



Short Communication

Depolymerization of oak wood lignin under mild conditions using the acidic ionic liquid 1-H-3-methylimidazolium chloride as both solvent and catalyst

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HIGHLIGHTS

- ▶ Lignin extracted from wood in ionic liquid through dissolution and precipitation.
- ▶ Lignin reacted with 1-H-3-methylimidazolium chloride at mild temperatures.
- ▶ Hydrolysis of lignin ether linkages with acidic ionic liquid was demonstrated.
- ▶ Acidic ionic liquid could be used for biomass pretreatment by lignin degradation.

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ABSTRACT

Oak wood lignin, which was separated from the wood using dissolution in the ionic liquid 1-methyl-3-ethylimidazolium acetate and subsequent precipitation, was successfully depolymerized in the acidic ionic liquid 1-H-3-methylimidazolium chloride under mild conditions (110–150 °C). Based on gel permeation chromatography results, an increase in temperature from 110 to 150 °C increased the rate of reaction, but did not significantly change the final size of the lignin fragments. Nuclear magnetic resonance and infrared spectroscopy were utilized to demonstrate that the depolymerization proceeded via a hydrolysis reaction that cleaved the alkyl-aryl ether linkages. Coupling of the lignin fragments was also shown to occur in the reaction mixture. These hydrolysis results are consistent with the literature on acid catalyzed depolymerization of lignin in conventional solvents and with recent model compound studies involving guaiacylglycerol- β -guaiacyl ether and veratrylglycerol- β -guaiacyl ether done in acidic ionic liquids.

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1. Introduction

As the demand for alternatives to petroleum based resources continues to grow, new and better methods must be developed to utilize “green” energy sources (Edenhofer et al., 2012). Biomass has been indicated as a major renewable resource that will continue to be developed in future generation energy production, with an annual yield of 1.37 million dry tons in the United States (Perlack et al., 2005). Lignin is one of the three biopolymers that comprise plant biomass; 15–30% is lignin, with the balance being cellulose and hemicellulose (Holladay et al., 2007). Lignin is a complex, amorphous biopolymer that is incorporated into the cell wall in plant matter. This structural component of biomass is comprised of phenyl-propanoid units that are connected through a number of different chemical structures (Chakar and Ragauskas, 2004; Holladay et al., 2007). The β -O-4 linkage is the most common of these

structures, accounting for 45–50% of the linkages in softwood lignin (Adler, 1977). The complex, amorphous structure of lignin is very resistant to biological attack, and only metabolized by a few species in nature. Lignin is also a major hurdle for the effective utilization of biomass as a fuel and chemical feed stock because it retards chemical and biological attack (Davis and Sello, 2010).

Currently, there are a few methods used to process biomass (Chakar and Ragauskas, 2004; Perlack et al., 2005; Elliott, 2007; Hicks, 2011). Pretreatment is often an important step in the effective utilization of biomass. Some work has already been done using steam explosion, ammonia fiber expansion, acid hydrolysis, and even ionic liquids in the pretreatment of lignocellulosic biomass to provide a more accessible structure for biological attack (Kumar et al., 2009). The work presented herein seeks to add to this body of pretreatment research by focusing on lignin degradation.

Ionic liquids (ILs) are a class of chemicals that are generally composed of an organic cation with an inorganic counter ion and melt at or below 100 °C. Ionic liquids are often considered a green solvent due to advantages in separations and reusability. ILs have also received attention in the field of biomass processing because of their ability to solubilize cellulosic biomass (Kilpeläinen et al.,

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2007; Sun et al., 2009). Studies utilizing model compounds that replicate the ether structures in lignin have shown that these acidic ILs are effective for the hydrolysis of the β -O-4 ether linkage, a common structure in lignin (Jia et al., 2010a; Cox et al., 2011).

Lignin can be degraded through a number of different chemical paths, such as base, acid, or metal chloride catalyzed depolymerization, or treatment under supercritical conditions (Chakar and Ragauskas, 2004; Yokoyama and Matsumoto, 2010; Jia et al., 2010b; Gosselink et al., 2012). Model compounds are commonly used to study the hydrolysis reactions; studies with the lignin model compounds, guaiacylglycerol- β -guaiacyl ether and veratrylglycerol- β -guaiacyl, revealed the same pathway when an acidic IL is used as both the solvent and the catalyst as conventional acid based lignin treatment methods (Jia et al., 2010a; Cox et al., 2011). In this study, we investigate the ability of 1-H-3-methylimidazolium chloride (HMIMCl), an acidic IL, to depolymerize lignin as a route to the effective pretreatment of biomass with HMIMCl and as an extension of earlier research with model compounds. The novelty of this study lies in utilizing an ionic liquid as a combination solvent and catalyst to depolymerize lignin as a method for biomass pretreatment.

2. Experimental

2.1. Material

1-H-3-methylimidazolium chloride (HMIMCl) (>95%), 1-ethyl-3-methylimidazolium acetate (EMIMOAc) (>90%), 1-ethyl-3-methylimidazolium chloride (>95%), dextran standard 12000, and dextran standard 5000 were purchased from Sigma Aldrich and used without further purification unless otherwise noted. Acetone (99.8%), toluene (99.9%), ethyl acetate (99.9%), 2-naphthol (98%), dimethyl sulfoxide (DMSO) (99.97%), dimethyl formamide (99.92%) dimethyl sulfoxide- d_6 (99.9%), light mineral oil, phosphoric acid (purity not given, labeled “pure”), lithium bromide (99%) and sodium hydroxide (98.7%) were purchased from Fisher Scientific and used without further purification unless otherwise noted.

Lignin was extracted from wood through the modified method developed by Sun et al. (2009). Scrap oak wood was ground to a powder using a pneumatic powered abrasive disk. In a typical extraction, 2 g of wood dust was dissolved in 25 g of EMIMOAc by stirring at 110 °C for 48 h. The stirring mixture was held under vacuum until the pressure stabilized below 13 Pa to remove any incidental water. Once the 48 h had elapsed, 400 ml of a 1:1 mixture of acetone and water was added and stirred for at least 3 h or until there were no more remaining biomass/IL clumps. The mixture was filtered and the precipitated cellulose discarded. The acetone in the remaining homogenous solution was evaporated under mild heating (50–75 °C) and vacuum. The precipitated lignin was then filtered from the solution, washed three times with distilled water, and dried under vacuum. The water was evaporated from the EMIMOAc, which was subsequently washed twice with 20 ml of toluene and twice with 20 ml of ethyl acetate. The IL, which maintained a dark brown color, was dried on a Schlenk line and reused in the next lignin extraction. Typical lignin recovery was about 150 mg. The structure of the lignin was verified by comparing the 2D heteronuclear single quantum coherence NMR (2D HSQC NMR) data (see Supporting Material) with published NMR measurements (Zhang and Gellerstedt, 2007). No peaks resembling structural carbohydrates were observed when the NMR results were compared to 2D HSQC NMR for cellulose triacetate (Zhang and Gellerstedt, 2007).

2.2. Experimental procedures

In a typical lignin depolymerization experiment, 10 mg of lignin and 2.5 μ l of water was added to a 300 μ l reaction vial. HMIMCl

was melted in a boiling water bath and 300 μ l transferred to the reaction vial via pipette. In the case of the 2-naphthol experiments, 4.5 mg of 2-naphthol was added to the vial as well. The vial was then placed into a Thermo Scientific Reacti-Therm heated/stirred module set at the prescribed temperature. Once the required time had elapsed, the reaction mixture was quenched in 1 ml of gel permeation chromatography (GPC) eluent (80:20 DMSO:DMF containing 20 mM phosphoric acid and LiBr). The samples were analyzed on a GPC using a Wyatt Optilab T-rEX differential refractometer detector and two Phenomenex Phenogel 5 μ m, 300 \times 7.8 mm linear columns held at 50 °C with an 80:20 mixture of DMSO and DMF that contained 20 mM phosphoric acid LiBr flowing at 0.6 ml/min.

For IR and NMR analysis, lignin depolymerization products needed to be separated from the HMIMCl after the reaction. In a typical HMIMCl removal procedure for a 300 μ l experiment, the mass of add IL was recorded and the reaction mixture was quenched in 4 ml of water and added to a separatory funnel with 10 ml toluene. Roughly 170 mg of NaOH was dissolved in 10 ml water. A stoichiometric amount NaOH solution was slowly added to the quenched reaction mixture with occasional gentle swirling of the solution. The resulting methylimidazole was extracted with three more rounds of 10 ml toluene. Only gentle, repeated inversion of the extraction funnel was used to prevent an emulsion from forming. The remaining water was removed from the aqueous phase using a hot water bath and aspirator. The product, a mixture of depolymerized lignin and sodium chloride, was then powdered with a mortar and pestle for use in NMR or IR experiments. The structure of lignin was unchanged through this process, as verified by C NMR and H NMR (see Supporting Material).

NMR measurements were made on a Varian Direct Drive 600 MHz NMR spectrometer. For NMR samples, the amount of IL was quadrupled and eight times the standard mass of lignin was used. Experiments were run at 150 °C for 60 min. Samples were prepared using the method above for removal of HMIMCl from lignin samples, but scaled for the larger batch size. To make the NMR sample, the powder of sodium chloride and lignin was mixed with 1.3 ml DMSO- d_6 . The sodium chloride was filtered from the solution using a pipette packed with a small amount of Kimwipe®. In the case of unreacted lignin, the lignin samples were suspended in 4 ml water and 300 μ l HMIMCl. This suspension then underwent the IL removal procedure to ensure that any differences observed between the reacted and unreacted lignin was caused by the depolymerization and not the extraction process.

IR samples were made by following the standard reaction and IL separation procedures for a 150 °C, 60 min reaction. As with the NMR samples, unreacted lignin was subjected to the same IL separation process as the reaction mixture. Because solutions in DMSO were too dilute for IR analysis, the powder of sodium chloride and lignin was suspended in 500 μ l of mineral oil. Measurements of the suspended powder were made on a Thermo-Mattson Infinity Gold FT-IR spectrometer using a liquid cell with sodium chloride windows and a 0.1 mm path length.

3. Results and discussion

Lignin was reacted in HMIMCl under the prescribed conditions and then analyzed using GPC as described in Section 2.2. The results, shown in Fig. 1, demonstrate that the size of the lignin molecules is being decreased, indicating depolymerization, when reacted in the HMIMCl under mild heat. Fig. 1A is the result of 12 k dextran ($\bar{M}_w = 11600$, $\bar{M}_n = 8110$) and 5 k dextran ($\bar{M}_w = 5220$, $\bar{M}_n = 3260$) standards run on the GPC as comparison for the lignin. Dextran was chosen as a reference because it is a readily available, well characterized GPC standard that, due to its

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