Enzymatic activation of dissolving pulp with cationic polyacrylamide to enhance cellulase adsorption

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ABSTRACT

Cellulase treatment is a promising technology to improve the properties of dissolving pulp in an environmental friendly way. Increasing the cellulase treatment efficiency is of practical interest. In the present study, the concept of using cationic polyacrylamide (CPAM) to enhance the cellulase treatment efficiency was demonstrated. The hypothesis was that the CPAM would attribute to the increased cellulase adsorption onto cellulose fibers based on the patching/ bridging mechanism. Results showed that the viscosity decrease was improved with the addition of 250 ppm of CPAM under the same conditions as those of the control. Degraded cellulose content was increased based on the alkaline solubility analysis, while alpha- cellulose content kept constant. The CPAM- assisted cellulase treatment concept may provide a practical alternative method for upgrading dissolving pulp.

Keywords: Cellulase treatment; Dissolving pulp; Alkaline solubility; Alpha- cellulose content

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. 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.1,2 The production of cellulose from lignocellulosic biomass (known as dissolving pulp in the paper industry) is increasing, and this is particularly true in China.

The well-commercialized dissolving pulp production includes acid sulfite process and pre-hydrlisis kraft process. Nowadays, the pre-hydrlisis kraft-based production, including both batch and continuous processes, has been growing. Additionally, the pre-hydrlisis kraft-based dissolving pulp production may fit well into the integrated forest biorefinery concept. The selective separation of hemicellulose in the form of oligo- and mono- saccharides during the pre-hydrlisis stage has attract numerous interests to produce high value products.3,4

There is a strong commercial interest in improving the quality of dissolving pulp from both the acid-sulfite and the pre-hydrlisis kraft-based processes. Enzyme treatment is a promising approach to decrease the viscosity and increase the reactivity, which can shorten/eliminate the pre-aging stage and decrease carbon disulfide dose. Many studies have been conducted for these purposes. For example, Kvarnlöf et al.5 adopted Carezyme treatment to decrease the viscosity of bleached sulfite spruce dissolving pulp for reducing chemical demand in the etherification stage. Miao et al.6 employed cellulase to increase the Fock reactivity of hardwood kraft-based dissolving pulp.

The enhancement of cellulase treatment efficiency is of practical interest to commercialize the process from both economics and technical feasibility. The initial cellulase adsorption is a prerequisite step in enhancing the cellulase treatment efficiency. It has been reported that the enzymatic hydrolysis reaction starts rapidly followed by a slow phase, which was proportional to the amount of cellulase that is sorbed.7,8 However, both cellulose and cellulase bear negative charges, which can reduce the cellulase adsorption onto cellulose fibers due to electrostatic repulsion. Cationic polyacrylamide (CPAM) possess high density of positive charges, which has been used in the papermaking process as an effective retention aid, can improve the cellulase adsorption onto cellulose fibers based on the bridging/patching mechanism. The charge neutralization mechanism of CPAM has been well established and used.

CPAM has been used in papermaking and waste water treatment process,9,10 most recently it was shown that CPAM can improve the enzymatic hydrolysis in the conversion of cellulose to ethanol in the field of biorefinery. However, the utilization of CPAM to enhance cellulase treatment efficiency for improving the quality of dissolving pulp has not been reported. The present study explored the potential of using CPAM to enhance the cellulase treatment
efficiency for the purpose of improving the quality of dissolving pulp.

2. EXPERIMENTAL

2.1 Materials

Bleached hardwood dissolving pulp sheets were received from a mill using pre-hydrolysis kraft-based production process. The characteristics of the dissolving pulp were: α-cellulose content 95.6%, intrinsic viscosity 566.5 mL/g.

FiberCare D, an endoglucanase-rich cellulase was provided by Novozymes A/S (Denmark). The cellulase activity is 35000 U/mL determined by sodium carboxymethyl cellulose activity. Cationic polyacrylamide (CPAM, molecular weight 1 MDa) was received from BASF, which was dissolved in water at 2 g/L prior to use. The CPAM charge was set at 250 mg/L, which was optimized from a set of experiments. Bis(ethylenediamine)copper(II) hydroxide solution of 1.0 M was purchased from Sigma-Aldrich. Deionized water was used for all the experiments.

2.2 Cellulase treatment

The enzymatic treatment experiments were carried out in plastic bags, which were placed in a water bath at temperature of 55 °C. Initially, 10 g (equivalent to oven dried) pulp was used, well disintegrated, and its pulp consistency was set at 3%. The pH of the pulp suspension was 4.8 for all trials. Subsequently, the desired amount of cellulase (0.5, 1, and 1.5 mg/g pulp) was added, followed by the addition of 41.5 mL of CPAM solution and thorough mixing. The treatment time was varied from 0.5 h to 48 h. Hand-kneading was provided to ensure a good mixing during the treatment. At the completion of the treatment, the pulp was filtered, washed and collected for further analyses.

2.3 Analysis methods

The cellulose viscosity was determined according to Tappi T 230 om-94 in cupriethylenediamine (CED) solution at 0.5% cellulose concentration. All measurements were carried out in duplicates, and the average was reported.

S10 or S18 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 by following a literature procedure on a GPC (Waters 600E), equipped with a differential refractometer detector (Waters 410), a Waters Styragel HT6E column was used.

3. RESULTS AND DISCUSSION

3.1 Proposed concept of CPAM-assisted cellulase treatment of dissolving pulp

CPAM is positively charged (+0.41 meq/g), while the charge density at pH 4.8 for cellulose and cellulase was -0.09 and -0.08 meq/g, respectively. Cellulase is a protein-based amphoteric molecule with both acidic and basic functional groups, and the electronegativity depends on the system pH. The proposed mechanism of CPAM to enhance the cellulase treatment of dissolving pulp is illustrated in our previous study. Cellulase adsorption onto cellulosic fibers is based on the electrostatic interactions. Due to the fact that both cellulase and cellulosic fibers bear negative charges, there would be repulsion force between the two, hence reducing the cellulase adsorption. By adding cationic polymers, such as CPAM to the system, the cellulase adsorption could increase through the patching/bridging mechanism, thus enhancing the cellulase adsorption.

3.2 Alkaline solubility

Fig. 1. Effect of cellulase treatment on the alkaline solubility of dissolving pulp

The alkali solubility data of dissolving pulp, i.e. S18 and S10-S18 represent the contents of hemicelluloses and degraded cellulose, respectively. As can be seen from Figure 1, the hemicellulose content was rather constant during the enzymatic treatment whether CPAM was added or not, while the degraded cellulose increased somewhat at a higher cellulase dosage and/or extending the treatment.
time. What’s more, the CPAM addition further increased the degraded cellulose content as indicated by the higher difference between the S10 and S18 values. The pulp yield was maintained at a high level (>99%). This is expected because CPAM addition increased the adsorption of cellulase onto cellulose, in particular in the cellulose amorphous region to depolymerize the cellulose chain, but without extensive hydrolysis to affect the yield.

3.3 Alpha-cellulose content

Fig. 2. Effect of cellulase treatment on the alpha-cellulose content

Alpha-cellulose is one of the important quality parameters for dissolving pulp, which was present in Figure 2. As can be seen, the alpha-cellulose content kept constant during the cellulase treatment at various treatment times, whether CPAM was added or not. A slight decrease of alpha-cellulose was observed when the treatment time was extended to 24 h, probably due to cellulose degradation. Wang et al.\textsuperscript{15} also observed a decrease of alpha cellulose content when using endoglucanases rich cellulase to treat paper grade bleached softwood pulp to upgrade it to dissolving grade.

3.4 Molecular weight distribution

The uniform molecular weight distribution (MWD) of dissolving pulp is one of the primary parameter that affects the cellulose processability and the end-use properties of the cellulose-derived end products. All MWD showed a single narrow peak of cellulose, while the original pulp has a higher molecular mass. After the cellulase treatment, the cellulose peak shifted towards the low molecular mass region, and the sample obtained from the CPAM-assisted process showed a greater shift although at a lower cellulase charge according to our previous study.\textsuperscript{12} all these were in agreement with the viscosity decrease data discussed earlier, suggesting that the CPAM addition enhanced the enzymatic actions on the cellulose chain. Engström et al.\textsuperscript{16} observed that the cellulose peak shifted towards the low molecular mass region after cellulase treatment, when using Novozyme 476 to treat an acid sulfite pulp made from the mixture of Norway spruce and Scots pine.

![Molecular weight distribution](image)

Fig. 3. Molecular weight distribution of the dissolving pulp before and after the cellulase treatment with or without CPAM addition

4. CONCLUSIONS

The cellulase treatment efficiency of dissolving pulp was enhanced with the addition of CPAM, in terms of viscosity decrease and alkaline solubility increase. Results showed that the cellulase treatment with CPAM addition gave a much lower viscosity in comparison with the control under otherwise the same conditions. With the addition of CPAM, the S18 alkaline solubility was almost unchanged, while the difference of S10 and S18 increased significantly. CPAM addition had little effect on the alpha-cellulose content of the cellulase-treated pulp, but it caused the molecular weight distribution to shift to lower molecular mass region, which is desirable for high quality dissolving pulp.

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