Extracting hemicelluloses prior to aspen chemi-thermomechanical pulping: Effects of pre-extraction on pulp properties

Wei Liu [a,b,c,*], Zhirun Yuan [b,**], Changbin Mao [b], Qingxi Hou [a], Kecheng Li [c]

[a] Tianjin Key Laboratory of Pulp & Paper, Tianjin University of Science & Technology, Tianjin 300457, China
[b] FPInnovations, Pointe-Claire, QC, Canada H9R 3J9
[c] Department of Chemical Engineering, University of New Brunswick, Fredericton, NB, Canada E3B 5A3

ARTICLE INFO

ABSTRACT

Pre-extraction of hemicelluloses prior to pulping and conversion of the extracted hemicelluloses to other by-products will provide additional revenues to traditional pulp and paper industry. The effects of hemicelluloses pre-extraction with sulfuric acid on aspen (*Populus tremuloides*) chemi-thermomechanical pulp (CTMP) properties were investigated in this study. The sulfuric acid pre-extraction resulted in a release of 11% of hemicelluloses (determined as xylan) and acetic acid, especially at the second press-impregnation stage. Compared with CTMP without acid pre-extraction, the acid pre-extraction significantly reduced refining energy to a given freeness, and the pulps produced from acid pre-extracted chips have lower shives, higher strength properties except zero-span breaking length, lower bulk, but lower brightness at a similar specific refining energy. This study provides useful information for integration of biorefinery in mechanical pulp mills in the future.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

The concept of value prior to pulping (VPP) (van Heiningen, 2006; Thorp & Raymond, 2004) has been proposed where the hemicelluloses are either partially or completely extracted for biofuel production. The remaining solids (mainly cellulose and lignin) can be further delignified for wood pulp or fiber production (Zhu & Pan, 2010). Extracting hemicelluloses prior to pulping can also benefit the energy recovery from chemical pulping liquors, because the heating value of hemicelluloses is just about one half of that of lignin (van Heiningen, 2006). However, this concept requires a balance between potential yield loss, pulp property changes and capital investments as well as any increased revenue from marketing a by-product (Kenny, 2006).

The VPP concept had been mainly studied for the kraft pulping process (Al-Dajani & Tschirner, 2008; Helmerius et al., 2010; Yoon, van Heiningen, & Krishnagopalan, 2008). Few attempts have been made in recovering hemicelluloses from various pressates and filtrates from traditional mechanical pulping processes. The

chemi-thermomechanical pulp (CTMP), as one of the main high yield pulps, has been widely used in the pulp and paper industry with increasing applications in many paper products, such as printing and writing paper, paperboard, and hygiene products (Hu, Ni, Zou, & Zhou, 2006; Xu & Zhou, 2007; Zhang, He, & Ni, 2011; Zhou, Zhang, & Li, 2005; Zou, Zhou, Raymond, & Jolette, 2009). Hardwood is the typical wood species for making CTMP and contains an average of 22% hemicelluloses (Boluk, Yuan, Tosto, Browne, & Atkinson, 2008). The extracted flows from hardwood CTMP mills would be rich in hemicelluloses and acetic acid depending on the type and extent of chemical treatments. Therefore, there are certain opportunities to obtain the streams for value-added by-products before making pulp.

There are some potential additional benefits for applying VPP concept to a CTMP process: (1) the chemical pre-treatment stage of a typical CTMP process can easily be served as the pre-extraction stage without major capital investment; (2) the pre-extraction of hemicelluloses would also help to decrease the effluent load and minimize runnability problems on a paper machine due to the reduced dissolved and colloid substances (DCS) from dissolved hemicelluloses in a typical CTMP process (Johnsen & Stenius, 2007; Miao, Hou, Qin, & Fu, 2008; Rundlöf, Eriksson1, Ström, & Wågberg, 2002; Svedman, Lonnberg, Holmbom, & Jakara, 1995); (3) acid pre-treatment, such as dilute sulfuric acid (Boluk et al., 2008) and oxalic acid (Kenealy, Horn, & Houtman, 2007; Meyer, Ruel, Petit-Conil, Valtat, & Kurek, 2004), can also help to reduce the refining energy. CTMP typically consumes 1500–2000 kWh/t refining energy which

* Corresponding author at: Tianjin Key Laboratory of Pulp & Paper, Tianjin University of Science & Technology, Tianjin 300457, China. Tel.: +1 5147824661.
** Corresponding author at: FPInnovations, Pointe-Claire, QC, Canada H9R 3J9. Tel.: +1 5147824661.
E-mail addresses: Wei.liu2009@hotmail.com (W. Liu), Zhirun.Yuan@fpinnovations.ca (Z. Yuan).
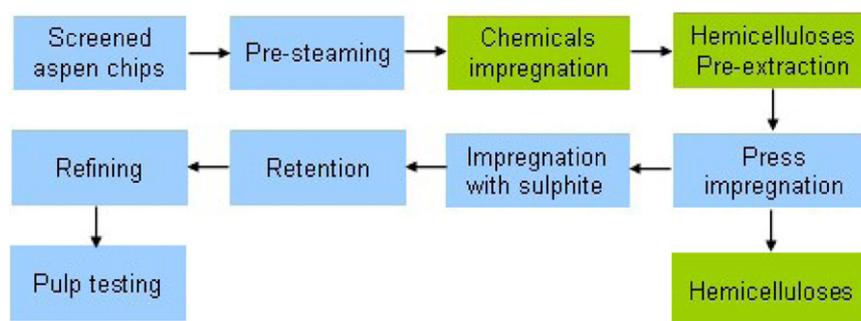
Fig. 1. The experimental scheme.

is a significant portion of the total production cost. Overall, it is expected that the VPP concept should fit well the CTMP process. Although there is a significant potential in pre-extracting hemicelluloses from wood chips prior to CTMP pulping, this needs to be demonstrated in lab studies. In addition, it is not clear how this would affect pulp properties. The impact is expected to be more significant than chemical pulping as wood chips need to go through an intensive refining process.

In this study, aspen chips were press impregnated with dilute sulfuric acid and cooked under various temperature and time to pre-extract hemicelluloses. The cooked chips were pressed and impregnated with sodium sulphite and then refined to produce CTMP pulps. The main goal of this study was to investigate the potential of hemicelluloses pre-extraction and the effects of acid pre-extraction on pulp properties of aspen CTMP.

2. Experimental

2.1. Materials

Aspen chips from an eastern Canadian mill were screened before the process. The chemical composition of the aspen chips is as follows: glucan 47.07%, xylan 16.50%, acid soluble lignin (ASL) 3.54%, acid insoluble lignin (Klason lignin) (AIL) 17.93%, and acetone extractives 1.07%. Acetone and H_2SO_4 used for acetone extractives and acid hydrolysis for chemical compositions analysis were of analytical grade.

2.2. Experimental procedure

The experimental scheme is shown in Fig. 1.

2.2.1. Hemicelluloses pre-extraction with sulfuric acid

The screened aspen chips were presteamed at 100 °C for 15 min. Then, an Andritz-Bauer 6″ MSD press impregnator was used for the impregnation of screened chips with 0.50% (w/v) sulfuric acid at 60 °C. The resulted sulfuric acid charges for CTMP2 and CTMP3 were both 1.0% based on oven dry wood chips. The impregnated chips were then cooked in a vapour-phase digester under different conditions to pre-extract part of hemicelluloses from wood chips, as shown in Table 1. After cooking, the cooked chips were fed into the press impregnator again to collect the pressates.

2.2.2. CTMP process

The CTMP pulps were made in the pilot plant of FPInnovations, Canada. The screened aspen chips were impregnated with 1.5% (w/v) sodium sulphite (Na_2SO_3) in the press impregnator. The impregnated chips were retained at 70 °C for 30 min and then preheated at 100 °C for 3 min before refining. The chips were then refined in two stages with a 22″ Andritz pressurized TMP refiner and a Bauer 400 36″ atmospheric refiner. Table 1 listed the

pre-extraction and pulping conditions of these trials: CTMP1 (without acid pre-extraction), CTMP2 (acid pre-extraction at 110 °C and 30 min) and CTMP3 (acid pre-extraction at 140 °C and 10 min). The sulfonation levels of CTMP pulps were similar between 17.2 and 18.2 mmol/kg, so the difference in pulp properties could be mainly attributed to the acid pre-extraction.

2.2.3. Pulp handling and testing

The refined pulps were hot-disintegrated and screened with a 4-cut plate. The pulp properties were tested according to Pulp and Paper Technical Association of Canada (PAPTAC) standard methods: C.1 (Canadian standard freeness, CSF); C.4 (handsheets forming for physical testing); C.8P (latency removal by hot disintegration); C.5U (fiber classification by Bauer-McNett); D.12 (physical and optical testing of handsheets); D.27U (zero-span breaking length); D.39P (Scott bond strength). And, the fiber length of pulp was measured by automated optical analyzer according to TAPPI method T221 cm-09.

2.2.4. Chemical composition analysis of aspen chips and resultant pulps

The aspen chips and resultant CTMP pulps were air dried and milled using a Thomas mill. Then, the milled powders passed through a 20-mesh (<0.5 mm) screen were kept in a sealed plastic bag and stored in a cold room with a temperature of about 4 °C for further analysis (Canettieri, Rocha, Carvalho, & Silva, 2007). The content of acetone extractives was determined according to the PAPTAC standard procedures G.13 and G.20. The total lignin content (acid soluble lignin and Klason lignin) was measured following PAPTAC standard procedures G.8 and G.9. The sugar analysis of aspen chips was performed by an ion chromatograph in accordance with the method described by Zhang, Qin, Paice, and Saddler (2009). The sugar monomers in the filtrate, including arabinose, galactose, glucose, xylose, and mannose, were separated by an anion exchange column (Dionex CarboPac™ PA1) in a Dionex DX-600 Ion Chromatograph system (Dionex, Sunnyvale, CA) equipped with an AS50 autosampler and a GP50 gradient pump.

Table 1
Pulping conditions for the pilot plant trials.

	CTMP1	CTMP2	CTMP3
H_2SO_4 on o.d. wood (%)	–	1.0	1.0
Pre-extraction temperature(°C)	–	110	140
Pre-extraction time (min)	–	30	10
Na_2SO_3 on o.d. wood (%)	2.6	3.0	3.1
Sulfonic groups (mmol/kg)	17.2	18.2	17.9
Preheating time (s)	180	180	180
Refining pressure in TMP refiner (kPa)	250	250	250
Refining consistency in 2nd stage (%)	15	15	15

Table 2
Sugar analysis of the pressates.

Sugar (ppm)	After the first and second press			After refining (PL3)		
	CTMP PL1	CTMP2 PL2	CTMP3 PL2	CTMP1	CTMP2	CTMP3
Arabinose	598.0	1961.4	2176.8	143.3	88.5	144.1
Galactose	438.8	777.0	590.0	151.2	82.0	99.0
Glucose	184.1	663.0	570.0	232.1	146.9	129.5
Xylose	1069.7	2904.7	6048.2	471.4	1046.5	1218.8
Mannose	754.2	717.5	934.2	114.4	90.4	87.6
Total sugar	4044.8	7023.6	9189.5	1112.5	1454.3	1678.9
Acetate	179.0	1069.0	2593.0	406.0	309.0	433.0

2.2.5. Analysis of pressates

The pressates obtained from the process were neutralized with dilute NaOH and stored in a cold room with a temperature of about 4 °C. The deposited solids were removed by filtration with Whatman filter paper. A 25 ml of filtrated pressates and 1.04 ml of 72.0% H_2SO_4 were mixed together in a COD test tube for each sample. All these tubes were autoclaved at 121 °C for 60 min. All these samples were filtrated through 0.45 μm Millipore filter and the filtrates were collected for the sugar analysis according to the method described by Zhang, Qin, Paice, and Saddler (2009). The acetic acid was measured with a Dionex 3000 ion chromatograph.

2.2.6. Sulfonic groups content measurement

The amount of sulfonic groups in CTMP pulps was determined in accordance with the conductometric titration method proposed by Katz, Beatson, and Scallan (1984).

2.2.7. FE-SEM observation of pulp fibers

Pulp fibers were screened with Bauer-McNett pulp classifier, and the fraction of R48 was collected for the analysis. The freeze-dried pulp samples were coated with platinum in a Polaron S150A sputter-coater. The prepared samples were then examined with a SU-70 field-emission scanning electron microscopy (FE-SEM) (Hitachi, Japan).

3. Results and discussion

3.1. Analysis of the pressates

The pressates from the first press impregnation (PL1), second press impregnation (PL2), and refined pulps (PL3) were collected from the pilot plant trials and analyzed for the chemical compositions, as shown in Table 2.

The sulfuric acid pre-treatment can release some hemicelluloses by cleaving the glycosidic linkages between lignin and carbohydrates (Sjöström, 1993). Canettieri et al. (2007) investigated the dilute acid hydrolysis on forest residues of *Eucalyptus grandis.* Their results showed that the concentration of xylose was about 0.5 g/L, and xylose extraction yield was about 4% under the conditions: 0.65% sulfuric acid, a residue/acid solution ratio of 1/9 (w/w), 130 °C for 20 min or 140 °C for 20 min. However, under the similar conditions (1% sulfuric acid, the liquid to solid ratio 2/1, 140 °C for 10 min), up to 11% of xylan would be possibly extracted from wood chips for CTMP3 (PL2 and PL3) in the present work, which possibly due to higher sulfuric acid charge in this study.

The results showed that more xylans than glucans were extracted from aspen chips, because (1) the xylosidic bonds between xylose units are more rapidly hydrolyzed by the acid pre-extraction than glucosidic bonds in cellulose (Boluk et al., 2008); (2) glucan in cellulose was not significantly affected by dilute acid pretreatment (Leenakul & Tippayawong, 2010). The pressates from CTMP2 and CTMP3 have a higher sugar concentration than that from CTMP1. Compared with CTMP1, the concentrations of hemicelluloses (arabinose, galactose, xylose, and mannose) obtained from both PL2 and PL3 stages increased significantly after sulfuric acid pre-extraction, especially under a high temperature (CTMP3). The factors affecting the acidic hydrolysis rate are basically pH and temperature. Increasing acidity and temperature will speed up the hydrolysis rate (Fengel & Wegener, 1989). The results showed the carbohydrate streams in PL2 would be a potential hemicelluloses source for producing bioproducts.

Acetic acid in pressates was also detected, as shown in Table 2. The results showed that the acetate concentrations in PL2 collected from CTMP2 and CTMP3 were about 6 and 15 times higher than that of PL1, respectively. The acetate concentration in CTMP3 PL2 was about 2.5 times higher than that of CTMP2 PL2 due to the stronger pre-extraction conditions. Aspen hardwood has seven acetyl and one methylglucuronic acid groups on every 10 xylose units which can be removed during the prehydrolysis (Boluk et al., 2008). Sulfuric acid pre-extraction can promote the release of acetic acid by cleaving of the acetyl groups from the xylan backbone, which may provide a way to generate acetic acid from pulp mills in the future.

The pre-extraction yields for both CTMP2 and CTMP3 were about 95%. So, the pulping yield for the CTMP process with hemicelluloses pre-extraction would be decreased slightly due to removal of hemicelluloses and some other carbohydrate polymers caused by acid pre-extraction.

3.2. Effects of pre-extraction on chemical compositions of CTMP pulps

The chemical compositions of pulp have a strong influence on fiber properties. Cellulose is the main strength-contributing component, hemicelluloses are softeners in the wet state, and lignin gives wet stiffness and resistance to strength development through refining (Annergren, 1999). Table 3 lists the chemical compositions of aspen CTMP pulps. It can be seen that acid pre-extraction resulted in a decrease of xylan and acid soluble lignin (ASL) percentages, and an increase of glucan, acid insoluble lignin (AIL) and acetone extractives percentages. Glucose concentrations in pressates were very low, and the percentage of glucan in produced pulps increased slightly (1.3–1.8 points) after acid pre-extraction. The result indicated that most of the cellulose remained in the extracted wood chips, which would benefit to the resultant pulp properties.

3.3. Effects of pre-extraction on pulp properties

Fig. 2(a) showed that at the same freeness, the acid pre-extraction significantly reduced refining energy to a given freeness.

Table 3
Chemical compositions of CTMP pulps.

	Glucan (%)	Xylan (%)	ASL (%)	AIL (%)	Extractives (%)
CTMP1	50.4	16.6	4.1	17.0	0.4
CTMP2	51.7	16.2	3.6	17.8	0.5
CTMP3	52.2	14.3	3.4	17.9	0.6
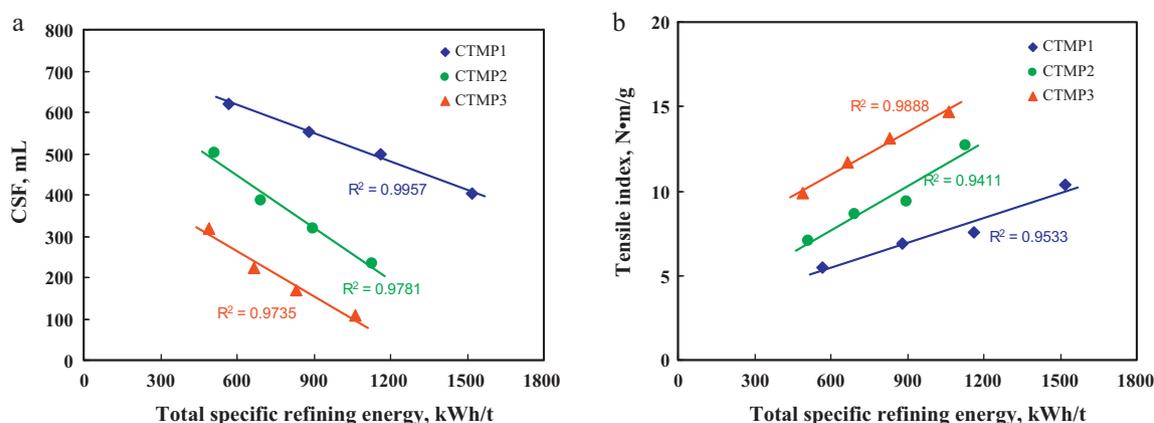
Fig. 2. Total specific refining energy vs. CSF (a) and tensile index (b) for CTMP pulps.

Compared with 1554 kWh/t for the CTMP1, only 712 kWh/t and 222 kWh/t of specific refining energy for CTMP2 and CTMP3 were required to reach a freeness of 400 ml, respectively. The specific refining energy was accordingly reduced by 54% and 86%, respectively. Compared with CTMP1, CTMP with acid pre-extraction resulted in a higher tensile index at a given refining energy level, as shown in Fig. 2(b).

The pulp properties were compared at similar refining energy consumption, as shown in Table 4. Compared with CTMP1, the pulps with acid pre-extraction (CTMP2 and CTMP3) had lower freeness, lower shives rate, and lower bulk at the similar specific refining energy. The lower shives rate indicated a better refining efficiency. The lower bulk for the acid pre-extracted pulps could be attributed to (1) less long fibers and more fines, the fines content of CTMP1 was 16.8%, while those of CTMP2 and CTMP3 were 25.2% and 33.5%, respectively (Fig. 3); (2) more pulp swelling caused by acid pre-extraction, as indicated by the higher water retention value (WRV). Pulp fibers would tend to collapse more and bond better between fibers during drying process, leading to a decreased sheet bulk. The results showed that the fiber strength itself was affected by the acid pre-extraction, as measured by zero-span breaking length. The zero-span breaking length was 7.6 km and 8.2 km for CTMP2 and CTMP3, respectively, while 9.8 km for CTMP1. The average fiber length was measured and the results showed that the length weighted fiber length decreased slightly from 0.8 mm to around 0.6–0.7 mm for the pulps with acid pre-extraction, as shown in Table 4. The above results suggested that acid pre-extraction could make aspen fibers more fragile and easier to be broken down in the refining process. However, most of the strength properties (except zero-span breaking length) of CTMP2 and CTMP3 were improved, which is mainly because the positive effect of bonding

between fibers overcomes the negative effect of strength loss of a single fiber. Better bonding for the acid pre-extracted pulps can be confirmed by the measurement of Scott bond and SEM analysis of pulp fibers.

Compared with CTMP without sulfuric acid pre-extraction, the brightness of pulps produced with acid pre-extraction decreased 5–7 points, because the light absorption coefficient increased much more than the increase of the light scattering coefficient, as shown in Table 4. The increase of light scattering coefficient mostly comes from the increased fibrillation. The strong cooking conditions (110–140 °C and 10–30 min) were probably the main reasons for the brightness loss. Methods to minimize the brightness loss during the cooking deserve further investigation.

3.4. Effects of pre-extraction on fiber surface morphology

Fig. 4 shows the SEM images of pulp fibers without (CTMP1) and with (CTMP3) acid pre-extraction. It can be seen that there are some smooth and patch-like materials (i.e., middle lamellas (Li, Tan, & Yan, 2006)), non-fibrillar patches and micro-fibrillar structures on these fibers. Particularly for the CTMP3 pulp fibers, these clear micro-fibrillar structures on fiber surface suggested that the fiber separation may occur mostly in the secondary wall (Li, Tan, & Yan, 2006). It is expected that acid pre-extraction could make aspen fibers more fragile and easier to be broken down in the refining process. Therefore, after acid pretreatment, the S1 layer became brittle and could be easily flaked off, which would benefit the fibrillation of fibers. The SEM analysis showed that the fibrillation degree of

Table 4
Properties of CTMP pulps.

	CTMP1	CTMP2	CTMP3
Total specific energy (kWh/t)	1160	1126	1062
CSF (ml)	499	234	107
Shives content (Somerville) (%)	1.4	1.0	0.7
WRV (%)	92	105	114
Bulk (cm^3/g)	3.9	2.8	2.5
Tensile index (N m/g)	7.6	12.7	14.7
TEA (mJ/g)	28.7	48.7	55.3
Tear index (mNm^2/g)	1.30	1.62	1.69
Zero-span breaking length (km)	9.8	7.6	8.2
Scott bond (J/m^2)	28.0	52.0	57.0
ISO brightness (%)	59.6	54.0	52.1
Light scattering coeff. (m^2/kg)	50.4	52.0	53.5
Light absorption coeff. (m^2/kg)	2.4	3.8	4.4
Length weighted fiber length (mm)	0.8	0.7	0.6
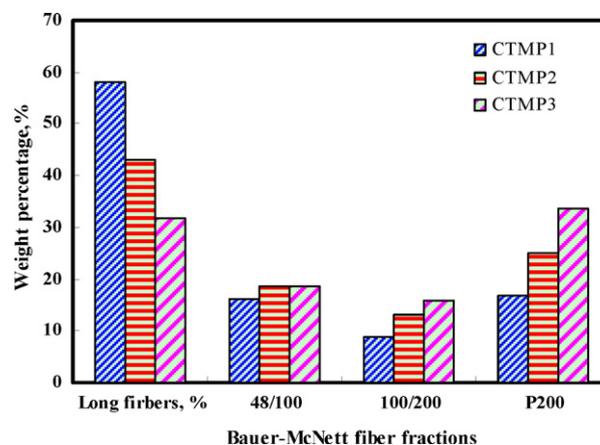
Fig. 3. Bauer-McNett fiber fraction of CTMP pulps that list in Table 4.
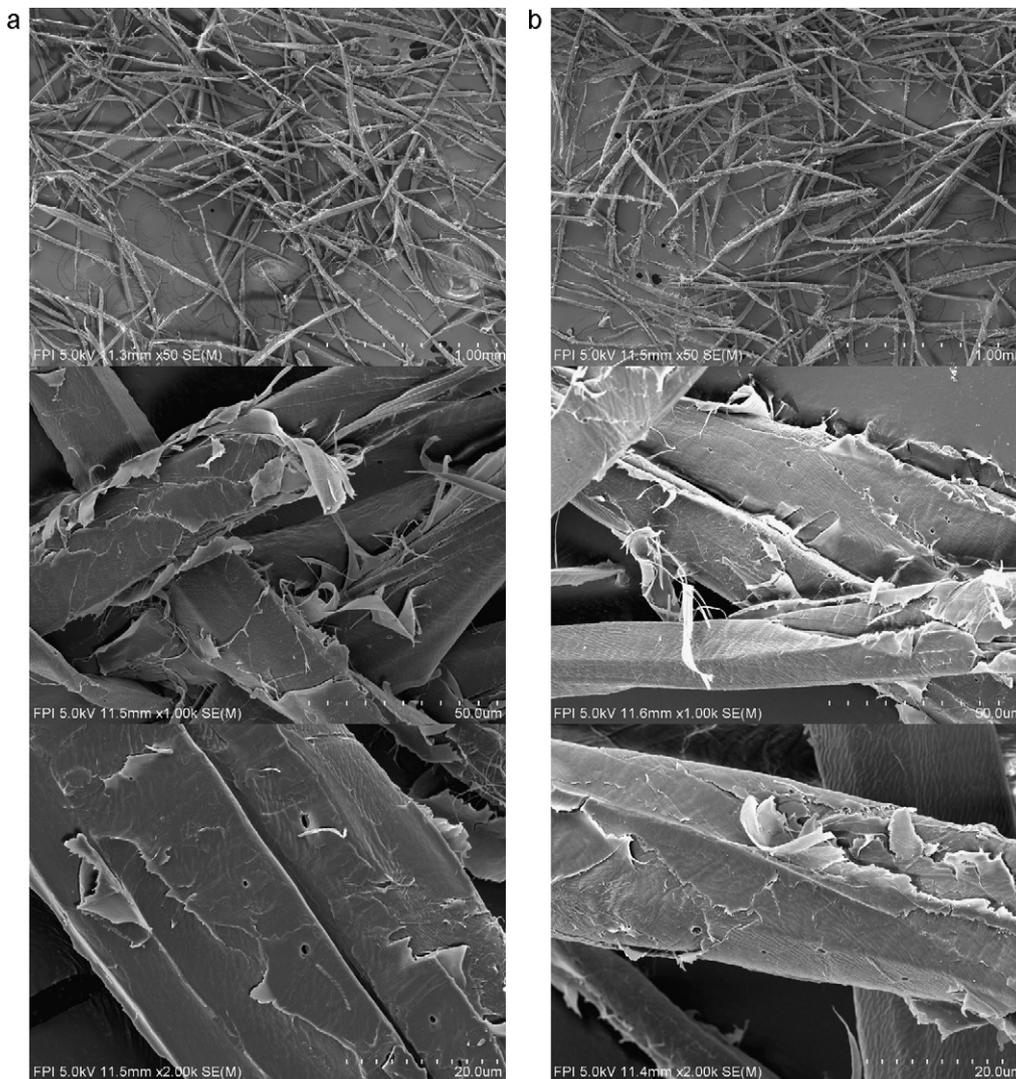
Fig. 4. SEM analysis of CTMP pulp fibers (a: CTMP1; b: CTMP3).

CTMP3 pulp fibers was much higher than that of CTMP1, as shown in Fig. 4.

4. Conclusions

Portion of the hemicelluloses and acetic acid can be pre-extracted prior to CTMP pulping with sulfuric acid and the resultant chips can still be used to produce mechanical pulps under suitable conditions. The carbohydrate streams collected from the second press-impregnation stage after acid pre-extraction have the potential to be one of the hemicelluloses streams. Acid pre-extraction significantly reduced refining energy consumption to a given freeness. Acid pre-extraction was found to have a very significant effect on pulp properties: at the specific refining energy, CTMP pulps produced with acid pre-extraction had a somewhat lower zero-span breaking length, lower bulk, higher fines content and lower brightness, but much higher tensile index and Scott bond.

Future works

(1) Further work is needed to optimize the acid pre-extraction process conditions to balance the extraction of hemicelluloses and pulp properties; and (2) pulp properties and bleaching abilities of pulps at similar freeness will be reported in another paper.

References

Al-Dajani, W. W., & Tschirner, U. (2008). Pre-extraction of hemicelluloses and subsequent kraft pulping. Part I. Alkali extraction. *TAPPI Journal*, *7*(6), 3–8.

Annergren, G. (1999). Fundamentals of pulp fiber quality and paper properties, vol. 1. In *TAPPI Pulping Conference* 31 October–4 November, Orlando, FL, USA, (pp. 29–39).

Boluk, Y., Yuan, Z., Tosto, F., Browne, T., & Atkinson, B. (2008). Dilute acid prehydrolysis and extraction of hemicellulose prior to aspen chemi-thermomechanical pulping. In *AIChE Annual Meeting, Conference Proceedings* New Orleans, Louisiana.

Canettieri, E. V., Rocha, G. J. M., Carvalho, J. A., Jr., & Silva, J. B. A. (2007). Evaluation of the kinetics of xylose formation from dilute sulfuric acid hydrolysis of forest

residues of *Eucalyptus grandis*. *Industrial & Engineering Chemistry Research*, *46*(7), 1938–1944.

Fengel, D., & Wegener, G. (1989). *Wood. Chemistry, ultrastructure, reactions*. Berlin, Germany: Walter de Gruyter., p. 613.

Helmerius, J., Vinblad, J., Walter, V., Rova, U., Berglund, K. A., & Hodge, D. B. (2010). Impact of hemicellulose pre-extraction for bioconversion on birch kraft pulp properties. *Bioresource Technology*, *101*(15), 5996–6005.

Hu, K. T., Ni, Y. H., Zou, X. J., & Zhou, Y. J. (2006). Substitution of hardwood kraft with aspen high-yield pulp in lightweight coated wood-free paper. I. Synergy on basestock properties. *TAPPI Journal*, *5*(3), 21–26.

Johnsen, I. A., & Stenius, P. (2007). Effects of selective wood resin adsorption on paper properties. *Nordic Pulp and Paper Research Journal*, *22*(4), 452–461.

Katz, S., Beatson, R. P., & Scallan, A. M. (1984). The determination of strong and weak acidic groups in sulfite pulps. *Svensk Paperstidning*, *6*, 48–53.

Kenealy, W., Horn, E., & Houtman, C. (2007). Vapor-phase diethyl oxalate pretreatment of wood chips. Part 1. Energy savings and improved pulps. *Holzforschung*, *61*(3), 223–229.

Kenny, J. (2006). How will biofuels affect the European wood market? *Solutions*, *89*, 16–20.

Leenakul, W., & Tippayawong, N. (2010). Dilute acid pretreatment of bamboo for fermentable sugar production. *Journal of Sustainable Energy & Environment*, *1*, 117–120.

Li, K. C., Tan, X. Q., & Yan, D. B. (2006). The middle lamella remainders on the surface of various mechanical pulp fibres. *Surface and Interface Analysis*, *38*(10), 1328–1335.

Miao, Q. X., Hou, Q. X., Qin, M. H., & Fu, Y. J. (2008). Characteristics of dissolved and colloidal substances released from poplar CTMP and BCTMP. *Transactions of China Pulp and Paper*, *23*(4), 13–18.

Meyer, V., Ruel, K., Petit-Conil, M., Valtat, G., & Kurek, B. (2004). Modification of the cell wall structure by oxalate associated with energy savings during mechanical pulping. In *9th International Conference on Biotechnology in the Pulp and Paper Industry* Durban, South Africa, (pp. 95–96).

Rundlöf, M., Eriksson1, M., Ström, H., & Wågberg, L. (2002). Effect of mannanase and lipase on the properties of colloidal wood extractives and their interaction with mechanical pulp fines. *Cellulose*, *9*(2), 127–137.

Sjöström, E. (1993). *Wood chemistry fundamentals and applications* (2nd ed.). San Diego, CA: Academy Press Inc.

Svedman, M., Lonnberg, B., Holmbom, B., & Jakara, J. (1995). Release of dissolved and colloidal substances in pressurized grinding with peroxide and alkali. *Paperi Ja Puu-Paper and Timber*, *77*(3), 117–121.

Thorp, B., & Raymond, D. (2004). Forest biorefinery could open door to bright future for P&P industry. *PaperAge*, *120*(7), 16–18.

van Heiningen, A. (2006). Converting a Kraft pulp mill into an integrated forest biorefinery. *Pulp and Paper Canada*, *107*(6), 38–43.

Xu, E. C, & Zhou, Y. (2007). Synergistic effects between chemical mechanical pulps and chemical pulps from hardwoods. *TAPPI Journal*, *6*(11), 4–9.

Yoon, S. H., van Heiningen, A., & Krishnagopalan, G. A. (2008). Kraft pulping integrated with mild alkaline pre-extraction of southern mixed hardwoods. In *Engineering, Pulping and Environmental Conference* 24–27 August, 2008, Portland, OR, USA, (pp. 2174–2233).

Zhang, H. J., He, Z. B., & Ni, Y. H. (2011). Improvement of high-yield pulp properties by using a small amount of bleached wheat straw pulp. *Bioresource Technology*, *102*(3), 2829–2833.

Zhang, X., Qin, W. J., Paice, M. G., & Saddler, J. N. (2009). High consistency enzymatic hydrolysis of hardwood substrates. *Bioresource Technology*, *100*(23), 5890–5897.

Zhou, Y. J., Zhang, D. J., & Li, G. L. (2005). An overview of BCTMP: process, development, pulp quality and utilization. *China Pulp & Paper*, *24*(5), 51–60.

Zhu, J. Y., & Pan, X. J. (2010). Woody biomass pretreatment for cellulosic ethanol production: Technology and energy consumption evaluation. *Bioresource Technology*, *101*(13), 4992–5002.

Zou, X., Zhou, Y., Raymond, S., & Jolette, D. (2009). Brightness and strength stability of high-yield pulps during short-term storage. *Pulp and Paper Canada*, *110*(2), 27–31.