



# Understanding lignin treatment in dialkylimidazolium-based ionic liquid–water mixtures



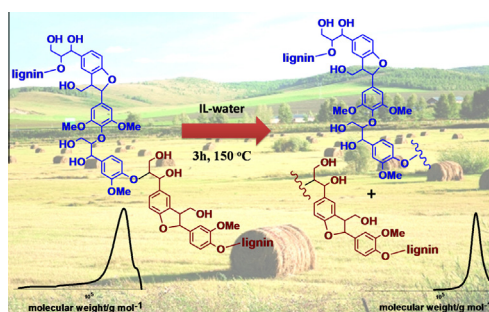
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## HIGHLIGHTS

- Lignin treatment in dialkylimidazolium-based IL–water mixtures was investigated.
- The pH, IL type and IL content influenced the degradation and structure of lignin.
- Adding water inhibited lignin depolymerization except for  $[\text{C}_4\text{mim}]\text{Cl}$ <sub>70%</sub>.
- Adding water affected the breakdown of inter-unit linkages and S/G ratio in lignin.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The treatment of enzymatically hydrolyzed lignin (EHL) in dialkylimidazolium-based ionic liquid (IL)–water mixtures (50–100 wt% IL content) was investigated at 150 °C for 3 h. pH, IL type, and IL content were found to greatly influence the degradation of lignin and the structure of regenerated lignin. 1-Butyl-3-methylimidazolium methylsulfonate–water mixtures with low pH facilitated lignin depolymerization but destroyed the regenerated lignin substructure. Regenerated lignin with low molecular weight and narrow polydispersity index (2.2–7.7) was obtained using a 1-butyl-3-methylimidazolium acetate-based system. Water addition inhibited lignin depolymerization at 50–100 wt% IL content, except for 70 wt% 1-butyl-3-methylimidazolium chloride–water mixture. Compared with pure IL treatment, obvious differences were observed in the breakdown of inter-unit linkages and ratio of syringyl to guaiacyl units in regenerated lignin with IL–water treatment.

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## 1. Introduction

Lignocellulosic biomass is a renewable material mainly composed of cellulose, hemicelluloses, and lignin (Singh and Mishra, 1995). The enzymatic hydrolysis of cellulose and hemicelluloses for fuels and chemicals is promising because of its environmental and economic benefits. Lignin, a three-dimensional amorphous polymer with methoxylated phenylpropane structure, can also be utilized as raw material for fuels and chemicals. Lignin can confer

mechanical strength to the cell wall with reinforced cellulose fibrils and polysaccharide matrix (Brandt et al., 2013). Thus, the accessibility of enzyme can be inhibited by lignin, which results in decreased extent and rate of enzymatic hydrolysis. Pretreatment can remove part of lignin to facilitate enzymatic hydrolysis and further lignin utilization (Kim et al., 2011; Hou et al., 2013).

The pretreatment of lignocellulosic biomass using an ionic liquid (IL)–water mixture is effective because of its low cost, ease of IL circulation, and low viscosity. This pretreatment is also known as the “Ionosolv” process (Brandt et al., 2013) and is characterized

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by the selective delignification of biomass through lignin dissolution.

The pretreatment process with IL–water mixture is commonly carried out at relative high temperature (120–180 °C) (Brandt et al., 2011; Fu and Mazza, 2011a,b). Lignin dissolution is accompanied by the cleavage of specific inter-unit lignin linkages during the traditional pretreatment process (Shi et al., 2014). The mechanism of lignin depolymerization during the pretreatment with pure IL was recently examined, and preferential lignin dissolution was observed due to the chemical nature of lignin including its building blocks and inter-unit linkages. In comparison with pure IL, only limited information on the depolymerization and structure changes of lignin during pretreatment with IL–water mixtures exists.

Sun et al. (2013) investigated the pretreatment of corncob in 1-ethyl-3-methylimidazolium acetate ([C<sub>2</sub>mim]OAc)–water mixtures followed by alkaline nitrobenzene to isolate lignin. Corncob lignin has a high weight-average molecular weight ( $M_w = 4310$  g/mol) and a low amount (Ar/100Ar, Ar represents aromatic units) of  $\beta$ -O-4 units than milled wood lignin. Shi et al. (2014) monitored the lignin molecular weight distribution in the pretreatment of [C<sub>2</sub>mim]OAc–water mixtures using gel permeation chromatography (GPC). They found that lignin dissolved and depolymerized during pretreatment and proposed that the addition of water has negative effects on delignification and lignin depolymerization. Sun et al. (2014) investigated the changes in molecular weight of formic acid and Alcell lignin after treatment of [C<sub>2</sub>mim]OAc–water mixtures. Nearly 40% lignin was found degraded into small molecules in the cases of [C<sub>2</sub>mim]OAc–water mixture (85 wt% [C<sub>2</sub>mim]OAc content) and pure [C<sub>2</sub>mim]OAc at 150 °C for 3 h, suggesting that a certain amount of water addition benefited lignin degradation. The role of water on delignifying biomass and lignin depolymerization is still unknown. Furthermore, the structural changes that lignin undergoes during the Ionosolv process are not fully characterized. Hence, an improved understanding of lignin characteristics before and after IL–water treatment will enable the development of a more efficient pretreatment process.

In our precious work (Wang et al., 2014), a series of dialkylimidazolium-based IL–water mixtures (above 40 wt% IL content) were found to dissolve lignin at 60 °C. In the present study, lignin treatment using three types of IL–water mixtures, namely, 1-butyl-3-methylimidazolium chloride ([C<sub>4</sub>mim]Cl)–water, 1-butyl-3-methylimidazolium acetate ([C<sub>4</sub>mim]OAc)–water, and 1-butyl-3-methylimidazolium methylsulfonate ([C<sub>4</sub>mim]MeSO<sub>3</sub>)–water, was investigated. Enzymatically hydrolyzed lignin (EHL) was used. EHL is isolated only from the enzymatic hydrolysis of biomass residues, which have high molecular weight and similar structure to lignin in untreated lignocellulosic biomass (Tolbert et al., 2014). In this work, we first investigated the treatment process using various IL–water mixtures. Solvent–solute interactions were then preliminarily investigated using attenuated total reflection infrared (ATR-IR) spectroscopy. Structural variations of lignin were characterized by two-dimensional <sup>1</sup>H–<sup>13</sup>C heteronuclear single quantum coherence (2D-HSQC) NMR, GPC, and elemental analysis.

## 2. Methods

### 2.1. Materials

EHL was supplied by Shandong Longlive Bio-Technology Co., Ltd. (China). EHL isolation involves the removal of a substantial amount of carbohydrate fraction with the cellulolytic enzyme hydrolysis of corncob; this procedure was followed by extraction

using diluted sodium hydroxide solution, and subsequently with diluted sulfuric acid (2 wt%) hydrolysis that cleaves lignin–carbohydrate bonds. According to the test results by the National Food Quality Supervision and Inspection Center (NFQSIC; China), the residual carbohydrates content in EHL is 0.17% and the phenolic hydroxyl group content is 8.0%. All ionic liquids (>98% purity) were supplied by Lanzhou Institute of Chemical and Physics, China. All chemical agents (purchased from Aladdin Co.) were of analytical grade and used without further purification.

### 2.2. Experimental procedure

IL and deionized (DI) water were mixed to form a treatment solvent with different IL weight percentages (50–100 wt%). To simplify the discussion, we devised a notation to indicate the IL content in mixture, with the remainder being water. For example, ([C<sub>4</sub>mim]Cl)<sub>70%</sub> represents a mixture of 70 wt% [C<sub>4</sub>mim]Cl and 30 wt% DI water.

IL–water (8 g) was transferred into a 50-mL reaction kettle. EHL (0.4 g) was then slowly added into the IL–water mixture under quick stirring. The mixture was then placed in oil bath and heated on a hot plate under magnetic stirring (720 rpm) at 150 °C for 3 h. After treatment, regeneration of the dissolved lignin was carried out by precipitation of the IL–water–lignin solution into 100 mL deionized water (pH 2.0) under vigorous magnetic stirring. The regenerated lignin was obtained by centrifugation, followed by thorough washing with DI water. The regenerated lignin was then lyophilized at –57 °C and weighed ( $m_r$ ). The recovery yield of lignin can be calculated using Eq. (1):

$$\text{recovery yield of lignin (wt\%)} = \frac{m_r}{m_0} \times 100\% \quad (1)$$

where  $m_0$  is the weight of the used EHL.

The interactions between solvent and solute molecules in the IL-based systems were investigated by ATR-IR spectroscopy. IR absorbance spectra of the IL–water mixtures and of mixtures with dissolved EHL were taken from 650 cm<sup>–1</sup> to 4000 cm<sup>–1</sup> with 2 cm<sup>–1</sup> resolution and with an ATR accessory from Perkin Elmer. A small droplet of the samples was placed on top of the ZnSe crystal, and each ATR-IR spectrum contained 16 signal-averaged scans.

### 2.3. Characterization of lignin samples

The weight-average molecular weight ( $M_w$ ), number-average molecular weight ( $M_n$ ), and polydispersity index (PDI,  $M_w/M_n$ ) of the lignin samples were determined by GPC with a refractive index detector on a HMW 6E tetrahydrofuran (THF) 4.6 × 300 mm column with THF as solvent. A lignin sample of 4 mg was dissolved in 2 mL of THF, and a 10  $\mu$ L sample in solution was injected. The column was operated at ambient temperature and eluted with THF at a flow rate of 0.6 mL/min. Monodisperse polystyrene was used as standard for the molecular weight of lignin.

For 2D-HSQC NMR spectroscopy, 80 mg of the lignin sample was dissolved in 0.5 mL of DMSO-*d*<sub>6</sub> (99.8% D). The Bruker standard pulse program hsqcetedgppp.3 was used for HSQC experiments. The spectral widths were 6010 Hz and 18,112 Hz for <sup>1</sup>H- and <sup>13</sup>C-dimensions, respectively. The number of collected complex points was 1024 for the <sup>1</sup>H-dimension with a recycle delay of 1.5 s. The number of transients was 128, and 256 time increments were recorded in the <sup>13</sup>C-dimension. The <sup>1</sup>J<sub>C–H</sub> used was 145 Hz. HSQC correlation peaks were assigned by comparing with those in the literature (Martínez et al., 2008; Sette et al., 2011). Data processing was performed using standard Bruker Topspin-NMR software. In the aliphatic oxygenated region, the relative abundances of side chains involved in various inter-unit linkages were estimated from C<sub>α</sub>–H<sub>α</sub> correlations, except for that of cinnamyl alcohol end groups

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