



The integration of different pretreatments and ionic liquid processing of eucalyptus: Hemicellulosic products and regenerated cellulose fibers



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ABSTRACT

The integrated biorefinery of woody biomass for the synthesis of cellulose materials and hemicellulosic products is nowadays considered attractive towards a sustainable standpoint. The effects of alkaline, hydrothermal and acidic pretreatments on the preparation of regenerated cellulose fibers from eucalyptus via ionic liquid wet-spinning, and the isolation and conversion of hemicelluloses using different pretreatments were explored. The structure of alkali-soluble hemicelluloses via 5% sodium hydroxide extraction was deduced to be D-Glcp-4-O-methyl-D-glucurono-D-xylan. The xylooligosaccharides (XOS, DP 2–6) yields by hydrothermal (180 °C, 30 min) and 0.25 mol/L dilute sulphuric acid (90 °C, 1 h) pretreatments were 37.30 and 52.12 mg/g respectively, and the main XOS productions were xylobiose (11.19–15.68 mg/g) and xylotriose (10.03–11.63 mg/g). The isolated cellulose could be completely dissolved in 1-butyl-3-methylimidazolium acetate ([bmim]OAc) and the chemical conformation of the regenerated fibers was similar to cellulose II. The viscosity of the spinning dopes, the morphology, molecular weights and mechanical strength of the fibers were highly dependent on the type of pretreatments. The multifilament fibers exhibited a smooth morphology and good mechanical property (1.55–2.01 cN/dtex) being close to commercial viscose rayon. The conversion of hemicelluloses to value-added products was achieved via different pretreatments in conjugation with cellulose spinning process.

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1. Introduction

Functional materials manufactured from renewable resources through environmentally friendly processes have attracted a great deal of attention recently due to their specific characteristics, such as low cost, biocompatibility, and biodegradability (Klemm et al., 2005). As one of the most important skeletal components in lignocellulosic biomass, cellulose is an almost inexhaustible resource with fascinating structure and properties for the preparation of ecofriendly materials (Huber et al., 2012). Cellulose is a high molecular weight linear polymer composed of D-anhydroglucopyranose units linked by β -(1-4)-glycosidic bonds (Loerbroks et al., 2013). The ordered cellulose chains form tightly packed crystalline regions of cellulose microfibrils, which are embedded within a matrix of hemicelluloses and lignin (Brandt et al., 2013). In addition,

the molecular chains of cellulose are held together by the inter- and intra-molecular hydrogen bonds, which make it insoluble in common solvents and further impede its potential applications (Chundawat et al., 2011). This triggers the development of novel solvents for cellulose to destroy the inter- and intra-molecular hydrogen bonds between cellulose chains and rearrange for the formation of multifilament fiber (Chen et al., 2016), membrane (Chen et al., 2015b), hydrogel (Setoyama et al., 2014), aerogel (Oshima et al., 2014), and other materials (Gelesky et al., 2009).

New developments for processing cellulose into fibers have widely expanded its potential for use in textile and materials science (Arola et al., 2012). A conventional method, termed viscose process, is still the predominate pathway to prepare cellulose fibers nowadays. In this process, cellulose need to be reacted with carbon disulphide (CS₂) and sodium hydroxide to form cellulose xanthate and then converted back to pure cellulose in sulfuric acid coagulation bath (Tian et al., 2014). However, substantial volumes of acids and alkalis are required while only a portion of the highly volatile and toxic CS₂ could be recovered during the viscose process, bringing about the serious consequences of water and atmospheric pollution. As a new class of environmental friendly solvents for

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cellulose, ionic liquids (ILs) have attracted considerable interest due to the wide range of melting temperature (−40 to 400 °C), high thermal stability (up to 400 °C), excellent conductivity, negligible vapor pressure, low flammability and weakly coordinating properties (Freudenmann et al., 2011). Their physical and chemical properties can be tuned by the permutation of cations and anions, which is barely possible in conventional solvents. Therefore, ILs have been considered as a distinguished candidate to replace traditional volatile solvents and hence classified as “green” solvents for a broad spectrum of potential applications in cellulose processing (Gupta and Jiang, 2015).

Hemicelluloses, the second most abundant carbohydrate of lignocellulosic biomass next to cellulose, are consisted of various sugar units in different proportions and with different substituents which have the potential to be integrated in a wide variety of applications, such as emulsifiers, stabilizers, and xylooligosaccharides (XOS) in the cosmetic, biomedical, and food industries (Xu et al., 2014a). Traditional pretreatment processes for filament fibers, paper making and other related industries have been widely dedicated to fractionate natural cellulose from biomass. These techniques are primarily focused on maximizing the cellulose yield, while most of the hemicelluloses are wasted (Sun et al., 2010). In fact, the utilization of hemicelluloses has been the linchpin in the development of economic cellulose-based technologies. The pretreatment of lignocelluloses with simultaneous recovery and conversion of hemicelluloses could offer a variety of new possibilities for converting biomass to valuable biofuels, chemicals, and biomaterials (Kilpeläinen et al., 2007). Among thermochemical pretreatments, hemicelluloses removal or alternation can be implemented using dilute acids, hot water, or base with reasonable costs (Mosier et al., 2005). A large portion of hemicelluloses could be effectively converted to its sugar derivatives during dilute acid and hydrothermal pretreatments, however, the hemicellulosic polymers could be isolated via the alkaline pretreatment of lignocelluloses at moderate temperature (Mosier et al., 2005). Moreover, physicochemical changes of biomass resulting from the action of different pretreatments have been advocated to improve the dissolution of cellulose in ILs, such as surface area, hemicelluloses removal, crystallinity, and reduced degree of polymerization (DP) for cellulose (Hu and Ragauskas, 2012).

With several pretreatments being effective in achieving high purity of cellulose, therefore, it is vital to develop a similar route on hemicelluloses recovery or conversion from pretreatment of holocellulose. In fact, although various thermochemical pretreatments of hemicelluloses have been explored for the multiple utilization of lignocelluloses such as eucalyptus, further research is imperative to evaluate the influence of key features influenced by each pretreatment to determine if the regenerated cellulose fibers via green wet-spinning can be related to any common characteristics (Wyman et al., 2005). Eucalyptus is a fast growing hardwood that has been targeted as one of the possible biomass sources for the production of lignocellulosic materials and chemicals, therefore, the full utilization of eucalyptus carbohydrates has attracted great interest. In line with these objectives, the purpose of this research is to analyze the effects of sodium hydrate, dilute sulfuric acid, and hydrothermal pretreatment of eucalyptus holocellulose on the hemicellulosic products and IL-based cellulose spinning fibers. In order to make full use of the multiple components from eucalyptus biomass, the isolation of hemicelluloses and its conversion to XOS during these pretreatments were both investigated. This present work not only opens up the feasibility of manufacturing high-purity cellulose for wet-spinning, but also sets up an economic and multifunctional platform to utilize hemicelluloses.

2. Experimental

2.1. Materials and reagents

Lignocellulosic biomass, eucalyptus (*E. urophylla*), was collected from Guangdong province and air dried, milled and sieved to obtain a wood meal of 200 μm diameter. The IL, 1-butyl-3-methylimidazolium acetate ([bmim]OAc), was purchased from Lanzhou Institute of Chemical Physics (Chinese Academy of Sciences, Lanzhou province, China). The rest of chemicals used in this study, including sodium hydrate, sulphuric acid, sodium chlorite and ethanol, were of analytical grade and used as received without further purification.

2.2. Different pretreatments

The dewaxed eucalyptus powder (20 g) was dispersed in 800 mL of deionized water and heated to 75 °C with stirring, and then 20 g of sodium chlorite were added. The pH of the mixture was gradually adjusted to 3.7–4.0 by acetic acid. The treatment with sodium chlorite was repeated twice at a 1 h interval to remove the lignin and obtain eucalyptus holocellulose (Chen et al., 2015a). The holocellulose was subsequently washed with distilled water and dried at 60 °C for 16 h prior to pretreatment. Different pretreatment strategies, including alkaline extraction (AE), dilute acid pretreatment (DAP) and hydrothermal treatment (HTT), were used to deal with eucalyptus holocellulose, and the specific pretreatment conditions are described as follows.

The holocellulose was extracted by 5% NaOH solution with a solid to liquid ratio of 1: 20 (g/mL) at 75 °C for 4 h. After the treatment, the insoluble residues were filtered through a nylon cloth on a funnel, washed with distilled water until the pH of filtrates was neutral, and dried at 60 °C to obtain cellulose sample which was termed as NaOH-C. The filtrate was adjusted to pH 5.5 with 6 mol/L acetic acid and concentrated to about 100 mL. Then the concentrated filtrates were mixed with 300 mL of ethanol to precipitate hemicellulosic fraction (Xu et al., 2014a). The DAP of holocellulose was conducted by 0.25 mol/L dilute H₂SO₄ with a solid to liquid ratio of 1: 20 (g/mL) at 90 °C for 1 h. The HTT of holocellulose was treated by deionized water with a solid to liquid ratio of 1: 20 (g/mL) at 180 °C for 30 min. The insoluble residues were filtered and washed with distilled water until the pH of filtrates was neutral, and dried at 60 °C to obtain the cellulose samples which were named as H₂SO₄-C and HTT-C respectively (Bian et al., 2014; Xiao et al., 2013). The filtrate was cryopreserved below 0 °C prior to the analysis of the contents of XOS and inhibitors.

2.3. Preparation of the regenerated fibers

[bmim]OAc of 40 g was loaded into a 50 mL round bottom flask and heated to 100 °C with an oil bath. Then, 2 g of cellulose sample (NaOH-C, H₂SO₄-C and HTT-C) was slowly added into the IL under vigorous stirring to obtain a spinning dope. After being degassed under vacuum, the dope was transferred to a syringe and extruded by wet-spinning method at a velocity of 1.2 m/min through an orifice of 0.21 mm diameter into a coagulation bath with water at 25 °C to obtain the regenerated fibers (Chen et al., 2015a). The regenerated fibers were soaked in water overnight to remove the residual IL, collected by a spool to prevent shrinkage, and then dried in ambient condition. The regenerated cellulose fibers were labeled as Re-NaOH-C, Re-H₂SO₄-C and Re-HTT-C corresponding to NaOH-C, H₂SO₄-C and HTT-C, respectively. The diagram of this experimental scheme is shown in Fig. 1.

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