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## COMMUNICATION

# Highly Selective and Efficient Extraction of Lignin in Kraft Pulp by Aqueous Ionic Liquids for Enhanced Bleaching Properties

Cite this: DOI: 10.1039/x0xx00000x

Received 00th XX 2014,  
Accepted 00th XX 2014

DOI: 10.1039/x0xx00000x

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**Aqueous ionic liquids (ILs) that selectively extract lignin in kraft pulp under benign conditions were reported. This study provided an innovative idea to isolate the three-dimensional lignin from recalcitrant matrix with benefits of decreased dosage of bleaching chemicals, degradation of cellulose and toxicity of bleaching effluent.**

Lignin is the second most abundant natural polymer on earth and comprise various phenylpropanoid units interlinked by carbon-carbon and ether linkages, which form a highly heterogeneous branched three-dimensional network.<sup>1</sup> The network characteristic of lignin and its covalent linkages with adjacent carbohydrates, coupling with highly crystalline cellulose are primarily responsible for the recalcitrance of lignocellulose, which hinders the selective isolation of lignin.<sup>2</sup> Lignin is generally isolated through oxidation and hydrolysis reaction at elevated temperature and pressure with acid, alkali, or organic solvents, so lignin is inevitably severely degraded with carbohydrate.<sup>3,4</sup> Lignocelluloses are currently mainly applied to pulping and paper-making. Kraft pulp production can roughly be divided into cooking and bleaching processes.<sup>5</sup> Cooking is the major delignification stage in the presence of Na<sub>2</sub>S and NaOH to disintegrate lignocellulosic plant into pulp, whereas bleaching subsequently increases brightness by eliminating chromophores.<sup>5</sup> After cooking, the majority of lignin is removed, with ca. 10% residual in pulp that generates chromophores. In kraft pulp bleaching, lignin is supposed to be selectively degraded and dissolved with little cellulose degradation, considering the loss of yield and strength properties of pulp. Bleaching is achieved after elimination of the chromophores or by thorough degradation and dissolution of lignin. Common bleaching chemicals, such as chlorine dioxide, hydrogen peroxide, and oxygen, can effectively increase brightness. However, cellulose is simultaneously degraded with poor delignification selectivity. Inevitably, the yield and strength of pulp are considerably lost, and even highly toxic polychlorinated phenols form in the effluent with chlorine-containing chemicals.<sup>6</sup> Environmentally friendly chemicals with efficient and high-selectivity delignification are urgently expected in innovative bleaching technology. Moreover, selective and efficient lignin isolation is a prerequisite of biorefinery with high value-added

processing.

Ionic liquids (ILs) have been receiving much attention because of their unique properties such as nearly total non-volatility, high oxidative and thermal stabilities, wide liquid temperature range, and tunable properties.<sup>7,8</sup> Efficient and environmentally friendly processing of lignocelluloses is gradually feasible when ILs are used as green solvent for its particular ability on breaking hydrogen bond networks.<sup>9</sup> The structure and reactivity of cellulose largely depend on the quantity and intensity of hydrogen bonds. Accordingly, cellulose is divided into crystalline and amorphous zones on the basis of glucose arrangement. The macromolecular matrix of lignin and hemicellulose also has extensive hydrogen bonds. Cellulose dissolution by ILs has been thoroughly investigated. However, the effect of ILs on lignin is still not fully understood. Many imidazolium-based ILs were demonstrated to be good solvent for lignin which contain methyl, ethyl, allyl, butyl, hexyl and benzyl groups in the imidazolium ring and chloride, bromide, tetrafluoroborate, acetate and methylsulfate as anions, especially the large non-coordinating anions were not favourable of lignin dissolution.<sup>10-12</sup> Complete dissolution of lignocellulose requiring harsh conditions, such as Norway spruce sawdust dissolved in 1-allyl-3-methylimidazolium chloride (AmimCl) at 110 °C for 8 h with a solubility of 8 wt%, has been widely accepted.<sup>13</sup> Particle size and water content are the two crucial parameters that define solubilization.<sup>14</sup> We showed in our previous study that mild treatment of pulps by ILs resulted in fiber swelling and decreased cohesive force.<sup>15</sup> The dissolution of cellulose by ILs was not necessary in pulp processing and was only a requirement for lignin removal. Several studies have examined the complete dissolution of lignocellulose by ILs. Developing an easy-to-make and cost-effective processing of lignocellulose by ILs would be highly welcomed. Although the application of ILs is still seriously hindered by cost, processing, and recycling,<sup>16</sup> elucidating the extraction mechanism by aqueous ILs would provide a powerful basis for an efficient novel molecular design and the isolation of a three-dimensional macromolecule.

In this paper, we present an innovative method of lignin extraction in lignocellulose for green bleaching of kraft pulp involving pretreatment with aqueous ILs under benign conditions. Deconstruction of compact woody lignocellulose using ILs is

difficult. Small particle-sized sample facilitates the diffusion of ILs, but the communiton of lignocellulose to small size consumes a considerable amount of energy. Kraft pulp is obtained by cooking with nearly 50 wt% loss of feedstock. Thus, woody lignocellulose separates into pulp with a loose structure, which results in the diffusion of ILs. Correspondingly, the energy-consuming communiton can be cancelled. The presence of water induces competitiveness between the hydrogen bonds of pulp with ILs, and the dissolving efficiency decreases markedly with water content. However, both ILs and lignocellulose naturally exhibit strong hygroscopicity and apt to absorb water from atmosphere. Dehydration is also extremely cost consuming, especially at low water content. Additionally, water itself is a solvent in paper making, and only the removal of lignin is expected without fiber dissolution in bleaching. Hence, kraft pulp is the ideal object for treatment by benign ILs and chosen as the lignocellulosic material in our study. We designed a process incorporating IL pretreatment under benign conditions with water to extract residual lignin with negligible degradation on cellulose for enhanced bleaching properties.

The performance of ILs was significantly affected by water molecules.<sup>17</sup> The presence of water in ILs decreased the solubility of cellulose. When water was added to IL at concentrations greater than ca. 1.0 wt % (approximately 0.5 mole fraction H<sub>2</sub>O), the solvent properties of ILs were remarkably impaired, leaving cellulose insoluble. Kraft pulps were treated with 1-butyl-3-methylimidazolium chloride (BmimCl) or AmimCl (at 70 °C with IL dosage of 3.0 mL/g pulp for 30 min) with varying water content. The intensity of the treatment was considerably weaker than that of the dissolution of lignocellulose by ILs, for example, lignin fractionation with 97wt% purity from wheat straw requires complete dissolution of biomass by 1-ethyl-3-methylimidazolium acetate ([emim][CH<sub>3</sub>COO]) pretreatment with biomass/IL ration of 5% (w/w) at 140 °C for 6 h.<sup>18,19</sup> Table 1 shows that residual lignin in pulp can be substantially extracted by BmimCl pretreatment when the water content was below 12.0 wt%. The percentage of lignin extraction exceeded 20.0 wt% when the water content was below 3.0 wt%. Aside from cellulose dissolution, water content also remarkably influenced lignin extraction. Lignin extraction of aqueous IL solutions decreased sharply with increased water content, and almost no lignin was extracted when the water content was higher than 12.0 wt%. AmimCl pretreatment was performed similar to BmimCl pretreatment (Table S1).

Despite the high degree of lignin extraction, the loss in viscosity of fiber was low; thereby the natural strength of cellulose was maintained. The pretreated pulp was thoroughly washed with water and bleached with chlorine dioxide – chelation – hydrogen peroxide (DQP) bleaching sequence. Compared with the control sample, the brightness of the bleached pulps increased with the degree of lignin extraction in IL pretreatment. Slight loss in viscosity occurred under identical conditions in the bleaching process. At 3 wt% water content, the brightness after DQP bleaching increased to 4.4%ISO, with a reduction in viscosity of only 8.1 mL/g. The pretreated pulp was subsequently bleached with decreasing dosage of bleaching chemicals. The chemical dosage of DQP bleaching could be decreased to as high as 25.0 wt% at the identical target of brightness with the control samples. Correspondingly, the viscosity increased to ca. 25.0 mL/g (Table S2). The reduction in the degradation degree of cellulose increased the yield of bleaching. Reduced dosage of bleaching chemicals resulted in lower load of pollution effluent, and pre-extraction of lignin decreased adsorbable organic halide (AOX) emission. Less lignin-derived pollutants that resulted in poor reactivity facilitated the effluent treatment.

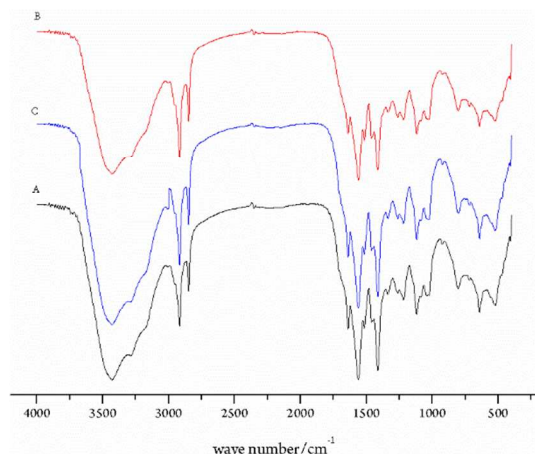
**Table 1.** Properties of pulps pretreated by BmimCl and DQP bleaching.

Water content, %	Lignin content, %	Viscosity, mL/g	Brightness, %ISO	Yield, %	CO <sub>2</sub> D, mg/pulp	BO <sub>2</sub> D, mg/pulp	AOX, mg/pulp
0	2.24	765.1	83.1	86.3	65.1	14.4	0.36
3	2.33	767.5	82.7	86.6	65.8	14.5	0.39
6	2.48	769.2	81.8	86.8	66.4	14.6	0.42
9	2.64	771.8	80.6	87.0	67.0	14.6	0.45
12	2.69	773.2	79.2	87.1	67.5	14.7	0.48
15	2.99	775.4	78.4	87.2	68.1	14.8	0.52
Control sample							
	3.00	775.6	78.3	87.2	68.2	14.8	0.53

The structural changes in pulp and lignin were analysed to reveal the mechanism of lignin extraction. The pulps were treated with 3.0 wt% water content (IL dosage of 3.0 mL/g pulp at 70 °C for 30 min). Given that no dissolution of cellulose occurred, the macrostructure of pulp was virtually untransformed by aqueous IL treatment and therefore could be used for paper making. The XRD pattern of cellulose was slightly changed by aqueous IL pretreatment (Figure S1). The crystallization index (CI) after BmimCl and AmimCl pretreatments was 66.2% and 67.5%, respectively. These values were slightly lower than those of the control sample (CI = 69.1%), which indicates that aqueous ILs mainly act on the amorphous zone of cellulose. The weak action on cellulose only resulted in a negligible loss in viscosity. However, the width of pulp increased from 19.34 μm to 20.12 μm and 19.40 μm for BmimCl and AmimCl pretreatments, respectively. The cellulose was significantly swollen after pretreatment with aqueous ILs under mild conditions. Larger volume of fiber led to a loose and porous structure, which facilitated the diffusion of lignin outside the fibers. Meanwhile, the diffusion of chemicals and degradation products in the subsequent bleaching stages was improved. Regarding the three-dimensional macromolecule of lignin, loosen structure of pulp can improve mass transfer performance favoring lignin extraction. The specific surface area of pulp increased from 2.14 m<sup>2</sup>/g to 2.36 m<sup>2</sup>/g (BmimCl pretreatment) and 2.34 m<sup>2</sup>/g (AmimCl pretreatment). Consequently, the reaction accessibility of pulp increased, which could be attributed to high bleaching efficiency.

Lignin, cellulose, and hemicellulose are the main components of the cell wall of lignocellulose. The effect of ILs on the hydrogen bonds in cellulose was comprehensively evaluated; this effect was believed to be the key factor in cellulose dissolution. However, hydrogen bonds also extensively existed in lignin and hemicellulose. A network of hydrogen bonds was formed in the lignin matrix and its neighboring hemicellulose, contributing a large portion of intermolecular forces of lignin. Under mild conditions, the breakdown of hydrogen bonds in cellulose mainly occurred in the amorphous zone, with a slight decrease in the degree of crystallinity. Thus, the degradation or even the loss of cellulose was avoided, which allowed the retention of the strength and yield of bleached pulp. Although a nonsignificant change with cellulose occurred, the lignin content in pulp after pretreatment decreased substantially. The hydrogen bonds (3000 cm<sup>-1</sup> to 3600 cm<sup>-1</sup>) in polymer was evaluated by IR.<sup>20</sup> The area of hydrogen bonds after aqueous IL pretreatment decreased to 17.53% (BmimCl pretreatment) and 15.89% (AmimCl pretreatment), whereas the other functional groups in pulp were

nearly unchanged (Figure 1). Breaking down the hydrogen bonds in lignin structure by aqueous IL pretreatment reduced the intermolecular forces.



**Figure 1.** IR spectra of pulps before and after IL treatment, (A) control sample, (B) sample after BmimCl treatment, and (C) sample after AmimCl treatment.

The hydroxyl groups in lignin, including aliphatic hydroxyl, phenolic hydroxyl, and carboxyl, substantially decreased after aqueous IL pretreatment (Table 2). The lignin units with more hydroxyls were easily dissolved for the disruption of hydrogen bonds.

**Table 2.** Quantitative analysis of groups in lignin from KP(m mol/g) by  $^{31}\text{P}$  NMR.

Groups	Control	BmimCl	AmimCl
Aliphatic hydroxyl	2.18	1.95	1.92
Condensed phenolic hydroxyl	0.63	0.54	0.52
Syringyl hydroxyl	0.52	0.47	0.46
Guaiacyl and demethylated hydroxyl	0.45	0.39	0.38
p-Hydroxy-phenyl hydroxyl	0.13	0.11	0.10
Total phenolic hydroxyl	1.73	1.50	1.46
Carboxyl	0.16	0.13	0.13

The molecular weight distribution and the polydispersity of lignin in pulps before and after aqueous IL treatment were analyzed by gel permeation chromatography. The number-average and weight-average molecular weights of lignin increased after aqueous IL pretreatment, whereas the polydispersity decreased. The extracted lignin had a small molecular weight. High-molecular weight lignin was still difficult to dissolve. Low-molecular weight lignin had weak intermolecular forces, and its diffusion ability was strong and easy to dissolve from pulp. This type of lignin also had low condensation degree with higher reactivity and readily reacted with bleaching chemicals in the subsequent bleaching stage and produced pollutants with higher toxicity. Therefore, pre-extraction of lignin by aqueous IL pretreatment could alleviate the toxicity of effluent in the following bleaching stage.

**Table 3.** Analysis of the molecular weight of lignin by IL pretreatment.

Pulp	Mn	Mw	Polydispersity (Mw/Mn)
Control	3215	5658	1.76
BmimCl	3458	5671	1.64
AmimCl	3423	5579	1.63

Deposited lignin layer formed on the fiber surface by adsorption of the dissolved lignin in the cooking stage. Thus, the diffusion paths were blocked, and the development on the diffusivity and bonds of fibers were hindered.<sup>21</sup> ILs with 1-butyl-3-methylimidazolium or 1-allyl-3-methylimidazolium cation exhibited the ability to form  $\pi$ - $\pi$  interactions with lignin for its aromatic groups. Moreover, ILs first acted on the deposited lignin layer. After pretreatment by aqueous ILs, the surface coverage of lignin decreased substantially from 32.34% to 21.83% (BmimCl pretreatment) and 21.54% (AmimCl pretreatment). The removal of deposited lignin on the fiber surface could open more diffusion channels.

## Conclusions

In conclusion, a highly selective and efficient method for extracting lignin in kraft pulp by aqueous ILs under benign conditions for green bleaching was proposed. The method could improve bleaching properties and was environmentally friendly, with nonremarkable degradation on cellulose. After pretreatment by aqueous ILs, the swelling level and specific surface area of pulp increased, which facilitated the diffusivity of pulp. Low-molecular weight lignin with a high content of hydroxyl groups was easily extracted because of its high diffusivity and decreased intermolecular forces caused by the breakdown of hydrogen bonds. The deposited lignin on the fiber surface that hindered diffusion was also substantially extracted. Given the diversity in its distribution, molecular weight, functional groups, and bonds, the dissolution or isolation of lignin cannot be simply described with only one model. Although the existence of water decreased the effectiveness of ILs, pre-extraction of lignin can effectively improve the bleaching properties of pulp. However, the rate of lignin extraction was confined to less than 30%, and only the low-molecular weight lignin deposited on the surface layer can be extracted. Designing ILs with high water content tolerance for strong affinity to lignin and selective cleavage of bonds between lignin monomers is required to determine the mechanism of intermolecular forces between complex polymer and ILs.

The authors are grateful for the financial support from the National Science Foundation of China (Grant Nos. 31370580 and 31100434), Talented Scientist of Shandong Province (BS2013HZ020 and BS2011CL035), and Open Fund of Jiangsu Provincial Key Lab of Pulp and Paper Science and Technology (201309).

## Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental and characterization details. See DOI: 10.1039/c000000x/

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