Carbohydrate Polymers 86 (2011) 1630–1636

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Chitosan as a flocculant for pre-hydrolysis liquor of kraft-based dissolving pulp production process

Abrar Saeed, Pedram Fatehi*, Yonghao Ni

Department of Chemical Engineering and Limerick Pulp and Paper Centre, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3

ARTICLE INFO

Article history:
Received 16 February 2011
Received in revised form 24 June 2011
Accepted 30 June 2011
Available online 7 July 2011

Keywords:
Forest biorefinery
Flocculation
Chitosan
Recovery
Pre-hydrolysis liquor
Dissolving pulp

ABSTRACT

In this work, the flocculation concept was employed to recover the dissolved lignocellulosic materials of industrially produced pre-hydrolysis liquor (PHL) using two different molecular weights of chitosan. The analysis revealed the maximum turbidity of 1000 NTU or 1900 NTU via adding 2.2 mg/g low molecular weight (LMW) or 1.7 mg/g high molecular weight (HMW) chitosan to the PHL, respectively. Also, the maximum furfural removal of 55% or 50% was obtained by adding 0.7 mg/g or 0.5 mg/g LMW or HMW chitosan to the PHL, respectively. The maximum recovery of oligomeric sugars was 20% or 25% by adding 1.5 or 0.5 mg/g LMW or HMW chitosan, while that of lignin was 40% or 35% by applying 2.2 mg/g or 1.7 mg/g LMW or HMW chitosan to the PHL, respectively. The removal of monomeric sugars and acetic acid was rather limited. The particle size and nitrogen analyses were also hired to characterize the properties of the formed complexes.

1. Introduction

The application of integrated forest biorefinery concept has received a great attention in the pulp and paper industry (Amidon et al., 2008; Saeed et al., 2010; van Heiningen, 2006). Such an application could improve the revenue of the mill, reduce its environmental impact and increase employment opportunities (Amidon et al., 2008; van Heiningen, 2006). Following this concept, different components of lignocellulosic materials are systematically separated and converted to various value-added bio-products.

In the kraft-based dissolving pulp production process, the hemicelluloses and a part of lignin are separated in the pre-hydrolysis stage, while the remaining lignin is removed from the solid residue (cellulose) in the subsequent kraft pulping and bleaching steps (T. Liu, He, Hu, & Ni, 2011; Saeed et al., 2010). The pre-hydrolysis liquor (PHL) from the pre-hydrolysis stage is presently mixed with black liquor and burned in the recovery boiler of the mill. However, the dissolved lignocellulosic materials could be potentially used for various purposes: wet end additives of papermaking from the recovered hemicelluloses (Ren, Peng, & Sun, 2009), fuel source from the recovered lignin (Leschinsky, Zuckerstätter, Weber, Patt, & Sixta, 2008; Z. Liu, Fatehi, Jahan, & Ni, 2011; van Heiningen, 2006), and ethanol production via fermentation of recovered hemicelluloses (Alvarado-Morales, Terra, Gernaey, Woodley, & Gani, 2009; Carvalheiro, Durate, & Girio, 2008; Huang, Ramaswamy, Al-Dajani, & Tschirner, 2010). One method to recover and subsequently utilize the lignocellulosic materials of the PHL is to employ flocculation concepts through a cationic polymer treatment. This method has been widely applied in various waste water treatment systems (Ji, Qiu, Wai, Wong, & Li, 2010; T. Liu et al., 2011; Mihai & Dragan, 2009; Saether, Holme, Maurstad, Smidsrod, & Stokke, 2008). In this system, the electrostatic interaction developed between oppositely charged polymers promotes the flocculation (Muzzarelli, 1990; Szygula, Guibal, Palacin, Ruiz, & Sastre, 2009). If the molecular weight of two oppositely charged polymers is significantly different, a patch flocculation may be developed, in which the low molecular weight polymer neutralizes a part of the charges associated with the high MW polymer (Guibal and Roussy, 2007; Schatz, Domard, Viton, Pichot, & Delair, 2004; Strom, Barla, & Stenius, 1985). If the molecular weight of polymers is relatively high, the charged polymer may bridge the formed complexes and create larger complexes (Guibal and Roussy, 2007; Schatz et al., 2004; Strom et al., 1985). As the PHL contains various anionic lignocellulosic materials (Li, Saeed, Ni, & van Heiningen, 2010; Saeed et al., 2010), the addition of cationic polymers to the PHL would facilitate the flocculation due to the formation of complexes of cationic polymers/anionic lignocellulosic materials.

Chitosan, a natural polysaccharide, is commercially prepared by partial deacetylation of chitin, which is a product found in crustacean shells. (Fredheim & Christensen, 2003; Guibal & Roussy, 2007; Saether et al., 2008). The abundance and comparative cost-effectiveness of chitosan with other cationic polymers make chitosan attractive for industrial usages in various areas (Fatehi, Kititerakun, Ni, & Xiao, 2010). One main advantage of chitosan is

---

* Corresponding author. Tel.: +1 506 450 5583; fax: +1 506 453 4767.
E-mail address: pfatehi@unb.ca (P. Fatehi).

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.06.075

its natural cationic charge, which facilitates its interaction with anionic charged polymers in various media (Fatehi, Kititerakun et al., 2010). In fact, the cationic charge of chitosan eliminates the need for its further modification/cationization, which is in opposition to the preparation methodology of cationic synthetic polymers used in waste water treatment and papermaking systems. The interaction of chitosan with various anionic polymers in water was investigated in the literature (Fredheim & Christensen, 2003; Guibal & Roussy, 2007; Saether et al., 2008; Szygula et al., 2009). The performance of chitosan on interacting with various components of a chemical pulp suspension (Li, Du, Xu, Zhan, & Kennedy, 2004) and with various dyes have been evaluated in the literature (Guibal & Roussy, 2007; Szygula et al., 2009). The objective of this study was to investigate the flocculation behavior and efficiency of chitosan on interacting with the lignocellulosic materials of the PHL and on removing them from the PHL.

In the literature, the efficiencies of acidification and liming on removing various components of the PHL have been comprehensively investigated (Horvath, Sjode, Alriksson, Jonsson, & Nilvebrant, 2005; Z. Liu et al., 2011; Martinez, Rodriguez, York, Preston, & Ingram, 2000; Sun, 2008). Our focus in this study was to further improve the removal efficiency of lignocellulosic materials of PHL via using chitosan. In this work, two chitosan samples with different molecular weights (MW) were applied to industrially produced PHL. The removal of various dissolved organics in the PHL was assessed at different dosages of chitosan. The properties of chitosan/PHL mixture and the formed complexes were assessed and related to the removal of organics. Depending on the compositions of the formed complexes, they may be used as fuel source, or wet end additive (retention aid) in papermaking, as described above. Thus, the flocculation process via using chitosan suits well with the biorefinery concept applied to the kraft-based dissolving pulp production process.

2. Experimental

2.1. Raw material

The pre-hydrolysis liquor (PHL) was collected from a dissolving pulp production mill, located in Eastern Canada, and used as received. Chitosan with 70–180 kDa (448869) and 200–300 kDa (448877) molecular weights, 79% deacetylated, were purchased from Aldrich Co., and dissolved in the solutions of 0.5 g/l prior to analysis. The standard solutions of potassium polyvinyl sulfate (PVSK) or polydiallyldimethylammonium chloride (PDADMAC) (0.5 mM) were purchased from Aldrich Co., and used for measuring the charge density of chitosan and the PHL (Fatehi, Kititerakun et al., 2010). NaOH (1 M) and H_2SO_4 (1 M) were obtained from Fisher scientific.

In the literature, acidification has been regarded as the first step of PHL utilization in biorefinery concept (T. Liu et al., 2011; Sun, 2008). In this research, the PHL (500 ml) has been acidified to a pH of 2 by adding sulfuric acid at room temperature and then kept for 2 h. The precipitated materials were then removed from the PHL via filtering (0.45 μm nylon filters) (Z. Liu et al., 2011). Then, the acidified PHL sample was treated by CaO to a pH of 6–7 for the chitosan treatment. The application of lime has also been respected as a method to reduce the lignocellulosic materials of the PHL in the past (Horvath et al., 2005; Martinez et al., 2000). Afterwards, the PHL was filtered and this pretreated PHL was applied for the flocculation analysis via the chitosan treatment.

2.2. Addition of chitosan to PHL

Various amounts of low or high MW chitosan were subsequently added to 20 ml of the pretreated PHL for removing of the lignocellulosic materials at room temperature, while stirring. Then, the zeta potential, particle size, and turbidity of the chitosan/PHL mixture were analyzed. Afterwards, the formed complexes were isolated by centrifuging at 3000 rpm for 5 min. The concentrations of lignocellulosic materials before and after chitosan addition were determined, and removal efficiencies were calculated. The chitosan content of the formed complexes was identified via the Nitrogen analysis.

2.3. Charge density, zeta potential, particle size and turbidity analyses

The charge density of the PHL sample and chitosan solutions were measured by using a particle charge detector (Mütek PCD 03, Germany) with the standard PVSK or PDADMAC solutions. The charge densities of low and high MW chitosan were 3.09 meq/g and 3.05 meq/g, respectively. The quasi-elastic light scattering (QELS) analysis was conducted for measuring the size of complexes formed in the chitosan/PHL mixture. Chitosan and PHL solutions (20 ml) were first filtered by using syringe filters, sterile 0.2 μm pore size, to remove the impurities of the solutions. Then, various dosages of chitosan were added to the PHL at room temperature, and the hydrodynamic sizes and zeta potential of the solutions were quantified before and after mixing. The data was obtained at 25 °C with a ZetaPlus Brookhaven (Holtsville, NY, USA) with the software of 90 plus/BI-MASS. The scattering angle and operating wavelength were 90° and 658 nm, respectively. Analysis was conducted automatically to yield the mean diffusion coefficient. Then, from the Stokes–Einstein equation, the apparent hydrodynamic sizes of the formed complex were assessed. This method has been widely applied for determining the size of complexes in solutions (Buchhammer, Mende, & Oelmann, 2003; Fatehi, Kititerakun et al., 2010). The zeta potential was calculated by measuring the electrophoretic mobility, using the Smoluchwski's approximation by a ZetaPlus Zeta potential analyzer (Brookhevan, Holtsville, NY, USA) (Onesippe and Lagerge, 2008). The turbidity of the PHL samples before and after the cationic polymer treatments was conducted by using a turbidimeter, 2100AN, HACH co., CO, USA at room temperature.

2.4. Sugar analysis

The concentration of sugars in the PHL was determined by using an ion chromatography unit equipped with CarboPac^{TM} PA1 column (Dionex-300, Dionex Corporation, Canada) and a pulsed amperometric detector (PAD) (T. Liu et al., 2011; Saeed et al., 2010). To convert oligosaccharide of PHLs to monosaccharide, an additional acid hydrolysis was carried out on the PHL under the conditions of 4% sulfuric acid at 121 °C in an oil bath (Neslab Instruments, Inc., Portsmouth, NH, USA) (Saeed et al., 2010). The PAD settings were E1 = 0.1 V, E2 = 0.6 V and E3 = −0.8 V. Deionized water was used as the eluant with a flow rate of 1 mL/min. NaOH with the concentrations of 0.2 M and 0.5 M were used as the regeneration agent and supporting electrolyte with a flow rate of 1 mL/min. The sugar analysis prior to this additional acid hydrolysis reveals the content of monomeric sugars, while that after the additional acid hydrolysis reflects the total monomeric sugars existing in the PHL. The subtraction of total sugars from monomeric sugars reflects the amount of oligomeric sugars in the PHL.

2.5. Lignin, furfural and acetic acid analyses

The lignin content of the PHL was measured based on the UV/Vis spectrometric method at a wavelength of 205 nm (TAPPI UM 250). A Varian 300 ^{1}H NMR spectrometer was employed for determining the concentrations of furfural and acetic acid of the PHL (Z. Liu et al.,