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Enhancing the Fock reactivity of dissolving pulp by the combined prerefining and poly dimethyl diallyl ammonium chloride-assisted cellulase treatment

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ABSTRACT

Dissolving pulp is an important source of cellulose raw material, and its key quality parameter is the Fock reactivity for viscose rayon application. Cellulase treatment is an effective method for improving the Fock reactivity of kraft-based dissolving pulp. In this study, a novel process concept of improving the cellulase treatment for this purpose was developed, and it consists of mechanical pre-refining and PDADMAC-assisted cellulase treatment. The hypothesis is based on: 1) opening up the fiber structures to improve the cellulase accessibility by pulp prerefining, 2) the addition of cationic poly DADMAC to the subsequent cellulase stage enhances the cellulase adsorption onto anionic fibers due to favorable electrostatic interactions. The results showed that the Fock reactivity of the resultant pulp from the combined treatment is much higher than that of the control, yet, achieved at a much lower cellulase dosage.

1. Introduction

Regenerated cellulose and cellulose derivatives as part of the so-called biorefinery concept have received much attention in recent years. Dissolving pulp as the raw material for producing cellulose derivatives is consistent with the biorefinery concept. Dissolving pulp has a high purity alpha cellulose (90–99%), which can be used for manufacturing viscose rayon, carboxymethyl cellulose, cellulose esters, cellulose ethers and other cellulose derivatives (Jahan et al., 2016; Tang et al., 2014). The production of dissolving pulp has exhibited a significant increase worldwide, particularly in China and Canada.

The global production of dissolving pulp was 5.6 million tons in 2013 and 7.5 million tons in 2015. More than 70% of the produced dissolving pulp around the world is used to manufacture viscose staple alone (Kumar and Christopher, 2017). In the viscose production process, the Fock reactivity of dissolving pulp is a key quality parameter. Dissolving pulp with a high reactivity can produce high-quality products with low demands of carbon disulfide, allowing a cost-effective production and low environmental impact (Ibarra et al., 2010). In order to do so, various treatments such as ultrasonic, oxidative hydrothermal, grinding or refining, and enzymatic, have been investigated (Koutu et al., 2001; Miao et al., 2015; Tian et al., 2014; Wang et al., 2014; Zhao et al., 2017). Among them, the cellulase treatment is an effective, mild and green method, which can not only improve the cellulose reactivity but also fine-tune the degree of polymerization of cellulose. For example, Duan et al. (2016) reported that cellulase can replace hypochlorite in the bleach plant, resulting in a higher Fock reactivity (from 46.7% to 72.0%).

However, the cost of cellulase is an obstacle to industrialization (Wang et al., 2016). Enzymes, such as cellulase, are biocatalysts, hence, enhancing the cellulase accessibility to the fiber structures and its adsorption, would be critical to improve the process efficiency. It has been reported that the cellulase reaction efficiency is dependent on the cellulase adsorption onto the fiber, which is the primary factor for a high effectiveness (Mansfield et al., 1999; Steiner et al., 1988). The pretreatment of the substrate has a significant effect on the adsorption of cellulase (Boussaid and Saddler, 1999). There are two methods to increase the adsorption of cellulase onto pulp fibers, namely, improving the fiber morphological/surface characteristics and using an additive.

The improvement of fiber morphological/surface characteristics can include: (1) breaking the primary fiber cell wall; (2) opening or exposing the voids and pores; (3) splitting the fiber aggregations; (4) increasing fiber fibrillation; (5) shortening the cellulose chains (Li et al., 2012; Schild and Sixta, 2011). These changes will improve the

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accessibility of cellulose fibers, thus, the cellulase adsorption onto fibers. Mechanical refining is an effective method for the above purpose. For example, Tian et al. (2014) improved the reactivity of kraft-based dissolving pulp from 49.27% to 71.75% by grinding for 6 min, or to 58.32% by PFI refining at 25,000 PFI revolutions.

The use of additives is another effective way to enhance the effectiveness of enzymatic treatment. The additive may include surfactants, proteins, and polymers (Lou et al., 2013). For example, Kristensen et al. (2007) reported that non-ionic surfactants and poly(ethylene glycol) can increase the conversion of cellulose to fermentable sugars, with up to 70% yield. Reye et al. (2011) reported that cationic polyacrylamides (CPAMs) increase the binding of cellulase to cellulose, thus the hydrolysis rate of substrates. In the enzymatic treatment, both cellulose and cellulase bear negative charges, which reduces the cellulase adsorption onto cellulose fibers due to electrostatic repulsion between cellulase and cellulose (Wang et al., 2015). If cationic polymer is added, the electrostatic repulsion will be minimized, thus increasing the adsorption of cellulase. Poly(diallyl dimethyl ammonium chloride) (PDADMAC) is a water-soluble cationic polymer with a wide range of molecular weight (MW) distribution, and charge density, and it is widely used in the industry, including the pulp and paper industry, and water treatment.

The two methods have their own advantages, but combining them for the purpose of increasing the efficiency of cellulase treatment for improving the reactivity of dissolving pulp has not been reported yet. In this study, mechanical prerefining and the use of cationic polymer (PDADMAC) as an additive, were combined to increase the efficiency of cellulase for improving the Fock reactivity of a hardwood kraft-based dissolving pulp, while decreasing the cellulase dosage. The hypothesis is as follows: 1) mechanical prerefining modifies the fiber morphology, exposing more reaction sites to cellulase and increasing the accessibility of fiber; 2) PDADMAC changes the interactions between cellulose and cellulase, and the cellulase adsorption onto fibers is increased on account of the favorable electrostatic attractions.

The combined prerefining and PDADMAC-assisted cellulase treatment has three advantages: 1) intensifying the efficiency of cellulase treatment; 2) improving the Fock reactivity of dissolving pulp; 3) decreasing the cellulase dosage. The cellulase adsorption onto cellulosic fibers was investigated. The cellulase treatment performance was evaluated in terms of reactivity increase and viscosity decrease. The fiber length and width, fines content, specific surface area, molecular weight distribution, and the morphological change of fibers were studied and discussed.

2. Materials and methods

2.1. Materials, cellulase and chemicals

A commercial bleached hardwood kraft-based dissolving pulp was provided by a pulp mill in Shandong province in China. The characteristics of the dissolving pulp were: cellulose content 92.6%, intrinsic viscosity 628.8 mL/g, and Fock reactivity 41.5%. A commercial cellulase FiberCare® was supplied by Novozyme. The activity of FiberCare® was 20000 IU/g, and its highest activity occurred at 40–60 °C and pH 4–6. PDADMAC (molecular weight 10 kDa, charge density 6.05 meq/g) was provided by a Chemical Company in Shandong province in China. The Fluorescein isothiocyanate (FITC) was purchased from Sigma-Aldrich (Shanghai, China).

2.2. Experimental design

Four different process concepts were studied: 1) the cellulase treatment alone; 2) addition of PDADMAC to the cellulase stage (the so-called PDADMAC assisted cellulase treatment) 3) the refining pretreatment, followed by cellulase treatment; 4) the combined prerefining and PDADMAC- assisted cellulase treatment.

2.2.1. The cellulase treatment alone

Equivalent to 10 g oven dried pulp was soaked in deionized water for 24 h, then disintegrated at the consistency of 2% for 25,000 revolutions. The cellulase treatment was carried out in plastic bags, which were placed in a water bath at 50 °C. The pulp consistency was 5%, and the pH was 4.8. Subsequently, the desired amount of cellulase was added. The time of reaction was 1 h. Hand-kneading was providing for a good mixing of cellulase and fibers. After the enzymatic treatment, the pulp sample was subjected to a hot water (100 °C) treatment for 20 min for denaturing the cellulase, and the sample was filtered, washed and collected for the analyses.

2.2.2. The PDADMAC assisted cellulase treatment

Equivalent to 10 g oven dried pulp was soaked and disintegrated. The pulp consistency was set at 5%. The concentration of PDADAMC solution was set at 1%. Subsequently, 0.5 g of PDADMAC solution and the desired amount of cellulase were added to the pulp. The reaction conditions were same as Section 2.2.1.

2.2.3. The refining pretreatment, followed by cellulase treatment

Mechanical refining pretreatment was performed in a PFI in accordance with Tappi T248sp-08. The pulp sample was impregnated and disintegrated. Then, the equivalent of 30 g oven dried pulp was refined at 10% consistency and 7000 revolutions with a PFI mill. Subsequently, the pulp was treated by cellulase according to Section 2.2.1.

2.2.4. The combined prerefining and PDADMAC- assisted cellulase treatment

Firstly, the pulp was treated with a mechanical refining pretreatment according to Section 2.2.3. Then, the PDADMAC assisted cellulase treatment was carried out according to Section 2.2.2.

2.3. Cellulase adsorption determination

The pulp samples were prepared with different methods according to Section 2.2, wherein the cellulase dosage was 2.0 mg/g (to oven dried pulp). Subsequently, the samples were filtered, and the filtrate was separated by 0.22 μm filter. The protein of free cellulase remaining in the filtrate was determined according to Bradford method (Bradford, 1976). The cellulase adsorption ratio on cellulose was calculated as follows (Yu et al., 2009):

$$\text{Cellulase adsorption ratio } (\%) = (w_1 - w_2) * 100 / w_1$$

where w_1 was the amount of protein of all added cellulase; w_2 was the amount of protein of cellulase in the supernatant.

2.4. Intrinsic viscosity and Fock reactivity determinations

The Fock reactivity of samples was determined based on an improved method (Tian et al., 2013). The intrinsic viscosity was measured according to the T230 om-99 standard. Repeating measurements were performed on some samples to verify the accuracy/repeatability of the analysis.

2.5. Fiber characteristics analyses

Fiber CLSM analysis: cellulase labeling followed an early reported method (Jervis et al., 1997). Briefly, 1 mg FITC was added to 100 g cellulase solution (1% concentration). The pH of mixture was adjusted to 9 by Na_2CO_3/$NaHCO_3$ buffer solution. The mixture was gently shaken in the dark at 4 °C in a biochemical incubator for 12 h. Subsequently, the mixture was transferred to a UF tube to separate unbound FITC. Then, the labeled cellulase was stored in the dark at 4 °C until use. The pulp samples were treated with the labeled cellulase according to Section 2.2, and then they were observed using a CLSM (TCS SP2 Nikon Instrument Inc., Japan).