Modifying the Refining Energy Consumption of Chemi-Mechanical Pulping with NaOH-Thiourea-Urea Aqueous Solution

Rui Zhai,* Bing Song, and Xiaofan Zhou

To reduce the refining energy consumption of chemi-mechanical pulping, treatment with NaOH-thiourea-urea aqueous solution was studied in this work. By means of single-factor experiments, the effects of alkali dosage, soaking time, and freezing time were evaluated. It was found that the optimal conditions were an alkali dosage of 8%, soaking time of 45 min, and freezing time of 105 min. The results revealed that refining energy consumption could be reduced by approximately 40% under optimal conditions compared with that of alkaline peroxide mechanical pulp, while other pulping or paper-making properties were similar. There were no significant effects on the structure of the functional groups, the crystalline region of the pulp, or the whole structure of the treated wood chips. However, damage to single wood fibers on the chips treated in NaOH-thiourea-urea aqueous solution was more obvious.

Keywords: NaOH-thiourea-urea aqueous solution; Refining energy consumption; Chemi-mechanical pulping; APMP

*Contact information: Key Lab of Pulping and Paper Science and Technology, Nanjing Forestry University, Nanjing, P. R. China, 210037; *Corresponding author: zhairui860916@sina.com*

INTRODUCTION

Recently, chemi-mechanical pulping has been used to prepare high yield pulp due to its high bulk, low fasciculus content, excellent optical properties, and other advantages (Sundholm 1999). However, the development of chemi-mechanical pulping has been limited due to its high refining energy consumption. It has been reported that refining energy consumption would be increased by two thirds if the pulping yield was increased by 10% (Liu 2010). Therefore, the problem has received significant attention recently.

A variety of methods, such as physical, chemical, or biological treatments before or during the refining process, have been adopted to solve this problem. Among these methods, chemical or biological treatments have been attracting growing attention. It was found that when white-rot fungi or manganese peroxidase were used to treat softwoods, the materials could be softened, and the refining energy consumption would be reduced with a reduction in the content of lignin (Dutton and Evans 1996; De Sousa-Cruz *et al*. 2004; Hunt *et al*. 2004; Hakala *et al*. 2005; Maijala *et al*. 2008). Wood materials could also be treated with pectinase or laccase (Mansfield 2002), and the results showed that the refining energy consumption and the physical properties of the paper could be modified. Oxalic acid or sulfuric acid were applied to treat hardwoods (Kenealy *et al*. 2007; Liu *et al*. 2012), and the treated materials could be used to prepare thermomechanical pulp or chemi-thermomechanical pulp, while the refining energy consumption could be reduced by 20%. Also, wood materials could be treated with alkaline peroxide (*e.g.*, H_2O_2/NaOH), which would be beneficial to softening the wood fibers (Cort and Bhon 1991; Xu and Zhou

2005; Zhan 2010) and reduce the refining energy consumption by 30% compared with that of chemi-thermomechanical pulping.

In recent years, NaOH-thiourea-urea aqueous solution has been enjoying growing attention as a new solvent for cellulose (Jin *et al*. 2007) due to its advantages of high solubility, low cost, rapid dissolution, and low environmental impact. Cellulose products could be obtained from NaOH/H_2O systems (Kamide *et al*. 1984; Yamashiki *et al*. 1992). Regenerated cellulose membranes could be prepared from cellulose in NaOH/urea aqueous solution using various coagulants (Zhou *et al*. 2002; Mao *et al*. 2006), and novel microporous membranes could be prepared from cellulose in NaOH/thiourea aqueous solution with ammonium sulfate aqueous solution (Ruan *et al*. 2004). NaOH-thiourea-urea aqueous solution, modified according to the three systems mentioned above, could also be used to generate cellulose membranes or other products.

To the best of the author's knowledge, there have been no reports on the modification of refining energy consumption with this solution. It is known that NaOH can degrade lignin, swell the amorphous regions of fibers, and soften wood materials (Yang 2008) and that lignin would contribute to the stiffness of wood chips, thereby increasing the refining energy consumption (Zhan 2010). Also, urea or thiourea could diffuse to the surface of the crystalline region of swelled fibers and modify the toughness of the fibers or soften the wood chips (Zhang *et al*. 2001, 2002). All of the effects mentioned above are beneficial for the refining energy consumption reduction of chemi-mechanical pulping. In the present study, the reaction conditions were mild (*e.g.*, low temperature and low alkali dosage), so the ratio of degraded lignin, hemicellulose, and cellulose was small, and there would be relatively little effect on pulp yield (about 85% under the optimal conditions). The goal of the present work was to determine whether such a mild treatment has the potential to reduce refining energy consumption.

EXPERIMENTAL

Materials

Poplar chips (Henan Province, China) were washed and extruded with an extruder (Andritz, Austria; compression ratio of 4:1). The extruded poplar chips were air-dried at room temperature for 7 days. Finally, the solid content of the chips was measured.

NaOH, thiourea, and urea were dissolved in deionized water at a mass ratio of 8:6.5:8:77.5 (NaOH:thiourea:urea:H_2O) (Jin *et al*. 2007); then the solution concentration was stabilized at room temperature for 72 h.

Methods

First, 150 g of oven-dried wood chips were added to NaOH-thiourea-urea aqueous solution. The concentration was regulated to 20%, and the mixture was soaked at room temperature to fully mix the chips with the solution. The corresponding mixture was then frozen at -10 °C (Wang *et al*. 2008) and refined to coarse pulp with a KRK refiner (Jilin Province, China) while the refining energy consumption was measured. The coarse pulp was dewatered with a centrifugal hydro-extractor, the moisture was balanced in a refrigerator for 24 h, and the solid content was measured to obtain the pulp yield. Then, all the coarse pulp was screened and the accept pulp (the pulp passing through the screened or filtrated instruments. In this work the mesh of the screening instrument was 100) was collected (STUMP, NaOH-thiourea-urea mechanical pulp). Finally, the accept pulp yield was measured.

The technological procedure of alkaline peroxide mechanical pulp (APMP) was utilized in accordance with a report in *Pulping Principles and Engineering* (Zhan 2010) and the bleaching conditions of unbleached STUMP under the optimal conditions were in accordance with that of APMP. Paper was made at 60 g/m^2 to compare the pulping and paper-making properties.

APMP, bleached STUMP, and the corresponding chips were dried in a freeze dryer (Thermo Scientific Heto Power Dry PL6000) for 48 h at -30 °C with an applied vacuum of -0.1 MPa.

The morphology of the chips was observed by a scanning electron microscope (SEM; FEI Quanta-200, USA). The magnifications were 100X and 3000X. Fiber attributes were quantified with a Fiber Quality Analysis system (Morfi, France), with a pulp concentration of 40 mg/L. Pulp samples were broken apart with a fiber mill, and the powder was screened to obtain the components passing through the screen of 100 mesh for the FT-IR spectrum analysis (Nicolet 380, USA) and X-ray diffraction (XRD; Bruker D8 Avance, Germany). The scanning range, in wave numbers, was from 500 cm^{-1} to 4000 cm^{-1}. The scanning angle of XRD was from 5° to 40°.

Some details on the experimental methods were as shown below:

(1) In this paper, the refining concentration was 20% (the same as the treatment concentration mentioned above), the rotational speed of the refiner was 3000 rpm, and the distance between the fixed disk and rotatable disk of the refiner was 4 mm. The refining time was chosen as 30 s to reduce the refining energy consumption as much as possible, while keeping suitable yield, pulp or paper-making properties and fiber qualities (The refining time of 30 s was the most suitable in our tests. With shorter refining time, the accept yield would be much lower, which meant that the wood fibers had not been dispersed fully. When the time was longer than 30 s and shorter than 40 s, the variations of the accept yield, pulp properties, and paper-making properties were not obvious. If the time was longer than 40 s, some of the pulp might be carbonized and the color would become black, which meant that the fibers had been damaged under the high temperature in the refiner.). The maximum throughput rate of the refiner was 150 g (oven-dried weight of wood chips), and a single pass was employed.

The refining energy was based on the oven-dried weight of the wood chips (150g, as a constant value in this paper). First, the refiner was operated without any loads for 30s (idling) and the consumed electric quantity was recorded. Then the materials were added in the refiner through the feeder and refined to prepare the chemi-mechanical pulp. And finally, the pulp was removed from the refiner by water (3 L, also based on our previous tests) at the refining time of 30 s (water was also added in the refiner through the feeder to flush all the pulp), and the consumed electric quantity in the refining process was also recorded. The calculation of the refining energy consumption was shown as below,

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

where, W_1 is the consumed electric quantity in idling process (kWh), W_2 is the consumed electric quantity in the refining process (kWh), and M is the oven-dried weight of the treated wood chips, (in this paper, M=1.5*10^{-4}tonnes)

(2) The content of degraded lignin (Removal Ratio of lignin) was calculated according to the formula as shown,

$$Removal\ ratio\ (\%) = \frac{X_1 - X_2 * Y}{X_1} * 100\% \quad (2)$$

where, X_1 is the lignin content in the fiber materials (%), X_2 is the lignin content in the chemi-mechanical pulp (%), and Y is the pulp yield.

The content of Klason lignin in pulp or fiber material was measured according to the methods GB/T2677.8-1994 and GB/T747-1989. The content of acid-soluble lignin in pulp or fiber material was measured according to the method of GB/T10337-1989, where the content of lignin is given by the sum of Klason lignin and acid-soluble lignin contents. The yield is given by,

$$Y\ (\%) = (M_2/M_1) * 100\% \quad (3)$$

where, M_1 is the oven-dried weight of wood material (g), and M_2 is the oven-dried weight of pulp (g).

(3) The crystallinity of STUMP and APMP was directly shown in the X-ray diffraction. The crystallinity calculation of this kind of fiber sample in the XRD analysis equipment was calculated as shown below,

$$\text{Crystallinity} = I_2 / (I_1 + I_2) \quad (4)$$

where, I_1 is the absorption intensity of the amorphous region of pulp, the absorption intensity at a horizontal ordinate of 15° in Fig.2 in this paper, and I_2 is the absorption intensity of the crystalline region of pulp, the absorption intensity at a horizontal ordinate of 22.5° in Fig. 2 in this paper.

RESULTS AND DISCUSSION

Effects of Alkali Dosage

Table 1 lists the energy consumption, yield, and Canadian Standard Freeness at different alkali dosages with a soaking time of 60 min and a freezing time of 120 min. The results indicated that the energy consumption and pulping yield were reduced with the increase of alkali dosage, while the accept yield was increased. However, the decrease of the accept yield was also observed with higher alkali dosages. There were no other significant effects on the drainage property of the accept pulp. A refining energy consumption of 522 kWh/t, pulp yield of 83.9%, and accept pulp yield of 72.5% were determined to be the optimum effects at an alkali dosage of 8%.

The degradation of lignin (*e.g.*, phenol structure of β-O-4 or α-O-4, non-phenolic structure of β-O-4), hemicellulose, cellulose, and the fiber softening process could be promoted with the increase of alkali dosage. Then the chips would become softer, and the content of the fiber fasciculus would decrease gradually, both of which would contribute to the reduction of refining energy consumption and the improvement of accept pulp yield. The ratio of degraded lignin, hemicellulose, or cellulose would be increased more significantly with higher alkali dosages, and the accept pulp yield would also be reduced. Moreover, the wood chips had been softened or swelled fully with an alkali dosage of 8%, and there would be little effect on the refining energy consumption with a higher alkali dosage. Therefore, an alkali dosage of 8% was chosen as the optimal condition.

Table 1. Effects of Alkali Dosage

Alkali dosage (%)	Energy consumption (kWh/t)	Pulp yield (%)	Accept pulp yield (%)	Canadian Standard Freeness (mL)
4	663	91.74	62.65	695
6	577	88.43	67.52	686
8	522	83.89	72.48	702
10	498	82.97	72.12	696
12	486	81.75	71.15	692

Effects of Soaking Time

Table 2 shows the effects of soaking time during the STUMP process with an alkali dosage of 8% and freezing time of 120 min. It was found that energy consumption and pulping yield were reduced with the increase of soaking time, and the accept yield was increased. However, variation in the pulping properties was not obvious with a longer soaking time. Also, there was little effect on drainage rates. The pulping properties of refining energy consumption of 535 kWh/t, pulp yield of 84.3%, and accept yield of 72.3% at a soaking time of 45 min were chosen as the optimum levels.

During the soaking process, NaOH-thiourea-urea aqueous solution was gradually absorbed by the chips; and with the increase of soaking time, the absorption became more sufficient, which would be beneficial for the subsequent reaction in the freezing process *e.g.*, the softening of wood fibers and chips, and the degradation of lignin or extracts. However, the absorption process could gradually reach equilibrium with the decrease of the difference between the solution concentration of the solution absorbed by wood chips and that of the unabsorbed solution, and then the solution could not be absorbed by the materials. Therefore, a soaking time of 45 min was chosen as the optimum condition.

Table 2. Effects of Soaking Time

Soaking time (min)	Energy consumption (kWh/t)	Pulp yield (%)	Accept pulp yield (%)	Canadian Standard Freeness (mL)
15	665	87.85	65.62	700
30	613	86.64	69.50	707
45	535	84.29	72.33	703
60	527	83.98	72.47	711
75	517	83.85	72.56	715

Effects of Freezing Time

Table 3 lists the pulping properties with different freezing times with an alkali dosage of 8% and a soaking time of 45min. The pulp yield or refining energy consumption was reduced, and accept yield was increased. However, the variation of the pulping properties was not significant with longer freezing times. The optimal pulping properties of energy consumption of 529 kWh/t, pulping yield of 84.6%, and accept yield of 72.6% at a freezing time of 105min were obtained. Also, there was little variation on the pulp drainage rate. Therefore, the freezing time of 105min was chosen as the optimal condition in this study.

Wood fibers could be softened by urea, thiourea, or NaOH at low temperatures, and the lignin, extracts, or other components might be degraded by NaOH during the freezing process. Then, the wood materials would be softened gradually and become more suitable for refining. Therefore, refining energy consumption or pulp yield were reduced and the accept pulp yield was increased. The reactions mentioned above would reach equilibrium gradually with the consumption of NaOH, thiourea, or urea, and the decrease of the solution concentration, and there would be little effect on pulping properties with longer freezing time.

Table 3. Effect of Freezing Time

Freezing time (min)	Energy consumption (kWh/t)	Pulp yield (%)	Accept pulp yield (%)	Canadian Standard Freeness (mL)
60	672	86.29	71.88	660
75	648	85.98	72.04	665
90	595	85.25	72.23	696
105	529	84.61	72.64	672
120	518	84.45	72.83	708
135	510	84.32	72.95	711

Pulp, Paper, and Fiber Qualities

As is shown in Table 4,the refining energy consumption of STUMP was 529 kWh/t, which represents a decrease by 40% compared to that of APMP (887 kWh/t). The pulping yield of STUMP was lower than that of APMP, although the accept yield was higher. Also, the STUMP exhibited better paper properties such as brightness, bulk, folding strength, and tensile and burst indices. The fiber length of STUMP was shorter than that of APMP, while the width was greater. There was little variation on the contents of kinked or curled fibers. The content of the fines (the pulp which could pass through the screen instruments of 200 mesh) was higher in STUMP.

The ratio of degraded components in NaOH/thiourea/urea aqueous solution was higher than that in H_2O_2/NaOH aqueous solution, *e.g.,* the ratio of degraded lignin in unbleached STUMP was 13.17% and that of APMP was 11.54%. Higher lignin content could contribute to higher fiber stiffness, refining energy consumption, paper bulk, and lower paper strength. Also, the toughness of fibers could be increased by urea or thiourea, which is also beneficial for the reduction of refining energy consumption and the improvement of paper properties (Zhan 2010).

Wood fibers could be swelled and some of the components (*e.g.*, lignin, extracts, and hemicellulose) would be degraded in NaOH-thiourea-urea or H_2O_2/NaOH aqueous solution; however, the behavior of the NaOH-thiourea-urea system was more significant. The fiber length of STUMP was shorter and the fiber width was wider than that of APMP. Usually, fibers might be kinked or curled by the refiners in the refining processes (Zhan 2010), and there would be no significant variation among the contents of kinked or curled fibers with different treatment methods.

Fines would contribute to the increase of paper strength of high yield pulp (Sain and Li 2002), and the fiber fragments peeled from the fiber surface by the solution would increase the amount of fines. This is similar to the beating process; thus it is appropriate to use the term “secondary fines” when referring to those released fragments (He 2010). Usually, under suitable treatment conditions, they come from the outer sphere of the primary wall or secondary wall of fiber (Bhardwaj *et al*. 1995). This also indicated that the effect of NaOH/thiourea/urea aqueous solution was more obvious than that of H_2O_2/NaOH system.

Table 4. Pulp, Paper, and Fiber Properties of STUMP and APMP

Pulp / Quality	STUMP	APMP
Energy consumption(kWh/t)	529	887
Pulp yield (%)	84.61	86.47
Accept yield (%)	72.64	62.92
Brightness (%ISO)	75.25	72.95
Canadian Standard Freeness (mL)	16	17
Tensile index (Nm/g)	17.96	14.75
Burst index (kPa·m^2/g)	0.798	0.751
Folding strength (time)	5	3
Bulk (cm^3/g)	2.066	2.419
Fiber length (mass average) (mm)	0.721	0.743
Width (μm)	30.5	29.6
Kinked fibers (%)	38.1	37.9
Curled fibers (%)	9.6	9.5
Fine elements (%)	33.6	29.8

FT-IR Analysis

The spectra of bleached STUMP and APMP are shown in Fig. 1.The peaks were assigned by data comparison with previous studies (Schmidt *et al*. 2002; Li *et al*. 2010). As shown in Fig. 1, both samples exhibited similar spectra, which indicated that the chemical composition of the samples did not change.

The absorption at 3423 cm^{-1} indicates the stretching of OH groups, and the peak at 2900 cm^{-1} is attributed to C-H stretching in CH_2 and CH_3 groups from hemicellulose, cellulose, and lignin.

The C-H deformation in CH_3 and CH_2 occurs at 1462 cm^{-1}, and the C-H asymmetric deformation appears at 1382 cm^{-1}. The peak at 1331 cm^{-1} is attributed to C-C and C-O skeletal vibrations. The bands between 1200 and 1000 cm^{-1} are dominated by ring vibrations overlapped by the stretching vibrations of C-OH side groups. The signal at 900 cm^{-1} is attributed to the dominant glycosidic linkages between sugar units. The peak at 1113 cm^{-1} is indicative of associated OH groups from cellulose and hemicellulose. A strong signal at 1055 cm^{-1} is indicative of C-O stretching at C-3 and C-C stretching.

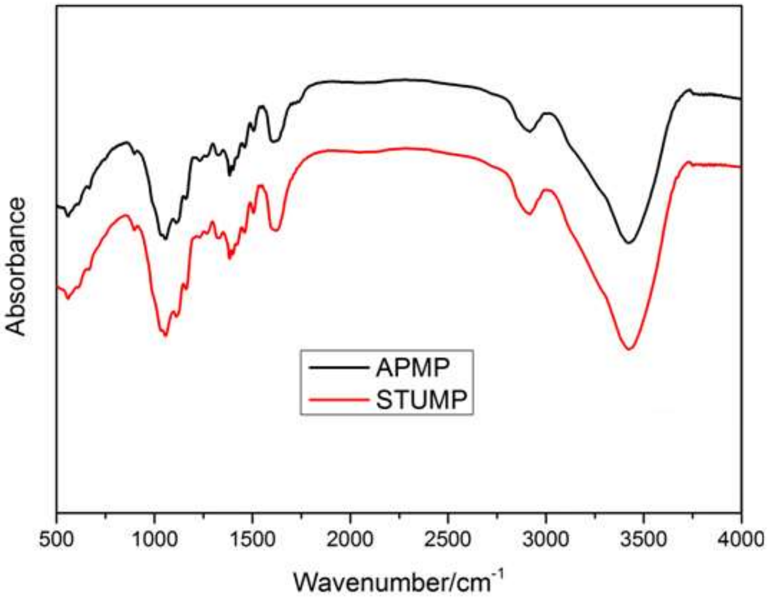

Fig. 1. Infrared spectrogram analysis of bleached STUMP and APMP

It is well known that lignin, extractives, and hemicellulose in wood materials can be dissolved or degraded by NaOH at room temperature, high temperature, or low temperature. Therefore, when the wood materials were treated in NaOH-thiourea-urea aqueous solution, the components would be reacted with NaOH, and some of them could be removed. However, a high temperature, such as 170 °C in the case of wood material, is needed in order to remove most of the lignin, extractives, or hemicellulose. Also, a high alkali dosage (20%) and high pressure (0.4 to 0.8 MPa) are also essential for this process (Zhai and Lee 1989). For example, during our tests in cooking poplar chips with NaOH, a temperature of 170 °C, an alkali dosage of 22%, a pressure of 0.5 MPa, and a cooking time of 200 min were applied. The results showed that all the hemicellulose or extract, and 90% of the lignin in wood materials could be removed in the cooking process. However, in the present work, a lower temperature (-10 °C), alkali dosage (8%), atmospheric pressure (0.1 MPa), and a shorter treating time (150 min) were used. During this reaction, only a minor proportion of lignin, extractives, and hemicellulose could be removed by NaOH, and the yield under the optimal conditions was about 85%, which meant that the total content of removed lignin, extract, and hemicellulose was about 15%, which is very low compared to a typical chemical pulping operation, which would remove 55%. So after the treatments of NaOH-thiourea-urea aqueous solution in this work, the chemical components or compositions in the STUMP would not be changed substantially (lignin, hemicellulose, cellulose, and extractives) compared with those in wood materials, while the chemical components in chemical pulp would be changed significantly (cellulose and a minor proportion of lignin). Also, the chemical components of APMP was similar to that of STUMP in our tests. Therefore, the variations of the FT-IR spectra were not significant.

XRD Analysis

Fig. 2 lists the XRD results of STUMP and APMP. The variation of the spectra was not significant. Through calculation, the crystallinity of STUMP was found to be 0.621, which is about 0.019 lower than that of APMP. This indicated that the effects on the amorphous region of the wood fibers were similar in the STUMP and APMP processes.

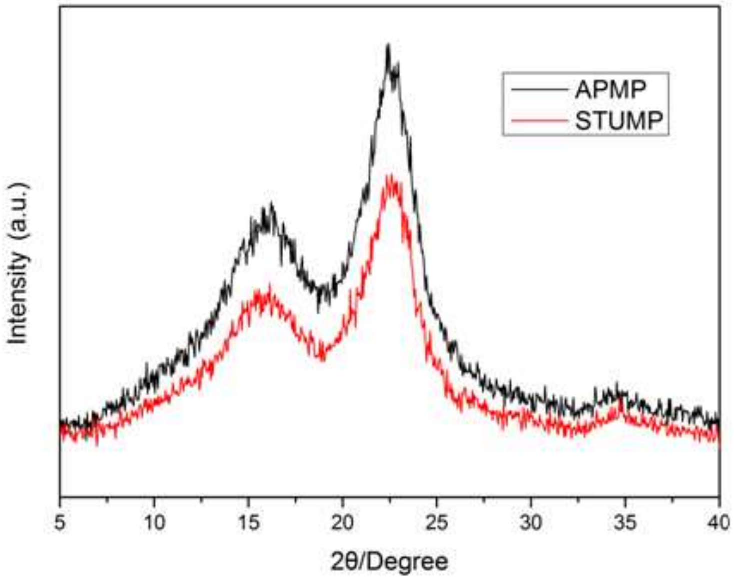

Fig. 2. XRD analysis of bleached STUMP and APMP

SEM Analysis

The surface morphology of the whole structure of the wood chips was investigated by SEM, and results are shown in Figs. 3a and 3b. Fig. 3a displays the surface morphology of the woodchips in APMP, and Fig. 3b displays that of STUMP. The magnification was 100X in Fig. 3a and 3b. The results indicated that the variation of the whole structure of the wood chips was not significant.

The ratio of degraded components in the STUMP process (15%) was higher than that of the APMP process (13%), but the ratio was much lower than that of the chemical pulping (50% to 55%). Therefore, there would be little variation on the whole structure of the treated wood chips. However, when the magnification was increased to 3000X, the surface morphology of single wood fibers on the material’s surface could be seen in Fig. 3c (APMP) and Fig. 3d (STUMP). It could be observed that there was more damage on the surface of the wood fibers when a higher ratio of degraded components (*e.g.*, lignin, extracts, and hemicellulose) was used in the treatment of NaOH-thiourea-urea aqueous solution.

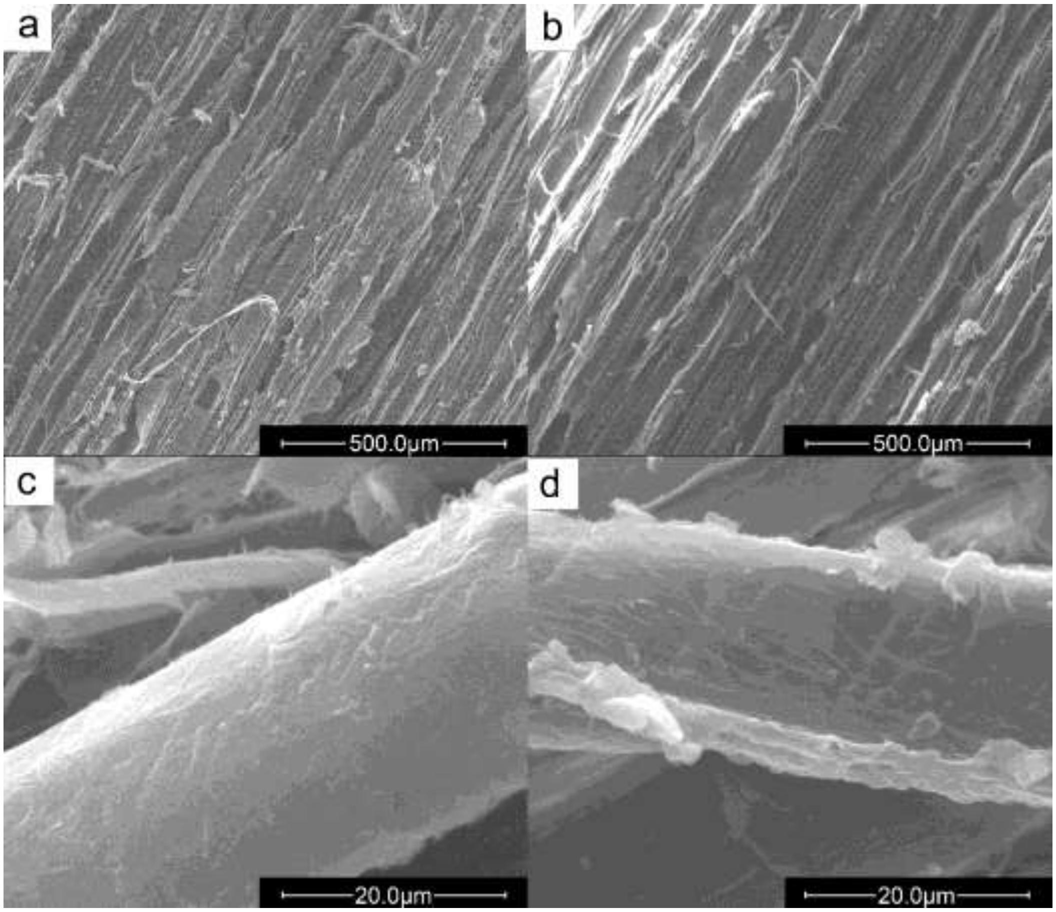

Fig. 3. SEM images of wood chip structure: a) APMP at 100x, b) STUMP at 100x, c) APMP at 3000x, d) STUMP at 3000x

Proposed Mechanism

When the NaOH-thiourea-urea aqueous solution was used in the cellulose dissolving or treating processes, a low cellulose concentration and a high alkali dosage (cellulose concentration of 5%, alkali dosage of 160%) were required (Jin *et al*. 2007). During these processes, the amorphous region of cellulose could be swelled by NaOH, the bonding of the amorphous region would be reduced by NaOH (the OH^- might combine with cellulose molecule, for there are lots of -OH in cellulose molecule, which is called hydrogen bonding or intermolecular hydrogen bonding between -OH and OH^-), and the bonding in amorphous region could hinder the reagents from soaking into the crystalline region of cellulose. Also, the reaction activity of cellulose would be increased at the same time (Yang 2008). Therefore, when the amorphous region of cellulose was fully swelled by NaOH, urea, thiourea, and the residual NaOH might interact with the crystalline region of cellulose; and then OH^- (NaOH), or the groups C=O, C=S, -NH (urea and thiourea) could combine with cellulose molecule, which is also called hydrogen bonding or intermolecular hydrogen bonding between -OH and OH^-, C=O, C=S, or -NH. Moreover, due to the strong polarity of C=O, C=S, -NH, it would be much easier for them to combine with -OH (Wang *et al*. 2008), which meant when the crystalline region was fully swelled, the internal bonding in original cellulose molecule would be decreased significantly by OH^-, C=O, C=S, and -NH. As a result, cellulose would become softer gradually, and be dissolved finally.

When the solution was used to treat chips in this work, the process would be different from the process of dissolving cellulose. Some distinctions are as explained below:

The lignin in wood materials could be removed or degraded by NaOH. Meanwhile, the softness of wood fibers or wood chips might be increased by urea and thiourea. For these reasons, wood materials could be softened and refined more effectively during the pulping process, and therefore, refining energy consumption would be decreased.

Some lignin in fibrous materials, *e.g.*, the lignin with lower molecular weight or phenol structure, or water-soluble lignin, could be removed or degraded by NaOH at room temperature or lower temperature (Liu and Lee 1991). Wood fibers or wood chips containing more lignin will tend to be stiffer than those with lower lignin content. Therefore, the materials with high lignin content would be more difficult to refine during the pulping process (Laivins and Scallan 1996), and the refining energy consumption might also be increased significantly. For these reasons, the removal or degradation of lignin during the wood pretreatments would be helpful in the reduction of refining energy consumption.

Wood fibers could be swelled by NaOH, and thereby, the reaction ability of fibers would be significantly increased (Sang and Dong 2005). As shown in the above introduction, the amorphous region of fibers could be swelled by NaOH, and then the thiourea, urea, and residual NaOH could diffuse to the crystalline regions and be present on the surface of crystalline region of wood fibers (Wang *et al*. 2008). Therefore, the softness of wood fibers would be increased with the swelling of these reagents (Chakravarty 1962; Zhang *et al*. 1994). For these reasons, wood chips or wood materials could gradually be softened during the NaOH-thiourea-urea aqueous solution pretreatment, and the treated wood chips would be more easily refined in the pulping process, effectively reducing refining energy consumption.

However, according to the results of the present single-factor experiments, the yield would be decreased with high alkali dosage, and at the same time, there would be no significant effects on the refining energy consumption.

A high temperature, such as 170 °C in the case of wood material, is needed in order to remove lignin or hemicellulose. Also, a high alkali dosage (20%) and pressure (0.4 to 0.8 MPa) are necessary for this process. In the present study, the treatment temperature was -10 °C, the optimal alkali dosage was 8%, and it was applied at ambient pressure. Under these conditions, only some of the lignin or hemicellulose could be degraded or dissolved by this solution. Under suitable conditions, most of the NaOH should be used to swell the wood fibers, increase the reaction activity of the fibers, or soften the wood chips. Therefore, the ratio of NaOH consumed in the degradation of the components was much smaller. However, with a higher alkali dosage, the content of residual NaOH could be much higher than that seen under the conditions of the present study. More polysaccharides or lignin would be removed by the alkali (Zhai and Lee 1989), and the yield might be decreased significantly. The most crucial advantage of chemi-mechanical pulping is the high yield (80% to 90%), and the pulping yield would be decreased with the removal of lignin and polysaccharides (Zhan 2010). When the alkali dosage was 15%, the yield was lower than 80% in the tests herein described. Therefore, a high alkali dosage could not be applied in the present study.

During treatment, NaOH-thiourea-urea aqueous solution would be gradually absorbed by the wood chips. NaOH could swell the amorphous regions of fibers (Fengel and Wegener 1984; Yang 2008), and urea or thiourea might interact with the crystalline regions of swelled fibers (Zhang *et al*. 2001, 2002). Both of the approaches mentioned above were helpful for the softening of wood materials and the reduction of refining energy consumption, especially the treatments of the crystalline region. However, solutions including NaOH, urea, thiourea, or H_2O could not be absorbed by the wood chips, and the swelling softening process might have been completed when the fibers had been fully swollen. Therefore, the effects on refining energy consumption reduction would not be significant with a higher alkali dosage. The internal hydrogen bonding of the fibers could be weakened by the groups C=O, C=S,-NH (urea and thiourea), or OH^- (NaOH) (Roy *et al*. 2001; Cai and Zhang 2006). Therefore, paper strength might be significantly decreased with high alkali dosage.

Low temperature or freezing was more suitable for the swelling or softening process of wood fibers or cellulose by thiourea or urea according to the reports of SCI literatures (Zhang *et al*. 2001; Zhou *et al*. 2002; Mao *et al*. 2006). Some detailed explanations are given below:

The swelling and softening processes of cellulose or wood fibers in alkali aqueous solution are exothermic reactions, so lower temperature is more suitable for the swelling or dissolving process according to Le Chatelier's principle.

Thiourea and urea could easily be oxidized by air at higher temperature. Also, when thiourea and urea are dissolved in NaOH aqueous solution, the reaction activities of thiourea and urea could be increased significantly (Yang 2008); thus it would be much easier for the chemical decomposition reaction of thiourea and urea to take place in air, and some toxic gas might be generated (nitrogen oxides and sulphur oxides), which could be harmful to the environment.

Finally, during the treatments, the functional groups (-OH, $-OCH_3$, -COOH, *e.g.*) in wood materials would react (chemical reaction) or combine with NaOH, thiourea, or urea (OH^-, C=O, C=S,-NH, *e.g.*), and the bonding between wood fibers and swelling agents was chemical in nature. Therefore, the swelling process investigated in this work can be regarded as a chemical swelling process (not a physical swelling process), and the wood materials would not revert to an unswollen condition after the removal of residual swelling agents. Also, the pulp and paper qualities would not be affected by the variation of the washing position (before refining process or after refining process, before screening process or after screening process) during the whole pulping process in our tests.

CONCLUSIONS

1. The optimal NaOH-thiourea-urea aqueous solution pretreatment conditions were determined to be an alkali dosage of 8%, soaking time of 45 min, and freezing time of 105 min.
2. Some of the components, *e.g.*, lignin, hemicelluloses, and extractives, could be degraded or dissolved by NaOH, and the toughness or softness of the fibers might be increased by thiourea or urea. Therefore, wood chips would be softened much more effectively during treatment with NaOH-thiourea-urea aqueous solution.
3. The whole structure of the wood chips, the functional group, and the crystalline region could not be substantially altered by NaOH-thiourea-urea aqueous solution, and the effects were similar to that of APMP.

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