), Fourier Transform infrared (FT-IR) spectra, and Nuclear Magnetic Resonance Spectroscopy (^{13}C -NMR) were used to characterize the structure of lignin.

EXPERIMENTAL

Materials

The solvents were purchased from Nanjing Reagent Co. (Nanjing, China) and were used as received. Black liquor lignin was obtained from the Shandong Tralin Group (Liaocheng, China). Ionic liquid ([Bmim]Cl > 99%) was purchased from the Lanzhou Institute of Chemical Physics in Lanzhou, China.

Purification of lignin

Black liquor lignin was dissolved in water to make a 10% solution and then titrated with 10% sodium hydroxide to a pH of 12. The mixture was stirred constantly until the lignin was completely dissolved. The solution was centrifuged at 4000 rpm for 5 min. The solid residue was discarded. The lignin was purified by adjusting the pH to 2 with 10% (wt.%) H_2SO_4 and stirring for 30 min at 60 °C. The acidified black liquor was then centrifuged at 4000 rpm for 5 min. The solid residue was collected and washed with deionized water until the solution was neutral. Lastly, the rough lignin was dried at 60 °C (for approximately 24 h) until a constant mass was achieved. The regenerated lignin (RL) was not further purified.

Methods

Pretreatment of lignin with ionic liquid

An amount of 1 g of RL was mixed with 10 g [Bmim]Cl under a N_2 atmosphere. The mixture was placed into a water bath with a magnetic stirrer at 85 °C for 2 h and 4 h, respectively. After the pretreatment, the lignin was extracted as per the above procedure. After pretreated, the solution is black liquor. After adding H_2SO_4 , the solid was collected and washed. The liquid part, which was black, was could be readily dissolved in both neutral and acid water. This dark black liquor may have contained minor molecular components, but it was not further analyzed in the current work. The IL-lignin (ILL1, ILL2) was collected for later use.

Characterization of lignin

Phenolic hydroxyl groups were detected by ultraviolet-spectroscopy (Zakis 1994). The spectra were recorded using a UV TU1080 (Beijing Purkinje General Company, Beijing, China). The infrared (FTIR) spectra were recorded on a Nicolet 360 spectrometer (Nicolet Company, Madison, USA) in the range of 4000 cm^{-1} to 400 cm^{-1} . The samples were formed into a KBr (2/100 mg) pellet. The spectra resolution was 4000 cm^{-1} to 400 cm^{-1} . All solution-state ^{13}C -NMR were performed on a BrukerAvance-600 spectrometer (Bruker Company, Fällanden, Switzerland) at 600 MHz and 150 MHz, respectively. For the ^{13}C -NMR spectrum, 100 mg of the sample was dissolved in 0.55 mL of DMSO-d_6 at 25 °C, and 20000 scans were collected. The inverse-gate decoupling sequence (Tong-Qi *et al.* 2011), which allows a quantitative analysis and comparison of

signal intensities, was used with the following parameters: 30° pulse angle, 2 s relaxation delay at 20000 scans.

The X-ray photoelectron spectroscopy (XPS) measurements were performed with a PHI 5000 VersaProbe (UIVAC-PHI, Osaka, Japan). The system was equipped with a monochromatic Al K α source. A C1s spectra at the binding energy (BE) of 285 eV was used as a reference. The thermal stability of samples was conducted using a TG 209F3 (NETZSCH, Selb, Germany). Approximately 5 mg of sample was loaded into an Al₂O₃ container. The samples were heated to approximately 800 °C at the rate of 10 °C/min. All of the tests were performed in a nitrogen atmosphere with a flow rate of 20 mL/min. The lignin was acetylated with acetic anhydride/pyridine (1:1 v/v) at room temperature for 72 h. The extracts were removed with ethanol (El Hage *et al.* 2009). After acetylation, the samples were dissolved in tetrahydrofuran (THF). 25 μ L aliquots of lignin solutions were injected and the run time was 25 min. The number average molecular weight (M_n) and weight average molecular weight (M_w) of lignin were determined by gel permeation chromatography (GPC, Waters 1515, Waters Company, Milford, USA) with an ultraviolet detector (UV) at 240 nm and using a Styragel HR1 column and Styragel HR2 column (Waters Company, Milford, USA) linked in series with tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min.

RESULTS AND DISCUSSION

Determination of Phenolic Hydroxyl Groups

The four structures of phenolic hydroxyl groups (namely [OH_I], [OH_{II}], [OH_{III}], and [OH_{IV}]) in lignin are presented in Fig. 2. The phenolic hydroxyl groups not only affect the acidity of lignin, but also its physical and chemical properties. Determining the phenolic hydroxyl content of lignin was critical to understanding its characteristics.

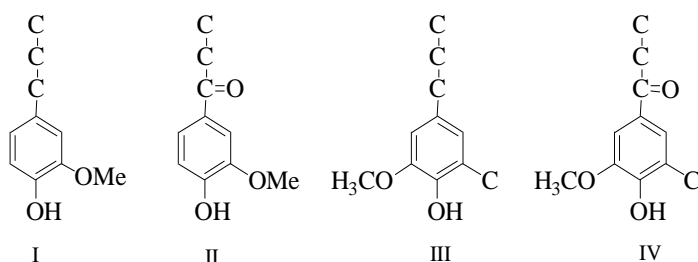


Fig. 2. Types of phenolic structures in lignin samples

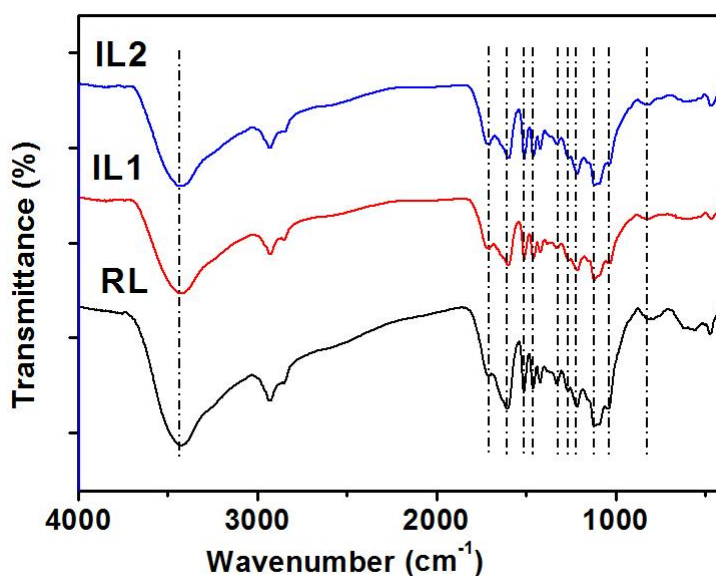
As shown in Table 1, the phenolic structures of lignin changed with the pretreatment of [Bmim]Cl at 85 °C for 2 h and 4 h. From Table 1, the main types of phenolic hydroxyl groups were [OH_I], [OH_{II}], and [OH_{III}]. The total content of phenolic hydroxyls also increased with increased time. Moreover, the content of [OH_I] increased most noticeably. It was deduced that this could be due to the reduction reaction that occurred in the ether linkages on the benzene rings, the cleavage of β -O-4 and formed phenolic hydroxyl (Brandt 2015). The contents of [OH_{II}] and [OH_{III}] phenolic hydroxyls increased to some degree. These results revealed that the structure of lignin was changed when processed with [Bmim]Cl.

Table 1. Phenolic Hydroxyl Content of RL, ILL1, and ILL2 L·g⁻¹·cm⁻¹

Sample s	Processing Time (h)	Total Phenolic Hydroxyl	[OH _i]	[OH _{ii}]	[OH _{iii}]	[OH _{iv}]
RL	0	1.54	0.17	0.18	1.12	0.07
ILL1	2	2.75	0.85	0.25	1.55	0.10
ILL2	4	2.98	1.02	0.33	1.60	0.03

FTIR Analysis

To investigate the structural changes that took place during the [Bmim]Cl process, the FTIR spectra of RL and ILL were recorded. The characteristic peaks of RL and ILL in the region of 400 cm⁻¹ to 4000 cm⁻¹ are shown in Fig. 3. A comparison between RL and ILL showed that the band shapes in the spectra generally had the same distribution. This meant that the backbone structure of lignin under the [Bmim]Cl treatment did not change noticeably. A wide absorption band at 3426 cm⁻¹ originated from O-H stretching. The band at 1705 cm⁻¹, which can be attributed to unconjugated carbonyl groups and which was found in all samples, notably increased in all ILL samples that had been subjected to the [Bmim]Cl treatment. The bands for aromatic skeleton vibrations, exhibited at 1604 cm⁻¹, 1512 cm⁻¹ (aromatic ring vibration), and 1470 cm⁻¹ (C-H deformation vibration of the aromatic ring), showed the typical signal pattern expected for a lignin moiety. The absorption at 1266 cm⁻¹ was attributed to guaiacyl ring breathing with C=O stretching and the absorption at 1327 cm⁻¹ was attributed to syringyl ring breathing with C=O stretching, both of which were notably decreased in all ILL samples subjected to the [Bmim]Cl pretreatment. This showed that the content of S units may have been reduced. The pretreatment in IL lead to the transform of S units. Meanwhile, the content of G and H units may increase. The absorptions at 1215 cm⁻¹ and 1041 cm⁻¹ were attributed to the stretching vibration of C-O. Moreover, the bands around 828 cm⁻¹ and 1120 cm⁻¹ indicated the existence of G, H, and S units. It can be concluded that all three of these lignins were GSH-type lignins (Faix 1991; Seca *et al.* 2000).

**Fig. 3.** FT-IR spectra of RL, ILL1, and ILL2

Gel Permeation Chromatography Analysis

The changes in the molecular weights of lignin could provide important insights into lignin's fragmentation and recondensation during an IL pretreatment (Wen *et al.* 2014). To determine the effect of [Bmim]Cl on the molecular weight of lignin, GPC was used for the analysis of RL, ILL1, and ILL2. Changes in the molecular weight of lignin are shown in Table 2 and Fig. 4.

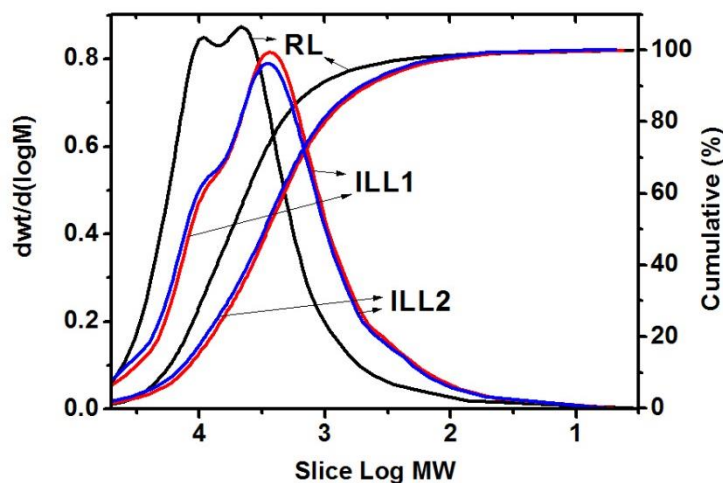


Fig. 4. Molecular weight distribution of lignin

Table 2. Weight-average (M_w) and Number-average (M_n) Molecular Weights (g mol^{-1}) and Polydispersity (M_w/M_n) of RL, ILL1, and ILL2

Samples	M_n	M_w	Polydispersity (M_w/M_n)
RL	1092	8791	8.1
ILL1	646	6224	9.6
ILL2	733	6873	9.4

The results showed that the molecular weight (M_w) and the polydispersity (M_w/M_n) of RL was 8791 g/mol and 8.1, respectively. After modification with [Bmim]Cl, the molecular weight (M_w) of ILL1 and ILL2 decreased to 6224 g/mol and 6873 g/mol , respectively. The polydispersity (M_w/M_n) of ILL1 and ILL2 increased to 9.6 and 9.4 as compared with the RL. This result indicated that compared to RL, ILLs was formed with a relatively uniform lignin fragment size and a lower number of condensed linkages (Tan *et al.* 2009). It also revealed that [Bmim]Cl had a noticeable effect on the molecular structure of RL and showed that the depolymerization of RL had occurred during the pretreatment with [Bmim]Cl. Moreover, the higher content of phenolic OH and the lower M_w value for ILL was good evidence for lignin depolymerization by an IL pretreatment (Jia-Long *et al.* 2013). This may have been due to cleaved linkages in lignin, like β -O-4 (Wen *et al.* 2014). While the cleavage of β -O-4 linkages could result in a decrease in the molecular weight of lignin, condensation reactions usually lead to a condensed and heterogeneous lignin structure with an increase in the molecular size (Pu *et al.* 2013). The molecular weight and polydispersity of ILL1 and ILL2 was nearly equal. The yields of ILL1 and ILL2 were 58.3% and 43.5%, respectively. Smaller

molecular compounds were washed away during regeneration. The ILL2 could have a higher degree of degradation than ILL1.

¹³C Nuclear Magnetic Resonance Spectroscopy

To understand the chemical structures of RL, IL1, and ILL2, spectra were obtained *via* ¹³C NMR. The peak assignments of lignin were based on previous literature (Lin and Dence 1992; Holtman *et al.* 2006). In the ¹³C-NMR spectra of RL and ILL, the characteristic tertiary carbon resonances from syringylpropane (S) (signals centered at 104.9 ppm) and guaiacylpropane (G) units (signals centered at 111.5 ppm and 119.3 ppm) were observed. The approximately calculated S/G ratios for RL, ILL1, and ILL2 lignins were 1.14, 0.90, and 0.96, respectively, which showed that the RL was richer in syringyl content than the ILL (Seca *et al.* 1998). This may result from the demethoxylation of S units. The quantitative ¹³C NMR spectra of RL, ILL1, and ILL2 are shown in Fig. 5. The integral at 160 ppm to 102 ppm was set as the reference, and the total aromatic carbons was assigned as 6. The integral values for the other structural moieties were expressed per one aromatic ring. A comparison of the integration values of the protonated aromatics, condensed aromatics, oxygenated aromatics, β-O-4, and OCH₃ are presented in Table 3. The content of aromatic C-O in RL increased from 1.83 /Ar to 1.86 /Ar in ILL1 and decreased to 1.62 /Ar in ILL2. The content of aromatic C-C in RL increased from 1.66 /Ar to 1.86 /Ar in ILL1 and 1.82 /Ar in ILL2, respectively. The condensation reaction occurred during this process. The content of aromatic C-H in RL decreased from 2.50 /Ar to 2.33 /Ar in ILL1, and increased to 2.55 /Ar in ILL2. These changes suggested that the [Bmim]Cl system had a minimal effect on the aromatic ring. The content of OCH₃ in RL decreased from 1.77 /Ar to 1.54 /Ar in ILL1 and 1.63 /Ar in ILL2. The methoxyl contents (as measured by NMR) of RL and ILL were in agreement with their relative compositions in the S and G units. The content of β-O-4 decreased from 0.22 /Ar to 0.18 /Ar in ILL1 and 0.13 /Ar in ILL2. This may have been due to the degeneration of the β-O-4 linkages. This meant that demethoxylation and the degeneration of β-O-4 linkages had occurred during the [Bmim]Cl system pretreatment. All of these results help to confirm the [Bmim]Cl break β-O-4 mainly on S units. Based on these results, the proposed [Bmim]Cl pretreatment mechanism of lignin is shown in Fig. 6.

Table 3. Assignment and Quantification of the Signals of the ¹³C-NMR Spectra (Results Expressed per AR)

δ/ppm	Assignment	RL	ILL1	ILL2
160 to 140	Aromatic C–O	1.83	1.86	1.62
140 to 123	Aromatic C–C	1.66	1.86	1.82
123 to 102	Aromatic C–H	2.50	2.33	2.55
61.2 to 58	β-O-4	0.22	0.18	0.13
58 to 54	OCH ₃	1.77	1.54	1.63
*δ/ppm- chemical shifts				

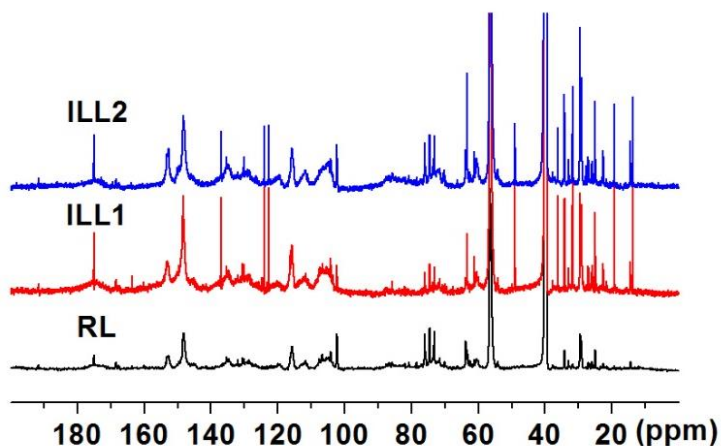


Fig. 5. ^{13}C -NMR spectrum of RL, ILL1, and ILL2

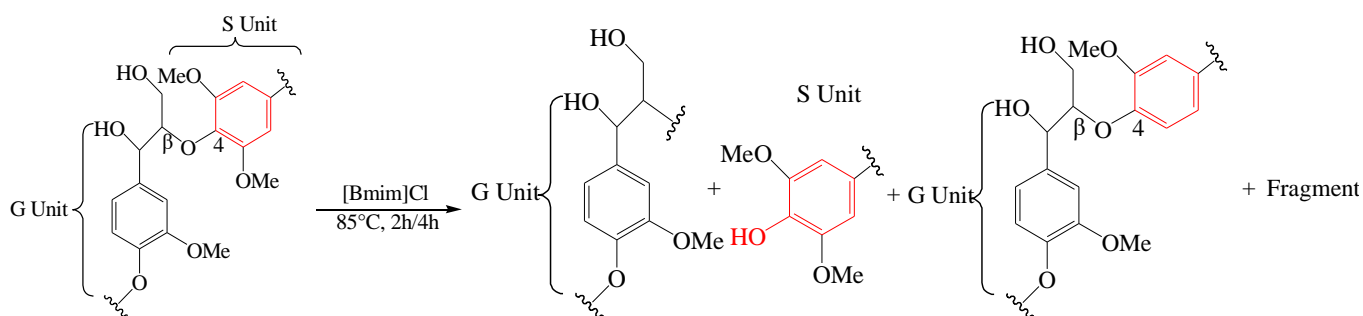


Fig. 6. Proposed [Bmim]Cl pretreatment mechanism of lignin

XPS Analysis

To determine the chemical composition of lignin, the samples were evaluated before and after the pretreatment with [Bmim]Cl via an X-ray photoelectron spectrometer (XPS), and high resolution XPS spectra were obtained, (Fig. 7). The characteristic peaks that corresponded to C1s and O1s appeared at approximately 286 eV, 532 eV, respectively.

According to previous research (Shen *et al.* 1998), the authors considered four classes of peaks and the different contribution of C1s groups could be classified, as shown in Fig. 7 and Table 4.

Table 4. XPS of RL, ILL1, and ILL2 (Wt.%)

Samples	O/C	C1	C2	C3	C4
RL	35.80	41.61	32.40	21.25	4.74
ILL1	35.09	43.21	33.01	18.33	5.45
ILL2	29.34	43.38	36.33	16.26	4.03

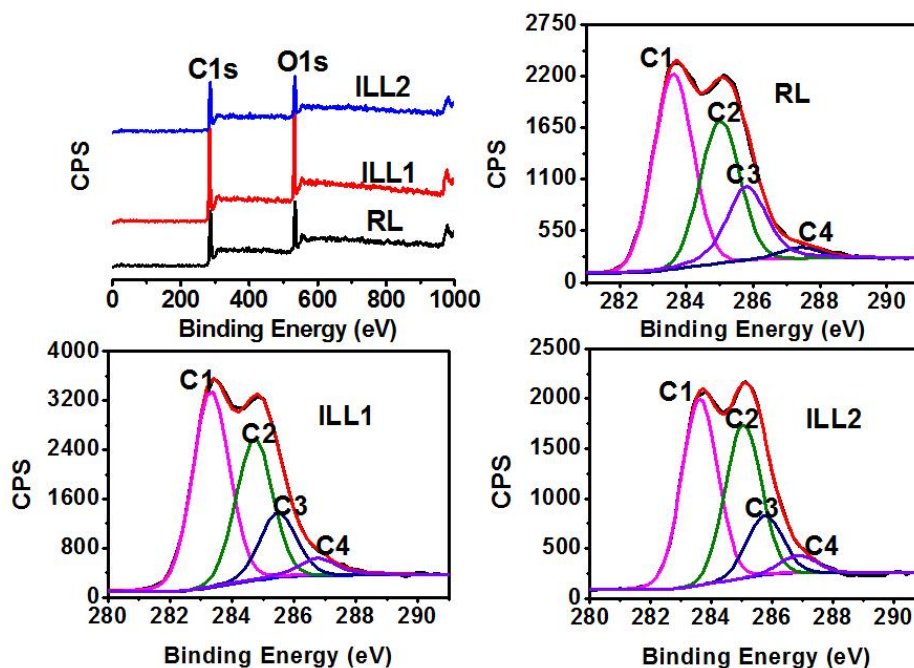


Fig. 7. XPS survey spectra and C1s XPS high-resolution spectra of RL, ILL1, and ILL2

The de-convolution of C1s XPS spectra gave the relative proportions of some important functional groups. The lignins were de-convoluted into four peaks. The results are shown in Table 4. The 285 eV corresponded to the C1s of the surface groups of nonoxidized carbon (C-H, C-C, C=C). The 286.5 eV corresponded to the C1s of the surface groups of carbon bound to one oxygen by a single bond (C-O, C-O-C). The 288 eV corresponded to the C1s of the surface groups of carbon with double bonds to oxygen (C=O and O-C-O), and 289 eV corresponded to the C1s of the surface groups of carbon with three bonds to oxygen (O-C=O), respectively (Li 2003; Wang *et al.* 2011).

The O/C ratio decreased and the content of C1 increased with the increased time of [Bmim]Cl pretreatment. Taking into account the GPC and ^{13}C -NMR results, this may have been due to the degradation of RL at first, which was then followed by condensation. When compared with the content of C2, the content of C-O increased. This resulted from the increase of phenolic hydroxyl (in accordance with the UV results), aliphatic hydroxyl, and ether bonds. The C3 was mainly attributed to carbonyl. The content of C=O decreased after processing by [Bmim]Cl; this was in accordance with the FTIR results. The C4 components could be attributed to the carboxylic moieties.

Lignin Thermal Stability Analysis

The results for the thermal decomposition of RL, ILL1, and ILL2 are shown in Fig. 6. The thermal decomposition of lignin took place in a temperature range of 120 °C to 800 °C. The TGA curves of the three samples showed a three-step thermal decomposition process. As can be seen in Fig. 8, the two samples began to decompose at <120 °C, associated with the loss of water and small organic molecules. The second weight loss temperature region between 120 °C and 500 °C

was due to carbohydrates in the lignin that decomposed into CO, CO₂, and CH₄ (Liu *et al.* 2008; Wang *et al.* 2009; Gu *et al.* 2013). At this stage, the weight loss ratio showed differences to some degree, RL < ILL1 < ILL2. This accounted for the degradation of lignin during the [Bmim]Cl pretreatment. Moreover, the DTG curve of the lignins appeared to be different, as there were two peaks in the RL. Only one peak was found in ILL1 and ILL2. This showed that the molecular weight distributions of ILL1 and ILL2 were more uniform. After the pretreatment with [Bmim]Cl, the molecular weights of ILL1 and ILL2 decreased and their distributions broadened. The thermal stability of ILL1 and ILL2 was increased after the [Bmim]Cl pretreatment. This result was consistent with the GPC results. The remaining residue after 800 °C was carbon (Brebú and Vasile 2010).

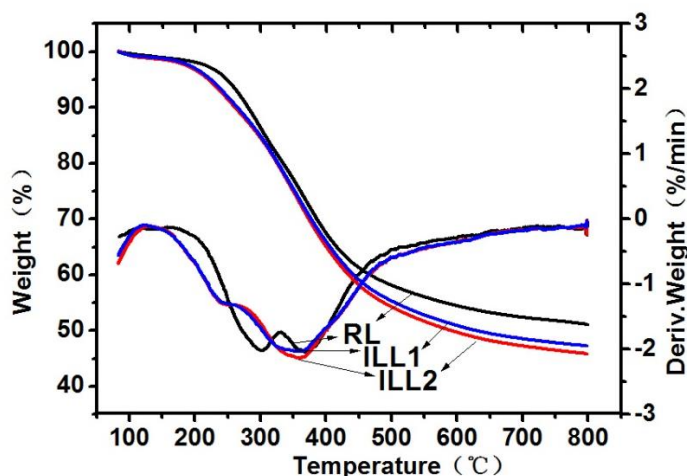


Fig. 8. TG and DTG curves for RL, ILL1, and ILL2

CONCLUSIONS

1. The results showed that the total content of phenolic hydroxyl in lignin increased when pre-treated in the ionic liquid. This can be attributed to the cleavage of β -O-4 linkages on S units.
2. The pretreatment with [Bmim]Cl enhanced the degradation of lignin, and the degree of lignin degradation increased with prolonged time of pretreatment.
3. After the pretreatment, lignin's molecular weight decreased and its molecular weight distribution broadened. This was due to the cleavage of β -O-4 linkages.

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