

Ionic liquids as green solvents: A selective approach to biomass fractionation and deconstruction

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Introduction

Lignocellulosic biomass is a valuable resource for fuels and chemicals which can be grown sustainably in areas where food crops cannot be produced. This plant matter is made up primarily of three components: cellulose, hemicellulose, and lignin. While many new technologies are being developed to facilitate efficient and cost effective conversion of these biopolymers into value-added fuels and chemicals, the implementation of these technologies on a large scale is greatly limited by current fractionation solvents and technologies.¹ Ionic Liquids (ILs) are highly adaptable and recyclable solvents with a number of properties that make them attractive for biomass processing. These “molten salts” consist primarily of large organic ions with multiple sites at which various functionalities can be attached. Many ILs are capable of completely dissolving lignocellulosic biomass.² Moreover, the development of solvents which selectively target specific biopolymers could greatly reduce the time and cost involved in processing these biopolymers to bioproducts. To this end, in this work a semi-continuous IL extraction system was developed and coupled with a catalytic depolymerization process in an effort to selectively extract and deconstruct switchgrass lignin.

Materials and Methods

Ionic Liquids utilized in this study were synthesized in house to a purity of 90-95%. A series of glass upright jacketed extraction columns were heated to 50°C using a recirculating heater. These columns were then loaded with 5 g of milled switchgrass (30-60 mesh) prior to being rinsed with 250 mL of water for one hour. Once this step was complete, 250 g of the desired IL was prepared for each column by adding 0.5 mL of concentrated HCl to act as a catalyst during the extraction of lignin. Next, the IL solution was pumped vertically through the column for a period of 24 h. Dissolved cellulose and lignin were precipitated from the IL by the addition and evaporation of sequential antisolvents.

Subsequently, an array of oxidative depolymerization strategies was employed in order to depolymerize the extracted lignin. In a first step, the benzylic hydroxyl groups of the lignin polymer (200 mg) were oxidized under O₂ using a mixture of TEMPO (40.8 mg) in BMIM-Cl (1.2 g), 12 M HCl (137 µL), NaNO₂ (135.6 mg), and NaCl (77 mg). This reaction was followed by Baeyer-Villager oxidation of the formed ketone groups using 30% aqueous H₂O₂ (277 µL) and HCOOH (105 µL) as the oxidant, and 1,2-dichloroethane as the solvent. The reaction mixture was stirred at 50 °C for 24 h.

Results and Discussion

In all, five ionic liquids were tested, each IL being chosen so as to yield insights into the impact of the cation and anion on the effectiveness of the extraction. The ions chosen for this study included the cations 1-allyl-3-methyl imidazolium (AMIM), 1-butyl-3-methyl imidazolium (BMIM), and 1-decyl-3-methyl imidazolium (DMIM) in addition to the chloride (Cl), and xylene sulfonate (XS) anions. Formic acid (FA), a common lignin solvent, was used as a baseline for comparison.² Figure 1 presents a clear trend towards preferential lignin solubility as the chain length on the 1-position of the imidazole ion increases.

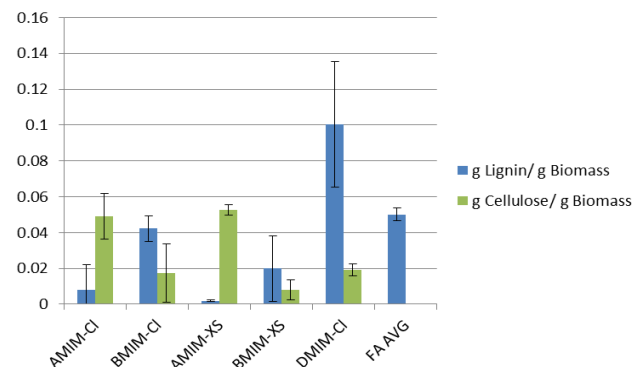


Figure 1. Yields of extracted material from switchgrass at 50 °C.

In order to depolymerize the extracted lignin, oxidative cleavage of the lignin β -O-4 linkages was targeted using BMIM-Cl as the reaction solvent and TEMPO as the oxidation catalyst, the latter being activated by nitrosyl chloride formed from the reaction of sodium nitrite and hydrochloric acid.³ Subsequent Baeyer-Villager oxidation of the formed ketone groups afforded a lignin product showing greatly increased solubility, while NMR analyses confirmed the formation of carboxylic acids, indicative of successful ester cleavage (and hence cleavage of the β -O-4 linkages). According to MALDI-MS data, depolymerization afforded mainly lower lignin oligomers, rather than monomeric aromatic compounds.

Significance

As fossil fuel supplies decrease, innovative approaches to the development of sustainable and renewable fuels and chemicals must be developed. This solvent extraction and lignin depolymerization system displays promise for biomass fractionation and processing.

References

1. Ritter, S. K. *Chemical & Engineering News* **2008**, 86, 10.
2. Dapia, S.; Santos, V.; Parajó, J. C. *Journal of wood chemistry and technology* **2000**, 20, 395.
3. Wang, X.; Liu, R.; Jin, Y.; Liang, X. *Chemistry-A European Journal* **2008**, 14, 2679.