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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.

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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