Application of Thermomechanical Pulping Method for Fabricating Bamboo Fiber

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Application of Thermomechanical Pulping Method for Fabricating Bamboo Fiber

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Abbreviation

Terms	Description
TMP	Themo-mechanical pulping
MDF	Medium density fiberboard
APTMP	Alkaline-peroxide mechanical pulping
NSSC	Neutral sulfite semi-chemical
S1	Fiber wall second layer 1
S2	Fiber wall second layer 2
NBO	Nitrobenzene oxidation
Py-GC/MS	Pyrolysis-gas chromatography/mass spectrometry
S/G ratio	Syringyl/Guaiacyl ratio
S/V ratio	Syringaldehyde/Vanillin ratio
SEM	Scanning electron microscopy
UV	Ultra violet

Chapter 1 Introduction

1.1 Bamboo as a wood alternative material

Bamboos are woody grasses that fast grow in diverse habitats from all continents of the world except Europe. There are over 1250 species in approximately 75 genera of bamboo that have ideal living environment in tropics and subtropics regions, where they can grow in mixed forests or pure stands. The most important part of bamboo for industries is the bamboo culm because it contains a huge amount of fibers, which appear as bundles in the culm's wall. Varied for species, the culm is often short-lived within 5-10 years. Japanese moso-bamboo is mature at 3-4 years and gradually become old and death in about 10 years. Culm's age also the important factor to consider in order to manage bamboo cavillation (Liese and Köhl 2015).

The anatomical structure of bamboo woody-culm is different and more uniform comparing with wood. The most unique structure of bamboo is the shape and the distribution of vascular bundles, which are surrounded by the parenchyma cells inside the internode. Vascular bundle is a group where fibers present and appears massively at the outer part of the culm's wall. Therefore, the outer part of the culm is denser with fibers and has far higher density than the inner, which almost filled by parenchyma cells. Amount of vascular bundles does not change with the height, while the parenchyma fraction declines (Liese 1998).

The bamboo fibers are presented by their slender form, long and tapered and sometimes forked at the ends. Content of fiber is about 40 % of the mass and to 60–70 % of the weight

of the bamboo culm. The length of fiber is varies between species but is recognized to be much longer than those of hardwoods or softwoods. In general, fibers wall is formed by the primary, secondary, and the tertiary wall. To be more specific, the secondary wall of a bamboo fiber is made up by up to 8 layers of microfibrils in different orientation. Especially, bamboo does not have any particular cells for radial transportation like ray cells in woods (Grosser and Liese 1971).

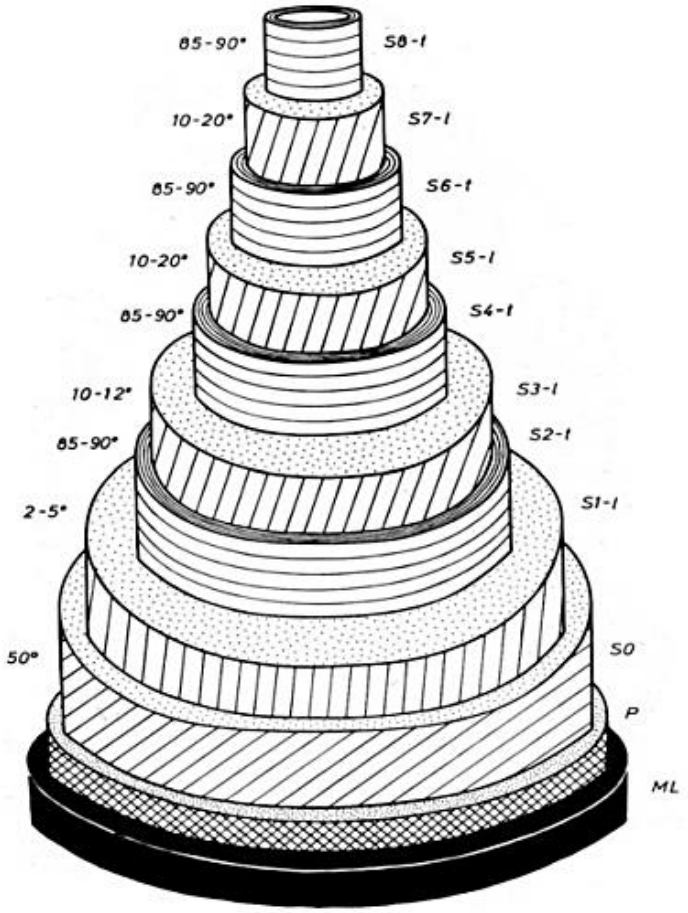

Figure 1. 1 Model of bamboo fiber with numerous of wall's layers (Liese and Köhl 2015)

As an overview of the bamboo resources, data reported by FAO in 2005 shown that there are more than 36 million hectares of bamboo worldwide or an average of 3.2 % of the total forest area. Asia countries poses the largest proportion of the resource, about 65%, and equal to approximately 24 million hectares of bamboo forest. India and China are the two major of bamboo producing countries (FAO, 2005).

The use of bamboo as a living plant is diversity, depends on the field of the application such as food industry or building and construction. Bamboo culm also becomes the important material for producing flooring and furniture, as commercial products like laminated bamboo or bamboo veneers. Chemical pulp from bamboo also take interest for years. The pulp yield in the Kraft process is comparable with hardwood Kraft pulp, however, cooking is more costly (Liese and Köhl 2015).

1.2 Pulping process

The basic target of every pulping method is to release the fibers from the lignin that adheres the fibers together in any lignocellulosic materials. Basically, there are five main types of pulping processes, includes: chemical, mechanical, semi chemical, recycled/secondary fiber pulping, and others (dissolving, nonwood) (Bajpai 2016). All chemical pulping methods rely on the effect of chemicals to separate fibers, whereas mechanical pulping methods depend on physical impact. The more that chemicals are involved, the lower the yield and lignin content since chemical action degrades and solubilizes components of the wood, especially lignin and hemicelluloses. Chemical pulping extracts individual fibers that are not cut and give strong papers since the lignin, which interferes with hydrogen bonding of fibers, is largely removed (Biermann 1996).

On the other hands, mechanical pulping remains mostly lignin from raw material, with pulp yield are around 90–95 %. This pulp are produced by two different commercial processes, in which wood is processed either in the form of logs treated in grinders, or in the form of wood chips that are converted to pulp by mechanical work in a refiner (Höglund 2009). However, the presence of lignin will alter fiber from swelling during pulping and result in less collapsible fibers. Mechanical pulp was considered as having low strength since the lignin interferes with hydrogen bonding between fibers when paper is made. Another aspect of mechanical pulping is this method is quite violent, the whole process is based on damaging fibers (Lehto 2011). Actions such as grinding or refining can damage fibers and contribute further to reduction in fiber's strength. The lignin also causes the pulp to turn

yellow with exposure to air and light, thus, mechanical pulps is confined mainly to non-permanent papers like newsprint and catalog paper (Biermann 1996). There are so-called chemi-mechanical pulping (CMP) and chemi-thermormechanical pulping (CTMP) processes that involves a gentle chemical treatment stage combined with mechanical defibration such as disc refining. The yields of these pulps are generally in the range of 80–95%, and their properties are intermediate between those of high-yield chemical pulps and mechanical pulps (Jürgen Blechschmidt, Sabine Heinemann 2006). In the broader sense as consider about the pulp yield, pulping processes that involve a chemical treatment before refining must be classified as semi chemical pulping (Marteny 1980).

To date, refiner pulp is usually produced in a so-called thermomechanical pulping, which will be described in detail in the current chapter and be further discussed thoroughly on this research.

1.3 Thermo-mechanical pulping (TMP)

Thermo-mechanical pulping (TMP) is now the most important mechanical process in pulping industry. This original was started from the Refiner mechanical pulping method (RMP) which was developed during 1948-1954 by Bauer Bros. and patented by Entherhard (Biermann 1996). RMP itself is a very complicated process combining the influences of several physical and mechanical elements. Basically, in refining moist wood chips and dilution water are fed into the first stage refiner. The chips are broken down when they contact with breaking bars of the rotor. Due to rotation of the disc and pattern of the refiner segment surface, rotational energy is transferred into the pulp by compression and frictional

forces. The outcome of the refiner are several different kinds of wood particles: shives, coarse fibers, fibrillated and flexible fibers, as well as fines (Illikainen 2008).

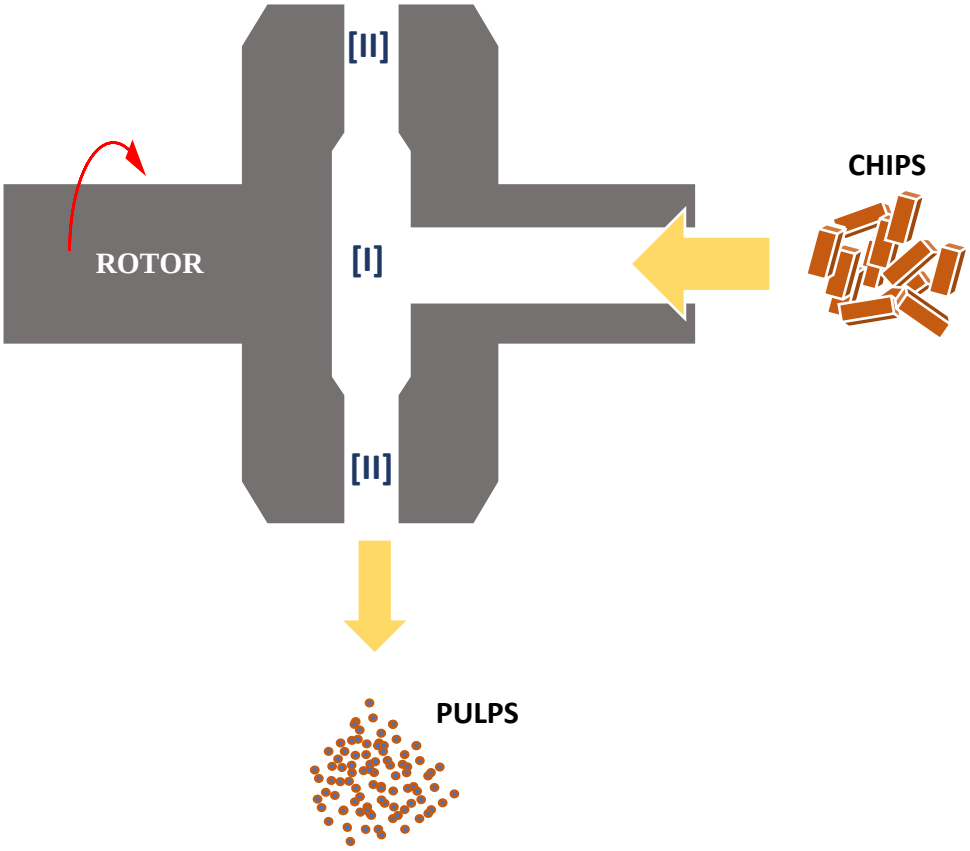

Figure 1. 2 The mechanism of a refining process

[I] – Breaking zone

[II] – Refining zone

The TMP process is very similar to the RMP process except that pulp is made in special refiners that are pressurized with steam in the first stage of refining. Commercial TMP is usually carried out in two stages of refining. In the first stage, the refiners are at elevated temperature and pressure to promote fiber liberation; in the second stage, the refiners are at ambient temperature to treat the fibers for papermaking. The high temperature during refining in the first step (normally 110-130°C) can help softening the fibers, loosing them from the matrix of wood components meanwhile be able to allow their recovery with less fiber damages compared to other mechanical process. To be more specific, refining happens at the temperature is just under the glass transition point of lignin, which is approximately 140°C, so that separation of fibers more likely occurs at the S-1 layer of the cell wall. This will improve fiber's external fibrillation (surface area) and expose more hydroxyl groups for hydrogen bonding when forming paper sheet (Belgacem and Pizzi 2016; Illikainen 2008; Karnis 1994). Increasing the refining temperature by operating at higher casing pressure is also expected to reduce energy consumption, thermomechanical pulp required more energy but produced a high-quality pulp that could be used as a single furnish for grades such as newsprint (McDonald et al. 2004).

Mechanism of thermomechanical pulping and fiber development phenomenon during this process has attracted a lot of interests from researchers in the field pulping and paper making. Accordingly, those parameters that are responsible for the pulp's properties can be listed as: (1) the pre-treatment condition (including duration, pressure and temperature); (2) the usages of additional chemicals; (3) the energy consumption and distribution; (4) the

pulping consistency; (5) the chip characteristic; and (6) the refining intensity (caused by plate design, rotational speed and feeding speed). Although the effectiveness of TMP depends on many factors, an ideal process is expected to meet these following requirements: the completely separation of fibers from wood matrix, fiber length must be retained, fibers must be delaminated, abundant fines must be generated by peeling off outer layers of the middle lamella, primary and secondary layers of fiber wall, and finally the surface of the remaining secondary wall must be fibrillated (Illikainen 2008).

In pulping industry, softwood is preferable than hardwood for TMP process because hardwood likely to give rather poor pulp strength properties. This can be explained by the fact that hardwood is more dense wood, and it's fibers do not form fibrils during refining but tend to separate into short debris (Bajpai 2015a). This phenomenon requires an addition chemical pretreatment to the wood chips prior to TMP in case of using such material that is considered as hard for refining.

1.4 Problem statement

Although bamboo has been used as an alternative wood material for years in a wide range of productions, the information of applying thermo-mechanical pulping on fabricating bamboo fiber has not clearly addressed in any published research. Furthermore, the unique anatomical structure of bamboo may lead to different fiber's characteristic comparing with wood. This issue also needs to be identified.

1.5 Objective of the study

The overall objective of this study is to investigate the possibility of using bamboo as the raw material for pressurized thermo-mechanical pulping. Application of pretreatment prior to refining will be focused. The characteristic of bamboo fiber generated from thermo-mechanical pulping method also under exanimated.

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Chapter 2 Alkaline – peroxide thermo-mechanical pulping of Bamboo

2.1 Introduction

In straight thermo-mechanical pulping, softwoods tend to break down to produce fibrillar material that has good sheet forming and bonding properties. However, hardwoods are more dense wood and have more rigid fiber structure that make the resulting pulp possesses lower fibrils content. Moreover, hardwoods tend to break up to nonfibrillar debris even with the preheating period is applied (Kurdin 1980). Chemical pretreatment of hardwood has been developed for decades due to it's potential to weaken the fiber – to-fiber matrix, subsequently cause the fiber development has possibility to happen at S1 and S2 layer of the fiber. Among those chemical pretreatment system, alkaline-peroxide has attracted research interest recently due to its advantages. Alkaline-peroxide can help to hydrolyze hemicellulose and lignin at high temperature, providing smooth defiberization while bleaching fiber when refining. Bleaching reaction is believed to majorly completed prior to refining (Miyanishi 2017). Alkaline-peroxide pretreatment also provide good quality of pulp and energy saving (Pan and Leary 2000). The application of this pretreatment has been first developed for low-density hardwood (Kofler et al. 1999), but then successfully applied for non-wood material due to their relatively open and easy to disintegrate structure (Jahan Latibari et al. 2012). The possibility of alkaline-peroxide mechanical pulping (APMP) of various non-wood species has been investigated, including wheat straw (Pan and Leary 2000; Zhao et al. 2004), oil palm empty fruit bunch (Ghazali et al. 2009; Owolabi et al. 2016), kenaf or bagasse (Xu and Narayana Rao 2001). Though, there is no

information about APMP of Bamboo so far. Bamboo characteristics are somewhat more likely similar with hardwood. The first chapter of this study has experienced the high debris content and darken pulp bamboo TMP, thus, it is necessary to investigate the possibility of applying alkaline-peroxide pretreatment on bamboo chips prior to refining. This research aims to examine the application of alkaline peroxide on TMP of Bamboo and its fiber's characteristic.

2.2 Material and methods

2.2.1 Material pretreatment

The raw bamboo chips used in this research were prepared in the same way as described in Chapter 1. Each 150 gram (oven dried) of bamboo chips were impregnated in $MgSO_4$ solution containing of 0.1% Mg^{2+} based on material weight prior to treating with a solution containing a mixture of 5.0% NaOH and 5.0% H_2O_2. Liquor to solid ratio was 2:1. Three kind of pulps then produced with following condition:

A：Cooking at 160℃ (maximum pressure was 1.7 MPa）in 40 minutes.

B：Cooking at 100℃（maximum pressure was 1.5 MPa）in 20 minutes.

C：Control experiment, cooking with tap water without any chemical involved. The cooking temperature was at 100ºC in 20 minutes.

As will be described later, the higher pressure than the water steam pressure in the treatment of A and B is due to the decomposition of H_2O_2.

2.2.2 Refining and fiber classification

The pretreated chips were then primary refined under pressurized conditions at 120ºC, followed by the secondary atmospheric refining. The disk clearance (plate gap) of the refiner gap for the primary and secondary refining was set at 1.0 mm and 0.1 mm, respectively. Refining was performed by the laboratory pressurized single disk refiner with a refiner plate (Type J) 305 mm in diameter was a model BRP45-300SS manufactured by Kumagai Riki Kogyo Co., LTD. (Nerima, Tokyo), equipped with a steam boiler (model SU-200 supplied by MIURA Co., LTD., Matsuyama, Ehime). Obtained pulp was fractionated by wet method in a Bauer McNett fiber classifier No.2593, mesh number was 14, 28, 48 and 100 (mess opening was 1180 µm, 600 µm, 300 µm and 150 µm respectively).

2.2.3 Pulp mechanical properties

The refined pulp was further treated with a PFI mill (ISO 5264-2:2011) at 10,000 revolutions according to ISO 5264-2:2011 standard. Forming handsheets for physical tests of the pulp followed the ISO 5269-1:2005 standard. The physical properties, as well as the tensile and tear indices of the handsheets were determined according to ISO 1924-2:2008, 1974:2012, and 5270:2012 standards.

2.2.4 Chemical analysis of materials and pulps

Contents of acid-insoluble lignin (Klason lignin) and acid-soluble lignin, a sum of which was reported as a lignin content, for each fraction were determined a modified method of TAPPI test methods T 222 om-15 (Harsono et al. 2016). Approximately 0.3 g of pulp was treated with 7.5 ml of 72% sulfuric acid for 2.5h. The mixture was diluted to 4% sulfuric

acid concentration, and then, the solution is heated for 1h in an autoclave at 121ºC. The acid-insoluble lignin is then separated as residue using a glass filter (1GP16), and it was dried to constant weight in an oven at 105ºC. The amount of acid-soluble lignin in the filtrate was determined according to UV spectrophotometry at the wavelength of 205 nm. The carbohydrate composition: the amounts of glucose, xylose in the acid hydrolysate for each fraction obtained from the previous lignin determination were determined using ion chromatography.

Nitrobenzene oxidation (NBO)

Fibers in each fraction were subjected to NBO to know chemical characteristics of lignin in the fraction. According to a modified NBO method (Nakagawa-Izumi et al. 2017), about 200 mg (oven-dried weight) of the prepared sample, 7 ml of 2 mol/L NaOH and 0.4 ml of nitrobenzene were placed together in a 10-ml steel bomb and oxidized at 170ºC for 2.5 h. After bombs were cooled down, using 8ml distilled water to wash the content of bombs into the 100 ml bottles. Then, ethyl vanillin (2 mg) as an internal standard was added to the reaction mixture. The mixture was extracted three times using 20 ml ether, and the lower (water) layers of the mixture were gathered and acidified to pH 3-4 using a small amount of 2 mol/L HCl. Then, the mixture was again extracted three times using 20 ml ether. The upper (ether) layers were gathered and washed with 5 ml of water to remove the remaining acid. Then, approximately 20 g of sodium sulfate anhydrous (Na_2SO_4) was added to the bottle and left it for 24 hours. After filtration of the mixture, the ether was evaporated, and syringaldehyde (S_a) and vanillin (V_a) in the ether were concentrated and ready for gas

chromatography (GC). From the molar yields of S_a and V_a, S_a ratios to V_a were defined as S/V ratios. The conditions for GC equipped with FID were as follows: GC system, GC-17A (Shimadzu, Japan); column, DB-1 (30 m × 0.25 mm; film thickness: 0.25 μm) with helium gas as a carrier. Temperature profile for analysis: 15 min at 110ºC, 110–160ºC (at a rate of 5ºC/min), 160–280ºC (at a rate of 20ºC/min), and 7 min at 280ºC.The FID response factors for estimating the amount of S_a and V_a obtained by making calibration lines between the weight ratios and area ratios of S_a and V_a to the internal standard.

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS)

Fibers in each fraction were subjected to Py-GC/MS to know chemical characteristics of lignin in the fraction. Approximately 150–180 μg of each sample prepared with *n*-eicosane (0.1 μg) as an internal standard (IS) was placed on a ferromagnetic pyrofoil and tightly wrapped. Then, the sample-loaded pyrofoil was inserted into a quartz sample tube. The sample holder with the sample tube was centered in the pyrolizer, and then Py-GC/MS started (Nakagawa-Izumi et al. 2017).

Pyrolysis condition (JHP-5, Japan Analytical Industry Co. Ltd. Japan): 500ºC for 4 s; GC/MS system, QP-5050A (Shimazdu, Japan); column, HP 1-MS (30 m × 0.25 mm; film thickness: 1.0 μm). Temperature profile for GC analysis: 1 min at 50ºC, 50–280ºC (at a rate of 5ºC /min), and 13 min at 280ºC.

2.3 Result and discussion

2.3.1 Effect of pretreatment on fiber fractionation

As shown in Table 3.1, the yield of pulp A and pulp B were about 8% lower than pulp C. The reason may due to the partially decomposition of cellulose and hemicellulose as well as the removal of organic acid and ash by pretreatment (Harsono et al. 2015).

According to fiber fractionation result, the amount of fibers passed through 100- mesh (mess opening 150 µm – fraction 5) of pulp A (43%) was the largest, there was no significant difference between pulp B and C from this last fraction. In addition, the amount of fibers which remained on 14-mesh (mess opening 1180 µm) of pulp A (4%) was lower than that of B and C. The increasement in cooking temperature in pulp A is advantageous for softening bamboo chips and may benefit to fiber defibration, but if the temperature is too high, the decomposition of carbohydrates accelerates, thus the amount of fibers remains on 14 to 100-mesh (mesh opening from 150 to 1180um - fraction 1,2,3,4) decreased.

Table 2. 1 Effect of pretreatment conditions on fractionation of thermomechanical pulps using fiber classifier.

Pulp name	Pretreatment conditions			Pulp yield (%)	Ratio of fractionation using fiber classifier [a] (%)				
	NaOH, H_2O_2 dosage (%)	Temperature (ºC)	Time (min)		Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5
A	5, 5	160	40	88.9	4 ± 1.0	13 ± 1.2	19 ± 0.4	20 ± 1.3	43 ± 0.7
B	5, 5	100	20	89.2	6 ± 0.1	29 ± 3.1	23 ± 1.3	20 ± 1.5	22 ± 1.7
C	0, 0	100	20	96.9	7 ± 1.1	23 ± 2.8	26 ± 3.2	19 ± 2.9	25 ± 1.2

[a] Bauer McNett Fiber Classifier No.2593

Note:

Fraction 1 – pulp remains on 14-mesh (>1180 µm mesh opening)

Fraction 2 – pulp remains on 14 to 28 mesh (1180-600 µm mesh opening)

Fraction 3 – pulp remains on 28 to 48 mesh (600-300 µm mesh opening)

Fraction 4 – pulp remains on 48 to 100-mesh (300 - 150 µm mesh opening)

Fraction 5 – pulp passed through 100-mesh (<150 µm mesh opening)

2.3.2 Effect of pretreatment on pulp strength

From the results shown in **Table 2.2**, the density, tensile strength, tear strength, and brightness of pulp B were higher than those of A and C. Comparing between pulp B and C, the different in pulp strength and brightness due to the involved of alkaline – peroxide system. However, between pulp A and C, the pretreatment temperature may take responsibility. In this study, pulp A was cooked at 160^{o}C whereas pulp C was cooked at 100^{o}C. At high temperature, hemicellulose and a part of cellulose could decompose, and colored lignin is diffused on the fiber surface, resulting in poor pulp strength and reduced the pulp brightness of pulp A. Meanwhile, although without bleaching agent system pulp C still have higher brightness value than pulp A.

Table 2. 2 Effect of pretreatment conditions on pulp properties.

Pulp name	**Density (g/cm^3)**	**Tensile index (N·m/g)**	**Tear index (mNm^2/g)**	**Brightness (% ISO)**
A	0.37	5.3	2.6	32.1
B	0.41	6.5	2.9	47.1
C	0.38	3.2	1.1	39.8

2.3.3 Chemical composition analysis

Figure 2.1 shows the lignin content of each fiber fraction TMP. From this result, the lignin content of pulp C was higher than that of A and B (except for the 600-1180 μm fraction). This because of the removal of lignin in pulp A and B due to the pretreatment with alkaline. The lignin content of A as was higher than that of B (except for pulp fractions which remain on 1180 μm mesh). The reason is due to the decomposition of carbohydrates in pulp A, which are susceptible to temperature, progressed more than the decomposition of lignin due to the high pretreatment temperature.

Figure 2.2 shows the xylan/glucan ratio of each fraction. Interestingly, the results showed that the xylan/glucan ratio tended to increase as the fiber became shorter. Comparing the average value of each pulp, it was 0.40, 0.51, 0.53 in the order of pulp A, B, C. This indicates that xylan decomposition progressed due to the effect of pretreatment with alkaline. Combining with the results of lignin content in **Figure 2.1**, a tendency to increase the content of lignin and xylan/glucan ratio when fiber became shorter was observed in pulp A and B.

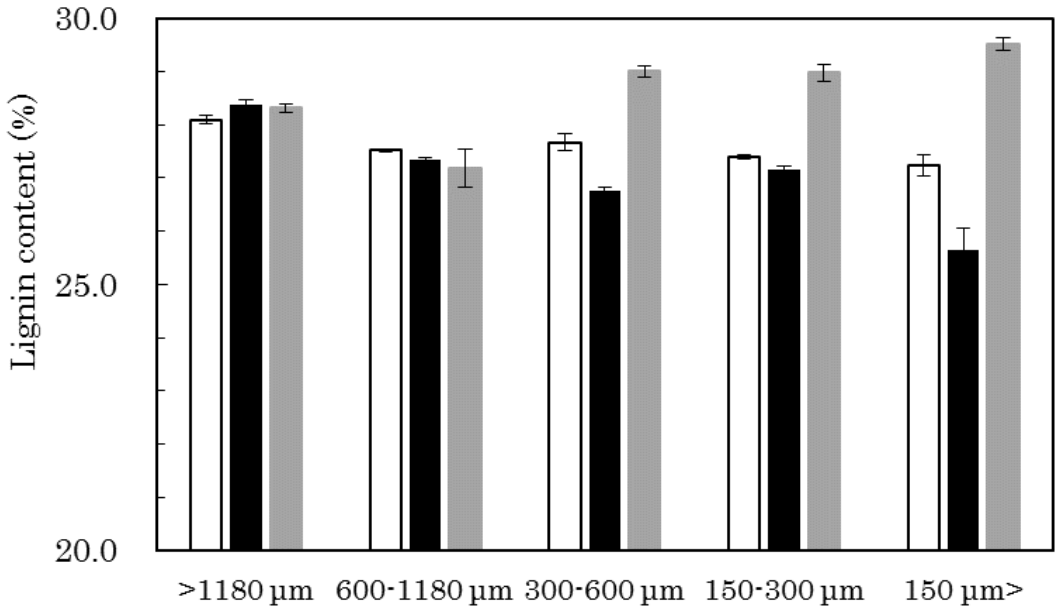

Figure 2. 1 Contents of acid-insoluble and acid-soluble lignin in TMP fractions.

Legend: □: Pulp A； ■: Pulp B； ▒: Pulp C

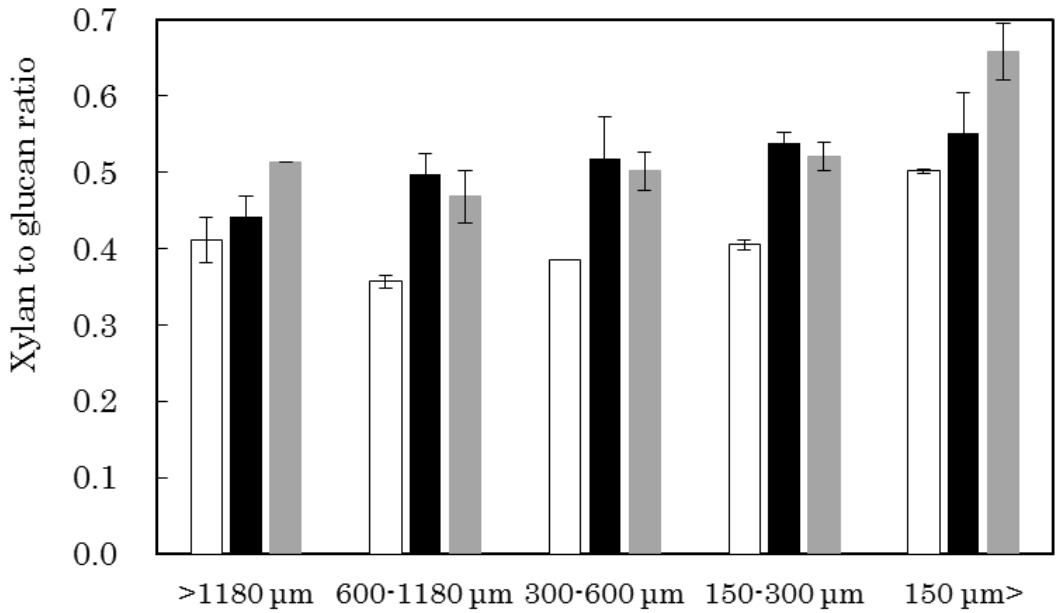

Figure 2. 2 Carbohydrate composition of TMP fractions.

Legend: □: Pulp A ; ■: Pulp B ;▩: Pulp C

2.3.4 Structural analysis by Py-GC / MS

Pulp B obtained the highest pulp strength in three pulp and was chose for further analysis. Py-GC /MS results for each fraction fiber of pulp B showed the same patent which shown in **Figure 2.3**, including 14 pyrolysis products of G1 ~ G7 and S1 ~ S7 and IS. From the peak areas of the total ion (TI) intensity of these degradation products, the ratio of the syringyl nucleus to the guaiacyl nucleus (S/G ratio) of the bamboo sample powder (75 μm or less) and each fraction fiber can be compared. It has been reported that there is a good correlation between this S / G ratio and the molar ratio (S / V ratio) between syringaldehyde and vanillin obtained by NBO.

Table 2.3 shows the S/G ratio of pulp A, B, and C by Py-GC / MS and the S/V ratio of pulp C by NBO. The S/G ratio of the bamboo sample powder was 0.96, and the S / G ratio of each pulp fraction was 0.83 to 1.55. The S/G ratio of the pulp A fraction remained on 1180 μm mesh (fraction 1) was the smallest. In pulp A and pulp C, the S/G ratio tended to increase as the fiber length decreased. Interestingly, the S/G of pulp passed through 150 μm mesh (fraction 5) of pulp A was the largest, at 1.54. The reason may due to lignin that has undergone condensation reaction of guaiacyl nuclei gathered in this fraction after pretreatment at 160ºC for 40 minutes. The S/V ratio of pulp C is 0.80 to 1.06, which is slightly larger than the S/G in the mean value. For comparison, the S/V ratio obtained by NBO is generally 0.5 to 4.0 for hardwood and non-wood fibers (Nakagawa-Izumi et al. 1995). However, in NBO there was no significant difference between pulp fraction of pulp C due to fiber length.

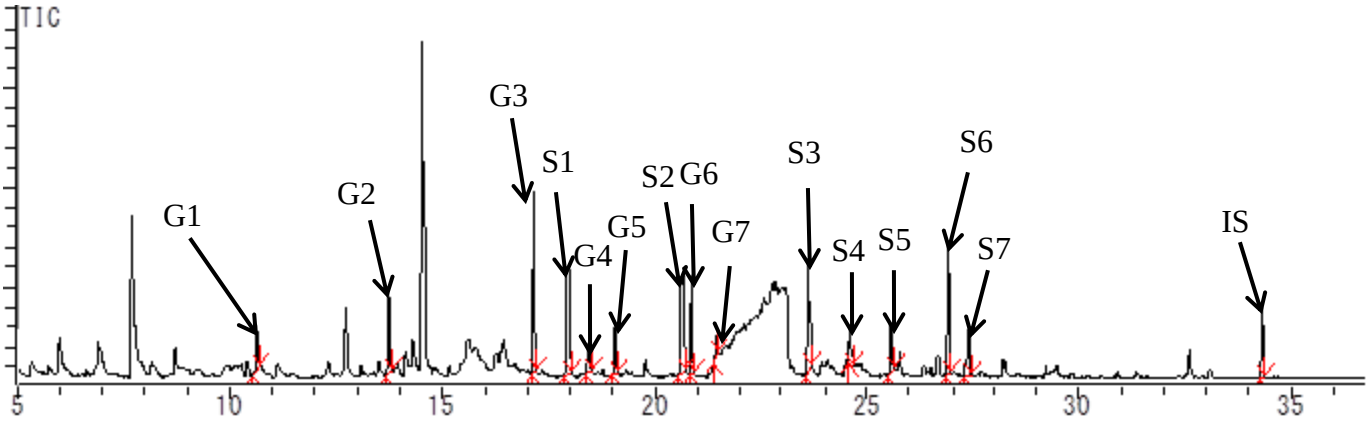

Figure 2. 3 Total ion chromatogram of pyrolysis products of pulp B fraction 5 by Py-GC/MS.

Note for G1-G7, S1-S7 and IS

Peaks	Pyrolysis products	Main ions	Retention time (min)
G1	Guaiacol	124, 109	10.6
G2	4-Methylguaiacol	138, 123	13.8
G3	4-Vinylguaiacol	150, 135	17.1
S1	Syringol	154, 139	17.9
G4	Eugenol	164, 149	18.3
G5	Vanillin	152, 151	19.0
S2	4-Methylsyringol	168, 153	20.6
G6	*trans*-Isoeugenol	164, 149	20.8
G7	Acetoguaiacone	166, 151	21.4
S3	4-Vinylsyringol	180, 165	23.6
S4	4-Allylsyringol	194, 179	24.6
S5	Syringaldehyde	182, 181	25.6
S6	4-*trans*-Propenylsyringol	194, 179	26.9
S7	Acetosyringone	196, 181	27.4
IS	*n*-Eicosane		34.3

Table 2. 3 S/G ion-intensity ratio by Py-GC/MS and S/V ratio by NBO from bamboo TMP

	Pulp name	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Average	Bamboo
S/G ratio	A	0.83	0.97	1.02	1.21	1.55	1.12	0.96
	B	0.85	1.30	1.22	1.25	1.10	1.14	
	C	0.94	0.95	1.00	1.21	1.32	1.08	
S/V ratio	C	0.80	0.77	1.02	1.06	0.89	0.91	-

3.3 Conclusion

Pulp A prepared by alkaline-peroxide pretreatment at 160ºC had the smallest amount of shive fiber (remained on 1180 µm mesh opening) compared to pretreatment at 100ºC. The fine fiber fraction (which passed through 150 µm mesh opening) was the highest.

Pulp B prepared by alkaline pretreatment at 100ºC had higher density, tensile strength, tear strength, and brightness than pulp A which was pretreated at 160ºC.

Both pulp pretreated with alkaline-peroxide declined in lignin content but increased in xylan/glucan ratio when fibers became shorter. In general, pulp A had a lower xylan/glucan ratio than pulp B.

The S/G ratio of the fine fraction of pulp A was the highest. The reason may due to fiber containing lignin had undergone the condensation reaction of guaiacyl nuclei gathered in this fraction after pretreatment at 160ºC for 40 minutes.

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Chapter 3 Neutral sulfite semi-chemical pulping of Bamboo

3.1 Introduction

Neutral sulfite semi-chemical process is a two-stage process in which wood chips are treated with a mild chemical condition at elevated temperature to soften and partially remove the lignocellulosic interfiber bonding material. This is followed by a mechanical refining to complete the fiber separation. The cooking liquor in the early development of the process contained sodium sulfite and buffered with sodium carbonate to reduce corrosion, thus the process became known as the neutral sulfite semi-chemical (or NSSC process).

The history or this process should be dated back to the year 1870's when mechanical pulping processes were quickly followed by chemical processes. In 1874, A. Mitsherlich proposed treating chips with a solution of sulfur dioxide or of bisulfite followed by grinding or rubbing to make pulp. Six years later C. F. Cross (1880) described the advantage of cooking chips in a neutral or slightly alkaline solution of sodium sulfite. For years of lacking adequate attention, researchers at the Forest Products Laboratory (USA) later found it advantageous to add a small amount of an alkaline agent to the sodium sulfite solution to control the pH and reduce corrosion on the equipment They also found that cooking to the fiber liberation point was not necessary, but partially pulped chips at 60 to 75% yield could be defibered mechanically without damage to the fibers. In 1925, the first NSSC mill started operations for manufacturing corrugating medium (Marteny 1980).

The semi-chemical wood pulping method yields more as compared to the wholly chemical wood pulping method. In the former process there is approximately 50% lignin retention and 30-40% hemicellulose. Both these factors make semi-chemical wood pulping more commercially attractive than chemical wood pulping. Semi-chemical wood pulp finds utility in important manufacturing processes, such as in the manufacturing of high-quality corrugated paper.

NSSC pulping uses a solution of sodium sulfite and carbonate or bicarbonate to impregnate the wood chips. The sulfonation of mainly middle lamella lignin causes a partial dissolution so that the fibers are weakened for the subsequent mechanical defibration. NSSC pulp remains significant amount of residual lignin (>15%) and is mostly used for unbleached products where good strength and stiffness are particularly important (Evtuguin 2016). To date, this is the most widespread semi-chemical process, and is mainly used with hardwood chips for corrugating medium, but the trend now is to use it as partial Kraft pulp replacement in linerboard and bag grades (Area et al. 2001; Vidaurre et al. 2018).

NSSC pulping is often integrated into a kraft mill to facilitate chemical recovery by a so-called cross-recovery, where the sulfite spent liquor is processed together with the kraft liquor. The sulfite spent liquor then provides the necessary makeup (Na, S) for the kraft process. However, with the greatly improving recovery efficiency of modern kraft mills, the NSSC makeup is no longer needed so that high-yield kraft pulping develops as a serious alternative to NSSC cooking. Semi-chemical pulps are still an important product category, however, and account for 3.9% of all virgin fiber material. It is also used as dichlorination

agent by the paper industry. Sodium sulfite also helps remove residual oxidants after bleaching of wood pulp (Bajpai 2015). To the recent interest of biorefinery, the spent liquor of a neutral sulfite semi chemical pulping process contains a considerable amount of lignocelluloses and can be used for producing value-added products (Dashtban et al. 2014; Tarasov et al. 2015).

The conditions of semi-chemical pulping vary depending to the raw material as well as the bleached or unbleached pulp is desired (Malo 1967). Research on NSSC pulping of three Eucalypt species showed substantially high yields of pulp with acceptable strength for corrugating medium (Franklin 1977). A process suitable for the manufacture of corrugating paper-board from New England hardwoods had been applied chemical ratio of sodium sulfite to sodium bicarbonate about 5:1, amount of chemical on the basis of wood was 14%, temperature of about 170^{o}C, pressure of about 100 psi (~0.7 MPa), time at maximum temperature of 2 to 3 hours and the yield was about 70% (Marteny 1980). Pulping hybrid poplar wood (*Populus deltoides*) with varied NSSC conditions to obtain pulp yield between 72%-80% showed that temperature presents the most important effects, sodium carbonate effect on yield is important only at low sulfite charges or high temperatures, whereas sodium sulfite charge has the highest influence on energy consumption, followed by temperature (Area et al. 2001). Recently, as the rising demand of using non-wood fiber sources, NSSC pulping of wood alternative material also takes interests. Study of NSSC pulping for bagasse at 165^{o}C with different sodium sulfite charge showed that the influence of pulping time is greater than chemical charge on yield and pulp strength (Khakifirooz et

al. 2013), this conclusion agrees with results of research on NSSC pulping Parcia wood and Eucalypt wood (Vidaurre et al. 2018). Pulping sunflower stalk for producing fluting paper grade revealed NSSC delignification rate of sunflower stalk is quite slow even at high chemical charge and cooking temperature, and to obtain good fibers pulping process should be done in relatively intensive condition with low yield and high kappa number (Rudi et al. 2016). In addition, anatomical structure of non-wood material, such as Silvergrass, with less amount of fibers on unit mass, thin wall of fibrous elements and high content of parenchyma cells would make the strength of NSSC pulp become poorer comparing with wood (Bocianowski 2019). To the best of our knowledge, research on pulping bamboo with NSSC method is limited, thus, the objective of this research is to provide necessary information for using NSSC method on pulping bamboo in terms of producing corrugating medium fiber grade.

3.2 Material and methods

3.2.1 Material

In this research, 2-year-old moso-bamboo (*Phyllostachys pubescens*) was used as raw material. After harvesting from the forest, the green bamboo was left dried naturally to moisture content of 10% with nodes removal. Then, all the internodes were split and cut into chips which have 5 mm in thickness and 20 mm in length. The chips then packaged in plastic bag to maintain dry condition.

3.2.2 Chemical compositions analysis

The contents of acid-insoluble lignin, acid-soluble lignin, extractives, and ash were determined using TAPPI Test Methods T 222 om-15, T 204 cm-07, and T 211 om-02. The amount of glucose, xylose, and others sugars in the acid hydrolysate of materials and TMP were determined using ion chromatography (Nakagawa-Izumi et al. 2017).

3.2.3 NSSC pulping and refining

NSSC pulping was done by using an oil-bath cooking system. Cooking liquor contained a mixture of sodium sulfite (Na_2SO_3) and sodium carbonate (Na_2CO_3) with a weight ratio of 1 to 0.5. Total chemical charge was 12% based on oven-dried weight of bamboo chips. Liquor to solid ratio was 4:1. Cooking temperature was set constantly at 160 □C, cooking time was 120 min and 80 min. Without removal of cooking liquor and washing materials, the cooked materials were subjected to the next refining step.

A laboratory pressurized single disc refiner (Model BRP45-300SS manufactured by Kumagai Riki Kogyo Co., LTD., Nerima, Tokyo) with a refiner plate (Type J, 305 mm in diameter), which connected to the pressure gauge and temperature sensor module in order to observe and control refining condition, was used to separate the fibers from cooked chips. The first-stage refining was done at 0.2 MPa pressure, and the second-stage refining was done at atmospheric condition. A gap of the disc was 1.0 mm for the first refining and 0.1 mm for the second refining. Control experiment was taken under the same condition with no chemicals in the cooking liquor.

Pulp properties

Obtained pulp was fractionated into five fractions using a Bauer McNett fiber classifier No.2593 with mesh opening 1180, 600, 300 and 150 µm (mess number 14, 28, 48, and 100 respectively). Fiber length and width distribution was determined by a fiber tester (Alva F5800). Scanning electron microscopy equipment (SU1510, Hitachi) was used to take SEM photo of the fibers, in order to identify the fiber surface characteristic of each fractions. Aspect ratio index was used for representing the relation ship between fiber size parameters, and calculated by the following ratio:

$$\text{Aspect ratio index} = \text{Fiber length (µm)} / \text{Fiber width (µm)}$$

To characterize pulp strength, pulp was firstly treated with a PFI mill at 10,000 revolutions according to ISO 5264-2:2011 standard. Forming handsheets for physical tests of the pulp followed the ISO 5269-1:2005 standard. Pulp brightness (%ISO), as well as the tensile and tear indices of the handsheets were determined according to ISO 1924-2:2008, 1974:2012, and 5270:2012 standards.

3.3 Results and discussion

3.3.1 Chemical components of moso-Bamboo

The glucans (cellulose) and lignin content of 2-year-old moso-Bamboo were determined as 36.2% and 28.8 % respectively (**Table 3. 1**). Comparing with wood, this lignin content of bamboo is in the range of 26-34 % of softwood, but the cellulose content is lower than both hardwood and softwood, which in the range of 38-49% (Rowell 2008).

Table 3. 1 Chemical compositions of raw material

Components	Content (%)
Acid-insoluble lignin	26.5 ± 0.2
Acid-soluble lignin	2.30 ± 0.04
Subtotal	28.8 ± 0.2
Glucan	36.2 ± 0.4[a]
Xylan	16.0 ± 0.3[b]
Other sugars	1.43 ± 0.02[c]
Subtotal	53.6± 0.7
Unknown	17.6

[a] As polymer of glucose.

[b] As polymer of xylose.

[c] As polymer of arabinose, galactose and mannose.

3.3.2 Fiber classification and pulp properties

Table 3.2 shows pulp response of NSSC in comparison with the control experiment. Effects of cooking liquor containing sodium sulfite and sodium carbonate were obvious on the cooking yield as well as the CSF value and physical strength of the pulp. NSSC provided much better pulp strength, however, the brightness of the pulp was lower than control experiment. Comparing between two NSSC treatment, pulp cooked for 120 min provided high pulp strength with slightly low pulp brightness. For the next pulp characteristics analysis, we use NSSC (1) pulp, which cooked for 120 min, as the representation of NSSC treatment.

Wet fractionation showed that NSSC pulp had smaller amount of fibers from 28 to 100 mesh but contained larger amount of pulp passed through 100 mesh (**Fig. 3.1**) Though, fiber aspect ratio of NSSC pulp was higher than that of control pulp in all fractions (**Fig. 3.2**). Fiber aspect ratio is an important parameter of fiber and is proved to have positive effect on mechanical properties, especially the tearing strength of pulp18). NSSC pulp had the fiber aspect ratio as 53.5 on average, and comparable to that of hardwood pulp which around 40 to 60 (Main et al. 2014).

Table 3. 2 NSSC pulp properties

Sample	Yield[a] (%)	Brightness (%ISO)	CSF[b] (ml)	Density (g/cm^3)	Tensile index (Nm/g)	Tear index (mNm^2/g)
NSSC (1)[c]	71.3	26.6	130	0.46	17.80	5.90
NSSC (2)[d]	87.6	27.4	150	0.44	14.50	5.05
Control	96.3	31.6	210	0.39	7.20	3.10

[a] Yield after cooking

[b] PFI at 10,000 revolutions

[c] NSSC (1): cooking for 120 min

[d] NSSC (2): cooking for 80 min

Table 3. 3 Lignin and carbohydrate contents and S/V molar ratio by NBO of NSSC pulp

Content (%)	Pulp fraction				
	>1180 μm (>14 mesh)	600–1180 μm (14–28 mesh)	300–600 μm (28–48 mesh)	150–300 μm (48–100 mesh)	<150 μm (<100 mesh)
Acid-insoluble lignin	26.5 ± 0.5	24.1 ± 1.4	24.4 ± 0.3	26.0 ± 0.5	22.5 ± 0.9
Acid-soluble lignin	1.53 ± 0.01	2.01 ± 0.01	1.76 ± 0.06	2.01 ± 0.03	2.75 ± 0.02
Subtotal	28.0 ± 0.5	26.1 ± 1.4	26.2 ± 0.4	28.0 ± 0.5	25.3 ± 0.9
Glucan	51.5 ± 3.1	52.2 ± 0.9	49.2 ± 0.5	47.7 ± 1.5	44.3 ± 0.2
Xylan	20.6 ± 1.2	20.7 ± 0.2	20.5 ± 0.1	22.1 ± 0.6	25.4 ± 0.5
Arabinan	1.10 ± 0.12	1.21 ± 0.01	1.27 ± 0.06	1.25 ± 0.02	1.30 ± 0.05
Subtotal	73.2 ± 4.4	74.1 ± 1.1	71.0 ± 0.7	71.1 ± 2.1	71.0 ± 0.8
Unknown	-	-	2.8 ± 1.1	0.9 ± 2.6	3.7 ± 1.7
S/V molar ratio	0.75	0.83	0.83	0.88	1.87

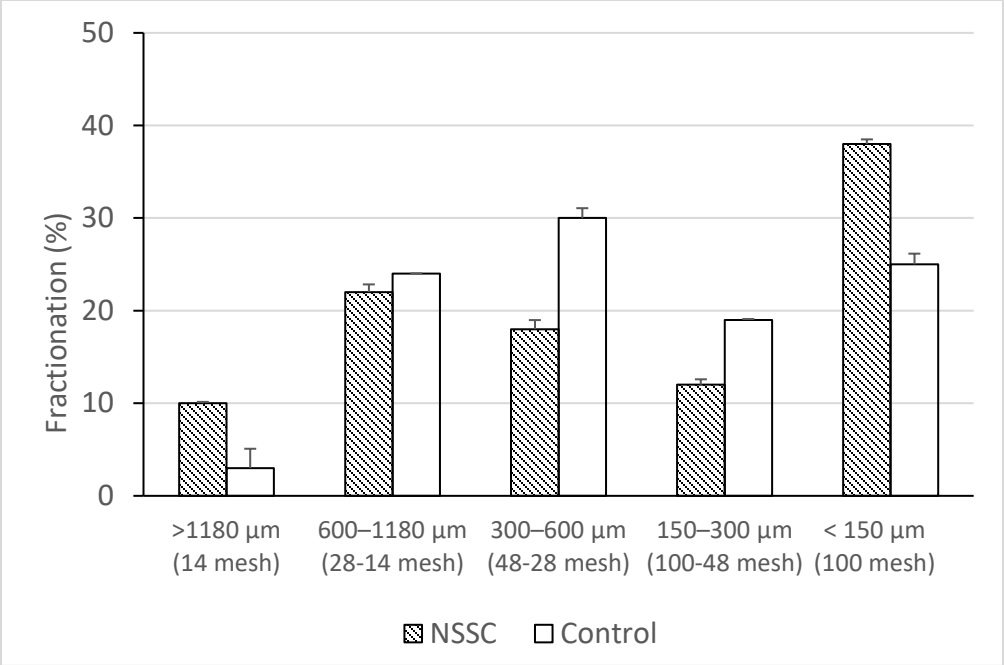

Figure 3. 1 Fiber classification

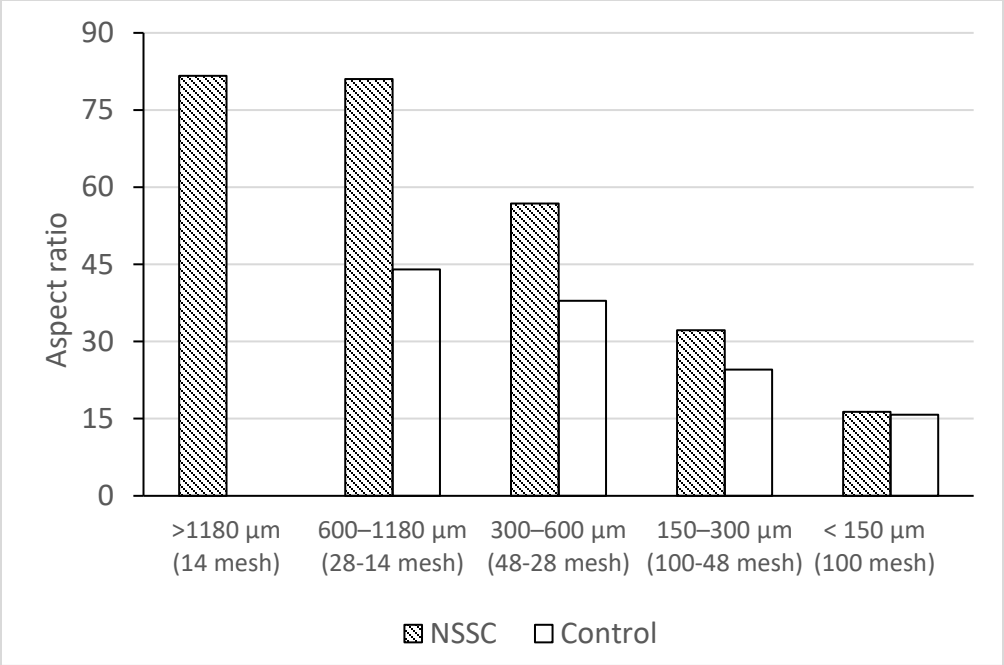

Figure 3. 2 Fiber aspect ratio of each fraction

In addition, it is well known that the fraction of mechanical wood pulp which passed through 100 mesh contains practically fines and ribbon fragments of fiber wall and S1 layer. The fines as flakes of the middle lamella or ribbons from fiber wall are rich in lignin content and can significantly affect to light absorption coefficient properties of the pulp. Mechanical pulp fines are believed to have light absorption coefficient about three to four times as high as that of the long fibre fraction (Odabas et al. 2016). In this case, the high content of fines in NSSC pulp may take responsibility for the overall pulp brightness, though, the elements of fines fraction still need further assessment. The content of glucan, xylan and lignin content in NSSC pulp are shown in **Table 3. 3**. There was a downward trend from lignin content and glucan content when fiber's size diminishes. However, the S/V ratio of NSSC pulp showed an upward tendency when fiber's size become shorter. The low S/V ratio indicated that NSSC pulp is not ready for further bleaching.

3.3.2 SEM observation

Evaluating the pulp fractions by SEM images reveals interesting information. The 14 mesh remain fraction from the both kinds of pulp contain mostly un-separated fiber bundles which shown clearly in **Fig. 3.3**. Fibers from control pulp were still stick together in a block-like shape including parenchyma cells. This indicated that this fraction was not suitable for making paper and should be treated as "rejects". The 14-28 mesh showed better isolated pulp fibers in the case of NSSC pulp, but still almost fiber bundles in the case of

control pulps as presented in **Fig. 3.4.** This fraction of NSSC pulp contained almost whole fibers with smooth surfaces of S1 layer of the fiber wall.

Fig. 3.5 shows the fraction 28-48 mesh of both pulps, reveals shorter and thinner but still whole fibers. These fibers should remain their intrinsic stiffness and they should be unable to create well fiber-to-fiber connection. There were some fibers of NSSC pulp that have been stripped of the fiber wall exposing S2 layer (Fernando et al. 2013). Fibrils can only be well observed from 48-100 mesh fraction. They are cell-wall segments in shape of ribbon-like or flake-like which shown in **Fig. 3.6**. NSSC pulp fibers were more fibrillated comparing with control pulp. This kind of fibrillation should have large specific-surface area and will contribute to pulp strength by providing high fiber-to-fiber contact.

In the 100 mesh pass fraction, parenchyma cells were concentrated in case of NSSC pulp, meanwhile with control pulp there were almost short fibers and fiber's segments (**Fig. 3.7**). It is known that with a suitable ratio, parenchyma cells have positive effect on paper tensile strength (Suzuki et al. 2008), therefore, this evidence can explain for the better tensile strength of NSSC pulp.

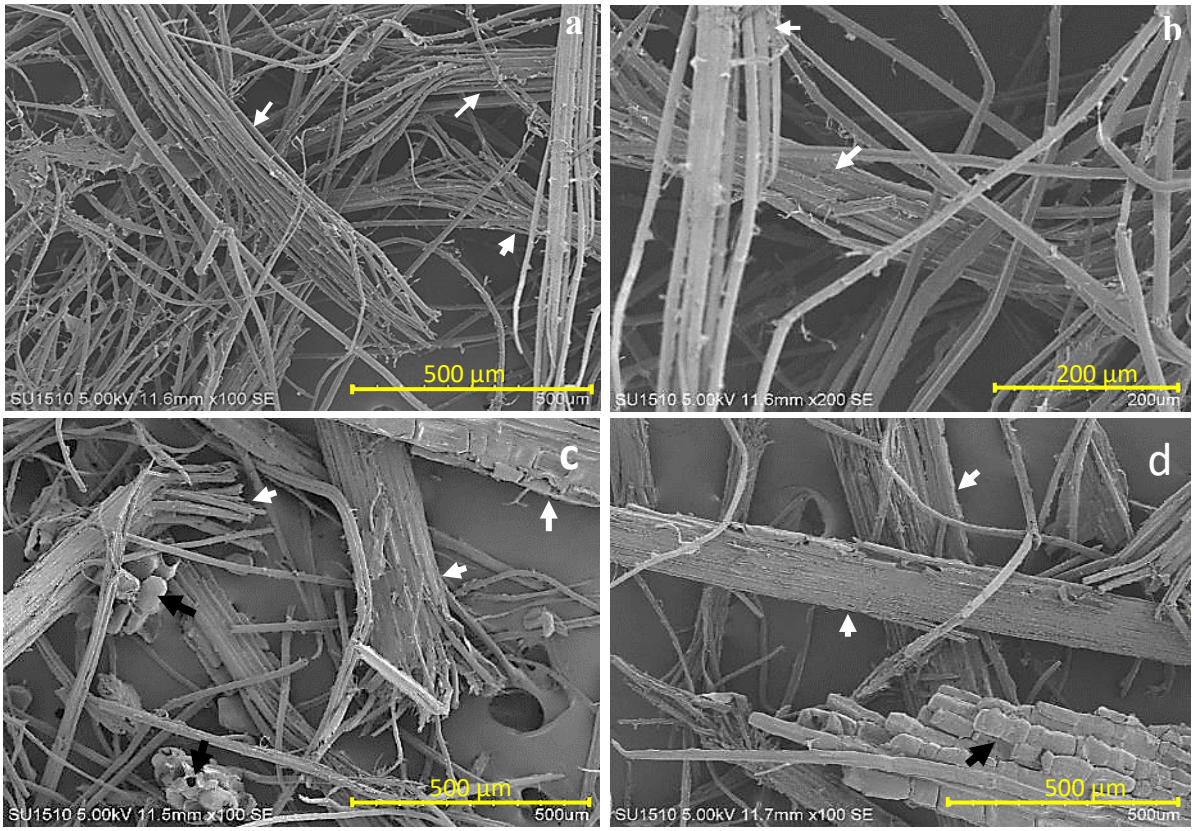

Figure 3. 3 SEM images from plus 14-mesh fraction of NSSC pulp (a, b) and control pulp (c, d). Un-separated fiber bundles (white arrows) and parenchyma cells (black arrows) are clearly shown.

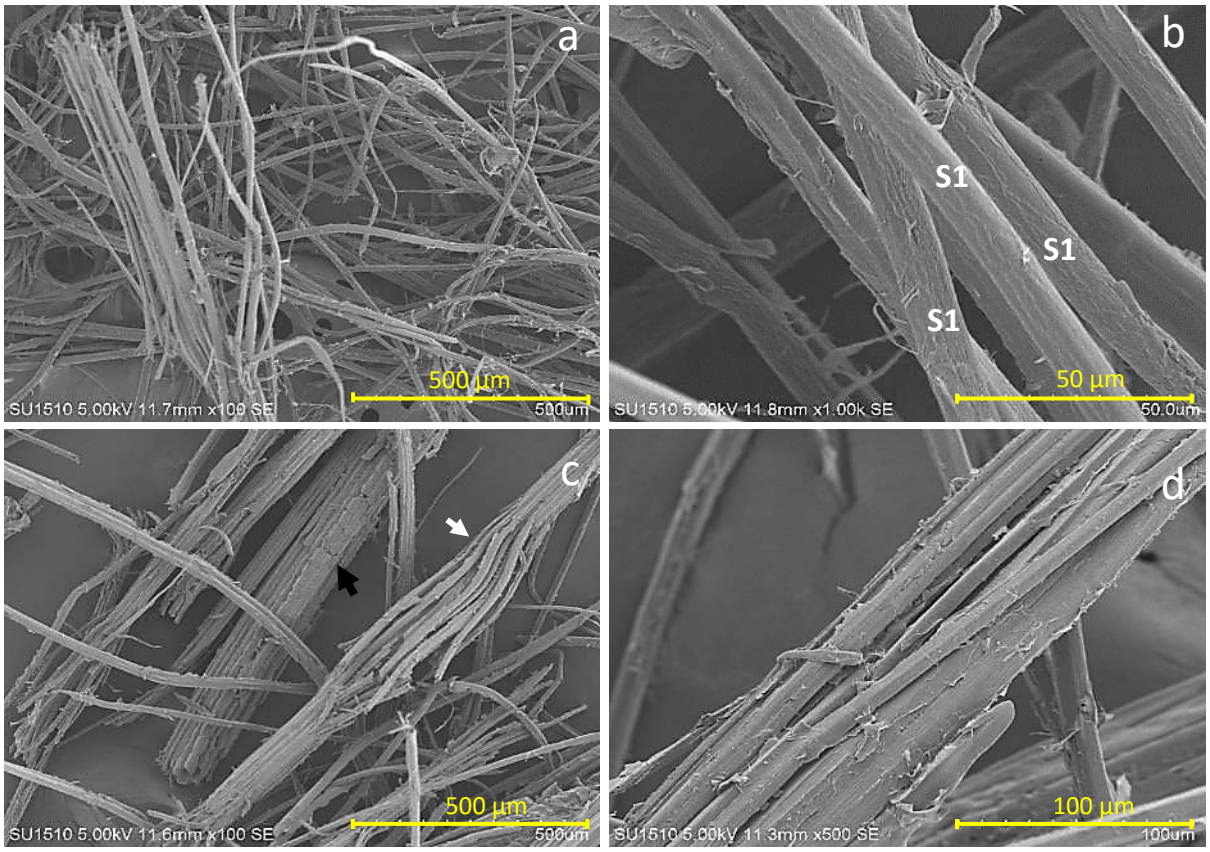

Figure 3. 4 SEM images from 14 to 28-mesh fraction of NSSC pulp (a, b) and control pulp (c, d). Only NSSC pulp shows smooth surface of individual fiber by exposing S1 layer of the cell wall (b).

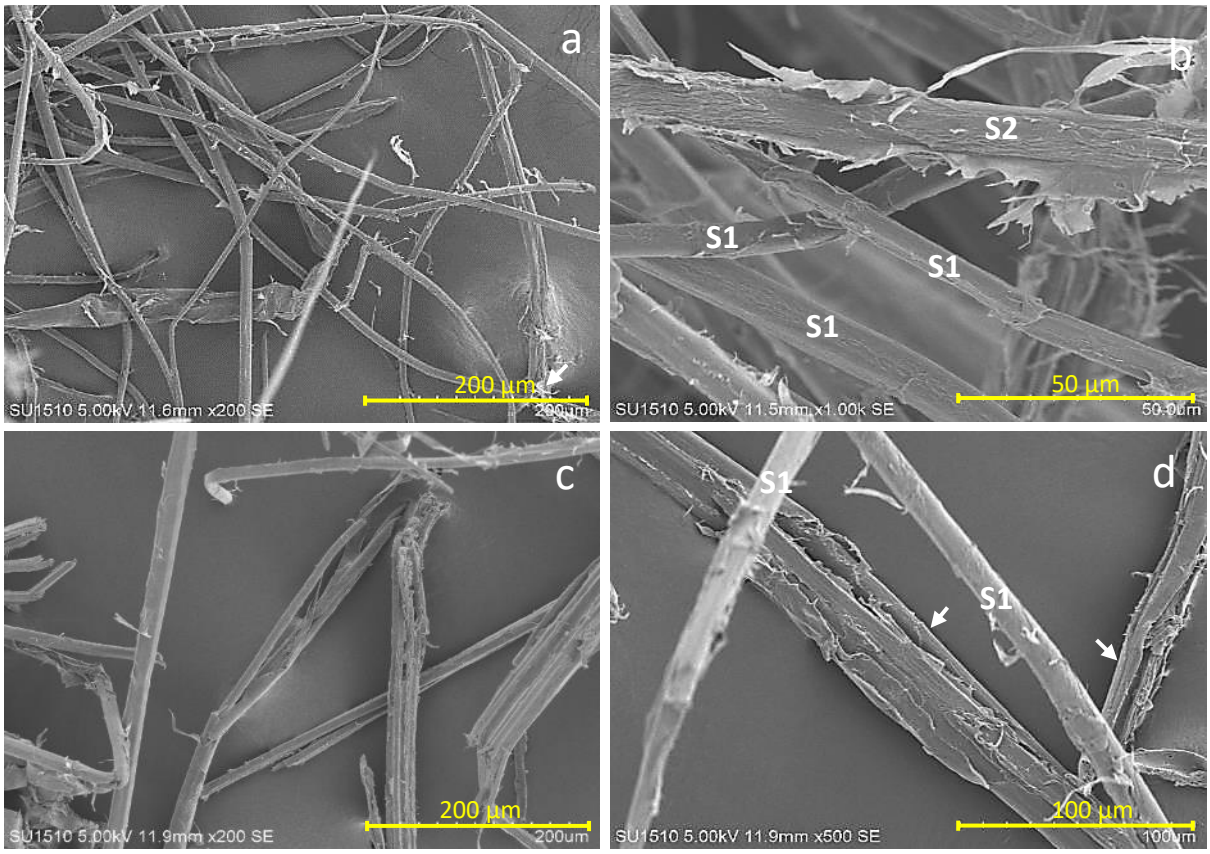

Figure 3. 5 SEM images from 28 to 48-mesh fraction of NSSC pulp (a, b) and control pulp (c, d). This fraction of both pulps contains almost whole fibers, exposing of S2 layer of the cell wall can only observable in NSSC pulp (b).

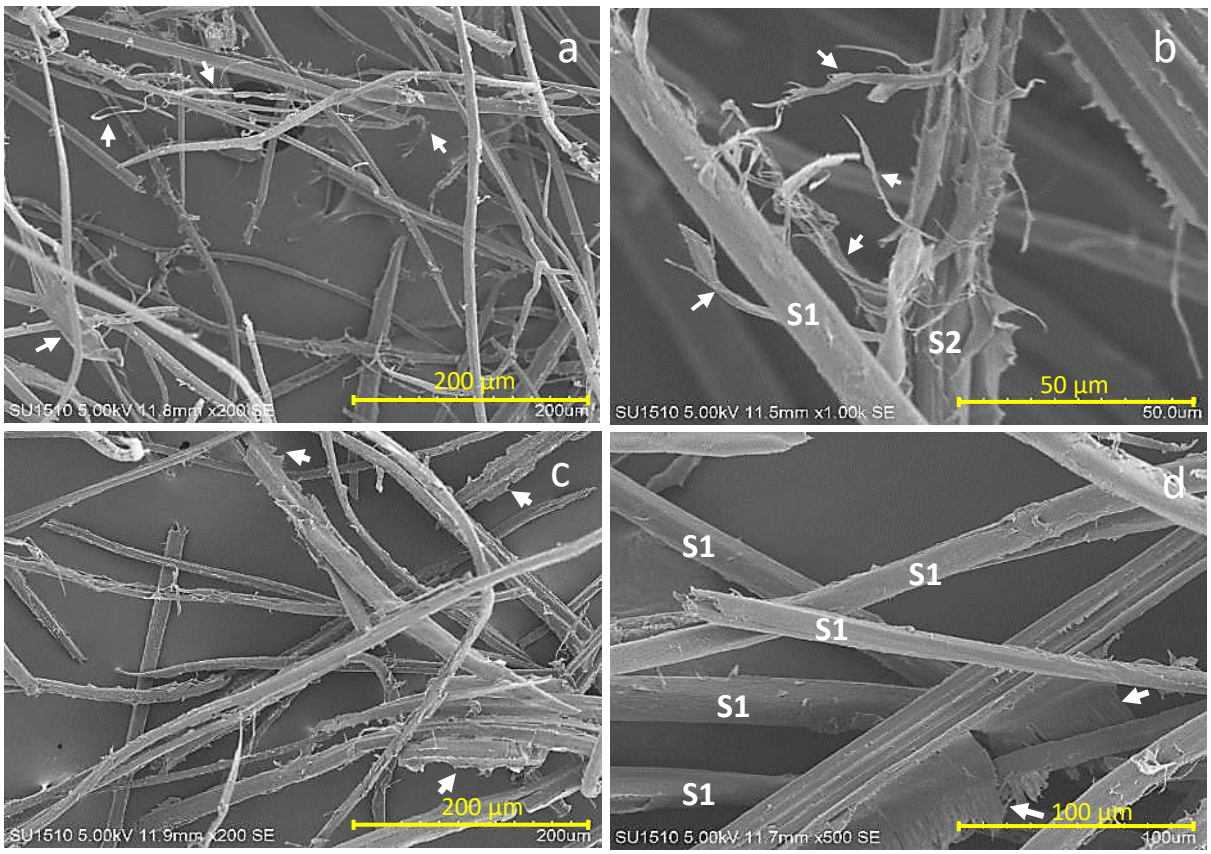

Figure 3. 6 SEM images from 48 to 100-mesh fraction of NSSC pulp (a, b) and control pulp (c, d). Fibrillation in shape of flake-like segments more likely appear in control pulp (c, d).

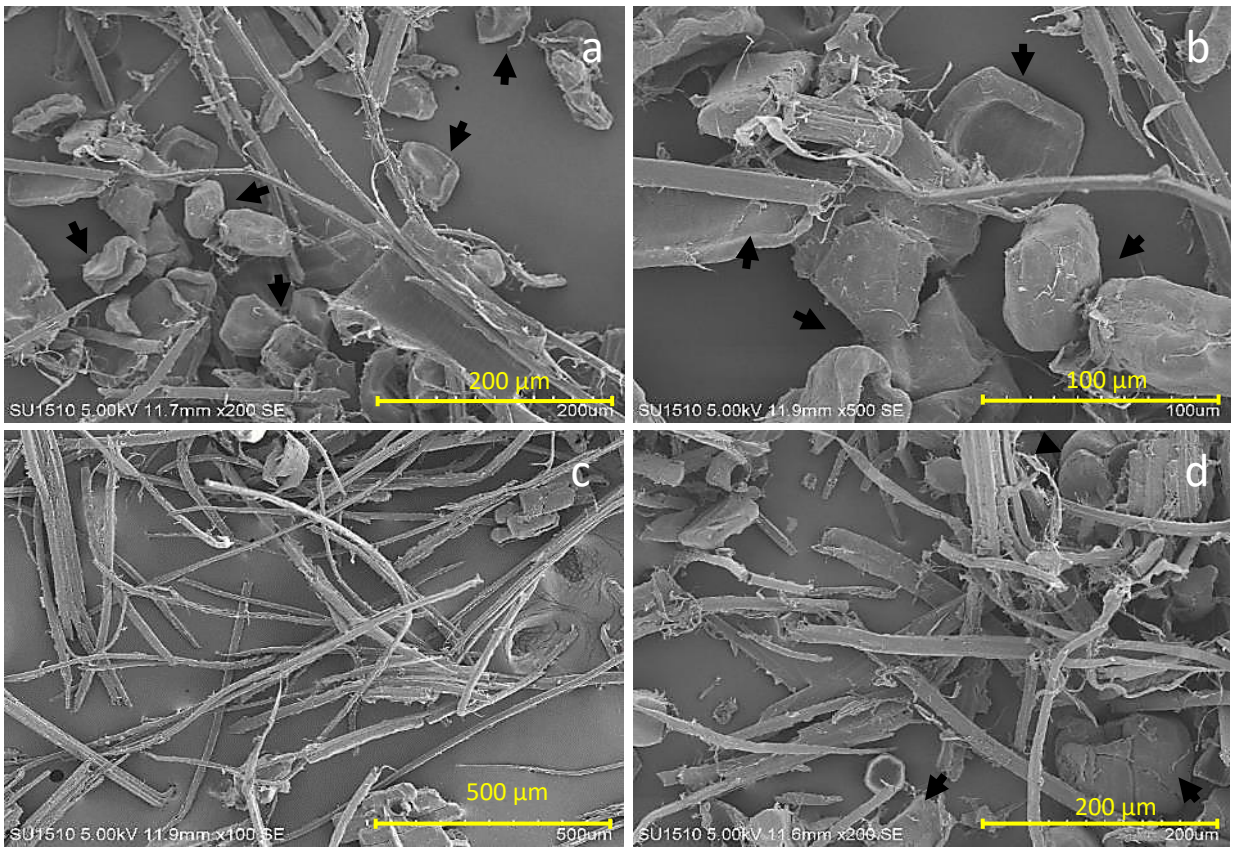

Figure 3. 7 SEM images from minus 100-mesh fraction of NSSC pulp (a, b) and control pulp (c, d). Parenchyma cell are concentrated in NSSC pulp (black arrows).

3.4 Conclusion

Pulping bamboo by NSSC results in a low brightness pulp but provided positive effect on pulp strength. NSSC method can help to reduce the amount of un-separated fiber bundles and shives content of pulp. Fibers development and fibrillation during refining do receive benefits, proving by higher Aspect ratio of NSSC pulp comparing with control pulp, also NSSC fibers contain more ribbon-like fibrillation which then response for high fiber-to-fiber connection. NSSC pulp had the fiber aspect ratio as 53.5 on average, and comparable to that of hardwood. There was a downward trend from lignin content and glucan contetn when fiber's size diminishes. However, the S/V ratio of NSSC pulp showed an upward tendency when fiber's size become sorter. The low S/V ratio indicated that NSSC pulp is not ready for further bleaching. Additionally, internal bonding of NSSC pulp might be increased reasonably by a significant amount of parenchyma cells appeared as fines in minus 100-mesh fraction, which revealed by SEM images evaluation.

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Chapter 4 General conclusion

This research had conducted several attempts to provide more information about applying the TMP method on fabricating fiber from moso-bamboo.

In Chapter 2, pretreatment of bamboo chips with alkaline-peroxide prior to refining was conducted, aimed to provide paper grade pulp with high value of brightness. Results shown that pulp B (pretreatment with 5% NaOH + 5% H_2O_2 based on oven dried weight of sample at 100^{o}C in 20 minutes) had better mechanical properties and brightness comparing with pulp A (pretreatment with 5% NaOH + 5% H_2O_2 based on oven dried weight of sample at 160^{o}C in 40 minutes) and pulp C (pretreated with H_2O in 20 minutes), though the properties of pulp B were still very low comparing with commercial TMP wood pulp. Both pulps pretreated with alkaline-peroxide declined in lignin content but increased in xylan/glucan ratio following the increased in mesh number (fiber became shorter). Pulp A had a lower xylan/glucan ratio than pulp B. The S/G ratio of the fine fraction of pulp A was the highest. The reason may due to fiber containing lignin had undergone the condensation reaction of guaiacyl nuclei gathered in this fraction after pretreatment at 160^{o}C for 40 minutes.

In Chapter 3, the Neutral Sulfite Semi-chemical pulping method were applied to fabricate bamboo fibers, aims to provide pulp for corrugating medium. It was suggested that pulping bamboo by NSSC results in a low brightness pulp but provided positive effect on pulp strength. NSSC method can help to reduce the amount of un-separated fiber bundles and shives content of pulp. Fibers development and fibrillation during refining do receive benefits, proving by aspect ratio of NSSC pulp was 53.5 on average, which

comparable to that of hardwood pulp. There was a downward trend from lignin content and xylan/glucan ratio of NSSC pulp when fiber's size diminishes. However, the S/V ratio of NSSC pulp showed an upward tendency upon the decrease of fiber size. The low S/V ratio indicated that NSSC pulp is not ready for further bleaching. NSSC fibers contain more ribbon-like fibrillation which then response for high fiber-to-fiber connection. Additionally, internal bonding of NSSC pulp might be increased reasonably by a significant amount of parenchyma cells appeared as fines in minus 100-mesh fraction, which revealed by SEM images evaluation.

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