



Enhanced mass transfer upon switchable ionic liquid mediated wood fractionation



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ABSTRACT

The fractionation of lignocellulosic biomass to its major components is the primary step towards the conversion of biomass-based biopolymers to commodity chemicals in the integrated biorefinery process. Wood chips encased in a SpinChem[®] device and attached to the stirrer of a batch autoclave were used together with switchable ionic liquids (SILs) for the selective fractionation of hemicelluloses and lignin. Stirring of the wood chips in the SpinChem[®] device facilitated the diffusion of SIL into the chips through forced recirculation and at the same time avoiding mechanical fibrillation. The treatment of birch chips (*Betula pendula*) with SILs comprising 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU), monoethanolamine (MEA) and CO₂ at 120 °C in a SpinChem[®] device resulted in the fractionation of 82 wt.% hemicelluloses and 90 wt.% lignin, leaving the cellulose-rich non-dissolved material partially fibrillated and softened. The dissolved hemicelluloses and lignin were selectively precipitated using isopropanol and recovered from the spent SIL.

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1. Introduction

Biomass constitutes an abundant and widely available source for bio-energy supplying about 10% of the current global primary energy. Through thermochemical and biochemical technologies lignocellulosic biomass may be converted to energy (heat, fuels), energy carriers (charcoal, torrefied 'bio-coal', bio-oil) and platform chemicals (Binder and Raines, 2009; Shishir et al., 2011; Klass, 2004; Taarning et al., 2011), allowing for the displacement and/or replacement of diminishing fossil fuels with carbon neutral resources. The composite micro-structure of lignocellulosic biomass consists mainly of cellulose, hemicellulose and lignin, with minor quantities of extractives and inorganic matter. The irregular and highly condensed cross-linked network of lignin cements hemicelluloses and cellulose together and also forms lignin-carbohydrate complexes in plant cell walls, thus, providing the lignocellulosic material with structural rigidity to resist external stress (Jing-Ke Weng and Clint Chapple, 2010). These complex chemical and structural mechanisms contribute to the superb resistance of the plant tissue against invasion of the living cells by fungi and other microorganisms in the living plant but also constitute the structural recalcitrance of biomass towards fractionation (Himmel et al., 2007).

Pretreatment of lignocellulosic biomass disrupts the complex polymer matrix of lignocellulosic materials via the cleavage of hydrogen, ether, ester and carbon-oxygen bonds thereby improving accessibility of enzymes or chemicals during processing. Steam explosion, carbon dioxide explosion, hot water treatment, dilute acid treatment, alkali treatment organosolv processes, ammonia treatment and ozonolysis have been proposed as pretreatment methods for lignocellulosic biomass through the breakdown of intra- and intermolecular hydrogen bonds and disassembling the crystalline lattice of cellulose (Kumar et al., 2009). However, extreme conditions such as, high temperature and pressure, use of acids or bases may result in sugar degradation, enzyme-inhibition products or necessitate special equipment. The release of pollutants, salts from acid/base neutralization and solvent consumption have prompted the search for efficient, recyclable pretreatment alternatives such as, ionic liquids.

Ionic liquids have recently attracted attention for the dissolution of cellulose, lignin and other non-wood products by facilitating partial or complete disassembly of the crystalline lattice of native cellulose and the deconstruction of the polymer network of lignin (Swatloski et al., 2002; Zhao et al., 2009; Li et al., 2010). Cellulose dissolution has been achieved using ionic liquids based on a multitude of designs though the use of acetate or phosphate anions is favoured due to their contribution to low viscosity, hydrogen bond interaction and their interaction with cations (Liu et al., 2010). The extraction of lignin has also been demonstrated using 1-ethyl-3-methyl imidazolium xylene sulfonate at 170–190 °C while

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1-ethyl-3-methyl imidazolium acetate has shown good performance as a solvent for wood dissolution (Tan et al., 2009; Zavrle et al., 2009). The selective cleavage of bonds in the complex polymer matrix is influenced by the composition of ionic liquid, operating conditions, chip size and wood composition (Fort et al., 2007). In addition, various wood species and different wood components were found to be completely or partially soluble in ionic liquids at mild operating conditions, with hardwoods apparently dissolving faster than softwoods (Arora et al., 2010; Swatloski et al., 2002; Sun et al., 2009; Viell and Marquardt, 2011; Kilpeläinen et al., 2007; Mäki-Arvela et al., 2010). In spite the apparent deconstruction of woody biomass, the water intolerance of some ionic liquids, high operating temperatures and the protonation of the acetate anion to yield acetic acid during wood treatment presents stability and recyclability problems justifying the search for alternative, recyclable and efficient ionic liquid systems for wood fractionation.

Thermally stable and water tolerating switchable ionic liquids (SILs) have recently demonstrated strong potential for the selective dissolution of hemicelluloses and lignin, resulting in enriched cellulose matrices (Anugwom et al., 2011a,b, 2012; Mikkola et al., 2010). SILs are ionic salts composed of a mixture of an organic superbase such as an amidine (e.g. 1,8-diazabicyclo-[5.4.0]-undec-7-ene, DBU), hydroxyl-containing compound and an acid gas (e.g. CO₂, SO₂) (Jessop et al., 2005). The carbonate ionic salts are capable of reversible compositional change (polarity switch) upon the release of the acid gas facilitated by heating, and/or bubbling an inert gas through the viscous ionic salt. The properties of SILs significantly affect the chemical processes involved during the deconstruction of hydrogen, esters, carbon and ether bonds in the hemicelluloses and lignin matrices.

Although progress in wood dissolution has been made by tuning the composition of ionic salts leading to enhanced yields of the fractionated wood components, significant improvements in activity can be obtained at mild reaction conditions in a properly designed reactor setup. The batch-wise operations often carried out during pretreatment, usually in the absence of mechanical agitation, results in hotspots and limitations due to diffusion of the fractionated components. Recently, we found that the flow of ionic liquid through the loop reactor created turbulence in the reactor, decreasing the liquid film thickness around the chips and improving the dissolution of hemicelluloses and lignin (Eta et al., 2014). It was observed that the reactor type and the mode of operation influenced the transport properties of the fractionated materials resulting in enhanced yields. However, the implementation of liquid recirculation necessitates understanding of the energy requirements as well as wood and solvent parameters vital for efficient fractionation. The current research is therefore devoted to the description and evaluation of the fractionation and dissolution of wood chips using switchable ionic liquids and a SpinChem® device to study the combined effects of agitation, chip size and loading on wood dissolution. Wood fractionation using SIL and the novel SpinChem® device as impeller provides the unique opportunity to investigate the dissolution efficiency in the absence of external mass and heat transfer limitations without mechanical fibrillation during treatment. The study is relevant in the biorefinery research as the manufacturing of materials and commodity chemicals may be added to the existing production of fuels and chemicals, and demonstrates the practical applicability, intensification aspects and evaluation of dissolution efficiency. The study will lead to improved understanding of the fractionation and dissolution of wood chips and other biomass in a reactor equipped with mechanical stirring over non-stirred reactors. The fractionation of wood to its major components will result in the creation of novel business ideas with envisaged products such as, regenerated fibres and chemicals, structural composites, novel packaging

and filtration materials, health-promoting products, wood preservatives, glues, polymers, resins and commodity chemicals.

2. Methods

2.1. Materials

A batch autoclave (Parr) equipped with an electric heater, an internal thermocouple and a mechanical stirrer affixed to a SpinChem® device (Nordic ChemQuest AB, Sweden) was used in this study. Birch (*Betula pendula*) chips were provided by the Finnish Forest Research Institute, Metla, and contained ca 10–15 wt.% water. 1,8-Diazabicyclo-[5.4.0]-undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), monoethanolamine (MEA), diethanolamine (DEA), glycerol, isopropanol and ethanol were purchased from Sigma Aldrich. CO₂ (99.999) was purchased from AGA. The chemicals were used as received.

2.2. Preparation and characterization of SILs

The carbonate ionic salts were prepared by bubbling CO₂ at atmospheric pressure in a solution containing appropriate amounts of amidine and hydroxyl-containing compound in a sealed reactor. The molar amount of amidine to the hydroxyl-compound in the mixture was calculated as a function of the number of OH-groups in the alcohol used. Prior to CO₂ treatment, trapped air was displaced from the solution by flushing with a stream of argon. The reactor was immersed in an ice bath and CO₂ was bubbled through the solution under vigorous agitation until the amount of CO₂ (determined gravimetrically) in the solution was equal to the molar amount of amidine in the solution. Three SILs, DBU/GLY/CO₂, DBU/MEA/CO₂ and DBN/GLY/CO₂, were synthesized and used in this study. The chemical and structural composition, viscosity and thermal decomposition of the salts were determined and details of the SIL characterization are reported elsewhere (Anugwom et al., 2011a, 2012; Mikkola et al., 2010).

2.3. Reactor setup and operation

The experiments were carried out in a stirred tank reactor (Parr) of 300 mL nominal volume equipped with electric heater and an internal thermocouple. Mixing and flow of SIL was achieved using a custom made impeller (SpinChem® device) driven by a variable speed motor (Parr 4843). The SpinChem® device consists of a hollow cylinder measuring 3.2 cm diameter and 2.9 cm long equipped with rounded orifices at the sides (Fig. 1) to permit SIL flux into and out of the embedded wood chips. Birch chips (2.3 cm long, 0.8 cm wide and 0.5 cm thick) were loaded into the SpinChem device, and the autoclave was filled with the appropriate quantity of switchable ionic liquid. Typically, 8 g of chips and 80, 120 or 160 g SIL was used giving the wood-to-SIL ratio of 10, 15 or 20 wt/wt, respectively. The setup was assembled, heated to 120 °C and stirred over a period of 4–30 h. After treatment, the reactor was cooled and the dissolved and non-dissolved materials recovered, washed and analyzed.

2.4. Analysis of hemicelluloses and lignin

The non-dissolved fraction was thoroughly washed and the content of hemicelluloses determined by acid methanolysis, while the acid insoluble material was determined as lignin. Samples of the non-dissolved wood materials were subjected to a mild acid treatment (HCl/methanol) for 3 h at 100 °C prior to derivatization by silylation. The derivatized samples were analyzed by gas chromatography equipped with a flame ionization detector. Klason lignin was determined as an ash-free residue of a two stage H₂SO₄ hydrolysis (Hatfield et al., 1994). The spent SIL separated from the

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