



Understanding structural changes in the lignin of *Eucalyptus urophylla* during pretreatment with an ionic liquid-water mixture

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ABSTRACT

Lignin is the second most abundant natural biopolymer found on earth. For sustainable use of lignin, the development of effective techniques for its depolymerization is necessary. In this study, the depolymerizations of enzymatic mild acidolysis lignin (EMAL) and Alcell lignin (AL), isolated from the eucalyptus urophylla using an ionic liquid (IL)-water mixture, were analyzed and compared. The results showed that the addition of a certain amount of water to IL could enhance the efficiency of lignin hydrolysis. The maximum solubilities of EMAL (41.5 wt.%) and AL (37.1 wt.%) were obtained in the [C₂C₁im][OAc]_{85%}-water and [C₂C₁im][OAc]_{15%}-water solutions, respectively. The structures of regenerated lignin fractions are changed according to the proportion of water added to the IL, and were thoroughly characterized by GPC, FT-IR, 2D-HSQC NMR, and TGA. The results indicated that the molecular weight of regenerated lignin decreased, especially in the AL fractions, which were dissolved due to a high proportions of water (35–85 wt.%) in the mixture. The increased syringyl (S) to guaiacyl (G) ratio (S/G) of EMAL indicated the preferential breakdown of G-unit lignin. For AL, the S-unit lignin was easy to be removed by the mixture, indicating different mechanism for the lignin depolymerization. The study provides a better understanding of IL-water mixture as a solvent for dissolving lignin, thus encouraging further use of lignin.

1. Introduction

After cellulose, lignin is the second most abundant biopolymer found on earth, and accounts for 15–35% of the typical dry lignocellulosic biomass (Azadi et al., 2013; Kim et al., 2011). It is estimated that the chemical pulp industry produces approximately 70 million tons of lignin per year globally (Bajwa et al., 2016). The most common application of lignin in the pulp and paper industry is the combustion process, which is used for energy generation, and accounts for around 95% of the total lignin market (Chakar and Ragauskas, 2004; Gordobil et al., 2016). Lignin has historically been viewed as a low value product, which was used in products such as binding, dispersing, or emulsifying agents (Calvo-Flores and Dobado, 2010), and has also been used as a resin manufacturing component (Sen et al., 2015). Lignin is rich in aromatic rings with various branches and is biosynthesized from three different monolignols of phenylpropane unit, namely the *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, which comprise of *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S)

units (Fig. S1, Supplementary data). Besides its use as a macromolecule, lignin can be catalytically depolymerized through hydrolysis, reduction and oxidation process to produce some high value added platform chemical and useful aromatic monomer (Farg and Chaouki, 2015; Li et al., 2015; Ma et al., 2015; Zakzeski et al., 2010).

For many years, lignin depolymerization has been investigated using a variety of methods, which convert lignin into useful chemicals. In industry, lignin was used to produce useful chemicals during the traditional pulping process. However, the production process was highly energy-intensive and associated with low-efficiency. For example, autohydrolysis and organosolv processes were used to treat lignin from stalks at 180 °C. However, only 2% of total phenols in the organosolv liquor could be recovered, which were almost completely mixed with lignin, making it difficult to separate from lignin (Amendola et al., 2012). Different catalysts were used to assist the conversion of macromolecular lignin into aromatic products. However, these catalysts were capital intensive, thus arising the need for a more economical catalyst (Gillet et al., 2017). Shu et al. (2018) reported a controllable

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method using a Pd/C catalyst which cooperated with metal chloride to produce guaiacols and phenols from lignin. The results showed that the selection of metal chloride played a leading role in the production of phenols, and the catalyst with strong Lewis acidity was an important factor to determine the phenols production. Furthermore, solid based catalysts were also used to depolymerize lignin into low molecular weight products at 250 °C. However, depending on the base catalysts used, different amounts of monomeric compounds were produced dependent on pH, the cation, the type, and concentration of basic sites (Chaudhary and Dhepe, 2017). Jiang et al. (2010) studied the pyrolysis of lignin and reported that the individual yield of compounds was less than 1 wt.%. Therefore, the main challenge in lignin depolymerization is the pretreatment process. The method that easily converts lignin into the depolymerization products is an important criterion for lignin utilization. In addition, lignin processing should first be favored in accordance with the green chemistry and the sustainable pretreatment technology principles. Therefore, it is essential to develop more effective and cost-competitive method for lignin degradation and for continuous production of chemicals from lignin.

Recently, ionic liquids (ILs) have received increased research attention for their potential to be used in the pretreatment of lignocellulosic biomass and lignin (Berglund et al., 2017; Lauberts et al., 2017; Ninomiya et al., 2018; Soudham et al., 2015). Ninomiya et al. (2018) showed that the yield of phenolic aldehydes through oxidation depolymerization of IL-pretreated/enzyme lignin increased up to 48.0%, which was the highest among all other pretreated lignin. In addition, the lignin fractionation with 1-butyl-3-methylimidazolium ([C₄C₁im]) cation-based IL resulted in high purity and antioxidant activity, while the obtained low molecular weight lignin could serve as an excellent antioxidants. The results also showed that ILs could act as suitable solvents for technical lignin isolation (Lauberts et al., 2017). After dissolution in protic ILs, the regenerated lignin showed higher thermal stability and reduced average molecular weight, which could promote the potential of lignin as a commercial commodity (Rashid et al., 2016). ILs dissolution is an important pretreatment technique for lignin utilization. Moreover, water has been successfully introduced in ILs to dissolve lignin (Akiba et al., 2017; Brandt et al., 2011, 2015; Sun et al., 2013). The reaction conditions and the presence of water are the determinants for the depolymerization of lignin mediated by ILs (Gillet et al., 2017). The results showed that ILs can break the β-O-4' ether bonds, glycosidic, and ester linkages in the presence of water, generating new lignin fragments, called "ionosolv lignins" (Brandt et al., 2011). The ionosolv lignin has a lower molecular weight and higher phenolic hydroxyl content, which can serve as value-added chemicals (Brandt et al., 2011, 2015). In addition, it was found that the addition of water to IL not only decreased the viscosity of IL, but also reduced the cost of treatment process to improve the practical application of ILs in the dissolution of lignin and lignocellulosic biomass. It is believed that IL-water mixture is a suitable alternative solvent for the extraction and depolymerization of lignin. However, there is a lack of understanding regarding the structural changes in lignin during its depolymerization in IL-water mixture.

In the present study, the structural features regarding the composition and chemical linkages of lignin, which was depolymerized in an IL-water mixture, were comprehensively analyzed. Two representative isolated lignin, namely the enzymatic mild acidolysis lignin (EMAL) and Alcell lignin (AL), obtained from eucalyptus urophylla were studied. To carry out the study, different amounts of water were added to the IL to evaluate the efficiency of lignin depolymerization. The most effective IL, 1-ethyl-3-methylimidazolium acetate ([C₂C₁im][OAc]), was used to dissolve the lignin (Chen et al., 2018; Wang et al., 2013). Furthermore, a comprehensive and effective pathway was proposed to explain the detailed structural changes taking place in lignin fragment. In addition, advanced two-dimensional heteronuclear essential single quantum coherence (2D-HSQC) NMR spectroscopy was applied by dissolving the lignin fragment into deuterated solvents. Quantitative analysis,

including S/G ratio and major linkages, such as β-O-4', β-β', and β-5' were calculated to facilitate the understanding of structural changes in lignin. The molecular weights of recovered lignin were determined using gel permeation chromatography (GPC) to explain the interplay between the degradation and the self-condensation reactions during the depolymerization process. The physicochemical properties of the regenerated lignin were also characterized using Fourier-transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA).

2. Materials and methods

2.1. Materials and chemicals

Eucalyptus urophylla (6 years old) was obtained from Guangxi province, China. The trunks of eucalyptus were cut into small pieces, and then, milled into flour in a planetary ball mill (FritschGMBH, Idar-Oberstein, Germany) for 3 h in a 10 min-on 10 min-off cycle (500 rpm). The obtained flour was dried at 60 °C for 12 h and vacuum-sealed for the next fractionation. Furthermore, 1-ethyl-3-methylimidazolium acetate ([C₂C₁im][OAc], purity > 98.5%) was obtained from Lanzhou Institute of Chemical Physics (Chinese Academy of Science), Lanzhou, China. All other chemicals were of reagent grade and used without any further purification.

2.2. Preparation of enzymatic mild acidolysis lignin and Alcell lignin

The EMAL fractions were extracted from the ball-milled samples according to the procedure described by Wu and Argyropoulos (2003) (Fig. S2, Supplementary data). AL was extracted from eucalyptus wood chips using ethanol-water mixture according to the method proposed by Ni and Hu (1995) with slight modifications. In a typical experiment, 50 g of small wood chips were incubated in a 1 L stainless steel reactor (Parr, USA) with a 5% (w/v) aqueous ethanol solution (70%, w/w) at 200 °C for 1 h. The collected filtrate was centrifuged to remove fine wood powder. After centrifugation, the filtrate was placed in acidic deionized water (pH = 2.0) and stirred to precipitate lignin. Finally, the obtained AL was washed with deionized water and freeze-dried.

2.3. Lignin solubilization in IL-water mixture

The solubilization of lignin was carried out in a [C₂C₁im][OAc]-water mixture at 150 °C for 3 h with continuous stirring in an oil bath on a hot plate (IKA magnetic stirrer, Germany), as shown in Fig. 1. Because the *T*_{onset} value for the [C₂C₁im][OAc] is 216 °C, the IL used in the experiment is thermally stable and can be easily recovered and reused (Clough et al., 2013). In certain cases, the ionic liquid was first

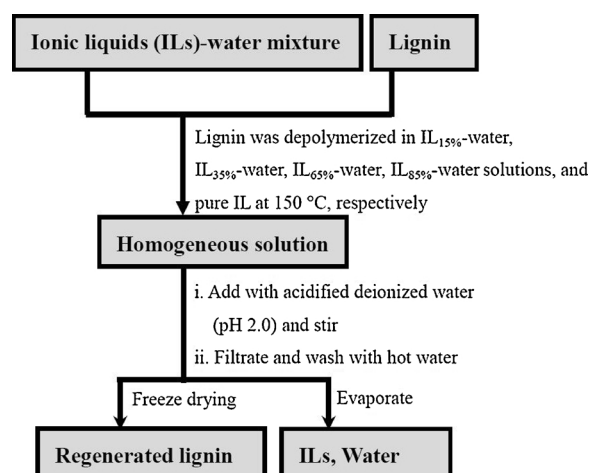


Fig. 1. Flowchart for lignin hydrolysis and regeneration in IL-water mixture.

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