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Deconstruction of Nordic hardwood in switchable ionic liquids and acylation of the dissolved cellulose

Valerie Eta[a,b,*], Jyri-Pekka Mikkola[a,b]

[a] Technical Chemistry, Department of Chemistry, Chemical-Biological Centre, Umeå University, SE-901 87 Umeå, Sweden
[b] Laboratory of Industrial Chemistry and Reaction Engineering, Johan Gadolin Process Chemistry Centre, Åbo Akademi University, Åbo-Turku FI-20500, Finland

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ABSTRACT

Nordic hardwood (*Betula pendula*) was fractionated in a batch autoclave equipped with a custom-made SpinChem® rotating bed reactor, at 120 °C using CO_2 and CS_2-based switchable ionic liquids systems. Analyses of the non-dissolved wood after treatment showed that 64 wt% of hemicelluloses and 70 wt% of lignin were removed from the native wood. Long processing periods or successive short-time treatments using fresh SILs further decreased the amount of hemicelluloses and lignin in the non-dissolved fraction to 12 and 15 wt%, respectively. The cellulose-rich fraction was partially dissolved in an organic superbase and an ionic liquid system for further derivatization. Homogeneous acylation of the dissolved cellulose in the presence or absence of catalyst resulted in cellulose acetates with variable degree of substitution (DS), depending on the treatment conditions. By varying the reaction conditions, the cellulose acetate with the desired DS could be obtained under mild conditions.

1. Introduction

Selective extraction and processing of the main wood components is an important area in bio-refinery research aiming for optimised utilisation of forest resources. The development of alternative and economically-viable fuels, materials and energy from sustainable, carbon-neutral energy sources is indispensable for the substitution of fossil-based products. Lignocellulosic biomass, consisting of cellulose, hemicellulose and lignin as major components have been recognised as potential feedstocks for the production of renewable fuels, materials and chemicals. Cellulose is the main constituent of the fibre wall of lignocellulosic biomass accounting for about 40–50 wt% of wood derived from linear chains of D-anhydroglucopyranose units which condense through β-(1–4)-glycosidic bonds. About 20–40% of the dry weight of Nordic wood is composed of heterogeneous group of polysaccharides. These hemicelluloses are principally present as glucomannans and galactoglucomannans in softwoods, and xylans in hardwood. Another major wood component is lignin, constituting between 20 and 35 wt% of wood depending on species. Lignin consists of polymers of phenylpropane units (coniferyl, sinapyl or *p*-coumaryl alcohols) linked via ester, ethers or carbon–carbon bonding during biosynthesis (Sjöström, 1989). Lignin has an irregular structure and is cross-linked to different polysaccharides in the cell wall such as lignin–carbohydrate network, resulting in a stiff and fluid impermeable wood matrix (Yuan, Sun, Xu, & Sun, 2011). Several pre-treatments methods aimed at limiting biomass recalcitrance have been proposed e.g. the removal of lignin and/or hemicelluloses, reduction of the crystallinity of cellulose, and increase in the porosity of the lignocellulosic materials prior to processing (Kumar, Barrett, Delwiche, & Stroeve, 2009; Soudham, Brandberg, Mikkola, & Larsson, 2014; Soudham et al., 2015). These pre-treatment strategies may be achieved via cleavage of ester groups, hydrogen bonds and lignin–carbohydrate interactions, or wood liquefaction, thus, releasing lignin, hemicelluloses and degraded cellulose into the solvents used (Lu et al., 2015; Wang, Yang, Guo, Yao, & Sun, 2014). Completely or partially solubility of wood has been achieved with ionic liquids at mild conditions, and the dissolution kinetics is dependent on the particles size, type of wood and the type of ionic liquid used (Fort et al., 2007; Kilpeläinen et al., 2007; Liu, Sale, Holmes, Simmons, & Singh, 2010; Mäki-Arvela, Anugwom, Virtanen, Sjöholm, & Mikkola, 2010). Although conventional ionic liquids based on acetate or phosphonate anions have demonstrated cellulose dissolution capabilities, these solvents suffer from major setbacks such as high viscosity, low water tolerance and existence of hydrogen bond interactions between

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[*] Corresponding author.
E-mail address: valerie.eta@abo.fi (V. Eta).

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ionic liquid ions and wood components, thus, rendering industrial implementation of these systems challenging. Recently, switchable ionic liquids (SILs) possessing high thermal stability formed from mixtures of an organic superbase such as an amidine (e.g. 1,8-diazabicyclo-[5.4.0]-undec-7-ene, DBU), a hydroxyl functionalised compound and an acid gas (e.g. CO_2), have demonstrated strong potentials for the selective extraction of hemicelluloses and lignin from wood, resulting in enriched cellulose matrices (Anugwom et al., 2011, Anugwom, Mäki-Arvela, Virtanen, Willför, Damlin, et al., 2012). The reactor design and agitation of the wood chips during treatment using a SpinChem® rotating bed reactor facilitated the diffusion of SIL into the chips through forced recirculation resulting in cellulose with low amounts of hemicellulose and lignin (Eta, Anugwom, Virtanen, Eränenm, et al., 2014). This cellulose-rich fraction may be dissolved in suitable solvent and further functionalised to commercially important cellulose derivatives like cellulose esters, widely used in applications such as films, textiles, coatings, membranes, composites, laminates, etc. Although commercial production is dominated by heterogeneous processes, homogeneous derivatization of cellulose has been the focus of cellulose research for the processing of partially substituted cellulose esters without using corrosive reagents and catalysts. Herein, we report the fractionation of Nordic birch using switchable ionic liquids based on CO_2 and CS_2 and the acylation of the cellulose-rich fraction to cellulose acetate in an organic base and ionic liquid systems. The extent of fractionation was dependent on the composition of SILs and treatment conditions employed. After separating the cellulose-rich fraction and motivated by our recent contribution on the dissolution of cellulose in ionic liquid (Jogunola et al., 2016), we focused on the dissolution of the extracted cellulose-rich fraction in 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 1,5-diazabicyclo[4.3.0]non-5-ene acetate ([DBNH][OAc]) in DMSO where 3 wt% cellulose solubility was obtained. The subsequent homogeneous reaction of the dissolved cellulose with acetic anhydride at 80 °C resulted in cellulose acetate with a wide range of DS depending on the reaction conditions. We believe that the partitioning and functionalisation of cellulose from wood would be of great relevance in the bio-refinery research for the manufacture of biomaterials and chemicals. The reported cellulose acylation may also be applied to other cellulose esters as well as cellulose etherification, alkylation, grafting, etc. in ionic liquids.

2. Materials and methods

Birch (*Betula pendula*) chips provided by the Finnish forest research institute were harvested from different areas in Finland and stored in a refrigerator. Prior to use, the moisture content of the wood chips was approximately 6–8 wt%. 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) glycerol, acetic acid, acetic anhydride, monoethanolamine (MEA), and carbon disulphide were purchased from Sigma–Aldrich with purities greater than 99.5%. CO_2 (99.999) was purchased from AGA Ab. The chemicals were used as received.

2.1. Preparation of SILs

Switchable ionic liquids were prepared from equimolar mixtures of DBU, MEA or glycerol, and CO_2 or CS_2. The switching reaction was achieved by bubbling CO_2 through a mixture of DBU/MEA or DBU/glycerol at atmospheric pressure until a highly viscous fluid was obtained. In the case of CS_2, the appropriate amounts of liquid CS_2 at −10 °C were added to the mixture of DBU/MEA or DBU/glycerol drop-wise under vigorous mixing for about 1 h. In the case of CO_2, the amount of CO_2 reacted was determined gravimetrically. The molar amount of amidine to alcohol or CS_2 in the mixture was calculated as a function of the number of hydroxyl groups in the alcohol. The exothermic reaction was controlled by intermittently adding CO_2 or CS_2 and by immersing the reactor in an ice bath for guaranteed cooling until the reaction was complete. The carbonate or sulphite salts formed were sealed and stored at 5 °C. The structure of CS_2 based SILs has been conformed as analogous to CO_2-based SILs. In our earlier paper, the carbonate ionic liquids were characterised (Anugwom, Mäki-Arvela, Virtanen, Willför, Sjöholm, et al., 2012) prior to testing for their efficiency in wood fractionation. [DBNH][OAc] was formed by equal molar amounts of DBN and acetic acid by dropwise controlled addition of acetic acid under stirring and cooling. The ionic liquid was used after preparation.

2.2. Reactor setup and operation

The experiments were carried out in a stirred tank reactor (Parr) of 300 mL nominal volume equipped with electric heater, stirrer and an internal thermocouple. Mixing was achieved using a custom-made impeller consisting of rotating basket specific for wood chips (SpinChem® rotating bed reactor) driven by a variable speed motor (Parr 4843). The moisture-free content of the wood was determined by drying reference samples at 105 °C overnight. Prior to SIL treatment, the wood chips were extracted with 1:1 v/v toluene–ethanol at 100 °C for 1 h to recover wood extractives.

25 g of birch chips of approximately 2.3 cm × 8 cm and 0.5 mm thick were carefully packed in the spinning reactor and assembled in the reactor. The autoclave was heated to 120 °C while stirring at 800 rpm for the desired duration. After treatment, fractionation was stopped by quenching the reactor followed by recovery of the spent SILs and non-dissolved fraction. The non-dissolved materials were recovered by washing the spent SIL from the treated material several times with 2-propanol. The cellulose-enriched fraction was also washed with ethanol and water to completely remove the SIL from the fractionated chips. When desired, the fractionated wood was treated with fresh SIL until the desired purity was obtained. The repeated sequential precipitation of the dissolved material in the spent SIL using 2-propanol resulted in a hemicellulose-rich fraction. Recovery of lignin was accomplished by addition of water and boiling the solution at 80 °C. The lignin fraction was recovered from the spent SIL by boiling the hemicellulose-free solution to induce lignin agglomeration, followed by protonation of phenolic hydroxyl groups via mineral acid treatment to decrease the pH (Helander et al., 2013). The amount of hemicelluloses in the non-dissolved and recovered materials was determined via acid methanolysis followed by gas chromatographic analysis (Sundberg, Sundberg, Lillandt, & Holmhom, 1996). The lignin-rich material was filtered from the SIL-water mixture. The molecular liquids constituting the SIL were recovered via evaporation of the solvents used. Reaction of the recovered molecular liquids with CO_2 or CS_2 resulted in SILs for reused.

2.3. Dissolution and acylation of non-dissolved cellulose fraction

After thorough washing and drying of the extracted non-dissolved cellulose fraction, the cellulose was crushed into a fine powder. About 2 g of cellulose powder was dispersed in 20 g DBN or DMSO (and mixed with [DBNH][OAc]) before heated to 60–70 °C for 3 h. After standing for ca. 10 min, sediments of non-dissolved cellulose were separated from the solution by decantation. The transparent solution containing about 3% (w/w) cellulose was transferred to a 250 ml glass reactor and 2 drops of pyridine were added where necessary. Appropriate amounts of acetic anhydride were added drop-wise to the cellulose solution and heated to 80 °C for 0.5–1 h under stirring at 250 rpm. After this treatment, the product was isolated by precipitated with excess isopropanol.