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Enhancement of colloidal particle and lignin removal from pre-hydrolysis liquor of aspen by a combination of pectinase and cationic polymer treatment

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ABSTRACT

The removal of colloidal particle and lignin from a pre-hydrolysis liquor (PHL) of biomass is essential for its processing as well as for the value-added utilization of saccharides in the PHL. In this paper, pectinase was used to treat an aspen PHL obtained by pre-hydrolysis at 160 °C, and a novel process in which pectinase treatment was followed by cationic polymer flocculation to enhance colloidal particle and lignin removal was investigated. The results showed that pectinase treatment caused an approximately 50% decrease in the cationic demand of the aspen PHL. For the controlled PHL, approximately 68 mg/L poly-dimethyl diallyl ammonium chloride (pDADMAC) was needed to remove nearly all of the colloidal particles with 40.3% maximum lignin removal; for the enzyme-treated PHL, only approximately 34 mg/L pDADMAC was needed to remove nearly all of the colloidal particles with 43.3% lignin removal. In addition, the enzyme treatment decreased the loss of saccharides during subsequent pDADMAC treatment at the concentration necessary for maximum lignin removal.

1. Introduction

In addition to cellulose and lignin, hemicelluloses are one of the three major cell wall components of lignocellulosic biomass such as wood, agricultural crop residues, and grasses [1,2]. The effective utilization of hemicelluloses is an important strategy for biorefineries. Hemicelluloses have been used as the feedstocks for producing platform chemicals such as furfural, hydroxymethylfurfuralxylitol and levulinic acid [3]. In recent years, many new applications of hemicelluloses have been developed such as hydrogels, surfactants, cosmetics, antibacterial materials, and films [4–7]. In addition, hemicelluloses have also been used as a source of saccharides for producing biofuels such as ethanol, 2,3-butanediol and methane [8–11].

Pre-hydrolysis, also called auto-hydrolysis or hot water extraction, is believed to be an environmentally friendly hemicellulose extraction process because no chemicals other than water or steam are involved in the process [12]. Pre-hydrolysis is also the method used to remove hemicelluloses from wood chips prior to kraft pulping to produce dissolved pulp for cellulose derivatives. During the pre-hydrolysis of wood, which occurs at high temperatures (140–180 °C or higher), most of the hemicelluloses are depolymerized through the cleavage of the glycosidic bonds and released into the pre-hydrolysis liquor (PHL), while the lignin is partially removed through the cleavage of the aryl-ether bonds and released into the PHL [13], where it forms the colloidal particles and dissolved lignin in PHL [14]. In addition, the carbohydrates degradation by-products such as acetic acid, formic acid, furfural and 5-hydroxymethyl-furfural (HMF) may also be formed and released into the PHL. Thus, PHLs are considerably complex and contain dissolved and colloidal substances derived from the carbohydrates and lignin [14].

The colloidal particles and lignin in PHL can cause the membranes fouling, which lowers their lifetime and the separation efficiency when ultrafiltration technology is used to concentrate and fractionate the saccharides of wood PHLs for high-value applications [15]. In addition, lignin can inhibit microbial fermentation during the energy utilization of the saccharides in PHL [16,17]. Therefore, the removal of the colloidal particles and lignin is important for the effective application of the saccharides in PHL.

Lignin removal can be achieved by adsorption with activated carbon [18,19], lime [20,21], or ion exchange resin [22,23], though some hemicellulose saccharides are also lost during the adsorption [15,18]. In addition to adsorption methods, other methods such as acidification, oxidation with pulsed corona discharge and solvent extraction [15,24] have also been used to remove lignin from PHL.

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Polymers, including cationic and nonionic polymers, have also been used to remove the colloidal particles, lignin and other impurities in wood PHLs by flocculation. A significant amount of lignin in wood PHLs can be removed by polyethylene oxide (PEO) treatment, and little of the hemicellulose saccharides are lost [25]. Cationic polymers, such as cationic poly acrylamide (CPAM), poly diallyl dimethyl ammonium chloride (pDADMAC), and poly ethylene imine (PEI), and the inorganic polymers polyaluminum chloride (PAC) have been used to remove the particulates and the lignin from wood PHLs [14,26,27]. Duarte et al. reported that pDADMAC effectively removed the particulates and lignin from a wood PHL with little carbohydrate loss [26]; however, our previous work showed that the pDADMAC treatment of a wood PHL resulted in the effective removal of the lignin with a significant loss of hemicellulose saccharides [27]. Enzymes have also been used to remove lignin from PHLs. Wang et al. reported that laccase treatment resulted in approximately 46–61% lignin removal because laccase could induce the polymerization of lignin present in the PHL, and the subsequent flocculation using cationic polymers further removed 10–15% of the remaining lignin; however, the cationic polymer treatment also caused a loss of 12–15% of the total sugar [28]. Piazza recently reported that a biobased protein flocculant hemoglobin (HEM) was an effective flocculant for the removal of non-sulfonated lignin in spent pulping liquor [29].

The negatively charged colloidal particles in wood PHLs are relatively stable, likely due to the negative charge of the system [26]. Therefore, when the cationic polymers are used to treat the wood PHLs for colloidal particles and lignin removal, the negative charge is very important for the efficiency of these polymers; however, resources of the negative charge in PHL systems has not been reported. Our previous study on the hemicellulose components of an aspen PHL showed that the content of 4-*O*-methyl-glucuronic acid and galacturonic acid (GalA) in the PHL was 3% of the total saccharides, and specifically, most of them existed in the form of polysaccharides and oligosaccharides [30]. These uronic acids may be an important source of the anions in PHLs. In the papermaking process, pectinases have been used to improve the efficiency of the cationic polymers because they depolymerize the dissolved polygalacturonic acid which can contribute to cationic demand [31,32]. We hypothesize that polygalacturonic acid is an important source of anions in PHLs. In the present work, a pectinase was used to treat a PHL prior to cationic polymer treatment. A novel process in which pectinase treatment was followed by cationic polymer pDADMAC treatment was developed, and the effects of this combined pectinase and subsequent pDADMAC treatment on colloidal particle and lignin removal and saccharide loss was studied.

2. Methods

2.1. Raw materials, enzymes and chemicals

Aspen wood chips were obtained from Huatai Group, China. The average size of the woodchips was approximately 33.0 mm × 42.0 mm × 3.6 mm, and they contained 21.0% pentosan, 20.5% Klason lignin and 2.6% acid-soluble lignin, as determined by TAPPI T 223, TAPPI T 222 and TAPPI UM 250, respectively.

The Pectinase P2611 (from *Aspergillus aculeatus*) and pectin were purchased from Sigma–Aldrich, USA. The pectinase activity was determined at pH 4.8 and 50 °C with a 10 g/L pectin solution. One activity unit was defined as the amount of pectinase that produced 1 mg galacturonic acid per hour by decomposing pectin at the measured conditions, and the measured pectinase activity was 1300 U/mL. In addition to the pectinase activity, according to the supplier's instructions, the enzyme also contains cellulase and hemicellulase activities.pDADMAC was provided by Jiangsu Feymer Technology Co., Ltd, China. Its average molecular weight was 200 kDa, and its cationic charge density was approximately 7.5 meq/g at pH 3.8.

2.2. Pre-hydrolysis of the wood chips

The pre-hydrolysis process was carried out in a 1-L pulp digester (rotary type autoclave No.2611, Kumagai Riki Kogyo Co., Ltd, Japan). The equivalent of 400 g of oven-dried aspen chips and the required amount of water were added to reach a1:6 wood to liquid ratio. The digester was heated from room temperature at a speed of approximately 2.2 °C/min to 160 °C and held for 60 min at the maximum temperature. At the end of autohydrolysis, the digester was removed and cooled with running water to approximately 60 °C in 5 min. The PHL was taken out and centrifuged for 15 min at 2000 r/min to remove the suspended wood particles.

2.3. Pectinase treatment

A total of 150 mL of PHL was added into a 250-mL Erlenmeyer flask; subsequently, the required amount of pectinase solution was added to the flask, which was then incubated in a shaking water bath at 40 °C at the original pH of the PHL (3.8). At the end of the treatment, the reaction was inactivated at 100 °C for 5 min. For the control samples, a deactivated enzyme was used to treat the PHL, and all other conditions were the same as those of the enzyme treatment.

2.4. pDADMAC treatment of PHL

A total of 5 mL of a pDADMAC solution of the desired concentration was added into 100 mL of the PHL samples in Erlenmeyer flasks, which were then shaken for 30 min at 120 rpm. After treatment, the PHL was centrifuged at 2000 rpm for 15 min to remove the flocs, and the supernatant was used for analysis.

2.5. Analysis of PHL

The saccharide concentration of the PHL was determined according to the methods described in our previous work [33]. In brief, the monosaccharide concentration of the PHL was determined using an ion chromatography ICS-5000 system (Thermo Fisher Scientific, MA, USA) with a pulsed amperometric detector (PAD), which was controlled by Chromeleon 7.0 SR1 software. A CarboPac PA20 (3 × 150 mm) coupled with a guard column (Dionex, CA, USA) was used. The column and detector temperatures were 30 °C and 25 °C, respectively. The injection volume was 20 μL, and the operating pressure was approximately 17.93 MPa to 20.68 MPa. The mobile phases consisted of 4% 50 mmol/L NaOH and 96% ultrapure water at 0–22 min; 40% 1 mol/L $NaCOOCH_3$, 20% ultrapure water and 40% 50 mmol/L NaOH at 22–27 min; and 20% ultrapure water and 80% 250 mmol/L NaOH at 28–35 min. The flow velocity was 0.4 mL/min. For the measurement of the total saccharide concentration, acid hydrolysis was carried out at 120 °C with 4% (w/w) H_2SO_4 for 60 min, according to the technical report from NREL [34]. Measurement of the saccharides concentration before and after acid hydrolysis was used to determine the monosaccharide and total saccharide concentrations, respectively. The polysaccharide content of (including oligosaccharides) of the PHL was obtained by subtracting the monosaccharides content from the total saccharides content. The saccharide concentration was analyzed in duplicate.

The saccharides arabinose, xylose, mannose, galactose and glucose were detected, and the saccharides concentration reported in the results is the sum of these saccharide concentrations, monomeric and polymeric.

The galacturonic acid in the PHL was determined according to the application note of Thermo Fisher Scientific by using an ion chromatography ICS-5000 system (Thermo Fisher Scientific, MA, USA) with a pulsed amperometric detector (PAD), and a Dionex CarboPac PA20 column was used [35].

The lignin content in the PHL was measured based on the UV/Vis