Separate Treatment of Long Fibres and Fines of Spruce CTMP in Laccase Mediator System Treatment

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Spruce chemithermomechanical pulp was treated with a laccase mediator system (LMS) and alkaline H_2O_2, and the whiteness and dye removal index of the long fibres fraction and fines fraction were compared. The long fibres fraction and fines fraction were treated separately with a LMS, and their whitenesses and strengths were tested. The results indicated that the lignin and extractives contents of the fines fraction were higher than that of the long fibres. Because of the strong adsorption capacity and higher reactive efficiency, the optimal laccase dosage of the fines fraction was lower than that of the long fibres. In the process of treatment using a LMS and alkaline H_2O_2, at the same laccase dosage, separate treatment of the long fibres fraction and fines fraction could improve pulp whiteness and pulp strength.

Keywords: Chemithermomechanical pulp; CTMP; Laccase mediator system; LMS; Fines

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INTRODUCTION

Chemithermomechanical pulp (CTMP) is produced by a relatively mild chemical treatment followed by pressurized refining and is used for the production of fluff pulp, printing paper, hygiene products, and newsprint. Compared with the chemical pulping, the CTMP process not only reduces the cost of the raw materials, but also improves paper quality, such as higher bulk, higher opacity, and better paper formation (Li *et al.* 2006). In the production of CTMP pulp, the fibres are separated from the middle lamella, and the lignin in the middle lamella most likely attaches to or remains on the surface of the adjacent fibres. The extractives also precipitate onto the fibre surface, so the CTMP fibre surface is rich in lignin and extractives, which hinders the formation of hydrogen bonds between fibres (Koljonen *et al.* 2003). Compared with chemical pulp, a higher fines fraction is one of the significant properties of CTMP pulp. The fines contain more lignin and extractives and have a larger specific surface area than long fibres (Karlsson and Agnemo 2010). Fines can enhance pulp network strength and play an important role in sheet formation (Kamaludin *et al.* 2012). Wong *et al.* demonstrated that laccase delignification can increase fibre bonding to enhance the strength of mechanical pulp (Wong *et al.* 2000). This study mainly discusses the treatment of spruce CTMP pulp with a laccase mediator system (LMS) and alkaline H_2O_2, with attention to the LMS treatment of different fibre fractions, *i.e.*, the long fibres fraction and fine fraction. The fractions were separately treated with LMS, the aim was to increase the efficiency of LMS treatment and improve spruce CTMP pulp strength.

EXPERIMENTAL

Materials

Spruce CTMP was kindly provided by Fujian Tengrongda Pulp Co. Ltd. (China). Laccase NS51003 with an activity of 1000 LAMU/g was supplied by Novozymes (Shanghai, China). One LAMU is defined as the amount of enzyme that oxidizes 1 micromole of syringaldazine per minute under standard conditions (pH 7.5; 30 °C). The mediator, 1-hydroxybenzotriazole (HBT), was purchased from J&K Scientific Beijing China. Chemicals (*i.e.*, HAc, NaAc, H_2O_2, NaOH, Na_2SiO_3, $MgSO_4$, and EDTA) were of analytical grade and were obtained from Qianhui Chemical Company (Guangzhou China).

Methods

Refining and screening

The spruce CTMP samples were beaten in a Mark V1 PFI mill (HAM-JERN; Hamar, Norway) at 3000 revolutions according to a standard method (ISO 5264-2 2002). The pulp samples were then fractionated in a Bauer-McNett fractionator (USA) with fibers being greater than 100 mesh and fines less than 100 mesh according to TAPPI method T233 cm-95 (1995). These fractions of pulp samples were stored for the analysis of chemical composition and further treatment.

Pulp treatment by Laccase mediator treatment (L stage)

Laccase mediator system (LMS) treatment of the fractions was carried out in a flask. To accomplish this, 12 g of oven dried pulp (odp) of the fractioned sample was treated with 7 LAMU laccase/g odp and 1.5% odp of HBT in a 50 mM HAc/NaAc buffer with a pH of 5, at 50 °C for 60 min at a 2.5% consistency, and agitated at a speed of 150 rpm. The treatment was aerated with air. After the treatment, the pulp was filtered and thoroughly washed with water.

Pulp treatment by hydrogen peroxide stage (P stage)

The pulp samples obtained from the L stage were subjected to a hydrogen peroxide treatment stage (P stage). To accomplish this, 10 g of pulp at 10% consistency was treated in a plastic bag with 4% odp H_2O_2, 3% Na_2SiO_3, 0.1% $MgSO_4$, 0.3% EDTA, and 4% NaOH at 70 °C for 120 min in each test. The L stage and P stage treatments are illustrated in Fig. 1.

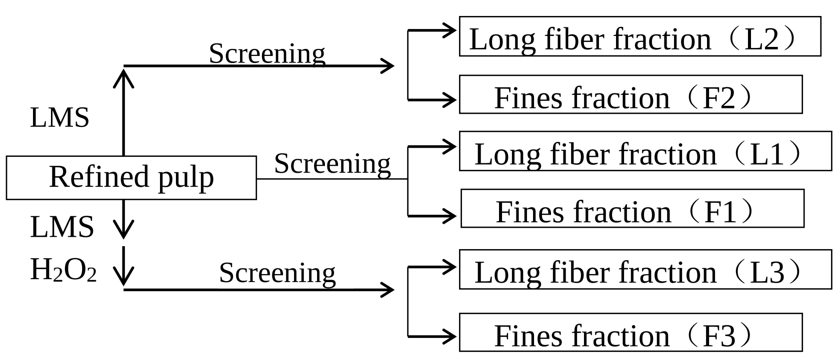

Fig. 1. Flow chart of laccase mediator treatment and peroxide hydrogen bleaching of the long fibres fraction and fines fraction

Chemical component of the fractions

A 3-g odp fraction sample was extracted with acetone for 4 h. The recycled rate of acetone was controlled at 4 times/h, and the acetone extractives were determined. The acid-insoluble lignin content of the fractions was determined according to TAPPI T 222 om-88 (1988).

Determination of optimal laccase dosage

The long fibres fraction and fines fraction were separately treated with LMS. The dosages of laccase were 0, 5, 10, 15, and 20 LAMU/g odp, and the other conditions were the same as the L stage treatment. The optimal laccase dosage was determined based on the whiteness and the dye removal index of the fraction samples

Whiteness, color difference, and dye removal index of the fractions

The fractions treated at different laccase dosages were made into handsheets with a Buchner funnel. The sheets were pressed twice under a pressure of 0.3 MPa and dried for 5 min at 90 °C. The whiteness and L^*, a^*, and b^* values of the handsheets were measured with a Technidyne Color Touch PC instrument (USA). The difference between the color of the pulp fraction and the ideal bleaching point (a^*=b^*=0, L^*=100) is determined by Eq. (1), where L^* is lightness, and a^* and b^* are color.

$$R = (a^{*2} + b^{*2} + (100 - L^*)^2)^{1/2} \tag{1}$$

Dye removal index (DRI) expresses the color reduction of the pulp fractions, shown by Eq. (2), where R_1 is the starting pulp (no laccase added). A negative DRI means the color has darkened, while a positive DRI means the color has lightened (Moldes *et al*. 2008).

$$DRI = -100\left[\left(R_2^2 - R_1^2\right) / R_1^2\right] \tag{2}$$

Comparison between separate and mixed treatment of the fractions in the L stage

The long fibres fraction and fines fraction were separately treated at the optimal laccase dosage; the other conditions were kept the same as in the L stage (Fig. 2).

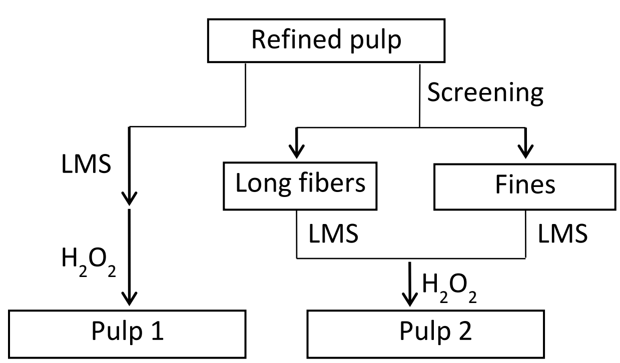

Fig. 2. Flow chart of separate and mixed treatments of the long fibres fraction and fines fraction with LMS

After being filtered and extensively washed, the fractions were mixed and bleached with alkaline H_2O_2, with the other conditions remaining the same as in the P stage. The unfractioned refined pulp sample was treated at the same laccase dosage as that of the separate treatment, and then bleached with alkaline H_2O_2. The process of separate and mixed treatment is illustrated in Fig. 2. The pulp strengths between the separate and mixed treatments were then compared.

Pulp strength

Handsheets with a basis weight of 60 g/m^2 were prepared according to the ISO standard 5269-1 (2005). The mechanical properties, including tensile, burst, and tear strength, were measured according to the ISO standard 5270 (2012).

RESULTS AND DISCUSSION

Chemical Component of the Long Fibres Fraction and Fines Fraction

Screening results indicated that the fines fraction of the spruce CTMP pulp was 35%. The spruce CTMP fibres were separated by pressure force, shear forces, and mechanical friction with mild chemical treatment, which retained most of the lignin. The lignin and acetone extractives contents in the long fibres and fines are shown in Fig. 3. The results indicate that the content of lignin and acetone extractives in the fines fraction (F1) were higher than that of the long fibres fraction (L1). The LMS can attack lignin, breakdown lignin molecular chains, and increase lignin solubility. The LMS can also attack the double bonds of fatty acids and conjugate structure of resin acid, and reduce the extractives content of hydrophilic and lipophilic (Kangas *et al.* 2007). Figure 3 indicates that the laccase mediator system can effectively remove lignin and acetone extractives of fines fraction (F2) and long fibres fraction (L2); however, H_2O_2 removed more lignin and extractives than the laccase mediator. Figure 3 also indicates that in the L stage and P stage, the lignin and extractives contents of the fines fraction (F3) were higher than that of the long fibres fraction (L3).

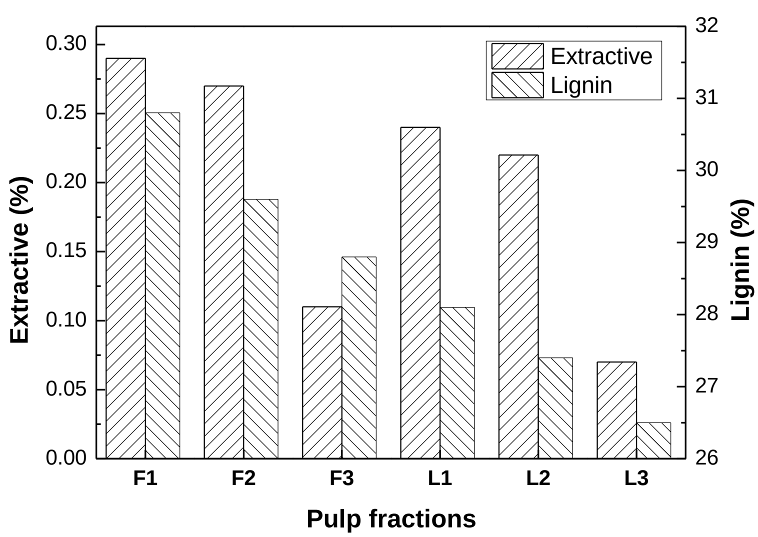

Fig. 3. Lignin and extractives contents of the long fibres fraction and fines fraction of refined pulp (L1, F1), LMS-treated pulp (L2, F2), and LMS+ alkaline H_2O_2 treated pulp (L3, F3)

Determination of the Optimal Laccase Dosage

The quinoniod chromophoric groups generated in the LMS treatment reduced the pulp brightness, so pulp brightness can indirectly reflect the reaction degree of LMS and lignin; with more chromophoric groups, the lower the pulp brightness, and the higher the reaction degree. In order to determine the optimal laccase dosage of the long fibres and fines, the fractions were treated with LMS at laccase dosages of 5%, 10%, 15%, and 20%, and the whiteness of the pulps were compared. The results indicated that the whiteness of the fines was higher than that of the long fibres (Fig. 4). According to the Kubelka-Munk theory, the pulp whiteness depends on the specific light scattering and specific light absorption coefficients (Kubelka *et al.* 1931). The specific light adsorption coefficient of the fines fraction was higher due to its higher lignin content; its specific light scattering coefficient was higher as well because of its larger specific surface area (Brannvall *et al.* 2007). It was speculated that the ratio of specific light absorption and scattering coefficient of the fines was lower, which caused the whiteness of the fines fraction to be higher than that of the long fibres fraction.

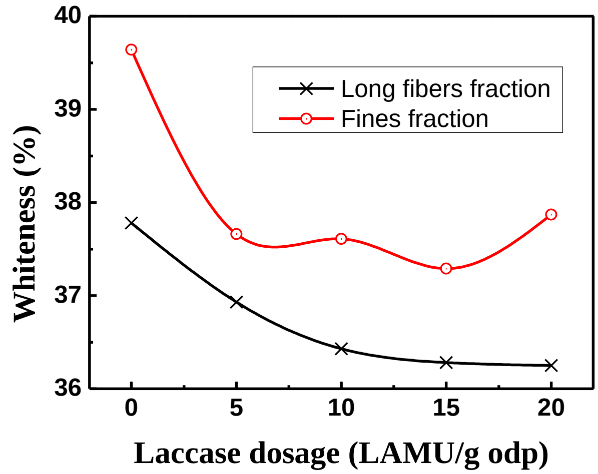

Fig. 4. The whiteness of the fractions treated with LMS

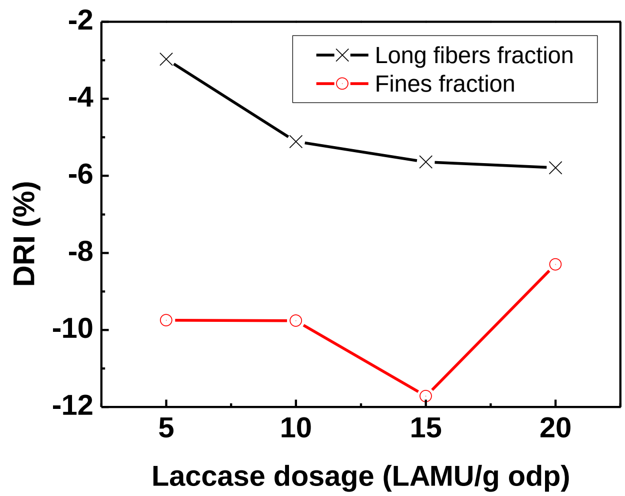

Fig. 5. The dye removal index of the fractions at the different laccase dosages

In the process of LMS treatment, covalent bonds evolved between the HBT and lignin, which made the pulp slightly red; this can be attributed to the quinonoid chromophoric groups produced in the LMS treatment (Yaropolov *et al.* 1994). The whiteness of the long fibres fraction and fines fraction decreased with the increase of laccase dosage (Fig. 4), and the dye removal index was negative and decreased with the increase of laccase dosage (Fig. 5). The whiteness of the long fibres fraction was lowest, and the dye removal index was at a minimum at the laccase dosage of 20%. The whiteness of the fines fraction was lowest and the dye removal index was at a minimum at the laccase dosage of 15%. The fines fraction had a larger specific surface area and strong adsorption capacity, allowing the HBT free radical to make good contact with the lignin thus causing the fines fraction to have a lower laccase dosage.

Comparison of the Pulp Properties

The long fibres fraction and fines fraction were treated separately at the respective optimal laccase dosages, and were then mixed for hydrogen peroxide bleaching. The non-screened pulp was treated with LMS at the same laccase dosage and bleached with hydrogen peroxide. The strength and optical properties of these two kinds pulp (separately treated and mixed treated) were compared. The laccase amount of the non-screened pulp (P = 18.25 LAMU/g) was calculated using Eq. (3), where P_1 is the long fibres fraction (65%), P_2 is the fines fraction (35%), d_1 is the optimal laccase dosage of the long fibres fraction (20 LAMU/g), and d_2 is the optimal laccase dosage of the fines fraction (15 LAMU/g).

$$P=P_1d_1+ P_2d_2 \tag{3}$$

The strength and optical properties of these two kinds of pulp are shown in Table 1. After treatment with LMS and alkaline H_2O_2, the pulp from separate treatment of the long fibres fraction and the fines fraction in L stage had higher pulp properties than pulp produced from the mixed treatment. Compared with the mixed treatment, the separate treatment had an increased tensile index, burst index, and tear index by 15.91%, 5.21%, and 4.65%, respectively, and an increased whiteness by 0.22%. This demonstrates that separate treatment of the fractions in the L stage effectively split the lignin molecular chain, increased lignin solubility, improved fibre flexibility, and increased fibre-fibre bonding.

Table 1. Properties of Pulp Fractions Separately or Mixed Treated with LMS and Mixed Bleached with H_2O_2

Properties	Mixed	Separate	Increase (%)
Whiteness (%)	63.30	63.44	0.22
Tensile index (N·m/g)	12.52	14.51	15.91
Burst index (Pa·m^2/g)	998.06	1050.09	5.21
Tear index (mN·m^2/g)	1.42	1.49	4.65

CONCLUSIONS

1. In the pulp treatment process using laccase mediator system (LMS) and alkaline H_2O_2, separately treating the long fibres fraction and fines fraction with LMS increased the whole pulp whiteness, tensile index, burst index, and tear index, compared with the mixed treatment.
2. The adsorption capacity of the fines fraction was stronger and its optimal laccase dosage was lower than those of the long fibres fraction.
3. The LMS removed the lignin and extractives of the spruce chemithermomechanical pulp (CTMP); however, alkaline H_2O_2 removed more lignin and extractives than the LMS.
4. The content of lignin and extractives of the fines fraction of spruce CTMP was higher than that of the long fibres fraction.

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