Energy Consumption and Morphological Development of Eucalyptus Alkaline Peroxide Mechanical Pulp by Carboxymethyl Cellulose-assisted Refining

Fengzhen Cheng, Youming Li,* and Donghai Chen

Carboxymethyl cellulose (CMC)-assisted refining was shown, by means of tests with a PFI mill, to have potential to save energy compared with conventional refining techniques. Previously it was thought that the energy-saving effect of CMC-assisted refining was caused by resultant lubrication that reduced friction. In this work, the refined fiber of eucalyptus alkaline peroxide mechanical pulp was analyzed. The mechanism of CMC-assisted refining is that the cell wall is fibrillated to peel and weaken cell wall strength. Then CMC permeates into the cell wall and swells it, and the fiber becomes more pliable. CMC-assisted refining is helpful in maintaining fiber length through resultant hydration to avoid more fiber cutting. In this work, fiber morphological changes in the course of PFI refining for different numbers of revolutions were shown in relation to CMC-assisted refining. The purpose of the research was to determine whether energy savings could be achieved by CMC-assisted refining and to study its influence on fiber morphological development. The study showed a linear relationship between fiber length and energy consumption, as well as an exponential relationship between fines and fiber length. These results are helpful for obtaining ideal fiber morphology in pulp and paper making, man-made board, natural nano-fibers and specialty fibers, and the food industry.

Keywords: Morphological development; CMC-assisted refining; PFI mill; Refining revolutions

*Contact information: Pulp & Paper Engineering State Key Laboratory of South China University of Technology, 381 Wushan Road, Tianhe District, Guangzhou, 510641, Guangdong, P.R. China; *Corresponding author: ymli3@scut.edu.cn*

INTRODUCTION

In the pulp and paper industry, refining is very energy intensive (Illikainen 2008; Sabourin 2003), especially mechanical pulp refining. Due in part to diminishing resources, the problem of high energy demand has become more and more serious. One type of mechanical pulp, alkaline peroxide mechanical pulp (APMP), is called a "high yield mechanical pulp" because of its high lignin content. Another similar type of pulp is chemithermomechanical pulp (CTMP). In the case of APMP about 85 to 96% of the original wood components are retained in the final product (Vena 2005). This pulping process results in less pollution and caters to the needs of environmental protection. Therefore, APMP is being used extensively for liquid package board (food industry) and light weight coating paper (culture and advertising field) production in place of semi-chemical pulps. In the papermaking process, APMP requires secondary refining for stock preparation (freeness drop from 450 CSF to 300 CSF for liquid package board or from 450 CSF to 150 CSF for light weight coating paper), which consumes a large amount of energy. However, there is also a trend in the development of certain specialty grades of

paper that the environment-friendly and cheap pulp APMP replaces chemical pulps cooked to relatively high yields, *e.g.* high-yield kraft and neutral sulfite semichemical (NSSC) pulps. This research mainly focuses on energy consumption and fiber morphological development during refining. In recent years, some low energy refining experiments have been based on process optimization (Senger *et al*. 2006; Muhic *et al*. 2010; Murton and Duffy 2005) and the aid of chemicals in sulphonation, carboxylation, oxidation, and enzymatic reactions (Johansson *et al*. 2011; Kumar and Wyman 2009; Decker *et al.* 2009). In those studies that involved refining, the focus was mainly on the refining equipment (Gorski *et al*. 2010; Kure *et al.* 1999), and there was less discussion on adjusting fiber morphology to reduce refining energy consumption.

Carboxymethyl cellulose (CMC) has been presented as an additive to improve the properties of the pulp and paper. Additionally, the characteristic of low molecular mass CMC that could reduce refining energy consumption was assumed to be its ability to lubricate (Huang *et al.* 2007; Rakkolainen *et al*. 2009), but the mechanism of energy consumption reduction has remained unclear. In this work, the energy consumption reduction was considered to be due to hydration, which resulted in the fiber being more pliable and there being more fibrillation instead of fiber cutting (*i.e*. peeling fibrillation is facilitated to a greater degree than fiber cutting and shortening when fibers are in a hydrated condition; thus, hydration is helpful in forming a liquid-lubricated film on the surface of the fiber wall.). In this paper, eucalyptus APMP, a common material, was used. Low molecular weight CMC-pretreated and standard eucalyptus APMP refining were compared. The energy consumption distribution and the development of fiber morphology at different PFI refining revolutions were analyzed.

EXPERIMENTAL

Materials

Flash-dried industrial eucalyptus APMP (29 ºSR, consistency 89%) was obtained from APP Jingui, China. The CMC (analytical reagent, dry powder, 0.6 mmol/g, degree of substitution 0.85) came from Tianjin Kermel Co., China. The distilled water (20 ºC) was self-made. The advantages of low molecular weight CMC are that the CMC solution preparation requires less time than high molecular weight CMC and the mixture of CMC solution and eucalyptus APMP has better electrostatic repulsion between the CMC and fiber. CMC with a larger molecular weight and a lower DS (0.2) is more difficult to handle because of its extremely low solubility in water (Rakkolainen *et al*. 2009).

Instruments

The instruments used in this work were a PFI mill, type 621 from Hamjern Maskin Company, Norway, an environmental scanning electron microscopy (ESEM), type Quanta 200 from FEI, Netherlands, a fiber lab analyzer, type Kajaani FS300 from Metso Automation, Finland, and a thermal magnetic stirrer, type DF-II from Changzhou Aohua, China. The PFI mill type of refining apparatus was chosen because the revolutions could be customized and the energy consumption could be shown; another reason for the selection was to simplify the interpretation of results. Generally, the nominal refining consistency is 10% in a PFI mill. It is known that higher refining consistency can save resources (energy and water, *etc*.), and avoid the big interference from fluid mechanics to refining mechanics that is inherent in low consistency refining conditions.

Methods

CMC solution preparation

Twenty-five grams of CMC dry powder were added gradually into 2475 mL distilled water, which was heated in the water box of the thermal magnetic stirrer up to a temperature of 60 ºC. At this temperature, the stirrer was used for 4 h until all flocs disappeared and the mixture became homogeneous. The CMC solution consistency was 1%, and the mass was 2500 g. Afterwards, the solution was cooled to 20 ºC.

Eucalyptus APMP pretreatment

PFI refining was done following TAPPI standard T248 sp-00. Fractions S1 and S2 were each split into seven equal portions and labeled S10, S11, S12, S13, S14, S15, S16, S20, S21, S22, S23, S24, S25, and S26. Portions S10 and S20 were used as stock samples for S1 and S2. The remaining portions of S1 and S2 were each refined at a PFI roll speed 1443 rpm and housing speed 696 rpm. S11 and S21 were refined at 1000 PFI revolutions, S12 and S22 at 2000 PFI revolutions, S13 and S23 at 2500 PFI revolutions, S14 and S24 at 2750 PFI revolutions, S15 and S25 at 3000 PFI revolutions, and S16 and S26 at 3300 PFI revolutions.

Table 1. Eucalyptus APMP Pretreatment

	Standard	1% CMC pretreatment
Sample	S1	S2
Mass of eucalyptus APMP (bone dry g)*	210	210
Distilled water at 20 ºC (g)	1864	-
1% CMC solution at 20 ºC (g)**	-	1864
Stirred time of eucalyptus APMP and CMC (min)**	40	40
Mixture temp. (ºC)**	20	20
Retained time at 20 ºC, atmospheric pressure (h)**	24	24
*The moisture measurement of wet eucalyptus APMP was done according to TAPPI methods T 210 cm-03 and T 240 om-02. **CMC solution consistency, mixed time, mixture temperature, and retention time were tentative, based on our earlier experiments		

RESULTS AND DISCUSSION

Fiber dimensions, deformation, and energy consumption (KJ) are shown in Table 2. The fiber dimensions and deformation data were obtained with a fiber lab analyzer (Kajaani FS300). Samples were prepared according to the recommendation of the equipment manufacturer. For latency, the fiber data were measured after all refined samples had been maintained at 10 ºC for one week. The energy consumption data was from the display panel of the PFI mill (type 621) and the numbers of revolutions were customized.

The fiber length, fiber width, fiber coarseness, fines, and vessels in Table 2 represent fiber dimensions; fiber curl and kink index represent fiber deformation.

Figure 1 presents the linear relationship of energy consumption and revolutions of PFI refining. Figure 2 presents a linear relationship of fiber length and energy consumption. Figure 3 presents an exponential relationship of fines and fiber length. Figure 4 presents a logarithmic relationship of kink index and fiber length. Figure 5 presents an irregular relationship between fiber curl and PFI refining revolutions.

Table 2. Energy Consumption, Fiber Dimensions, and Deformation

Sample	PFI revol. (rev.) *	Energy consum. (KJ)	Fiber length (mm)	Fiber width (μm)	Fiber coarse. (mg/m)	Fines (%)	Vessels (mm^2/mg)	Fiber curl (%)	Kink index (1/m)
S10	0	0	0.525	18.93	0.209	14.39	7.63	8.21	362.26
S11	1000	50.4	0.46	19.31	0.186	18.7	9.87	8.5	334.06
S12	2000	100.8	0.4	19.1	0.195	25.15	9.64	8.35	238.9
S13	2500	129.6	0.375	19.25	0.212	27.18	7.32	7.76	208.69
S14	2750	140.4	0.375	19.87	0.224	27.46	7.33	7.72	206.65
S15	3000	147.6	0.34	20.09	0.222	31.09	5.19	7.29	154.56
S16	3300	165.6	0.325	19.65	0.217	33.71	6.77	7.74	164.89
S20	0	0	0.54	18.62	0.19	13.79	9.74	8.13	313.34
S21	1000	46.8	0.52	18.82	0.168	15.45	10.92	8.62	341.56
S22	2000	93.6	0.47	19.42	0.192	18.78	8.17	8.39	290.71
S23	2500	118.8	0.44	19.18	0.197	21.57	7.7	8.3	264.15
S24	2750	129.6	0.46	18.95	0.189	19.3	7.74	8.15	294.05
S25	3000	133.2	0.45	19.13	0.193	19.54	9.08	8.22	290.27
S26	3300	154.8	0.43	19.38	0.182	22.27	7.9	8.19	254.93

*PFI revolutions were starting from 0 rev., i.e. 0-1000 rev., 0-2000 rev., 0-2500 rev., … instead of 0-1000, 1000-2000, 2000-2500 rev.…

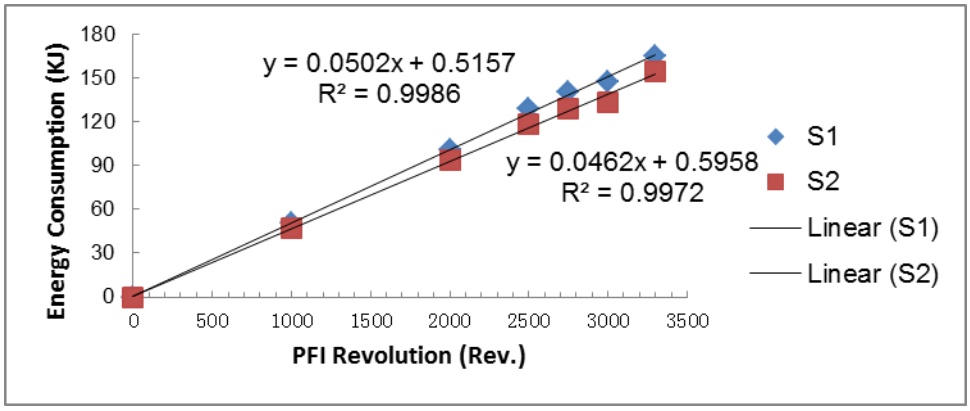

Fig. 1. The linear relationship of energy consumption and PFI refining revolutions

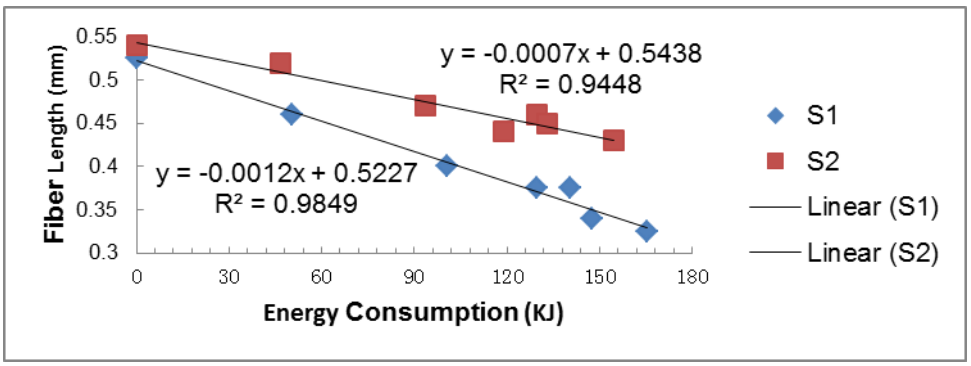

Fig. 2. The linear relationship of fiber length and energy consumption

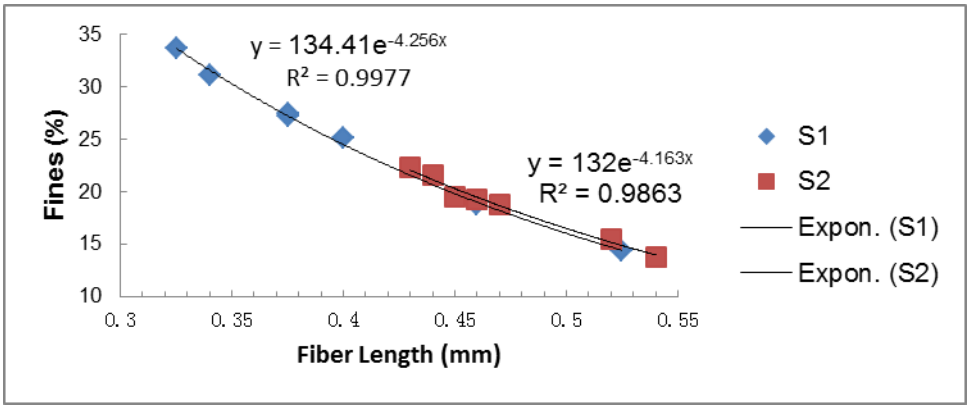

Fig. 3. The exponential relationship of fines and fiber length

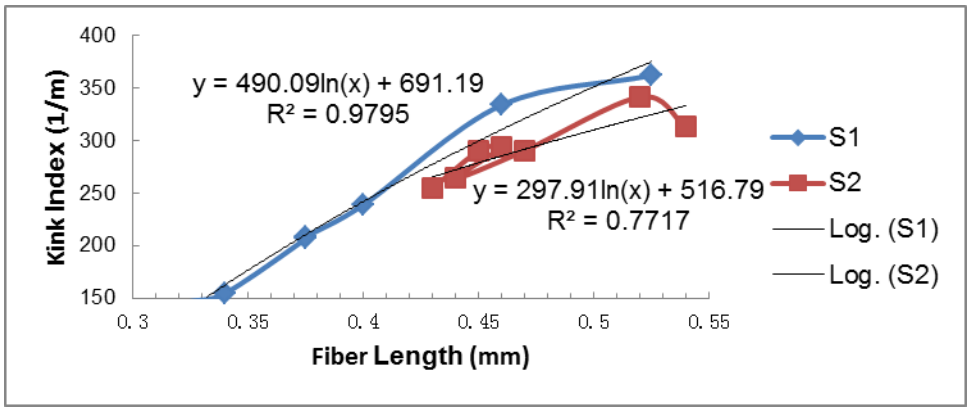

Fig. 4. The logarithmic relationship of kink index and fiber length

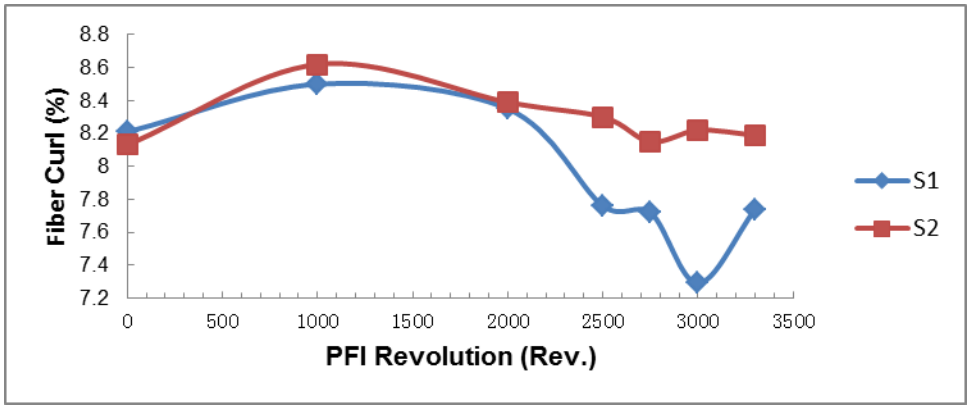

Fig. 5. The irregular relationship of fiber curl and PFI refining revolutions

Energy consumption, fiber length, and fines are three important indices of refining performance. From the experimental results in Table 2 and Fig. 1, the energy consumption increased almost linearly with PFI refining revolutions, and CMC-assisted refining could consume less energy, which was attributable to less fiber cutting action.

From Table 2 and Fig. 2, the fiber length decreased almost linearly with energy consumption and refining revolution increase. CMC-assisted refining was helpful in maintaining longer fiber lengths than standard refining at the same revolutions, and the

smaller energy consumption in CMC-assisted refining was one of the reasons accounting for the longer fiber length at the same number of revolutions as standard refining.

From Table 2 and Fig. 3, the fines increased almost exponentially with fiber length decrease, and the fines increase in CMC-assisted refining was less than standard refining at same revolutions.

From Table 2 and Fig. 4, the kink index decreased almost logarithmically with fiber length decrease for standard refining; however, in CMC-assisted refining, the relationship was changed.

From Table 2 and Fig. 5, the relationship of fiber curl and number of PFI refining revolutions was irregular; however, it still showed a trend that PFI refining could decrease fiber curl (*i.e.* latency removal action) under certain revolutions for standard PFI refining, whereas in CMC-assisted refining the action was changed.

From the above, the equations in Figs. 1, 2, and 3 could be used to control the fines, fiber length, and energy consumption through the PFI refining revolution in stock preparation. The standard PFI refining could be helpful in latency removal.

Regarding latency, Myers *et al.* (1996) described a latency method in which 15% CTMP was soaked in 90 ºC water for a minimum 30 min with occasional stirring; Wong *et al.* (2000) reported that the latency was removed by agitation at 90 ºC and 1.25% stock consistency for 10 min. In the present work, thinking about the potential effects of heating on the action of CMC, the further purpose for latency treatment was to make the measured fiber data more stable in the subsequent step, not to make the fiber straightened.

In the following discussion, fiber curl in Table 2 is a reference to measure the latency degree. If the change of fiber curl value has a large range, which shows an inadequate latency, then the measurement value in Table 2 is not reliable. However, in Table 2, the fiber curl value is in a small range (7.94 ± 8% for S1 and 8.29 ± 4% for S2). Therefore, the latency is adequate and the measured value in Table 2 is reliable. Figure 6 presents the ESEM images of surface morphologies of S1.

Côté (1967) presented that the fiber cell wall consists of the middle lamella (ML), primary wall (P), secondary cell wall layers (S_1, S_2, S_3), and warty layer (W) (Berg 2008). Franzén (1986) proposed that the rupture of the fiber wall during refining takes place preferentially in the primary layer (P) and in the lignin rich middle lamella (ML) in the CTMP pulping process. In this respect APMP can be regarded as similar to CTMP. In this paper, it is proposed that the re-rupture of the APMP fiber wall during PFI refining first takes place in primary layer (P).

Figure 6 and Table 2 show that from S10 to S12 (*i.e.*, PFI revolutions from 0 to 1000 to 2000), during fibrillation, the fibers widened and vessels' specific surface area increased in the primary layer (P) of the fiber cell wall. Further, the P layer peeled off, fiber coarseness decreased, and cell wall strength decreased, resulting in shortened fibers. The kink index decreased, fines increased, and the vessels' specific surface area increased. From S13 to S15 (*i.e.*, PFI revolutions from 0 to 2500 to 2750 to 3000), the outer layer (S_1) of the secondary wall peeled off due to fibrillation and the fiber ends split, which resulted in larger measured fiber width. Thus, water penetrated into the split fiber ends more easily and the fiber coarseness increased. Meanwhile, the fibers shortened, kink index decreased, fines content increased, and vessels' specific surface area decreased. From S16 (*i.e.*, PFI revolution from 0 to 3300), the inner layer (S_2) of the secondary wall fibrillation, the fractures/cracks caused the fines to increase and the vessels' specific surface area to increase. At the same time, fiber distortion occurred, which shortened the average fiber length. When the contained water in the cell was squeezed out by PFI mill

teeth, pits became clearly visible, fiber coarseness decreased, and kink index increased (fibers more pliable than S15).

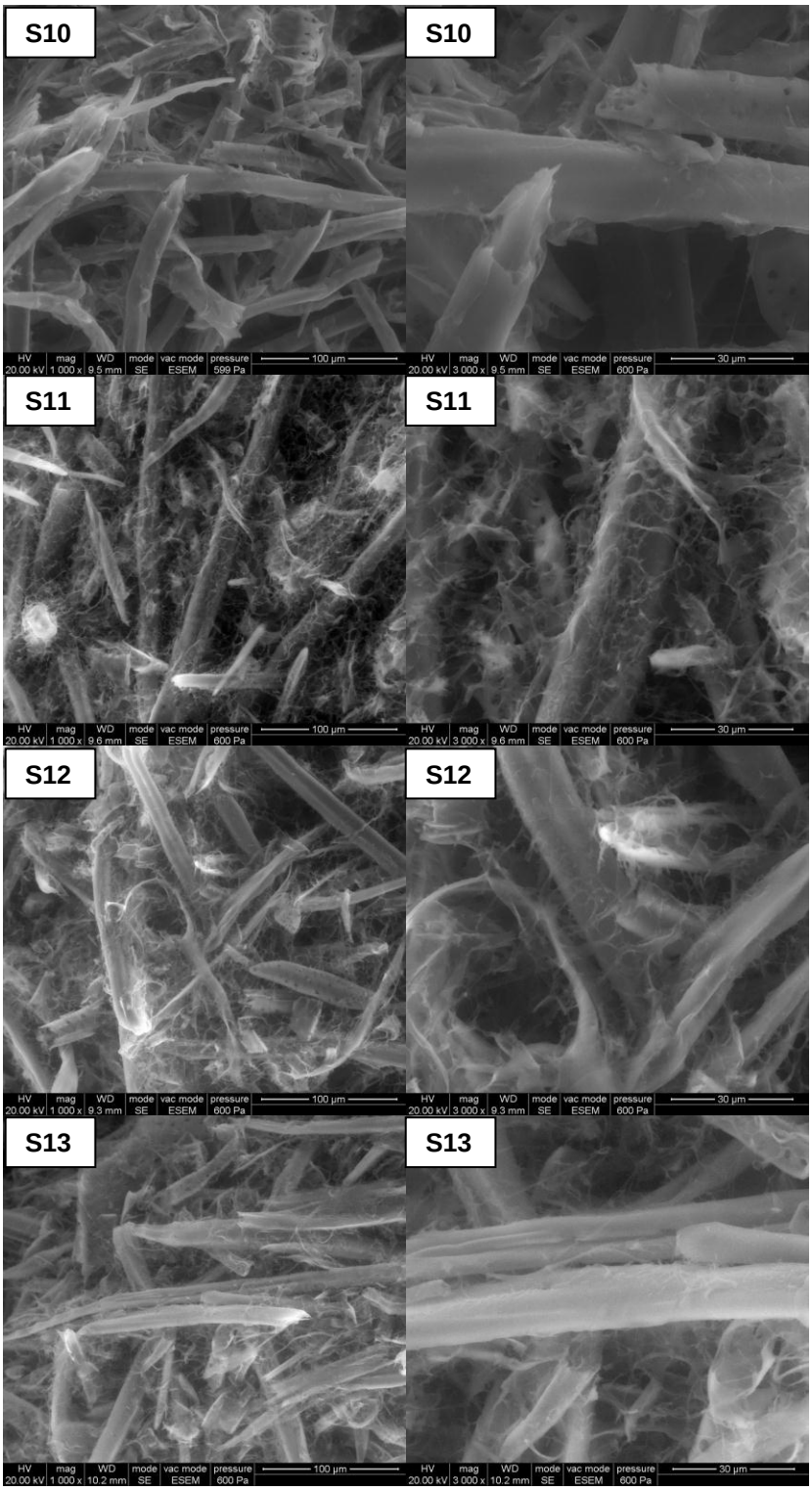

Fig. 6A. Surface morphologies of refined sample S1

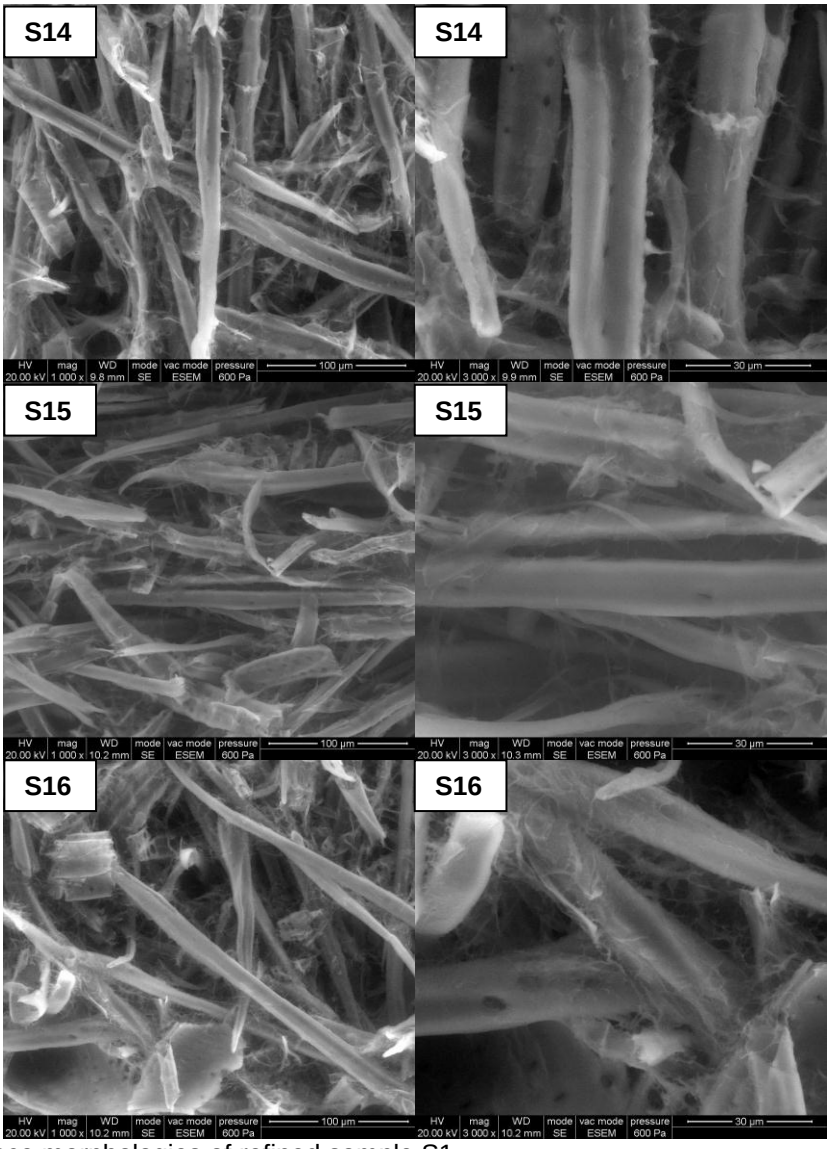

Fig. 6B. Surface morphologies of refined sample S1

Sundholm (1999) suggested that in an ideal refining process, the following phenomena should happen: fibers must be separated from the wood matrix, fiber length must be retained, fibers must be delaminated, abundant fines must be generated by peeling off P and S_1 layer of fiber cell wall, and the surface of S_2 of the remaining secondary wall must be fibrillated (Illikainen 2008). The experimental steps in this paper covered an ideal refining process; therefore, rpm greater than 3300 are not necessary.

Figure 7 presents the ESEM images of surface morphologies of S2. From Fig. 7 and Table 2, it is shown that in S20, the fiber was straighter than S10 (the fiber curl of S20 in Table 2 is shown as less than S10). The fiber length of S20 was longer than S10, the S20 vessels' specific surface area was bigger than S10, and the fiber coarseness of S20 was less than S10. The fiber width of S20 was smaller than S10 because of CMC's tendency to draw the fiber wall together more during drying. From S20 to S21 (*i.e.*, PFI revolutions from 0 to 1000), CMC was evenly dispersed in the water and on the fiber surface during refining. CMC passes through the pits to enter the cell wall P layer and S layer.

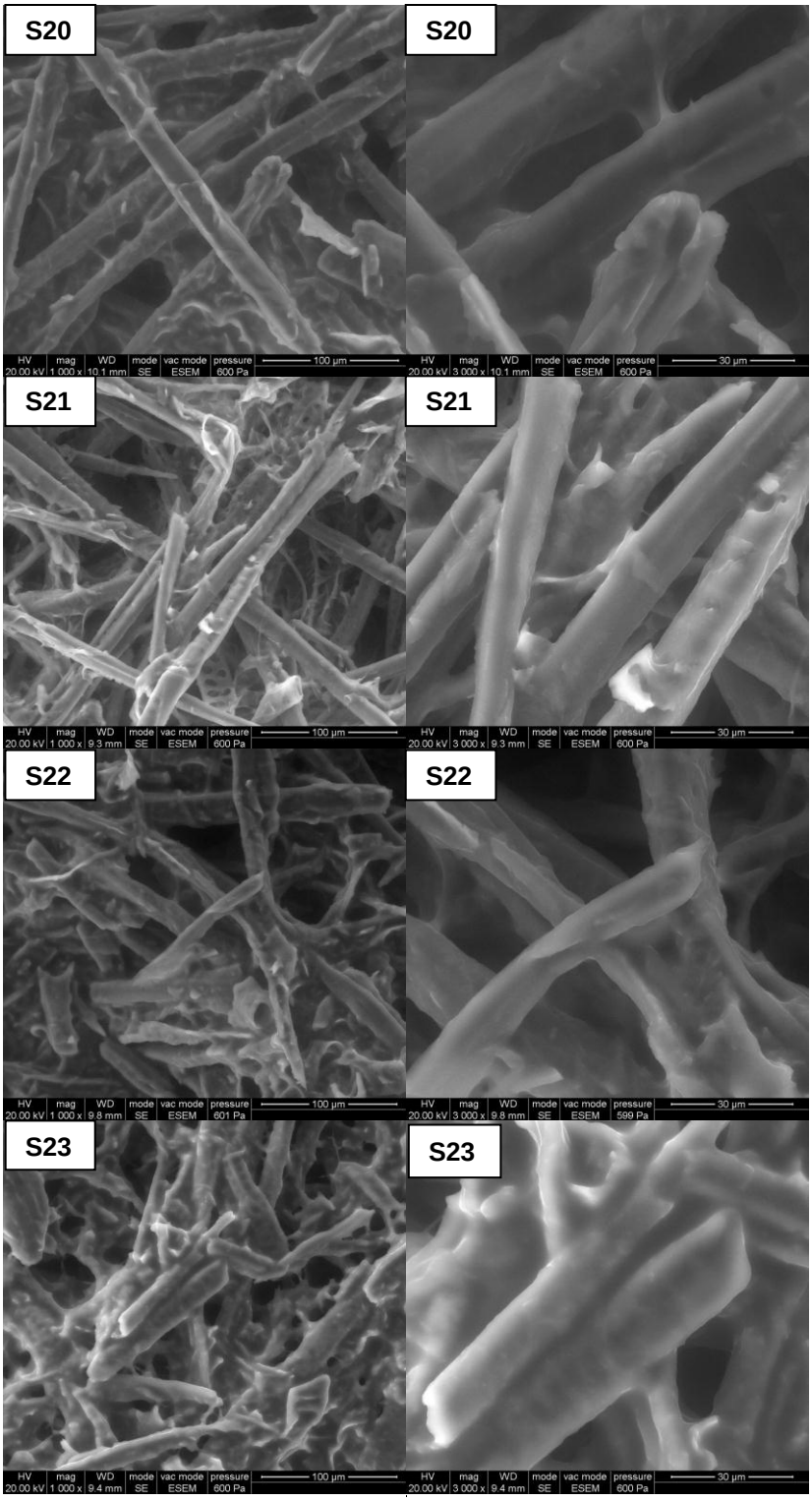

Fig. 7A. Surface morphologies of CMC-assisted refined S2

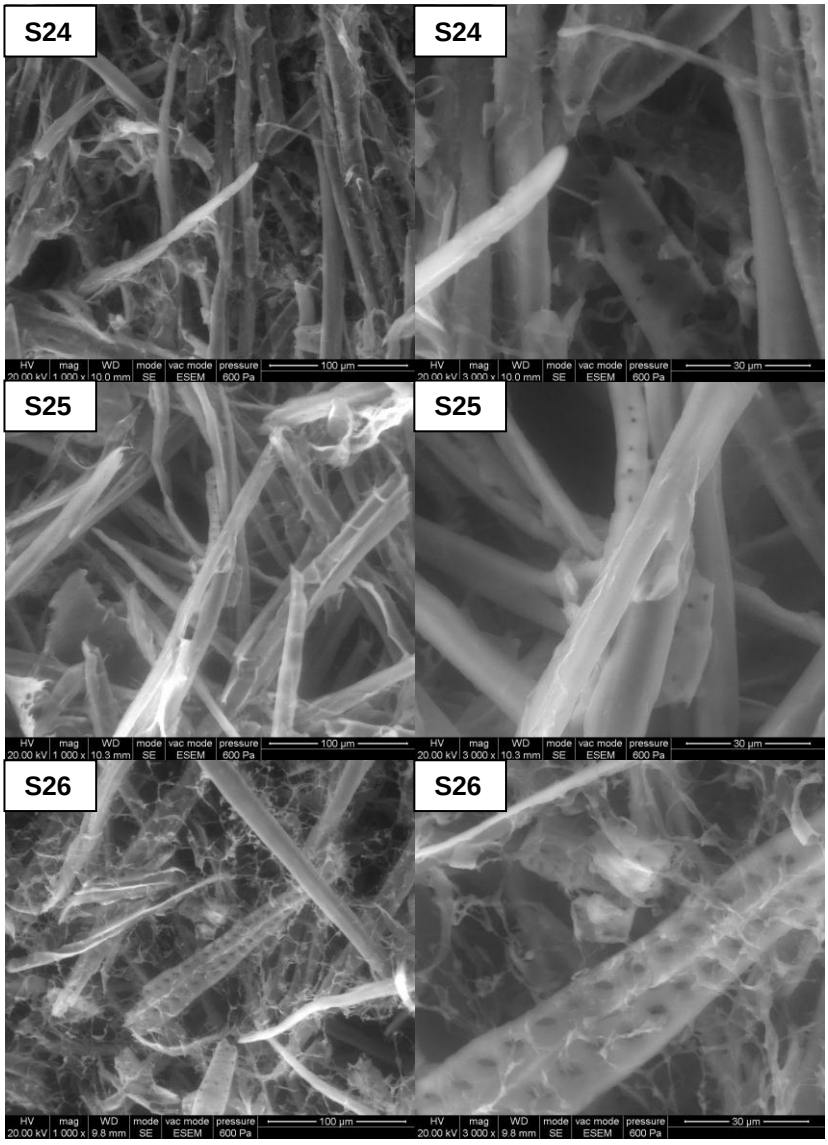

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Fig. 7B. Surface morphologies of CMC-assisted refined S2

With the protection of CMC lubrication, S21 fibers were cut less than S11 and the fines increased less than S11. However, the increase in vessels' specific surface area of S2 was more than S1. A small amount of fibrillation of the P layer and the resulting peeling caused the fiber width to increase, while the displaced water in the cell tube led to less fiber coarseness. An increase in kink index means that fibers are more pliable.

With the progress of refining, from S22 and S23 (*i.e.*, PFI revolution from 0 to 2000 to 2500), CMC was sheared and thinned (shear thinning) (Cross 1979), most fibers were coagulated together, which increased the chances of fiber cutting (leading to shorter fibers, an increase in fines content, and a decrease in vessels' specific surface compared with S21) and more fibrillation (leading to an increase in fiber width). Fiber coarseness increased due to CMC gel hydration with more hydroxyl groups. Hydration helps CMC into the secondary layer of cell wall and swells the S layers. For S2, the kink index changed with the fiber length.

From S24 and S25 (*i.e.*, PFI revolution from 0 to 2750 to 3000), the hydrated CMC between the S_1 and S_2 layers made the S_1 layer fibrillate and peel off easier, which led to a decrease in fiber width and fiber coarseness, a decrease in fines content, an increase in vessels' specific surface area compared with S22 and S23, and the kink index increased (the fibers were more pliable than S23).

From S26 (*i.e.*, PFI revolution from 0 to 3300), the S_1 layer peeled off, leading to decreased cell wall strength, shortened fibers, a decrease in kink index, an increase in fines, a decrease in vessels' specific surface area, and less fiber coarseness than S24 and S25. Fibrillation of the S_2 layer into a net structure made the fibers widen. However, the similar net structure of carrageenan/milk gels was also reported in the food industry (Michon *et al*. 2005).

In this experiment of CMC-assisted refining, the vessel specific surface area was greater, the fines rate was lower, and the fiber length was longer than in the case of a standard refining process. A CMC-assisted refining process can help reduce energy consumption in the pulp and paper or man-made board industries, using the appropriate design process parameters and chemical additives during refining, according to the needs for the morphological development of fiber.

CONCLUSIONS

1. Compared with standard refining, CMC-assisted refining can reduce energy consumption with the same refining revolutions, providing longer fiber length, fewer fines, bigger vessel specific surface area, smaller fiber width, and less coarseness. CMC-assisted refining saves energy because of less fiber cutting action. The fiber length decreased almost linearly with energy consumption and refining revolution increase. The fines increased almost exponentially with fiber length decrease, and the fines increase in CMC-assisted refining was less than standard refining at the same revolutions. The kink index decreased almost logarithmically with fiber length decrease for standard refining; however, in CMC-assisted refining, the relationship was changed. The relationship of fiber curl and PFI refining revolution was irregular. The trend is that PFI refining could decrease fiber curl (*i.e.* latency removal action) under certain revolutions for standard PFI refining.
2. A standard refining process is as follows: the P layer fibrillates and peels off (the fiber wall weakens), fibers shorten, fines increase, and vessels' specific surface area increases. Next the S_1 layer fibrillates and peels off (the fiber wall weakens), fibers shorten, fiber ends split, fines increase, and vessels' specific surface area decreases. Then the S_2 layer and fiber fractures fibrillate, fibers distort, fibers shorten, fines increase, vessels' specific surface area increases, kink index increases, and pits pass through.
3. The CMC-assisted refining process is as follows: CMC coats fibers' P layer surface (fiber is pliable), the P layer fibrillate and peels off, and there is less fiber cutting, less fines increases, and vessel's specific surface area increases. Then CMC enters the secondary layer of fiber wall and swells the S_1 layer (fiber is more pliable), resulting in the S_1 layer peeling off more easily, and then the S_2 layer fibrillates into a net structure.

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