$ZnCl_2$ Pretreatment of Bamboo Chips to Produce Chemi-thermomechanical Pulp: Saving Refining Energy and Improving Pulp Properties

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The pretreatment of biomass materials is critical for improvement of the overall production process and product quality. In this work, a dilute zinc chloride ($ZnCl_2$) solution was used to pretreat bamboo chips, followed by defiberization (mechanical pulping). Compared to the results from the traditional chemi-thermomechanical pulping process, the results from this study showed that the refining energy consumption of the modified process was lowered 27%, and the tensile and burst index of the resultant pulp increased 22% and 82%, respectively. The morphological changes on the fiber surface, functional groups, and crystallinity of resultant pulps due to the $ZnCl_2$ treatment were also analyzed.

Keywords: Biomass refinery; $ZnCl_2$; Pretreatment; Swelling; BCTMP; Refining energy; Fiber properties

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INTRODUCTION

High efficiency of biomass utilization with lower energy consumption is one of the most important parameters for converting a pulp mill to an integrated forest biorefinery. Bleached chemi-thermomechanical pulp (BCTMP) has been widely used in different paper grades, and the replacement ratio of BCTMP for chemical pulps has increased significantly in the past decades due to the high pulping yield, low pollution, low cost, and the excellent optical properties of BCTMP (Sundholm 1999; Zhang *et al.* 2007). However, BCTMP has the drawbacks of high refining energy consumption (Liu 2010), low pulp strength (Aricri *et al*. 2012), and high surface lignin (Ma *et al*. 2012).

To reduce the energy consumption of BCTMP, physical, chemical, and biological methods have been explored for the pretreatment of wood chips prior to mechanical refining (Fardim and Duran 2003; Aracri *et al*. 2012; Duan *et al*. 2016). In one study, wood chips were extruded before the chemical pretreatment to increase the specific surface area of the wood chips to facilitate the soaking and softening processes in the chemical pretreatment stage, and thus the refining energy consumption could be reduced (Zhan 2010). In another study, wood chips were treated with a diluted acidic solution to partially remove the lignin, and the refining energy consumption was reduced 20% (Liu *et al*. 2012). Liu *et al.* (2015) reported that the pretreatment of poplar wood chips by auto hydrolysis led to a 26% energy reduction in pressurized refining, and the resultant pulp had higher tensile and tear indices. However, hydrolysis pretreatments are difficult to incorporate into the existing mechanical pulping processes. White-rot fungi have also been used to soften softwood chips by decreasing their lignin contents, and thus the refining energy was reduced (Maijala *et al*. 2008). However, the duration of biological treatments were 2 to 3 weeks, which is too long in comparison with the existing mechanical pulping process. There is a need for an efficient pretreatment process for BCTMP pulping to meet the requirements of biorefinery performance and energy saving.

Zinc chloride ($ZnCl_2$) is a highly effective swelling reagent for biomass, and it has been frequently used for cellulose hydrolysis and derivatization (Almeida *et al.* 2010; Yang *et al.* 2011). The Zn^{2+} ions can diffuse into the amorphous and crystalline regions of cellulose fibers, causing the fibers to swell. With the increase of the swelling degree, the softness and toughness of fibers also increase, leading to the softening of the fibrous biomaterial (Zhang *et al.* 2010). Zinc chloride has been applied to dissolve cellulose fibers for the preparation of cellulose-based functional materials (Yuan *et al.* 2015), to treat the body paper to prepare vulcanized paper (Fischer *et al.* 2003), and to activate biomass for the development of micropores of activated carbon (Simsek *et al.* 2017). Despite considerable interest in zinc chloride aqueous solution as a solvent for cellulose, little has been reported in the literature on using $ZnCl_2$ solution to pretreat wood or bamboo chips to improve the mechanical refining process.

In many developing countries, non-wood biomass, such as straw, bagasse, cotton stalks, and bamboo, are important pulping raw materials (Jahan *et al.* 2012, 2013). The authors' previous work shows that high-strength paper can be prepared by treating bleached bamboo chemical pulp with $ZnCl_2$ solution. The aqueous zinc chloride solution is acidic. Acid-catalyzed hemicellulose hydrolysis may occur during the $ZnCl_2$ pretreatment, which would facilitate the subsequent refining of bamboo chips. Some acid-soluble lignin may be dissolved in the pretreatment (Zhai and Lee 1989). However, this may not explain a major decrease of lignin content. According to our previous tests, under mild treatment condition (*e.g.* $ZnCl_2$ dosage of 6%, temperature of 55 °C, treating time of 30 min), the lignin content in the pulps was about 23.3%, and the removal ratio was about 15.5% through our calculation; however, under drastic conditions (*e.g.* $ZnCl_2$ dosage of 12%, temperature of 70 °C, treating time of 70 min), the lignin content in the pulps was about 21.4%, and the removal ratio was about 28.6%, indicating that the lignin content had been decreased significantly. Even though the ratio was still much lower than that in chemical pulping process (at least 80%, it was not suitable for the preparation of chemi-mechanical pulp.) after the pretreatment and the refiningprocess, as the acid-soluble lignin content was much lower than the acid-insoluble lignin (Lourenco et al. 2012) in bamboo chips.

It has been shown that a portion of the hemicellulose in wood chips can be extracted with $ZnCl_2$ solution (Simkovic *et al.* 1994). Moreover, due to the linkage of lignin-carbohydrate complex (LCC) (Yang 2008), part of the lignin can also be removed along with hemicellulose (Gosselink *et al.* 2004; Wu *et al.* 2012), which results in opening up the cell wall structure followed by the access of $ZnCl_2$into the cellulose. Cao *et al.* (1995) and Weng *et al.* (2004) have shown that $ZnCl_2$ solution can cause cellulose to swell and dissolve. The swelling action of $ZnCl_2$ solution on cellulose fibers is stronger than that of the $NaOH$-Na_2SO_3 solution (Leipner *et al*. 2000; Amarasekara and Ebede 2009; Roy *et al*. 2009). From the analysis mentioned above, during the chemical pretreatment with $ZnCl_2$ solution, the bamboo fibers swell, and part of the cellulose, hemicellulose, and lignin dissolve from bamboo fibers, softening the bamboo chips to facilitate the subsequent refining process, so that less energy is required to separate and develop pulp fibers. Therefore, after the pretreatment with $ZnCl_2$ solution, the bamboo chips became softer and easier to break down into pulp fibers in the refining process. Furthermore, swelling of the fiber cell wall may promote the removal of lignin-rich middle lamella from the fiber surface by the high shear force in the refining zone of the refiner (Sain and Li 2002) and may expose more hydroxyl groups for inter-fiber bonding. Therefore, in the present study, the authors explore a new approach of pretreatment using a low concentration $ZnCl_2$ solution in BCTMP pulping of bamboo chips, with the objectives of saving refining energy and improving pulp properties.

EXPERIMENTAL

Materials

The bamboo chips were obtained from Linan in Zhejiang province, China. The chips were washed and then extruded with an extruder (Andritz, Graz, Austria) (compression ratio of 4:1) followed by air-drying at room temperature for 7days.

All of the chemicals used in this work were analytical grade and were purchased from commercial sources (Huipu Co., Ltd., Hangzhou, China). The $ZnCl_2$ was dissolved in deionized water at a mass ratio of 65:35 ($ZnCl_2$:H_2O), and then stabilized at room temperature for 120 h.

Methods

Preparation of bleached $ZnCl_2$ thermomechanical pulp (BZTMP) and BCTMP

Bamboo chips were washed with running water to remove the dust and scraps, and the washed chips were steamed to remove the air in the chips. Then the steamed chips were extruded and screened to obtain the qualified chips (length smaller than 2.5 cm, width smaller than 2 cm, thickness smaller than 5 mm). The qualified chips were treated withspecified concentrations of$ZnCl_2$ aqueous solution and refined.

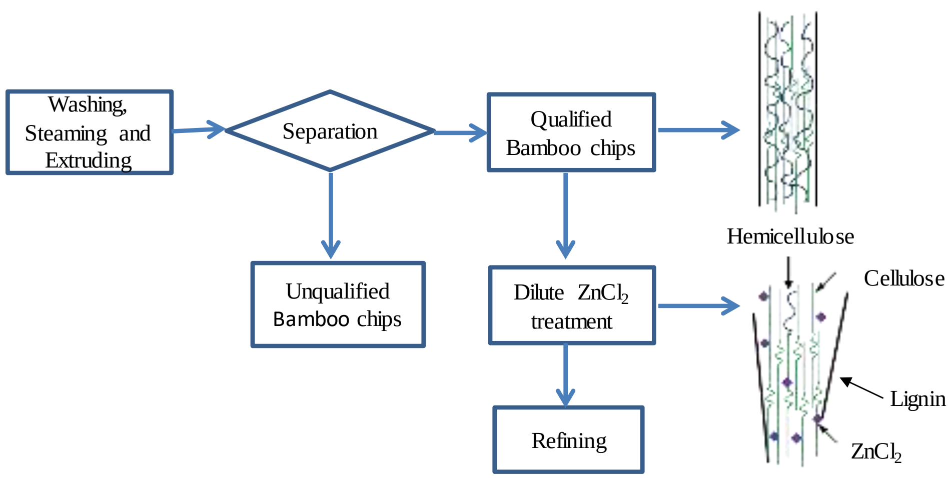

Fig. 1. Flow diagram of the $ZnCl_2$ pretreatment of bamboo chips

First, 100 g of qualified bamboo chips (equivalent to oven-dry) were added to 400 mL of $ZnCl_2$solutionand mixed at room temperature to fully mix the chips with the solution. The mixture was then treated at a higher temperature (Wang *et al*. 2014) and refined to coarse pulp with a refiner (Kumagai Riki Kogyo Company Ltd., Tokyo, Japan), and the refining energy consumption was measured. The control run conditions were: 0% $ZnCl_2$, with water treatment only for 60 min at 65 °C. The coarse pulp was washed and dewatered, and the solid content was measured to obtain the pulp yield.

Then, the coarse pulp was screened with a 100-mesh screen to obtain the accept (passing through the screen) ZTMP (zinc chloride thermal mechanical pulp), and the accept pulp yield was measured. Figure 1 shows the flow diagram of the BZTMP process for bamboo chips.

For comparison, bamboo CTMP (chemical thermal mechanical pulp) was prepared in accordance with a report by Zhan (2010), with the chemical pretreatment conditions of 3% NaOH, 5% Na_2SO_3, and 15 min at 100 °C. For the bleaching of the ZTMP and CTMP, the first stage was performed with 2% H_2O_2 and 1% NaOH, and the second stage with 4% H_2O_2 and 1% NaOH. The obtained pulp fibers were diluted to 3% consistency with hot water (90 °C) and stirred at this temperature for 30 min to remove the latency. Standard lab paper sheets (handsheets) were prepared with the pulp fibers and conditioned at 23 °C and 50% relative humidity for 24 h before testing.

Determination of refining energy consumption

The specific refining energy was based on the bone-dry mass of bamboo chips (100 g). The refining process was performed at 20% pulp consistency, with the rotational speed of the refiner at 2700 rpm and a refining gap of 6 mm. First, the refiner was operated without any loads (idling process) for 25 s, and the baseline of electric energy consumption was recorded as W_1. Then, the bamboo chips were fed to the refiner to go through the refining process in 25 s, and the electric energy consumption was recorded as W_2. The calculation of the refining energy consumption is shown below,

$$\text{Refining energy consumption} \left(\frac{\text{kWh}}{t}\right) = \frac{W_2 - W_1}{M} \quad (1)$$

Where W_1 is the energy consumption in the idling process (kWh), W_2 is the energy consumption in the refining process (kWh), and M is the bone-dry mass of the bamboo chips (t).

Fiber morphology, functional groups, and elemental analysis

The morphologies of the bamboo chips and pulp fibers were observed *via* a scanning electron microscope (SEM; FEI Quanta-200, FEI, Hillsboro, USA), under 100× and 1000× magnifications. The fibers of the bamboo BCTMP and BZTMP were characterized with a Fiber Quality Analysis system (Morfi, Techpap, Grenoble, France) with a fiber consistency of 40 mg/L. Dried bamboo chip and pulp samples were milled to pass a 100-mesh sieve for FT-IR analysis from 0 $cm^{-1}$to 4000 cm^{-1} (Nicolet 380, Nicolet, Madison, WI, USA), X-ray diffraction (Bruker D8 Advance XRD device, Bruker, Karlsruhe, Germany), and elemental analysis (Vario EL cube, EA, Elementar, Langsenselbold, Germany) for the contents of C, H, O, and N elements at 600 °C in an O_2 atmosphere.

RESULTS AND DISCUSSION

Effects of $ZnCl_2$ Dosage in the Pretreatment

Table 1 shows the effects of the $ZnCl_2$ dosage on the specific refining energy consumption, pulp yield, and strength properties, while the other pretreatment parameters were unchanged: fiber concentration of 20%, soaking time of 15 min, treating temperature of 70 °C, and treating time of 70 min. As can be seen in Table 1, with the increase of the $ZnCl_2$ dosage, the refining energy, total pulp yield, and bulk decreased, while the tensile and burst indices increased. When 6% $ZnCl_2$ was added in the pretreatment stage, the specific energy consumption (SEC) in the mechanical refining process decreased approximately 30%, compared with the control (0% $ZnCl_2$ added in the pretreatment). The screening accept yield first increased and then decreased. When the $ZnCl_2$ dosage was lower than 10%, the screen accept yield increased as the $ZnCl_2$ dosage increased; when the $ZnCl_2$ dosage was higher than 10%, the screening accept yield decreased with the increase of the $ZnCl_2$ dosage. This was explained by the two opposite actions of the pretreatment with $ZnCl_2$ solution. Either as the $ZnCl_2$ dosage increased, the bamboo chips became softer and easier to be refined into good pulp fibers and thus lowered the reject rate. In contrast, as the $ZnCl_2$ dosage increased, the pretreatment liquor acidity increased and caused dissolution of more organic matters from the bamboo chips, and thus the total pulp yield and screening accept yield decreased. As discussed above, hemicellulose, cellulose, and lignin-carbohydrate complexes can be removed or degraded during the pretreatment with an acidic $ZnCl_2$ solution. Moreover, some organic extractives (*e.g.*, flavone, terpene, and organic acids) were dissolved in the pretreatment. Under the optimal conditions in terms of accept pulp yield, the results were: specific refining energy of 826 kWh/t, pulping yield of 84.1%, accept yield of 75.5%, tensile index of 12.76 N·m/g, burst index of 1.01 kPa·m^2/g, and bulk density of 2.39 cm^3/g.

Table 1. Effects of $ZnCl_2$ Dosage on the Refining Energy, Pulp Yield, and Strength Properties of Resultant Pulp

$ZnCl_2$ Dosage (%)	Refining Energy (kWh/t)	Total Pulp Yield (%)	Accept Pulp Yield (%)	Tensile Index (N·m/g)	Burst Index (kPa·m^2/g)	Bulk (cm^3/g)	Beating Degree (°SR)
Control	1384±16	95.2±1.4	62.8±0.95	6.33±0.085	0.39±0.006	2.81±0.036	16
6	965±14	89.2±1.2	69.3±1.01	11.35±0.13	0.91±0.012	2.47±0.032	15
8	894±12	86.4±1.4	72.6±1.05	12.14±0.16	0.97±0.013	2.44±0.032	17
10	826±12	84.1±1.1	75.5±1.11	12.76±0.17	1.01±0.015	2.39±0.029	18
12	779±11	81.8±1.0	72.9±1.08	12.98±0.19	1.06±0.014	2.35±0.027	17
14	732±11	79.5±1.1	70.2±1.06	13.22±0.21	1.13±0.017	2.30±0.027	17

Because $ZnCl_2$ has a specific swelling effect on cellulose and hemicellulose, the secondary layers of the cell wall (S1 and S2) that are rich in cellulose and hemicellulose will be swollen and weakened in the pretreatment step with $ZnCl_2$ In the subsequent refining process, fiber separation is more likely to take place at the S1 or S2 layers rather than at the middle lamella, which in turn will increase the inter-fiber bonding potential of resulting pulp due to the exposure of more hydroxyl groups of cellulose and hemicellulose on the fiber surface.

Besides, with the increase of fiber swelling degree, the chips would be refined and fibrillated more easily in the refining process, leading to the increased fiber specific surface area and the bonding area between fibers or fiber bonding strength. Swelling is beneficial for the modification on the fiber toughness or flexibility, leading to the increase of single fiber strength. During the treatment process, some lignin would be removed. As is known, with the increase of lignin content, the fiber stiffness is increased; therefore, the decrease of lignin content is also beneficial for the fiber toughness or single fiber strength (Lee *et al.* 2009). As reported previously, the paper strength mainly depends on the strength of single fibers and the fiber bonding strength. Therefore, the fiber swelling process in $ZnCl_2$ aqueous solution was helpful to the increase of the paper strength of chemi-mechanical pulp.

For the reasons mentioned above, compared with the control, the tensile index, and the burst index of the resultant pulp increased 79% and 133%, respectively, at a 6% dosage of $ZnCl_2$. Further increasing the $ZnCl_2$ dosage slightly improved the strength properties of the resultant pulp. The strength improvement can be explained by the swelling effect of $ZnCl_2$ on the fiber cell wall structure of bamboo chips, because fiber swelling increases the chance of fibers to separate between the secondary layers (S1 and S2) instead of the middle lamella in the refining process. Compared with the middle lamella, the concentrations of lignin in the secondary layers were lower and the concentration of cellulose and hemicellulose were higher, which can provide more hydroxyl groups for inter fiber bonding. The swelling of cellulose fibers in $ZnCl_2$ solutions have been observed by other researchers (Yamashiki *et al.* 1992; Mao *et al.* 2006; Jin *et al.* 2007).

Effects of Pretreatment Temperature

Table 2 shows the effects of the pretreatment temperature on the refining SEC, pulp yield, and pulp strength properties, with all the other reaction parameters fixed at: $ZnCl_2$ dosage of 10%, fiber concentration of 20%, soaking time of 15 min, and pretreatment time of 70 min at the temperature.

Table 2. Effects of Treating Temperature on Refining Energy, Pulp Yield, and Fiber Strength

Treating Temperature (°C)	Refining Energy (kWh/t)	Total Pulp Yield (%)	Accept Pulp Yield (%)	Tensile Index (N·m/g)	Burst Index (kPa·m^2/g)	Bulk (cm^3/g)	Beating Degree (°SR)
55	917±16	89.5±1.4	67.6±0.96	11.54±0.15	0.91±0.011	2.52±0.039	16
60	882±14	87.7±1.2	72.4±1.04	12.18±0.17	0.94±0.014	2.46±0.036	18
65	851±12	85.4±1.2	76.2±1.07	12.76±0.20	1.01±0.013	2.41±0.036	17
70	822±13	83.6±1.1	74.9±1.06	12.95±0.21	1.04±0.016	2.38±0.033	17
75	794±13	81.5±1.3	73.3±1.06	13.21±0.18	1.10±0.018	2.34±0.030	16

With the increase of treating temperature, the refining SEC, total pulp yield, and bulk decreased, while the accept pulp yield, tensile, and burst indices increased. However, when the pretreatment temperature was higher than 65 °C, the accept pulp yield began to decrease. At a higher temperature, more chemical components (*e.g.*, lignin, cellulose, and hemicellulose) were degraded and removed in the pretreatment with an acidic $ZnCl_2$ solution, and therefore the total pulp yield was lower. In contrast, the swelling degree of the bamboo chips increased with the increase of the pretreatment temperature, which in turn improved the refining process and resulted in a higher accept pulp yield, stronger inter-fiber bonding strength, and a lower SEC. However, a pretreatment temperature that was too high (>65 °C) caused excessive dissolution of cellulose and hemicellulose, and the accept pulp yield started to decrease.

Effects of Pretreatment Time

Table 3 shows the effects of pretreatment time on the SEC, pulp yield, and the strength properties of the resultant pulp, with all other reaction parameters fixed at: $ZnCl_2$ dosage of 10%, fiber concentration of 20%, soaking time of 15 min, and treating temperature of 65 °C.

The pretreatment time had a similar effect on the pretreatment temperature. As shown in Table 3, with the increase of the pretreatment time, the refining SEC, total pulp yield, and bulk decreased, and the accept pulp yield, tensile, and burst indices increased. However, when the treating time was longer than 60 min, the improvement on the strength properties of the pulp was minimal, and the accept pulp yield started to decrease. Therefore, the pretreatment time should not be longer than 60 min under the conditions in the current study.

Table 3. Effects of the Pretreatment Time on the Refining Energy, Pulp Yield, and Pulp Strength

Treating Time (min)	Refining Energy (kWh/t)	Total Pulp Yield (%)	Accept Pulp Yield (%)	Tensile Index (N·m/g)	Burst Index (kPa·m^2/g)	Bulk (cm^3/g)	Beating Degree (°SR)
40	924±14	88.5±1.5	72.5±1.0	11.65±0.13	0.95±0.012	2.47±0.035	17
50	886±13	87.1±1.3	74.7±1.2	12.08±0.16	0.98±0.015	2.44±0.037	16
60	847±11	85.6±1.3	76.9±1.2	12.71±0.19	1.02±0.017	2.42±0.032	17
70	832±11	84.8±1.2	75.6±1.1	12.78±0.20	1.04±0.018	2.40±0.036	18
80	821±12	84.2±1.1	74.8±1.2	12.82±0.21	1.05±0.018	2.39±0.033	10

Table 4. Analysis of Paper Properties and Fiber Qualities

Index	BCTMP	BZTMP
Beating degree (°SR)	15	17
Refining energy (kWh/t)	1076±14	847±12
Total pulp yield (%)	87.2±1.3	85.6±1.1
Accept pulp yield (%)	75.7±1.1	76.9±1.0
Whiteness (%)	76.8±1.2	78.4±1.0
Tensile index (N·m/g)	10.42±0.14	12.71±0.18
Burst index (kPa·m^2/g)	0.56±0.0072	1.02±0.0015
Folding strength (Time)	3	5
Bulk (kPa·m^2/g)	2.64±0.039	2.42±0.034
Fiber length (mm)	0.693±0.0056	0.668±0.0051
Fiber width (μm)	28.5±0.016	29.7±0.019
Kinked fibers (%)	23.6±0.11	23.9±0.13
Curled fibers (%)	11.5±0.087	11.8±0.082
Fines (%)	26.4±0.18	28.5±0.21
Lignin content (%)	23.51±0.27	22.28±0.25
Cellulose content (%)	53.75±0.79	55.52±0.84
Hemicellulose (%)	22.44±0.34	21.16±0.31
Organic extractives content (%)	1.84±0.025	1.57±0.020

Comparison of BZTMP with Conventional BCTMP

Table 4 compares the pulp qualities of the BZTMP (bleached zinc chloride thermal mechanical pulp) and BCTMP (bleached chemical thermo-mechanical pulp), both of which were prepared in the current study with the same batch of bamboo chips. The BZTMP was prepared by the $ZnCl_2$ pretreatment process under the optimal conditions found in the current study (6% $ZnCl_2$, 65 °C, and 60 min), while the BCTMP was prepared by the conventional pretreatment method (3% NaOH, 5% Na_2SO_3, 15 min at 100 °C).

Compared with the bamboo BCTMP, the specific refining energy consumption of the bamboo BZTMP decreased approximately 27%, and the accept pulp yield increased 1.6%. The whiteness, tensile index, and the burst index increased 2.1%, 22%, and 82%, respectively. The mean fiber length of the BZTMP was smaller, while the mean fiber width was larger than those of the BCTMP, which was probably caused by the swelling effect of $ZnCl_2$. For the same reason, the BZTMP also had more kinked and curled fibers.

The contents of lignin, hemicellulose, and organic extractives in BZTMP were lower than those in BCTMP, indicating that the removal ratios of these chemical components in BZTMP process were higher than those in BCTMP process. During the preparation process, cellulose could not be degraded by $ZnCl_2$, leading to the increase of cellulose content in BZTMP. However, the variations were not obvious, which was beneficial for the pulping yield. Some details on the pulping and paper-properties of BCTMP and BZTMP were shown as below:

(1) The basis of the compared decrease or increase ratio was the factor value of BCTMP, such as the refining energy of BCTMP, the total pulp yield of BCTMP, and the tensile index of BCTMP.

(2) During the measure of paper properties, especially the strength, an equal or similar beating degree usually is required. Besides, chips should be refined fully to increase the content of accept pulp in the coarse pulp. Therefore, in order to obtain the fibers with similar fiber beating degree and decrease the content of the fasciculus in the refined fibers, the refining time and temperature in the preparation of BCTMP and BZTMP should be controlled strictly.

During the process of chemical pulp (*e.g.* soda-AQ pulp and kraft pulp), the chemical reagents (*e.g.* NaOH, Na_2S, Na_2SO_3) can be recycled by alkali-recycling process. According to our discussion, the $ZnCl_2$ aqueous solution could also be recycled by physical and chemical treatment. Some details are shown below:

(1) The main chemical components in the waste water after the $ZnCl_2$ treatment in this paper were lignin, hemicellulose, and $ZnCl_2$. Through the calculation, the solid content of the waste paper obtained under the optimal conditions was about 5%; however, the content was usually in the range of 16% to 20%. Therefore, the waste water could be mixed with the fresh $ZnCl_2$ aqueous solution for the 2nd treatment before refining process, and the solid content of the waste water would be increased. If the content was still lower than 16%, the water could be used for the 3rd treatment or more until the value was higher than 16%.

(2) After the process mentioned above, the water would be evaporated and combusted (similar to the alkali-recycling process). During this process, the organic components in the waste water would be transformed into CO_2 and H_2O, which could be absorbed by NaOH aqueous solution (the generation of Na_2CO_3). However, at high temperature, $ZnCl_2$ can be hydrolyzed and transformed into $Zn(OH)_2$ and HCl; then $Zn(OH)_2$ will be decomposed, leading to the generation of ZnO and H_2O. HCl and H_2O

can be absorbed by NaOH (the generation of NaCl). Na_2CO_3 can be used in chemical pulping and other industries, NaCl can be used to prepare HCl, and HCl can be reacted with ZnO to prepare $ZnCl_2$. According to the analysis above, there can be almost no loss of chemical reagents in the whole process, which is also similar to the alkali-recycling process in kraft pulp or the BCTMP processes.

(3) Before the chemical treatment process of BCTMP or APMP , the chips should also be washed, steamed, and extruded, and after the refining process, pulp would be washed, screened, and cleaned (all of these are the same as those in BZTMP), indicating that the energy consumption in these processes was similar. Compared with those of BZTMP, the treating temperature of BCTMP was higher. However, the treating time was shorter, indicating that the energy consumption in chemical treatment of BCTMP was lower, which was also the main disadvantage of BZTMP.

(4) According to these analysis, the chemical costs of BCTMP and BZTMP were similar, and the total energy consumption of BZTMP was a little higher than that of BCTMP (the refining energy consumption of BZTMP was lower).

(5) The details in this paper can be regarded as a theoretical study, and it might not be ready to be applied in current industrial practice. However, the approach appears to be feasible on a theoretical basis.

Characterization of the BZTMP and BCTMP

Elemental analysis

Table 5 shows the results of the elemental analysis of the BCTMP and BZTMP. There was no remarkable variation on the contents of carbon (C), hydrogen (H), or oxygen (O) elements. This indicated that the removal ratios of lignin, cellulose, and hemicellulose in bamboo fibers during the treatment processes of NaOH-Na_2SO_3 or the $ZnCl_2$ solution were similar in the two processes.

Table 5. Elemental Analysis

Element	BCTMP	BZTMP
C (%)	47.42±0.072	47.55±0.069
H (%)	6.25±0.0088	6.39±0.0094
O (%)	44.26±0.096	44.42±0.092
N (%)	1.17±0.0043	0.75±0.0012

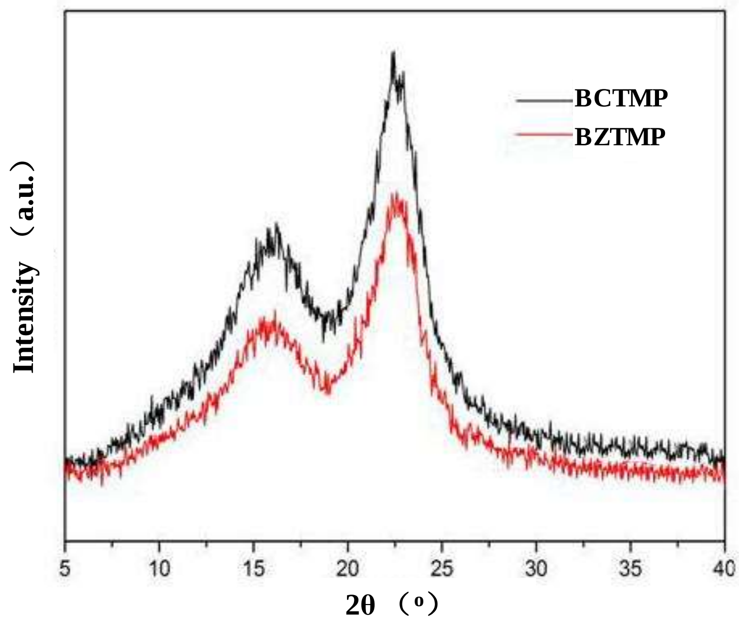

Fig. 2. XRD analysis of BCTMP and BZTMP

XRD analysis

Figure 2 compares the XRD results of the BCTMP and BZTMP.The variation of the spectra was not noteable. Through calculation, the crystallinity of the BZTMP and BCTMP was similar (approximately 0.64), but higher than that of the bamboo raw material. This value indicated that the chemical pretreatments did not affect the crystalline regions of the bamboo fibers in both the BCTMP and BZTMP processes, due to the relatively mild conditions of the chemical pretreatment (Fengel and Wegener 1984) applied in the present study.

SEM analysis

The SEM images in Fig. 3 illustrate that the BZTMP fibers swelled to a larger extent than that of the BCTMP fibers, probably due to the stronger swelling effect of the $ZnCl_2$ solution. The BZTMP fibers also had a rougher surface than the BCTMP fibers, indicating that the BZTMP fibers were more likely to expose the secondary layers of the cell wall structure in the refining process, which would contribute to the improved tensile and burst strengths.

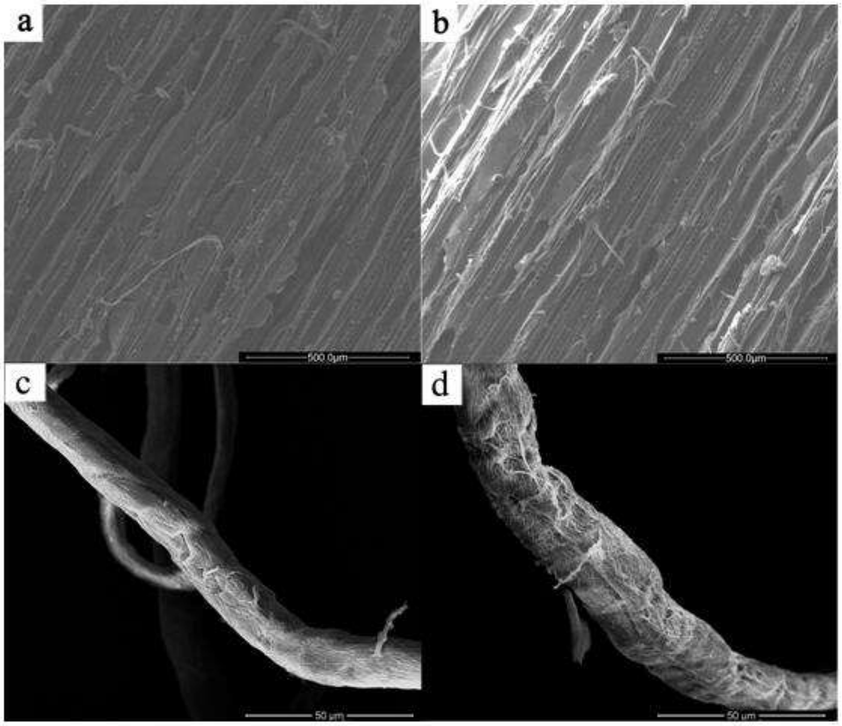

Fig. 3. SEM images of (a) bamboo chips after the chemical pretreatment in BCTMP process, (b) bamboo chips after the chemical pretreatment in the BZTMP process, (c) a BCTMP fiber, and (d) a BZTMP fiber

The morphology of the cross section of the chips are shown in Figs. 4a and 4b. It is apparent that the diameter of the chip fibers in BZTMP process was increased compared with that in BCTMP process(magnification of 1600), indicating that under the optimal conditions in this work, the swelling action of $ZnCl_2$ was more obvious than that of $NaOH$-Na_2SO_3 system. With the increased swelling degree, the volume of the fiber increased, leading to the increase of fiber diameter. According to the previous reports, swelling is also helpful to the fiber softening, resulting in the modification on the refining property.

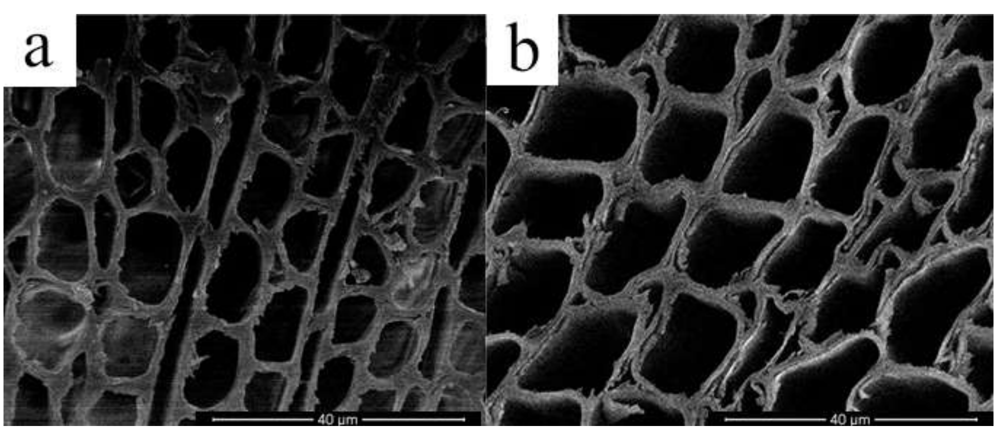

Fig. 4. SEM images of (a) the cross section of the bamboo chips after the chemical pretreatment in BCTMP process, (b) the cross section of the bamboo chips after the chemical pretreatment in the BZTMP process

CONCLUSIONS

1. Due to the swelling, softening, and degradation effects on cellulose fibers from $ZnCl_2$ pretreatment, the refining energy efficiency and cellulose fiber properties was greatly improved.
2. A 27% savings of refining energy could be achieved during the subsequent mechanical defiberization process. Meanwhile, the tensile and burst indices increased 22% and 82%, respectively, and the bulk density decreased9%.
3. The changes of the fiber morphology, functional groups, and crystallinity were negligible.

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APPENDIX

FT-IR Analysis

Figure A1 shows the FT-IR spectra for the BCTMP and BZTMP. The similarity of the FT-IR indicated that the chemical composition and the functional groups of BZTMP and BCTMP were similar. The absorption at 3423 cm^{-1}indicated the stretching of OH groups, and the peak at 2900 $cm^{-1}$is attributed to C-H stretching in the $CH_2$and CH_3groups from hemicellulose, cellulose, and lignin(Li *et al*. 2010).The C-H deformation in $CH_3$and CH_2occurred at 1462 cm^{-1}, and the C-H asymmetric deformation appeared at 1382 cm^{-1}. The peak at 1331 $cm^{-1}$was attributed to C-C and C-O skeletal vibrations. The bands between 1200 cm^{-1} and 1000 cm^{-1}were dominated by ring vibrations overlapped by the stretching vibrations of C-OH side groups. The signal at 900 $cm^{-1}$was attributed to the dominant glyosidic linkages between sugar units. The peak at 1113 $cm^{-1}$was indicative of associated OH groups from cellulose and hemicellulose. A strong signal at 1055 $cm^{-1}$was indicative of C-O stretching at C-3 and C-C stretching.

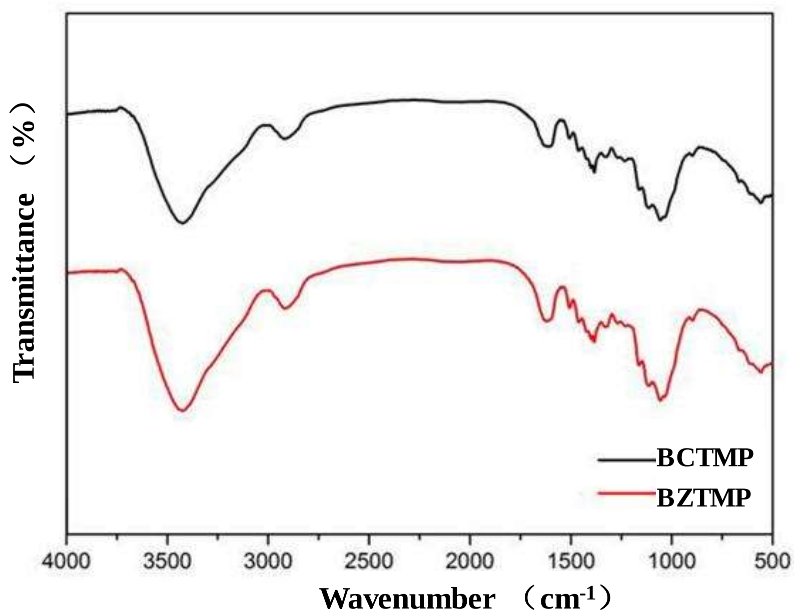

Fig. A1. FT-IR analysis of BCTMP and BZTMP

According to the previous reports, $ZnCl_2$ aqueous solution is a non-derivative cellulose solvent, indicating that there were no derivates during the cellulose dissolving process in this solution. As is known, there is almost no lignin or hemicellulose in cellulose fiber. Therefore, in this paper, FT-IR analysis was used to detect whether the cellulose or other components could be derived in the treating process of $ZnCl_2$ aqueous solution (as reported previously, during BCTMP process, there are no derivatives generated).