



Cellulose fractionation with IONCELL-P



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ABSTRACT

IONCELL-P is a solvent fractionation process, which can separate pulps almost quantitatively into pure cellulose and hemicellulose fractions using IL-water mixtures. In this work the role of the molecular weight of cellulose on its solubility in ionic liquid-water mixtures is studied. The aim of this study was to understand and identify the determining factors of this IONCELL-P fractionation. Cotton linters (CL) served as model cellulose substrate and was degraded by ozone treatment to adjust the molecular weight to that of hemicelluloses and low molar mass cellulose in commercial pulps. The ozone treated CLs were subjected to the IONCELL-P process using 1-ethyl-3-methylimidazolium acetate ([emim][OAc]) and water mixtures with a water content between 13.5 and 19 wt%. Based on the molar mass distributions of dissolved and undissolved cellulose the effect of the molecular weight of cellulose in IL-water mixture appears to be a key factor in the fractionation process.

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1. Introduction

Cellulose is a versatile molecule which bears potential for many applications in native or modified forms. Cotton has an undoubtable relevance in textile industry. However, cotton production of the world is predicted to fail to meet the natural-fiber based textile demands of the growing world population (Haemmerle, 2011). Not only is there a need to fill this appearing so called cellulose-gap, but in the mindset of environmentally sustainable agriculture, the high land, irrigation and pesticide requirements of cotton production also urges to find alternative cellulose sources for textile applications. This resulted in a number of new dissolving pulp mills to produce high purity cellulose from wood (TheFiberYear, 2015). The dominant industrialized processes to produce dissolving pulps, prehydrolysis kraft and acid sulfite pulping, have drawbacks such as severe cellulose losses and limited efficiency in hemicellulose removal (Sixta et al., 2013). Subsequent hemicellulose removal via cold caustic extraction, complex solvents or enzymatic treatments typically do not allow for the uncompromised isolation of hemicelluloses and cause changes in the residual cellulose.

The increasing environmental consciousness triggered a significant amount of research on novel, environmentally benign and economically feasible processes and solvents to replace the existing ones. Ionic liquids (ILs) are considered as a new generation of “green” solvents due to their tunable physicochemical properties, low flammability, low vapor pressure and reasonably high chemical and thermal stability and several of them have been shown to be desirable solvents for polysaccharides including cellulose (Gericke, Fardim, & Heinze, 2012; Gericke, Liebert, Seoud, & Heinze, 2011; Heinze, Schwikal, & Barthel, 2005; Karatzos, Edye, & Wellard, 2012; Peng, Ren, & Sun, 2010; Peng, Ren, Zhong, & Sun, 2011; Pinkert, Marsh, Pang, & Staiger, 2009; Welton, 1999). Thus, ILs quickly gained popularity in the past decade in cellulose modification and processing (Abbott, Bell, Handa, & Stoddart, 2005; Barthel & Heinze, 2006; Castro, Rodriguez, Arce, & Soto, 2014; Gericke et al., 2012; Gericke, Liebert, & Heinze, 2009; Gericke et al., 2011; Heinze et al., 2005; Karatzos et al., 2012; Kosan, Dorn, Meister, & Heinze, 2010; Liu, Zhang, Li, Yue, & Sun, 2009; Pinkert et al., 2009; Welton, 1999). Several ionic liquids can also dissolve other lignocellulosic components and even wood itself (King et al., 2009; Sun et al., 2009). Different ionic liquid based fractionation schemes were suggested in literature to separate the constituents of lignocellulosic biomass (Brandt, Graesvik, Hallett, & Welton, 2013; Sun et al., 2009). Dissolution of cellulose in IL-water or solvent-antisolvent mixtures also gained more attention recently (Hauru, Hummel, King, Kilpeläinen, & Sixta, 2012; Kuzmina, Sashina, Troshenkowa, & Wawro, 2010). However, the detailed mechanism of the dissolution and fractionation phenomena is not yet fully understood.

Abbreviations: BH, sodium borohydride; COS, cello-oligosaccharides; CED, cupriethylenediamine; CL, cotton linters; DMAc, *N,N*-dimethylacetamide; [emim][OAc], 1-ethyl-3-methylimidazolium acetate; DP, degree of polymerization; GPC, gel permeation chromatography; IL, ionic liquid; MMD, molar mass distribution; Mw, weight average molecular weight; PDI, polydispersity index; WAXS, wide angle X-ray scattering.

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Numerous studies have reported the negative effects of water on the cellulose dissolution capacity of ILs (Hauru et al., 2012; Mazza, Catana, Vaca-Garcia, & Cecutti, 2009; Pinkert et al., 2009; Zakrzewska, Bogel-Lukasik, & Bogel-Lukasik, 2010). However, by choosing the right cosolvents/antisolvents mixture the selective dissolution of different wood components has been demonstrated allowing for the fractionation of lignocellulosics and paper pulp (Froschauer et al., 2013; Hauru et al., 2013; Roselli, Asikainen et al., 2014; Roselli, Hummel, Monshizadeh, Maloney, & Sixta, 2014). Froschauer et al. presented a new methodology for the quantitative separation of bleached paper-grade pulps into high purity cellulose and hemicellulose fractions, without significant yield losses (Froschauer et al., 2013; Roselli, Hummel et al., 2014; Sixta et al., 2013). There, the [emim][OAc]-water fractionation solvent system did not facilitate cellulose solubility, while the hemicelluloses were still soluble in the mixture. The extraction efficiency and selectivity was highly influenced by the water content and the temperature of the system. Later Roselli et al. investigated the effect of different pulp sources and different IL-water mixtures on the fractionation efficiency (Roselli, Asikainen et al., 2014; Roselli, Hummel et al., 2014). [Emim][OAc] is one of the most studied and best understood cellulose dissolving ILs with also industrial scale availability (Gericke et al., 2012). Thus, [emim][OAc]-water was chosen as solvent system in this work to elucidate the mechanism of the IONCELL-P fractionation. The key importance of this process lies in the production of structurally unchanged cellulose and delivery of polymeric hemicelluloses, which could be a potential new raw material for industry.

This process also allows for the production of narrowly distributed high molecular weight cellulose which is very attractive for material applications and derivatizations, especially if the native cellulose I crystal structure is preserved. Low molar mass celluloses and cello-oligosaccharides (COS) also have several potential applications such as prebiotics in food products (Mussatto & Mancilha, 2007; Roberfroid, 2007; Tolonen et al., 2015). The low availability of COS is one of the reasons for the lack of extensive knowledge on them. Up to today there are only a few ways of preparing lower molecular weight cellulose. COS production requires strong acid treatment at low temperatures, while cellulose with a DP lower than the level off DP can be produced by medium acid treatment at elevated temperature or supercritical water treatment (Tolonen et al., 2015), which are both accompanied by severe losses. With enzymatic degradations of cellulose it is also possible to produce low molecular weight cellulose. However, below a certain DP around 100 yield losses also become more prevalent (Zhang & Lynd, 2005).

Cellodextrins also have been found to have health benefits such as lowering cholesterol levels and in preventing diabetes when consumed in certain daily doses (Cummings & Macfarlane, 1997; Wakabayashi, Kishimoto, & Matsuoka, 1995). Miller et al. has published numerous work on cellodextrins and their preparation already half a century ago, which still give the basis of today's processes (Miller, Dean, & Blum, 1960; Miller, 1963). The most common ways of preparing cellodextrins are HCl fuming of cellulose microcrystals combined with various methods to recover and purify the cellodextrins. Mixed acid treatments are also commonly used (Zhang & Lynd, 2003). By fractionating pure cellulose a new set of properties can see daylight simply by having cellulose available in low molecular weight cellulose II with a narrow distribution (Meiland, Liebert, & Heinze, 2011).

Understanding of the principle behavior of cellulose in ionic liquid solutions is essential to improve and to commercialize the IONCELL-P process in the near future. However, hitherto the effects of chemical and physical properties of biopolymers on the fractionation efficiency in IL-water solutions have not been evaluated. This work has several similarities to the study done by Meiland et al. and

Eckelt et al. on cellulose fractionation where different molecular weight celluloses were fractionated by changing solvent properties, though their work did not address a deeper understanding of the polysaccharide fractionation as a process (Eckelt, Stryuk, & Wolf, 2003; Meiland et al., 2011).

The aim of this work is to understand and establish the relationship between the polysaccharides' molecule size and the dissolution properties in [emim][OAc]-water system with different water contents. To exclude any effects of chemical variability of the fractionated molecules and, thus, study the purely physical factors governing the fractionation mechanism, pure cotton linters were used as model cellulose substrate and its molecular weight range was adjusted to mimic the size of hemicelluloses and low molecular weight celluloses. To understand the dominant mechanism behind the IONCELL-P fractionation, the newly obtained results are then reflected on the results reported earlier by Froschauer et al. about fractionated birch pulp containing both cellulose and hemicelluloses, meaning biopolymers of different chemical structures. The results of this study contribute to the understanding of the cellulose dissolution in ILs in general and will help to improve the IONCELL-P fractionation process.

2. Materials

The cotton linter was purchased from Milouban, Israel, with cellulose purity higher than 99.5%. The cotton linter had a weight average molecular weight (Mw) of 253.77 kg/mol (with a polydispersity index (PDI) of 2.2) which corresponds to a degree of polymerization of 1430. The intrinsic viscosity of the sample was 570 ml/g.

1-Ethyl-3-methylimidazolium acetate [emim][OAc] was purchased from BASF, Germany, and used as received. Deionized water was used to prepare the IL water mixtures. Ozone was produced by a Wedeco GSO30 device using oxygen as feed gas. The other chemicals used in this work were: KI from VWR, Finland, (26846.268), Na₂S₂O₃ from Merck, Germany, (1.06516.0500), cupriethylenediamine (CED) from VWR (5761.5000), HCl from VWR (20252.335), DMAc from Sigma-Aldrich, Finland, (270555), LiCl from Sigma (62476), acetone from VWR (20066.330), NaOH from VWR (28244.295) and NaBH₄ from Sigma (45,289-0) from which adequate solutions were prepared at Aalto University. A syringe filter from Sigma-Aldrich (Supelco-57183, polyethylene frit, with a porosity of 20 μm) was used for filtration of smaller batches and a metal mesh filter in a nitrogen pressurized steel filtration unit with a metal mesh with a cutoff size of 5–6 μm was used for the filtrations of bigger batches.

3. Methods

3.1. Molecular weight adjustment of cellulose by ozone treatment

The ozonization was performed in a rotary reactor where the ozone was fed through a tube directly in the mixing pulp (Table 1).

The cotton linter's initial pH level was adjusted to 5 ± 0.5 to prevent the formation of undesired byproducts and reduce the yield losses. The pH was adjusted by controlled addition of sulfuric acid at 3 wt% consistency. After the pH adjustment the excess water was removed from the sample by centrifugation to reach a consistency close to 55–60 wt%. The ozone flowrate was measured 3–4 times and after defining the average of generated ozone rate, the pH adjusted cotton linters is placed in the round bottom flask and the ozone is injected to the sample through a tube while the bottle is rotated. 50 g of cotton linter was ozone treated at ambient temperature and high cellulose consistency of 55–60 wt%. The obtained

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