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Short Communication

High consistency cellulase treatment of hardwood prehydrolysis kraft based dissolving pulp

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HIGHLIGHTS

- A high pulp consistency condition favors the cellulase adsorption.
- The improvement in the pulp properties was enhanced under the high consistency cellulase treatment.
- The high pulp consistency concept has better industrial relevance.

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ABSTRACT

For enzymatic treatment of dissolving pulp, there is a need to improve the process to facilitate its commercialization. For this purpose, the high consistency cellulase treatment was conducted based on the hypothesis that a high cellulose concentration would favor the interactions of cellulase and cellulose, thus improves the cellulase efficiency while decreasing the water usage. The results showed that compared with a low consistency of 3%, the high consistency of 20% led to 24% increases of cellulase adsorption ratio. As a result, the viscosity decrease and Fock reactivity increase at consistency of 20% were enhanced from 510 mL/g and 70.3% to 471 mL/g and 77.6%, respectively, compared with low consistency of 3% at 24 h. The results on other properties such as alpha cellulose, alkali solubility and molecular weight distribution also supported the conclusion that a high consistency of cellulase treatment was more effective than a low pulp consistency process.

1. Introduction

Green and natural raw material, characterized as sustainable and compatible with the environment, is in high demand, in light of the depletion of petroleum resources (Dodds and Gross, 2007). Cellulose, as the most abundant biopolymer on earth, is a green raw material that can be used to produce many products, such as rayon, cellulose acetate, nitrocellulose and cellulose ether (Jahan et al., 2011; Tian et al., 2014). The production of cellulose (known as dissolving pulp in the paper industry) from lignocellulosic biomass, is increasing, and this is particularly true in Canada and China (Miao et al., 2014; Wang et al., 2015).

Prehydrolysis kraft (PHK) – based dissolving pulp (cellulose) production process is dominant in the recent expansion of dissolving pulp. In the process, the impurities such as hemicellulose, lignin and extractives that were originated from wood (or other lignocellulosic biomass) are almost completely removed during the production process, i.e. pre-hydrolysis, pulping and bleaching (Mozdyniewicz et al., 2013). The viscosity and reactivity are the most important quality parameters for dissolving pulp in terms of processability of downstream production process. Low viscosity and high reactivity cellulose can improve the homogeneity and quality of cellulose-end products and lower the demands of reactants (Ibarra et al., 2010). But, a good control of viscosity and increase reactivity are not a simple task due to the compact fibrillar structure of cellulose. Various treatment such as chemical, mechanical and biological have been assessed to improve the properties of dissolving pulp (Wang et al., 2014; Tian et al., 2014; Miao et al., 2014). Among these, cellulase treatment is one of the promising approaches for this purpose, which is not only a naturally compatible process, but also a very mild processing condition.

Endoglucanases rich cellulase can effectively attack the cellulose structure, which will increase its accessibility towards

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reactants and facilitates the xanthation reactions in the rayon manufacturing process. In the literature, many studies were carried out, for example: Ibarra et al. (2010) reported that the endoglucanase with cellulose binding domain was effective in increasing the reactivity and decreasing viscosity of dissolving pulp. Miao et al. (2014) observed the enhancement of accessibility and reactivity of hardwood dissolving pulp when using cellulase treatment. Wang et al. (2014) reported that the high reactivity (about 80%) was achieved by endoglucanases rich cellulase treatment when upgrading bleached softwood paper grade pulp to dissolving pulp.

Enzymatic treatment of pulp, for example, xylanase treatment of brown stock to improve the bleachability, is usually performed at a low pulp consistency, e.g. 3–4% (Sharma et al., 2014), which was to improve the mixing between the used enzyme and pulp fibers. The medium technology (a pulp consistency of 8–14%), or even high consistency technology (20–35% pulp consistency) have often been practiced in a modern pulp and paper mill, with many advantages, for example, saving water, decreasing operating cost (Zhang et al., 2009). If the cellulase treatment would be performed at a higher pulp consistency, one would expect an improved interaction of cellulase and cellulose, which can then increase the cellulase adsorption, thus improving the cellulase efficiency (Liu et al., 2011). In fact, the high consistency enzymatic treatment of biomass was studied in the lignocellulose bioconversion process. Zhang et al. (2009) reported that a higher glucose content of 158 g/L was achieved at a 20% lignocellulose substrate concentration (a 750% higher than that of 2% lignocellulose concentration). Várnai et al. (2013) observed that increasing the substrate concentration during the enzymatic hydrolysis can increase the enzyme adsorption, thus improving the hydrolysis efficiency when studying the enzymatic hydrolysis of lignocellulose. Similarly, Le Costaouec et al. (2013) found the increased cellulase adsorption onto Avicel at 20% Avicel concentration than at 10% Avicel concentration.

Cellulase treatment of PHK – based dissolving pulp to improve its properties, e.g. viscosity control, Fock reactivity, etc., has a significant commercial potential; how to improve the process will be critical for its commercial viability. In this project, we studied the high consistency cellulase treatment technology to improve its performance. The hypothesis was that a high pulp consistency during the cellulase treatment can improve the interactions between cellulase and cellulose, which can lead to the enhancement of cellulase adsorption, hence improving the cellulase treatment efficiency. The scope of this study was to further improve the cellulase treatment technology of dissolving pulp for the purpose of control the pulp viscosity and reactivity, so that it is more commercially relevant. The proposed high consistency condition can not only improve the cellulase treatment efficiency, but also decrease the overall production costs by using less water, less energy, and less effluent treatment.

2. Methods

2.1. Materials

FiberCare D, a customized blend of cellulases that contains high levels of selected endoglucanases, was provided by Novozymes A/S (Denmark) and used as received. The cellulolytic activity of the cellulase was 35,000 U/mL as reported in our early paper (Wang et al., 2015). All other chemicals used were of ACS reagent grade and purchased from Sigma–Aldrich. Deionized water was used for all the experiments.

Bleached hardwood dissolving pulp was provided by a mill using pre-hydrolysis kraft-based production process in Eastern Canada, and the characteristics were alpha cellulose content of 95.6%, intrinsic viscosity of 566.5 mL/g and Fock reactivity of 49.3%.

2.2. Cellulase adsorption determination

Coomassie (Bradford) protein assay kit purchased from Fisher Sci. was used for the protein determination. Cellulase adsorption experiment was conducted at pH 4.8 and 25 °C using a shaker at a speed of 200 rpm. The pulp consistency was 3%, 10% and 20% (w/v) at cellulase charge of 10 mg/g pulp. After treatment of 1 h, the free cellulase in supernatant (after 0.45 μm syringe filter) was determined. The cellulase adsorption ratio (q) was calculated according to Eq. (1):

$$q = \frac{c_t - c_f}{c_t} \quad (1)$$

where, c_t and c_f are the total and free cellulase concentrations (mg/mL), respectively.

2.3. Cellulase treatment

The cellulase treatment was carried out in plastic bag by using a water bath. The treatment condition of cellulase charge of 1.5 mg/g pulp, pH 4.8 and 55 °C were set for all trials. Pulp consistency was set at 3%, 10%, 20% and 25% (w/v). Hand-kneading was providing for a good mixing of cellulase and fibers. Once the specified reaction time was completed, the sample was filtered and washed, then air-dried in constant temperature-humidity room for further analysis.

2.4. Analytical methods

The cellulose viscosity was determined according to Tappi T 230 om-94 in cupriethylenediamine (CED) solution at 0.5% cellulose concentration. The intrinsic viscosity [η] was then calculated according to a previous study (Mazumder et al., 2000).

Fock reactivity of dissolving pulp was conducted according to the modified method (Tian et al., 2013), in which the xanthation of cellulose was performed at 19 °C in a water bath, and all of the pulp samples were air dried to constant moisture content at constant temperature/humidity room.

S_{10} or S_{18} of pulp samples were determined according to TAPPI T 235 cm-00 using sodium hydroxide solution of 10% or 18% for the extraction.

The molecular weight distribution of samples was determined on a gel permeation chromatography (Waters 600E), equipped with a differential refractometer detector (Waters 410); columns were Waters Styragel HT6E. Prior to the determination, sample was firstly dissolved in the 8% LiCl/ DMAc solution. The mobile phase of 0.5% LiCl/DMAc was pumped into the system at a flow rate of 1 mL/min; the system was operated at column temperature of 55 °C; the injection volume was 10 μL.

3. Results and discussion

3.1. Cellulase adsorption ratio

The amount of cellulase adsorption is known to affect the enzymatic treatment efficiency. Increasing pulp consistency increases the interactions of cellulase and cellulose, therefore, improving the cellulase adsorption onto cellulose fibers. The cellulase adsorption ratio was 59%, 74% and 83% for pulp consistency of 3%, 10% and 20%, respectively. These results were in agreement with the hypothesis that higher pulp consistency will lead to higher cellulase adsorption. Similarly, Várnai et al. (2013) also observed the increases of cellulase adsorption ratio from 50% to 90% at the substrate concentration increases from 1% to 20% during the Avicel bioconversion process.