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Addition of ammonia and/or oxygen to an ionic liquid for delignification of miscanthus

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ABSTRACT

Ammonia and/or oxygen were used to enhance the delignification of miscanthus dissolved in 1-ethyl -3-methylimidazolium acetate at 140 °C. After dissolution of the gas at 9 bar, water was added as antisolvent to regenerate the dissolved biomass. In a next step, an acetone/water mixture was used to remove carbohydrate-free lignin from the regenerated biomass. The lignin content in the final product was around 10%, much lower than the ca. 23% lignin content of the raw dry miscanthus. This lignin reduction is achieved without diminution of cellulose or of total carbohydrates recovered, relative to the recovery achieved with the ionic liquid pretreatment in contact with air or nitrogen.

1. Introduction

Depletion of fossil fuels and increasing energy demand have prompted a search for alternative and sustainable sources of energy, including transportation fuels (U.S. Energy Information Administration, 2010). A promising option is to replace fossil fuels with bioethanol, i.e., ethanol from biomass (Office of Policy Analysis and Office of Policy and International Affairs, U.S. Department of Energy, 2008). While food crops such as corn have been used to produce bioethanol, now there is a preference for non-edible raw materials. One suitable source is a wild grass, miscanthus (Sørensen et al., 2008).

For production of bioethanol, the biomass is first pretreated to make cellulose and hemicellulose more easily hydrolyzable, to yield glucose that is then fermented to alcohol. This pretreatment step is critical for a good yield of bioethanol (da Costa Sousa et al., 2009; Hendriks and Zeeman, 2009; Yang and Wyman, 2008). In recent years, ionic liquids have become popular for the pretreatment of biomass (Cetinkol et al., 2010; Fu et al., 2010; Li et al., 2010; Samayam and Schall, 2010; Simmons et al., 2010; Singh et al., 2009).

Ionic liquids are salts that melt below 100 °C. Ionic liquids provide useful physical properties, including negligible volatility, wide liquid range and relatively high thermal stability as well as ability to solubilize organic, inorganic, or polymeric substances (MacFarlane and Seddon, 2007; Seddon, 1997; Welton, 1999). Almost a decade ago, Rogers and co-workers reported that some ionic liquids can dissolve cellulose in a non-derivatizing manner (Swatloski et al., 2002). More recently, it was discovered that some ionic liquids can dissolve wood and other recalcitrant lignocellulosic biomass (Fort et al., 2007; Kilpeläinen et al., 2007; Zavrel et al., 2009). Therefore, it appears that dissolution in ionic liquids may be useful for pretreatment of biomass toward bioethanol.

It has been recently shown that pretreatment of miscanthus with 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]) leads to improvement in conversion of carbohydrates to sugars by enzymes (Shill et al., 2011). However, there is an accumulation of lignin in the recycle stream of ionic liquid. Toward reducing this accumulation, an enhanced pretreatment of biomass has been investigated, with [C_2mim][OAc] accompanied by ammonia and/or oxygen as delignifying agents.

Ammonia and oxygen are currently used in traditional delignification processes in the pulp and paper industry (Gullichsen and Fogelholm, 1999). Gaseous ammonia and oxygen are easily separated and recovered from liquid mixtures containing lignocellulose dissolved in an ionic liquid. Nguyen et al. (2010) recently reported that addition of ammonia enhances pretreatment of rice straw with an ionic liquid. While Nguyen et al. used an aqueous solution of ammonia, it is expected that gaseous ammonia may have advantages in an industrial process because gaseous ammonia and

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oxygen are easily recycled. Also, Stärk et al. (2010) have recently described oxidative depolymerization of lignin in ionic liquids. It is reported here the effect of (gaseous) ammonia and oxygen to delignify miscanthus dissolved in [C_2mim][OAc].

2. Methods

2.1. Materials

Miscanthus particles (80 μm) from the University of Illinois at Urbana-Champaign were dried in an oven at 105 °C, at atmospheric pressure. The final water content was 6.5 wt.%, measured by the Karl-Fischer titration method in an AquaStar C2000 titrator (EM Science).

[C_2mim][OAc] was purchased from Iolitec with a nominal purity of >95%, and used as received. Its water content was 0.5 wt.%.

Compressed air, anhydrous ammonia, and oxygen were supplied by Praxair, with a purity of 99.99%.

2.2. Process

Fig. 1 presents a flowchart of the proposed process. Miscanthus (ca. 0.3 g) and [C_2mim][OAc] (ca. 5.7 g) were placed inside each of several batch pressure reactors (Parr Instruments), each with a capacity of ca. 15 cm^3. The biomass concentration was approximately 5 wt.%. The mixtures were reacted at 9 bar absolute of air, or ammonia, or oxygen, or a combination of ammonia and oxygen, at 140 °C for 3 h. Because the high solubility of ammonia in [C_2mim][OAc] (Yokozeki and Shiflett, 2007) may diminish its ability effectively to dissolve biomass, independent experiments with ammonia were made in two steps: first, for 3 h at atmospheric pressure, and then for 3 h with ammonia at 9 bar.

Following dissolution, water was added (approximately 50–60 mL) as an antisolvent to precipitate the biomass while keeping the hydrophilic [C_2mim][OAc] in solution. Stepwise washings of the precipitated biomass (ca. 20 mL each time) with fresh water removed any residual ionic liquid. All filtrates were combined and analyzed as described in Section 2.3.3. After analysis, water was eliminated by evaporation at atmospheric pressure by heating to 80–100 °C. The remaining liquid was analyzed by ^{1}H NMR in a Bruker Avance AVQ-400 spectrometer, to confirm the preservation of the chemical identity of the ionic liquid.

The precipitated biomass was oven-dried at 105 °C for a minimum of 4 h to achieve constant weight. This biomass was then placed in ca. 20 mL of a 1:1 v/v mixture of water and acetone (Fisher Chemical, 99.7%), and vigorously stirred for a few hours to dissolve "carbohydrate-unbonded" lignin (Sun et al., 2009, 2011). The suspension was filtered under mild vacuum, and the solid residue was collected. This "carbohydrate-enriched" material was dried and weighed again, following the same protocol as above, and prior to analysis as described in Section 2.3.1. The filtrate was heated for evaporating acetone and water; a small residue was collected. The latter was also weighed, and characterized as described in Section 2.3.2.

All weighings used a Mettler Toledo MS204S balance precise to $\pm 1 \times 10^{-4}$ g.

2.3. Composition analyses

2.3.1. Analysis of the carbohydrate-enriched materials

Analysis of cellulose, hemicellulose and lignin in the pretreated biomass samples (*Analysis 1* in Fig. 1) followed a procedure based on the Laboratory Analytical Procedure developed and recently

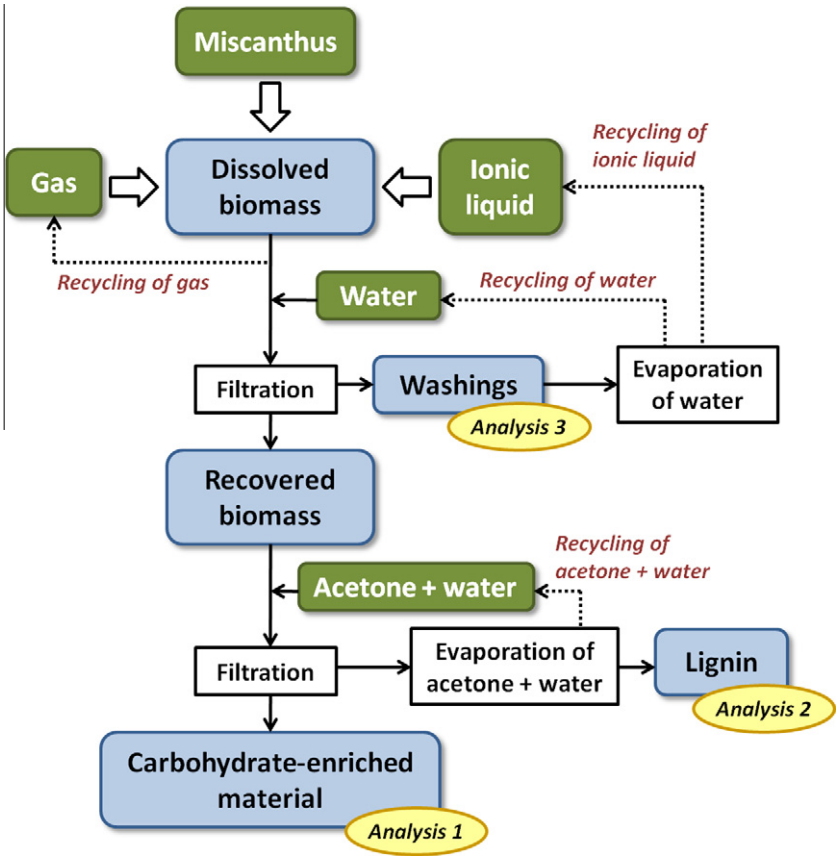

Fig. 1. Proposed process for delignifying miscanthus. The gas is either NH_3, or O_2, or a mixture of both. The ionic liquid is [C_2mim][OAc].