



Increasing efficiency of enzymatic hemicellulose removal from bamboo for production of high-grade dissolving pulp



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HIGHLIGHTS

- Sequential refining-xylanase treatment upgraded bamboo dissolving pulp.
- Mechanical refining improved the accessibility of xylan to enzymes.
- Combined refining-xylanase treatment improved delignification during bleaching.
- Proposed process increased reactivity and brightness of the final pulp.

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ABSTRACT

To improve the efficiency of enzymatic hemicellulose removal from bamboo pre-hydrolysis kraft pulp, mechanical refining was conducted prior to enzyme treatment. Refining significantly improved the subsequent hemicellulose removal efficiency by xylanase treatment. Results showed that when PFI refining was followed by 3 h xylanase treatment, the xylan content of the bamboo pre-hydrolysis kraft pulp (after first stage oxygen delignification) could be decreased to 2.72% (w/w). After bleaching of enzyme treated pulp, the alpha-cellulose content was 93.4% (w/w) while the xylan content was only 2.38%. The effect of refining on fibre properties was investigated in terms of freeness, water retention value, fibre length and fibrillation characteristics. The brightness, reactivity and viscosity were also determined to characterize the quality of final pulp. Results demonstrated the feasibility of combining refining and xylanase treatment to produce high quality bamboo dissolving pulp.

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1. Introduction

With the continuing increase in the population and the limited supply of non-renewable fossil-based resources, the proposed biorefinery concept, in which numerous consumer products are produced from lignocellulosic materials, is of great interest. Dissolving pulp, regenerated cellulose and cellulose-based products made from renewable lignocellulosic biomass are at the forefront of this biorefinery concept. Dissolving pulp is the raw material used in the manufacture of various cellulose-based products, including viscose rayon, cellulose nitrate, cellulose acetate, methyl cellulose, and carboxymethyl cellulose (CMC) (Christov et al., 2000; Hiett, 1985). Viscose rayon is one of the most important raw materials in the textiles industry. Cellulose nitrate can be used to man-

ufacture explosives while cellulose acetate has been used for the production of cigarette filters, eyeglasses frames and photography films. Methyl cellulose and carboxymethyl cellulose (CMC) are widely utilized in the food, pharmaceuticals, and construction industries (Gübitz et al., 1997; Hiett, 1985; Schild and Sixta, 2011). Moreover, the production of nanofibrillated cellulose (NFC), nanocrystalline cellulose (NCC) and microcrystalline cellulose (MCC) from dissolving pulp has been extensively studied (Sixta et al., 2013; Wang et al., 2015).

In general, dissolving pulps are characterized by high alpha-cellulose content and minor amounts of non-cellulosic impurities such as lignin, hemicellulose and ash (Hinck et al., 1985). In addition, uniform molecular weight distribution of alpha-cellulose, high brightness and high reactivity are all important characteristics of dissolving pulp (Hinck et al., 1985; Sixta, 2006). As one of the undesirable components of dissolving pulp, hemicellulose causes several problems in downstream conversion processes

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and adversely affects the final quality of cellulose derivatives. For example, during the viscose rayon manufacturing process, when the hemicellulose content in dissolving pulp is higher than 5% (w/w), the xanthation and filtering stages are adversely affected, and the physical properties of viscose are also negatively affected (Christov and Prior, 1993; Rydholm, 1965). In the production of cellulose ethers, hemicellulose dissolved in the steeping lye greatly impairs the conversion process (Gehmayer et al., 2011). In the case of cellulose acetate, hemicellulose levels even as low as 2.8% in the dissolving pulp can severely affect acetate filterability, dispersion, solution color and can cause thermal instability of the product (Funaki et al., 1993; He et al., 2009; Wilson and Tabke, 1974).

For the production of dissolving pulp, cotton linter, softwoods and hardwoods are the primary raw materials. However, due to the limited availability of land for cotton growth and diminishing wood resources in developing countries, non-woody raw materials have attracted increasing attention. Of the non-woods, bamboo, abundantly available in Asia and South Africa, is considered to be one of the most attractive feedstocks due to its similar chemical composition to that of softwood and hardwood. In the kraft-based dissolving pulp production process, pre-treatment with hot water/steam or dilute acid (named pre-hydrolysis) prior to kraft pulping is used commercially to remove hemicellulose (Kapu and Trajano, 2014; Liu et al., 2010; Sixta, 2006). Although this step is effective in removing hemicellulose from woody materials, in at least some studies it has been observed to be not as equally effective when treating bamboo (Batalha et al., 2012; Colodette et al., 2011). This lower efficiency of hemicellulose removal during pre-hydrolysis of bamboo might be due to differences in chemical composition and anatomical structure (Batalha et al., 2012). Therefore, to develop bamboo as a raw material for producing dissolving pulp, it is necessary to incorporate a hemicellulose removal step after kraft pulping.

Several methods have been investigated to remove hemicellulose from pulp (Christov et al., 2000; Ibarra et al., 2010; Li et al., 2015). Among the used methods, the environmentally friendly enzyme treatment is considered to be one of the most promising due to its selective reaction with hemicellulose without detrimental effects on cellulose. More than 90% of hemicellulose in bamboo is xylan (Salmela et al., 2008), and previous studies have shown that xylan in hardwood and several non-wood pulps could be removed by applying xylanase (Bajpai and Bajpai, 2001; Christov et al., 2000; Gübitz et al., 1997; Ibarra et al., 2010; Köpcke et al., 2010; Roncero et al., 2005; Senior et al., 1988).

However, during xylanase treatment of bamboo pulp, similar to many studies with other lignocellulosic feedstocks, the efficiency of xylanase treatment is not as high as when treating isolated birch xylan (Lian et al., 2012a,b; You et al., 2009a,b). This is probably due to the low accessibility of xylan inside the fibre wall to xylanase. Based on past studies (Lian et al., 2012a,b; Tian et al., 2014), we hypothesized that mechanical refining can lead to fibrillation and increase the accessibility of xylan, thereby promoting the reaction efficiency of xylanase with pulp. The present study used the proposed concept of combining mechanical refining and enzymatic treatments to remove hemicellulose to convert conventional bamboo kraft pulp into high grade dissolving pulp.

2. Material and methods

2.1. Raw materials and chemicals

The wet pre-hydrolysis kraft-based dissolving bamboo pulp, used as the control sample, was provided by Lee and Man Paper Manufacturing Ltd. China. This pulp was prepared by pre-hydrolysis, kraft cooking and oxygen-delignification. The obtained

pulps were thoroughly washed with distilled water at a consistency of 3.5% with a laboratory mixer to remove impurities and produce a homogeneous stock. The washed pulps were centrifuged to a moisture content of 80% and stored in sealed plastic bags at 4 °C for subsequent treatments and analysis. The control pulp used in this study had a kappa number of approximately 6 and a brightness 43% ISO. Its composition was: 87% w/w glucan, 3.5% w/w xylan, 1.5% w/w other polysaccharides (galactan, arabinan, mannan), and 4.6% w/w lignin. Small amounts of other components such as ash and extractives were also present.

A commercial xylanase was provided by Iogen Bio-products Corporation. The supplier recommended a range of xylanase dosage (100–1500 mL/tonne oven dried pulp), reaction temperature (40–75 °C) and pH value (5–8). Its highest activity (2,050,928 nkat/mL) occurred at 70 °C and pH 5.

2.2. Mechanical refining and grinding

The mechanical treatment was performed using a PFI refiner according to TAPPI standard T248 sp-00. A 24 g (equivalent to oven dried) pulp sample was refined at a 10% pulp consistency for 0, 3000, 6000, 7000, 9000, 12,000, and 15,000 revolutions.

Pulp powder was prepared by grinding bamboo pulp, dried for two days in the constant temperature (23 ± 0.5 °C) and humidity (50 ± 1%) room, with a Wiley mill. The pulp powder which passed through a 20 mesh screen was collected for subsequent xylanase treatment and analysis.

2.3. Xylanase treatment

The xylanase treatment was conducted in a water bath. For each sample, 20 g (oven dried weight) of bamboo pulp or pulp powder was treated with 1500 mL xylanase per tonne oven dried (O.D.) pulp at 10% pulp consistency for 1–8 h at 70 °C in citrate buffer (pH 5) in a polyethylene bag. Every 30 min, the samples were removed from the water bath and kneaded 40 times by hand. After the completion of the xylanase treatment, the samples were placed in hot water to boil for 15 min to denature the xylanase, and subsequently filtered and washed with 1 L deionized water three times. The xylanase treated pulp and powder samples were stored at 4 °C for subsequent analyses.

2.4. Pulp bleaching

The dissolving pulp was bleached to full brightness with a D-EP-D sequence, in which D is chlorine dioxide and EP is oxidative extraction reinforced with hydrogen peroxide. Table 1 shows the conditions used for each bleaching stage.

2.5. Compositional analysis

The moisture content of solid samples was measured by drying at 105 ± 2 °C to constant weight. The extractives content of bam-

Table 1
The D-EP-D bleaching conditions.

Conditions	D0	EP	D1
Consistency (%)	10	10	10
Temperature (°C)	70	80	80
Time (min)	90	60	180
ClO ₂ as Cl ₂ (% of dry weight pulp)	1.3	–	0.5
NaOH (% of dry weight pulp)	–	0.6	–
H ₂ O ₂ (% of dry weight pulp)	–	0.3	–
Final pH	2.4	10.8	4.4

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