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Specific lignin precipitation for oligosaccharides recovery from hot water wood extract

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HIGHLIGHTS

- OS recovery from HWE by specific lignin precipitation and subsequent dialysis.
- Controlled charge neutralization by PAC for specific lignin precipitation.
- Selective removal of large molecular lignin facilitates OS purification by membrane.
- OS production from HWE by proposed process attains 56.36 g per kg wood.

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ABSTRACT

Hot water extraction is an important strategy of wood fractionation, by which the hemicelluloses can be separated for value-added products, while the residual solid can still be processed into traditional wood products. In this study, a combined process consisting of specific lignin precipitation and dialysis was proposed to recover hemicellulosic oligosaccharides (OS) from hot water extract (HWE). The results showed that polyaluminium chloride (PAC) precipitation was highly specific to large molecular lignin, leading to 25.1% lignin removal with negligible OS loss through charge neutralization mechanism. The separation was further enhanced by dialysis, reaching 37.6% OS recovery from HWE with remarkable purity of 94.1%. By the proposed process, 56.36 g OS, mainly xylooligosaccharides with two fractions of 5.2 and 0.51 kDa was recovered from one kg dried wood. This process can be envisaged as a great contribution to wood biorefinery.

1. Introduction

Conventional pulping processes focus on separating cellulosic fiber physically or chemically from lignocellulosic feedstocks like woody and herbaceous crops. The non-cellulosic components, lignin, extractives, and most of hemicelluloses are primarily dissolved in spent liquor which is ultimately combusted for the production of thermal energy and the recovery of chemicals (Gullichsen and Fogelholm, 2000). In this context, the economical performance of the conventional pulping process is not favorable and limits the further development. To overcome this deficiency, the concept of biorefinery, which is analogous to today's petroleum refinery, is introduced to repurpose the pulping process so that a spectrum of more profitable bio-based products (food, feed, chemicals, and materials) and bioenergy (biofuels, power and/or heat) can be produced from biomass (FitzPatrick et al., 2010). Recently, hot water extraction has been developed to extract hemicelluloses, mainly oligosaccharides (OS), prior to wood cooking process as a strategy of wood fractionation (Amidon and Liu, 2009; Sainio et al., 2013). On one hand, the residual plant materials remain intact in fibrous form but become softer after hot extraction, and consequently are actually improved for subsequent manufacture of pulp, paper, fiberboard, and especially suitable for dissolving pulp (Duarte et al., 2011). On the other hand, the OS in hot water extract (HWE) had been proved to be bio-based products with multiple values as long as it can be recovered and purified. OS can be used as readily fermentable feedstocks for biomaterials and biofuels production (Gírio et al., 2010). In food industry, there has been an emerging interest in the use of OS as prebiotic and biopreservative additives because chemical additives are becoming less and less welcome (Barreteau et al., 2006). Glycobiology research demonstrated the increasing reorganization of the therapeutic importance of OS based molecules in basic cellular processes (Seeberger and Werz, 2007; Turnbull and Field, 2007). This makes OS high-value-added products in a wide range of areas (Dube and Bertozzi, 2005; Koeller and Wong, 2000), including inflammation, immunity, oncology, neurodegenerative disease, and infection.

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The recovery and purification of OS from HWE is challenging because of the fact that the HWE contains not only OS but a diverse palette of the byproducts, including dissolved lignin, monosaccharides, furfural, fatty acids, and methanol (Amidon and Liu, 2009; Garrote et al., 2007). Hence an effective separation of OS is critical for the overall biorefinery concept of hot water extraction. A number of processes had been developed for OS separation, e.g. gel filtration (Palm and Zacchi, 2004), membrane filtration (Al Manasrah et al., 2012; Buranov and Mazza, 2010), ethanol precipitation (Liu et al., 2011), and polyelectrolyte flocculation (Duarte et al., 2010). Among these processes, membrane filtration are the most effective strategy but the problems of fouling and flux decay that caused by dissolved lignin macromolecules render membrane separation unpractical on a large scale (Dal-Cin et al., 1995; Koivula et al., 2011, 2013; Ramamurthy et al., 1995). Ethanol precipitation is a traditional method used to purify and/or fractionate hemicellulose sugars (Peng et al., 2009) and nucleotide (Gaillard and Strauss, 1990; Jeanpierre, 1987) from aqueous solution by adding ethanol as an antisolvent, but showed poor performance in OS selectivity as demonstrated by Vázquez et al. (2005). Polyelectrolyte flocculation had received great attention as a pretreatment strategy of membrane filtration because it can decrease fouling by removing the lignin compounds, which are most dominant foulants in HWE. The study of Duarte et al. (2010) demonstrated that the polydiallyldimethylammonium chloride (*p*-DADMAC) induced flocculation was highly specific to lignin because of the negatively charged surface of colloidal particles. This means that the lignin concentration is reduced while the sugar content remains unchanged after precipitation. However, the different opinion from Yasarla and Ramarao (2012) showed the *p*-DADMAC-induced precipitation was not specific to lignin because the loss of total sugars (from 37.91 to 23.97 g/L) was as significant as the removal of lignin (from 5.547 to 1.645 g/L). Polymeric resins XAD-7 and XAD-16 were also used for OS separation as recently reported (Koivula et al., 2013), but they were observed to be nonselective between lignin and the carbohydrates. To clarify the mechanism of the specific precipitation, more efforts should be contributed to the characterization of colloidal particles in HWE in the level of molecules, such as particle size, surface potential and structure.

The present study aimed at the recovery of OS from wood HWE by specific precipitation and dialysis filtration. Various precipitation strategies will be compared in the terms of lignin selectivity because precipitation is supposed to work only with large molecular lignin and thereafter the separated OS containing small molecular impurities could then be purified by dialysis.

2. Methods

2.1. Materials

Poplar wood chips were prepared from debarked wood log harvested from the southwest region of Shandong province, China. The wood chips were then screened to remove all particles greater than 38 mm and less than 6 mm in length. The thickness of the accepted chips ranged from 1 to 5 mm. The wood chips were then air-dried to the solid content of 89.28% for hot water extraction. *p*-DADMAC was provided by Ashland Inc. with electric density of 2 mEq/g and molecular weight of 100–1000 kDa. The PAC used in the present study was purchased from Aspirit Chemical Co., Ltd. Qingdao, China. Dialysis tubes with molecular weight cut off (MWCO) of 1.0 kDa and 3.0 kDa were provided by Spectrum Laboratories, Inc. Pullulan standard set (Mp 342-710,000 Da) for gel permeation chromatography (GPC) analysis was from Sigma–Aldrich Co., LLC.

2.2. Hot water wood extraction

Hot water extraction was carried out in a pulp digester with capacity of 23 L. The digester was heated electrically and rotated at 2 rpm for mixing. About 1.0 kg (on OD basis) of wood chips was placed in the digester and 6 L of deionized water was added. The digester temperature was increased from the initial room temperature up to 170 °C and held for 60 min. At the end of extraction, the digester was cooled, depressurized and the reaction mixture was withdrawn. About 4 L HWE was separated and collected from the hot water treated wood chips. The HWE was then subjected to microfiltration with 0.45 micron membrane to remove the suspended solids and particles for the subsequent flocculation experiments.

2.3. Flocculation experiments

The flocculation experiments were performed with the neat wood HWE. The flocculants used were ethanol, *p*-DADMAC and PAC. Various dosages of flocculant were added in centrifuge tubes filled with 2 mL HWE. All tubes were strongly agitated by a plate vibrator for 5 min. After agitation, the mixtures were left for settling. The particle size and zeta potential of the suspension were measured during the settling process. For fast settling, centrifugation was applied at 10,000 rpm for 5 min. The supernatant was then taken for measurements of solid content, chemical components, and molecular weight distribution. Besides the dosage of flocculants, the effect of pH and temperature was also studied.

2.4. Dialysis purification

The supernatant from flocculation experiment was then subjected to dialysis for OS purification by removing impurities with low molecular weight, including lignin, phenolic compounds, furan aldehydes, organic acids and salts. 10 mL supernatant was filled into the dialysis tube with 1.0 or 3.0 kDa MWCO. The dialysis was conducted in 200 mL deionized water at room temperature. The pH and conductivity of the solution were measured during dialysis to determine the end time. After dialysis, the solid content, chemical composition, and molecular mass distribution of the retentates inside the tube were measured.

2.5. Analysis methods

Solid content was determined by weighting aliquots of solution before and after oven drying. Lignin content was determined via UV/Vis spectroscopy at 205 nm with absorptivity of 110 L/g/cm by dilution the solution with deionized water according to the acid soluble lignin method from TAPPI Standard T222. The OS was measured by an indirect method based on quantitative acid hydrolysis of the samples with 4% w/w of H_2SO_4 at 121 °C for 60 min according to technical report from NREL (Sluiter et al., 2006). The OS concentration was expressed as the increase in sugar monomers, as analyzed by HPLC (Shimadzu LC-20T equipped with a refraction index detector and a Shodex sugar SP0810 column, pure water as eluent at 0.6 mL/min). The molecule weight of the OS before and after the steps of precipitation and dialysis were analyzed by GPC using a Shimadzu SB-803 HQ column and refraction index detector with pure water as mobile phase at 35 °C (flow rate 1.0 mL/min). Particle size and zeta potential was measured by DLS analyzer equipped with a laser Doppler microelectrophoresis (Zetasizer Nano ZS90, Malvern Instruments, UK) at 25 °C. All the dilutions required were made with 20 mM NaCl solution in order to ensure a good conductivity of the solution.