Bioresource Technology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Fractionation and cellulase treatment for enhancing the properties of kraft-based dissolving pulp

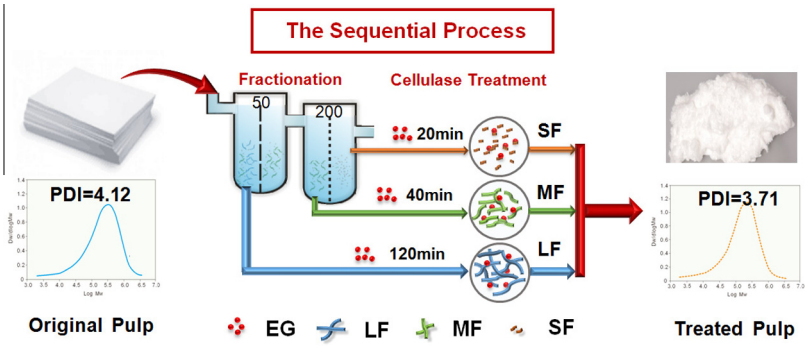
Chao Duan [a,b,*], Xinqi Wang [a], YanLing Zhang [a], Yongjian Xu [a], Yonghao Ni [a,b]

[a] College of Bioresources Chemical and Materials Engineering, Shaanxi University of Science and Technology, Xi'an 710021, China
[b] Limerick Pulp and Paper Centre, University of New Brunswick, Fredericton, New Brunswick E3B 5A3, Canada

HIGHLIGHTS

- A combined process to improve MWD and reactivity of dissolving pulp was proposed.
- Pulp fractionation and cellulase treatment of each fraction were involved in the combined process.
- The SF had the highest accessibility and highest cellulase adsorption capacity.
- The proposed process led to a narrower MWD and a higher reactivity due to more homogenous reactions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 October 2016
Received in revised form 22 October 2016
Accepted 25 October 2016
Available online xxxx

Keywords:
Dissolving pulp
Kraft-based process
Fractionation
Cellulase treatment
Molecular weight distribution
Fock reactivity

ABSTRACT

The aim of this study was to investigate a combined process involving pulp fractionation and cellulase treatment of each fraction for improving the molecular weight distribution (MWD) and reactivity of a kraft-based dissolving pulp. Three pulp fractions, namely long-fiber, mid-fiber and short-fiber fractions (LF, MF and SF, respectively), were used as the substrates. The results showed that the SF had the highest accessibility, lowest viscosity, and highest cellulase adsorption capacity, while the opposite was true for the LF. At a given viscosity, the combined process led to a lower polydispersity index (3.71 vs 4.98) and a higher Fock reactivity (85.6% vs 76.3%), in comparison to the conventional single-stage cellulase treatment.

1. Introduction

Dissolving pulp (i.e., lignocellulose-derived pulp with a high cellulose content) has attracted intensive interest in recent years due to its green and sustainable nature for many applications, including cellulose rayon, cellulose esters, cellulose ethers, and other cellulose-based new products (e.g. cellulose nano-crystals, cellulose filaments) (Miao et al., 2014; Sixta et al., 2013; Wang et al., 2015a). As a dominant consumer, viscose rayon manufacturers always have a high demand for the quality parameters of dissolving pulp (e.g. a narrow molecular weight distribution and a high reactivity), to ensure homogenous and efficient reactions in downstream processes, such as mercerization and xanthation (Ibarra et al., 2010b; Strunk et al., 2011; Tian et al., 2014). However, in practice, in order to mitigate the material shortage and save the cost, mills often manufacture the dissolving pulp using mixed

* Corresponding author at: College of Bioresources Chemical and Materials Engineering, Shaanxi University of Science and Technology, Xi'an 710021, China.
E-mail address: duanchaonba@126.com (C. Duan).

http://dx.doi.org/10.1016/j.biortech.2016.10.077
0960-8524/

wood chips as their feedstock, which results in products with poor homogeneity (Chen et al., 2016; Duan et al., 2015a).

Wood-derived pulp fibers can be fractionated based on fiber sizes to minimize the size-induced differentiation, and the fractionation treatment has been practiced or demonstrated in terms of pulp and paper production (Abubakr et al., 1995; Lei et al., 2013; Li et al., 2015). For the paper industry, Abubakr et al. (1995) studied the fractionation of mixed office waste fibers to upgrade fiber quality, and found that fractionation was effective in upgrading the long-fiber component, thus increasing the strength indices of paper. In the area of dissolving pulp, Li et al. (2015) developed a sequential process consisting of fiber fractionation and followed by cold alkali extraction (CCE), and the results showed that hemicelluloses removal for the long-fiber fraction was more pronounced than the short-fiber fraction.

Recently, cellulase treatment has shown to be effective in improving the critical properties of kraft-based dissolving pulp because it can not only adjust pulp viscosity, but also enhance pulp reactivity (Duan et al., 2016; Engstrom et al., 2006; Gehmayr and Sixta, 2012; Wang et al., 2015b). The efficiency of cellulase treatment is closely related to substrate-related factors: the intimate contact between enzyme and cellulose is the prerequisite for efficient enzymatic treatment (Arantes and Saddler, 2011; Meng and Ragauskas, 2014). For dissolving pulp, cellulose accessibility is mainly governed by fiber morphology, crystallinity and degree of polymerization (DP), etc. (Duan et al., 2015a; Gehmayr and Sixta, 2012; Leu and Zhu, 2012). Generally, the cellulase preferentially adsorbs onto substrates with a high cellulose accessibility, and these substrates can be characteristic of smaller size, high specific surface area, large porosity, and low crystallinity (Ju et al., 2013; Ko et al., 2011).

The objective of this study was to develop a sequential process consisting of pulp fractionation and cellulase treatment to improve the molecular weight distribution and reactivity of kraft-based dissolving pulp. The effect of pulp fractionation on cellulase treatment efficiency was investigated. Three fiber fractions, namely long-fiber fraction (LF), mid-fiber fraction (MF), and short-fiber fraction (SF), fractioned from a kraft-based dissolving pulp, were used for this purpose. Cellulose accessibility, cellulase adsorption, and viscosity reduction (chain scission) kinetics of each fiber fraction were also discussed.

2. Experimental

2.1. Materials

A commercial hardwood-derived dissolving pulp from the prehydrolysis kraft-based process was provided by a pulp mill in Eastern Canada. The whole pulp (WP) was subjected to rewetting and dispersion, and then used for the preparation of the three fiber fractions, namely the long-fiber fraction (LF), mid-fiber fraction (MF), and short-fiber fraction (SF), respectively. All the samples were stored in sealed plastic bags and refrigerated prior to subsequent treatments and analyses. The properties of pulp samples with respect to yield, purity, viscosity and Fock reactivity are listed in Table 1.

A commercial endoglucanase-rich cellulase (FiberCare D, EG) was supplied by Novozymes A/S (Denmark) and its cellulase activity of 460 U/mL was determined as sodium carboxymethyl cellulose (CMC-Na) activity. The protein concentration of FiberCare D solution was 68 mg protein/mL cellulase, as determined by following the Bradford method using a coomassie protein assay kit that was purchased from Sigma-Aldrich.

2.2. Methods

2.2.1. Pulp fractionation

Fractionation was carried out with a Bauer-McNett fiber classifier (MC Tec Co., Ltd, Giessen, Netherlands) by following Tappi T 233 cm-95. Pulp fibers that were retained on the 50-mesh screen were the LF, those fibers passed through 50-mesh screen but retained on the 200-mesh screen were the MF, while the SF was defined as those fibers that passed through the 200-mesh screen.

2.2.2. Enzyme adsorption kinetics and protein content measurements

The cellulase adsorption experiments were conducted using a buffer (pH 4.8) in a 500 mL beaker placed in a water bath shaker (25 °C, 200 rpm). Approximately 5 g of the slurry was taken out at intervals and filtered through a 0.45 mL syringe membrane to collect the fiber-free permeate. The amount of cellulase adsorbed to pulps was determined as the difference between the initial amount of cellulase added to the beaker and the amount of free cellulase in the aqueous medium.

The amount of free cellulase (protein) was determined by following the Bradford method using bovine serum albumin (BSA) as the standard (Duan et al., 2015b).

2.2.3. Cellulase treatment

Cellulase treatment was conducted using 5 g (oven dry weight) of pulp (whole pulp or each pulp fraction, 10% pulp consistency) at varying treatment times in a citrate buffer system (pH 4.8), and a polyethylene bag placed in a water bath (55 °C) was used. For a homogeneous distribution, cellulase was added to the buffer, and the mixture was then added to the pulp. The cellulase e dosage was 0.23 U/g odp or 0.5 mg cellulase/g odp unless otherwise stated. The samples were periodically taken out of the bath and kneaded for 10 to 15 s, in particular within the initial 10 min. After the completion of the cellulase treatment, the samples were placed in hot water (90 °C) for 15 min to denature the enzymes, and subsequently filtered and washed.

For the conventional process, namely a single-stage cellulase treatment of the whole pulp, 0.5 g of the pulp was treated with 0.5 mg cellulase/g odp for 60 min to obtain a cellulase-treated sample with a viscosity of 460 ml/g.

In the case of the combined process, namely an initial pulp fractionation followed by a cellulase treatment on each fraction, 0.5 g of the LF, MF and SF were treated with 0.5 mg cellulase/g odp for 20, 40 and 120 min to obtain three samples with viscosities of 458, 463 and 465 mL/g, respectively. After that, the three cellulase-treated samples were mixed together based on their weighted percent (shown in Table 1) to re-make the pulp sample with a final viscosity of 462 mL/g. All the cellulase treatment times

Table 1
Characteristics of pulp samples.

Sample	WP	LF	MF	SF
Yield, %	–	62.5 ± 0.5	26.1 ± 0.3	11.4 ± 0.2
Glucose, %	94.76 ± 0.25	95.39 ± 0.22	94.02 ± 0.32	93.03 ± 0.28
Hemicellulose, %	4.43 ± 0.08	4.02 ± 0.10	5.21 ± 0.12	6.45 ± 0.13
Intrinsic viscosity, g/mL	560 ± 4	591 ± 5	548 ± 4	500 ± 3
Fock reactivity, %	48.9 ± 0.4	45.5 ± 0.2	42.3 ± 0.3	56.4 ± 0.4

Please cite this article in press as: Duan, C., et al. Fractionation and cellulase treatment for enhancing the properties of kraft-based dissolving pulp. Bioresour. Technol. (2016), http://dx.doi.org/10.1016/j.biortech.2016.10.077