

Kinetics of Viscosity Decrease by Cellulase Treatment of Bleached Hardwood Kraft-Based Dissolving Pulp

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A dissolving pulp of low cellulose viscosity represents a pulp of high quality; hence, it is often necessary to decrease the initial dissolving pulp viscosity. One so-called environmentally friendly approach to further reducing the dissolving pulp viscosity is to treat the dissolving pulp with cellulase enzymes. In this study, the kinetics of the decrease in cellulose viscosity during a cellulase treatment was investigated. The study showed that the kinetics of the cellulose degradation during a cellulase treatment can be divided into at least two phases, where the initial phase is very fast and the final phase is very slow. The kinetic two-phase model for the viscosity degradation that has been developed in this project can be used to predict and control the final pulp viscosity of dissolving pulps.

Keywords: Dissolving pulp; Cellulose; Viscosity; Kinetics; Cellulase treatment

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INTRODUCTION

Effective fractionation of lignocellulosic material into its three main components (*i.e.*, cellulose, hemicellulose, and lignin) is necessary to produce a broad range of products, such as bio-based material, chemicals, and energy, which form the base for the integrated forest-based biorefinery concept (van Heiningen 2006; Peng *et al.* 2011). Commercial kraft-based dissolving pulp production naturally fits into this concept (Yang *et al.* 2012; Miao *et al.* 2014).

Dissolving pulp contains a high amount of cellulose (92% to 99%), while the level of impurities such as hemicellulose, lignin, extractives, and minerals is low, even negligible. Cellulose in this process is a platform material that can be further converted to such value-added products as regenerated cellulose (rayon), cellulose esters (acetate, nitrate), cellulose ethers, or cellulose nanocrystals (CNCs) (Jahan *et al.* 2011; Tang *et al.* 2014). In many of the downstream processes, *e.g.*, rayon, the cellulose viscosity is a critical parameter for processing and final product quality (Rahkamo *et al.* 1998).

In many applications, the cellulose viscosity would need to be further decreased prior to post-chemical processing, *e.g.*, xanthation in the viscose rayon process. For this reason, the cellulase treatment technology is considered in the present study. In the literature, cellulase has been used for the treatment of dissolving pulp for different purposes. Kvarnlöf *et al.* (2007) adopted Carezyme to treat bleached sulfite spruce dissolving pulp for reducing chemical demand in the etherification stage and found that the viscosity decreased from 15 mPa·s to 10 mPa·s at a cellulase charge of 4500 ECU/g. Wang *et al.* (2014) used cellulase treatment followed by alkaline peroxide treatment for

purifying the cellulose from a bleached softwood kraft pulp and observed that the intrinsic viscosity decreased from 916 to 507 mL/g at a cellulase charge of 300 IU/g and NaOH and H₂O₂ charges of 9% and 1% (based on oven-dried pulp), respectively.

Although many studies related to cellulase treatment on dissolving pulp have been conducted, there are no reports on the kinetics of the viscosity decrease as a result of cellulase treatment, which is one of the key issues when using cellulase to control the viscosity. In this study, the objective was to increase the knowledge on the kinetics of cellulose viscosity reduction during cellulase treatment. The pulp used was a Canadian hardwood dissolving kraft pulp, and the study focused on two parameters, *i.e.*, cellulase charge and treatment time.

EXPERIMENTAL

Materials

A sample of bleached hardwood pre-hydrolysis kraft-based dissolving pulp was provided by a mill in Eastern Canada. The alpha cellulose content was 95.6%, and the intrinsic viscosity was 566.5 mL/g.

An endoglucanase-rich cellulase (FiberCare D) sample was supplied by Novozymes A/S (Denmark), and the cellulase sample was used without any further purification. A 1.0 M bis(ethylenediamine) copper(II) hydroxide solution was purchased from Sigma-Aldrich. Deionized water was used for all the experiments.

Methods

Enzymatic treatment of bleached hardwood kraft-based dissolving pulp

Enzymatic treatment experiments were carried out in plastic bags, which were placed in a water bath at a temperature of 55 °C. Initially, 20 g (equivalent to oven-dried) of 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 2 mg/g o.d. pulp) was added and thoroughly mixed. The treatment time varied from 20 min to 72 h. The bags were hand-kneaded every 30 min for the first 2 h to ensure good mixing during the treatment. At the completion of the treatment, the pulp was filtered, washed, and collected for further analyses.

Determination of pulp intrinsic viscosity and degree of polymerization (DP)

The cellulose viscosity (unit in mPa·s) was determined according to TAPPI T 230 om-94 (1994) in cupriethylenediamine (CED) solution at 0.5% cellulose concentration. All measurements were performed twice, and the average was reported.

The intrinsic viscosity $[\eta]$ (unit in mL/g) was then calculated based on Eq. 1 (Mazumder *et al.* 2000):

$$[\eta] = 954 \times \lg(\text{viscosity}) - 325 \quad (1)$$

The average degree of polymerization (*DP*) was calculated from the intrinsic viscosity using Eq. 2 (Sihtola *et al.* 1963):

$$DP^{0.905} = 0.75[\eta] \quad (2)$$

RESULTS AND DISCUSSION

Cellulose Chain Scission due to Cellulase Treatment

A schematic of cellulase treatment and its effects on dissolving pulp is presented in Fig. 1. It is expected that the cellulose amorphous region is easily accessed by cellulase, which will lead to fast cellulose degradation. On the other hand, the cellulose crystalline region is much less accessible to cellulase, but given enough time, some cellulose degradation by cellulase would also be expected. In the literature (Hall *et al.* 2010), it was reported that the initial crystallinity degree of cellulose plays a major role in determining the enzymatic hydrolysis rate in the saccharification process for the purpose of producing bio-ethanol.

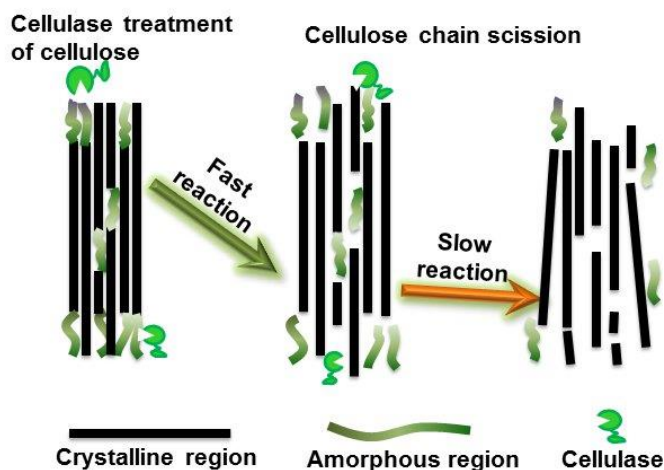


Fig. 1. Hypothesis of cellulose chain scission due to cellulase treatment

The effect of cellulase treatment on the intrinsic viscosity of the bleached hardwood kraft-based dissolving pulp is shown in Fig. 2. At least two phases can be identified: an initial fast phase, followed by a second slow phase. The majority of the decrease in viscosity occurred in the first 12 h for all three cellulase charges, which may be related to the extensive cellulose degradation in the amorphous regions.

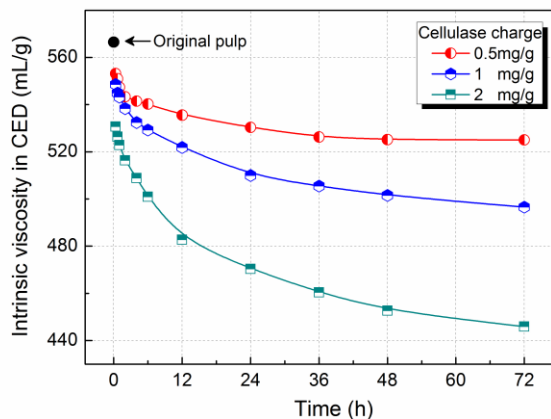


Fig. 2. Decrease in cellulose intrinsic viscosity during the cellulase treatment. Other conditions: temperature 55 °C, pulp consistency 3%, pH 4.8

By extending the enzymatic treatment time to 72 h, the viscosity decreased further. It is therefore clear that degradation from cellulase treatment can lead to a significant decrease in viscosity. Similarly, a viscosity decrease from 517 to 489 mL/g was reported by Henriksson *et al.* (2005) when using endoglucanase to increase the reactivity of softwood sulphite dissolving pulp. Miao *et al.* (2014) also observed a viscosity decrease from 634.8 to 490.8 mL/g after cellulase treatment of hardwood kraft-based dissolving pulp at a cellulase charge of 0.5 U/g.

Development of Kinetic Model

The cellulase-induced viscosity decrease is a result of cellulose depolymerization. In the literature, it was reported that the overall process of cellulase treatment involves: cellulase adsorption into the cellulose, formation of cellulose-enzyme complexes, breakdown at the interactions, and ultimately dissociation (Johnson and Goody 2011). A generic reaction of cellulose depolymerization due to enzymatic degradation may be considered as:



The cellulase-induced cellulose degradation reaction can be expressed based on the cellulose chain scission according to a reported study in the literature (Calvini 2014). In the present case, the reaction is affected by the cellulase charge; therefore, the kinetic equation is as follows,

$$v = \frac{d[\text{Chain}]}{dt} = k[\text{Cellulase}]^a [\text{Bond}] \quad (4)$$

where [Chain] is the concentration of the cellulose chain, t is the cellulase treatment time (h), k is the rate constant of the reaction between cellulase and cellulose, [Cellulase] is the cellulase concentration (mg/g), a represents the exponent of [Cellulase] (Tu *et al.* 2008), and [Bond] is the concentration of cellulose glycosidic bonds.

The concentration of cellulose chains ([Chain]) is equal to [Bond]/ DP , where DP is the degree of polymerization of the cellulose chains (Zhang *et al.* 2000). The cellulase-induced cellulose degradation reaction can be expressed based on the cellulose chain scission according to a reported study in the literature (Calvini 2014). In the present case, the reaction is affected by the cellulase charge; therefore, the kinetic equation is as follows:

$$d\left[\frac{1}{DP}\right] = k[\text{Cellulase}]^a dt \quad (5)$$

Integrating Eq. 5, the kinetic equation was obtained as Eq. 6,

$$\frac{1}{DP} - \frac{1}{DP_{ini}} = k[\text{Cellulase}]^a t \quad (6)$$

where DP and DP_{ini} are the average degree of polymerization at a time “ t ” and $t = 0$, respectively.

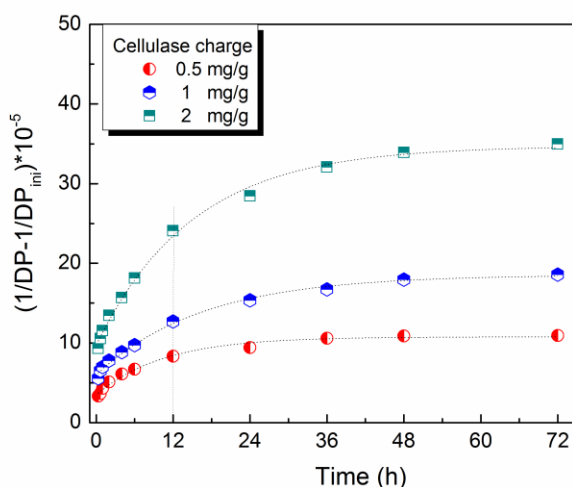


Fig. 3. Cellulose depolymerization due to cellulase treatment. Other conditions: temperature 55 °C, pulp consistency 3%, pH 4.8

The plot of $1/DP - 1/DP_{ini}$ against time (Fig. 3) based on Eq. 6 is an exponential model; this supports the hypothesis that the cellulose chain scission progress included two distinct phases. During the first 12 h, the reaction rate for all cellulase charges was higher than that of the second phase. Equation 7 was assumed for the k decrease by a typical first type process, as proposed by Emsley *et al.* (1997),

$$k = Ke^{-bt} \quad (7)$$

where K and b are constants; substituting Eq. 7 into Eq. 6, leads to Eq. 8:

$$\frac{1}{DP} - \frac{1}{DP_{ini}} = K[\text{Cellulase}]^a(1 - e^{-bt}) \quad (8)$$

The parameters K , a , and b (Eq. 8) were obtained by the nonlinear curve fitting procedure of Matlab (R2010b) based on the experimental data. Thus, the kinetic parameters of K , a , and b were found to be 1.26×10^{-4} , 0.83, and, 0.22, respectively. The kinetic model of intrinsic viscosity of cellulase treatment was obtained by substituting Eq. 2 into Eq. 8 and is shown in Fig. 4. Equation 8 corresponds to the approximate pseudo zero-order Ekenstam equation.

Model Prediction

In order to verify the reliability of unavoidable approximations, another set of independent data for the same dissolving pulp was obtained by varying the cellulase charge and treatment time.

The intrinsic viscosity of the model calculated data and the experimentally measured results are presented in Fig. 4. It can be seen that the two sets of data correlate, implying that the model can be used for prediction of the viscosity under the conditions studied.

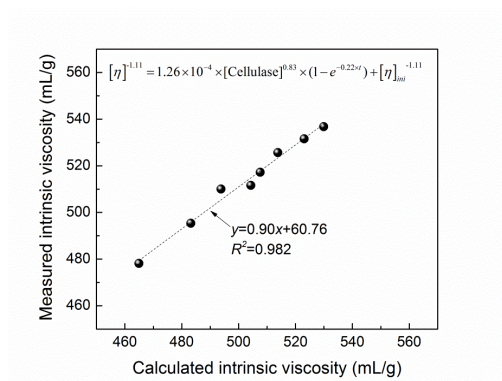


Fig. 4. Comparison of experimentally determined viscosity and model prediction during cellulase treatment. Conditions: cellulase charge of 0.8, 1, 1.5 and 2 mg/g; time of 5 and 20 h; temperature of 55 °C; pulp consistency of 3%; pH 4.8

CONCLUSIONS

1. A kinetic model was developed that details the relationship between the cellulose viscosity decrease and the cellulase charge and treatment time during the cellulase treatment.
2. The kinetics of the viscosity decrease includes at least two phases, *i.e.*, a first fast phase and a second slow phase. The established model can predict the viscosity development very well from the changes in the cellulase charge and treatment time.

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