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Contributed Paper

Preliminary Study of Anthraquinone in Sweet Bamboo (*Dendrocalamus asper* Backer) Alkaline Sulfite Pulping

Suphat Kamthai
Department of Packaging Technology, Faculty of Agro-Industry ,Chiang Mai University, Chiang Mai, 50100 Thailand, e-mail: Suphat_61@hotmail.com

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ABSTRACT

Sweet Bamboo (*Dendrocalamus asper* Backer) was raw material in this investigation and it was used to study all of basic bamboo properties and the effect of anthraquinone (AQ) addition on alkaline sulfite (AS) pulping. The results of laboratory indicated the important physical properties and fiber morphologies of sweet bamboo. They were 725 kg/m^3; basic density, 60.2%; moisture content and their fiber dimensions were fiber length 3.1 mm, fiber width 18.0 mm, cell wall thickness 6.9 mm and cell lumen 4.4 mm, respectively. The chemical compositions of sweet bamboo illustrated holocellulose 76.3%, alpha-cellulose 68.1%, lignin 28.7% and ash 1.4%. Considering the increment of alkaline charge from 25 to 35% and the addition of 0.1% AQ in AS – pulping found that the kappa number of alkaline pulping with anthraquinone (AS-AQ) pulp was reduced 12.5 to 9.6 points but AS-pulping condition hadn't affect AS-AQ pulped yield. The highest kappa number of AS-AQ pulps was evaluated unbleached pulp properties by PFI mill beating. The pulp beating revolution had more affect properties and less influenced optical properties of AS-AQ pulp. At 4,000 revs, presented the highest tensile index, 60.1 Nm/g and tear index, 27.9 mN.m^2/g. In contrast to the highest burst index and fold endurance was observed at 5,000 and 7,000 revs. They were 3.3 kPa.m^2/g and 405 r/c respectively.

Keywords: *Dendrocalamus asper* Backer, alkaline-sulfite pulping, alkaline-sulfite pulping with anthraquinone, holocellulose, alpha-cellulose, lignin, screened yield.

1. INTRODUCTION

It was long time ago the environmental impact in pulp and paper industries are important to concern such as air and water pollution. The pollutions were as a result of pulping and bleaching processes which were difficultly managed when the pollution discharged. Today, kraft pulping processes are the most popular pulping process that can produce highest strength pulp and handle wide variety of wood species. On the hand, this process has many disadvantages, such as more chemical is required for bleaching. Secondly, it produces dark pulp and, emits odorous pollution to the air. Smook concluded, the kraft pulping odor was principally four reduce sulfur gases include hydrogen sulfide, methyl mercaptant, dimethyl sulfide and dimethyl disulfide [1]. The odors from kraft process had unpleasant smell and it health hazard if odorous gases discharged to the air at over critical level.

In order to eliminate the hazardous gases emission from karft pulpin-g, the modification of pulping processes was modified by anthraquinone (AQ), addition alkaline-sulfite to the pulping process with anthraquinone (AS-AQ). AQ is an organic substance with aromatic molecule and their characteristic are a pale yellow, low toxicity, not an alkaline or acid substance and insoluble in water but it can soluble in alkaline solution as cooking liquor. AQ has great effect on the degradation of lignin and stabilization of carbohydrate in the pulping process. Compared to the ordinary kraft pulping, AS-AQ pulping had more advantage than kraft pulping such as accelerated delignification rate, reduced kappa number, protected cellulose degradation, increased pulp yield, much easier to beat, easier to bleach, high brightness bleached pulp and reduce sulfur pollution into the air [2,3,4].

The non-wood fiber will play an important role in the world's pulp and paper industries. It will increase the growth rate if necessary to sustain the increasing pulp and paper requirement. Casey reported, fiber morphology of bamboo had 1.5 – 4.4 mm; averaged fiber length and fiber width widely from 7 – 27 micron, with an average 14 micron [5]. In South-East Asia paper mills have been established using some bamboo species as raw material, such as *Bambusa bambos*, *B. blumeana* and *Dendrocalamus strictus* (Roxb.) Nee) [6]. For Thailand bamboo utilization, Sweet bamboo (*Dendrocalamus asper* Backer) is more popular and is more utilize than other species and it continues to use in pulp and paper industries. In 1998, sweet bamboo plantation was occupies about 153,227 rai (24,516 ha) [7].

The objectives of this study is : (1) to study the fiber morphology, physical and chemical properties of sweet bamboo (2) to optimize AS-AQ pulping condition for Sweet bamboo (3) to evaluate properties of obtained pulp from AS-AQ pulp and (4) to investigate the effect of beating revolution on strength improvement.

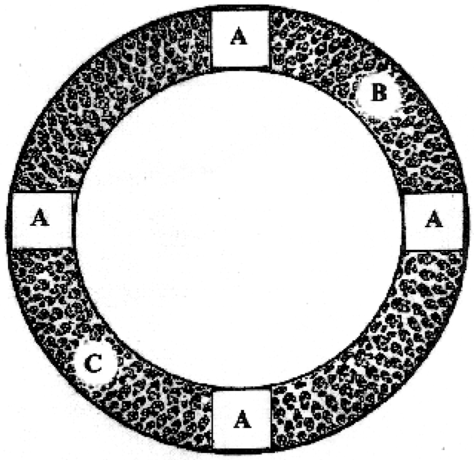
2. MATERIALS AND METHODS

2.1 Raw Material Preparation

In this study, 3 – year old sweet from bamboo plantation in Prachinburi province was utilized. The bamboo culms were selected and cut at 0.30 m above ground. They separated into two groups for experiment as (I) for analysis of physical and chemical properties, and fiber morphology, and (II) for pulping process. For pulping experiment, sweet bamboo culms were chipped and screened in through 19-25 mm hole screen. The accepted chips were left on the 22 mm and under 19 mm hole screen. The moisture content of screened chip was determined using TAPPI T258 om-02, then the sweet bamboo chips were dried at atmosphere temperature and packed in plastic bag around 700 g, oven-dry weight.

2.2 Analysis of Sweet Bamboo Properties

Sweet bamboo culms were cut into disk in every 2 m long and each disk was cut into 4 pieces for basic density and moisture content analysis according to TAPPI T258 om-02. The rest of each disk was chopped into small pieces and milled to wood meal with laboratory mill. Wood particles were screened and the accepted particle (over 60 mesh and under 40 mesh), then was collected for chemical analysis as followed: holocellulose (Wise method), alpha cellulose content (TAPPI T203 om-99), ash content (TAPPI T211 om-93), and lignin content (TAPPI T222 om-02). The solubility of sweet bamboo was also investigated such as water solubility (TAPPI T207 cm-99), 1% NaOH solubility (TAPPI T212 om-98), and alcohol-benzene solubility (TAPPT T204 cm-97). Franklin's method was used for fiber maceration and then continued to fiber length, fiber width, cell wall thickness and cell lumen measurement and they were measured by high capacity light microscope.



A = Basic density
B = Chemical Composition
C = Fiber morphology

Figure 1. Sweet bamboo disks for physical properties, chemical composition and fiber morphology.

2.3 Pulping Process

Cooking method in this study was alkaline sulfite pulping with anthraquinone (AS-AQ). The white liquor used in AS-AQ cooking was prepared from fresh sodium sulfite (Na_2SO_3) and sodium hydroxide (NaOH). 0.1% AQ was added in white liquor and stirred. The 700 g oven-dry weight chips were cooked in a 7-liter rotating digester by cooking conditions that were listed in Table 1.

After pulping, brown stock was washed with excess tap water and followed by mechanical disintegrator disintegrated pulp. Then cooked pulp was screened through 0.15 screen plate (TAPPI T275 sp-98) and separated for screened yield and yield reject. The yield obtained was estimated for kappa number (TAPPI T236 om-99) and determined for dry matter content of screened yield and reject (TAPPI T258 om-02). The pulp yields and reject content, as percentage on an oven dry weight, were calculated.

Table 1. Cooking conditions of AS-AQ pulping.

Cooking conditions	AS-AQ
Chemical charge (%)*	25 - 35
Na_2SO_3/NaOH	70 : 30
AQ (%)*	0.1
Liquor to wood ratio	4 : 1
Time to max (min)	90
Time at max (min)	90
Temperature (^oC)	170

*Based on oven-dry weight

2.4 Testing of Papermaking Properties

The unbleached pulp was beaten in PFI mill according to TAPPI T248 sp-00. Freeness and pulp physical properties demonstrated the effects of beating levels and papermaking properties. Freeness of beaten pulps was measured according to TAPPI T227 om-99. The handsheet for testing of papermaking properties was formed according to TAPPI T205 sp-02 and optical and strength properties such as brightness (TAPPI T452 om-98), basis weight or grammage (TAPPI T410-om-98), thickness (TAPPI T411 om-97), density and bulk (TAPPI T426 wd-70), tensile strength (TAPPI T494 om-01), tearing strength (TAPPI T414 om-98), bursting strength (TAPPI T403 om-97) and folding endurance (TAPPI T511 om-02).

3. RESULTS AND DISCUSSION

3.1 Physical Properties, Fiber Morphology and Chemical compositions

The physical properties, fiber morphology and chemical properties of sweet bamboo are presented in Table 2-3. Table 2 reveals the principle properties of sweet bamboo such as basic density, moisture content and fiber anatomy. The results were presented basic density and moisture content of sweet bamboo culm and they were 725 kg/m^3 and 60.24%, respectively. The density of this research was similar to the work of Parkeeree which reported density of same species and it was 730 kg/m^3 [8].

Table 2. Physical properties and fiber morphology of sweet bamboo.

Bamboo Properties	Results	SD.
Density (kg/m^3)	725.0	12.6
Moisture content (%)	60.2	6.6
Fiber length (mm)	3.1	0.7
Fiber width (mm)	18.0	2.8
Cell wall thickness (mm)	6.9	1.3
Cell lumen (mm)	4.4	0.3

The anatomy of sweet bamboo is illustrated in Figure 2 It has similar cell structure as compared with other bamboo species. It consists of parenchyma ground tissue and vascular bundle. The importance of sweet bamboo fiber morphology reported the average fiber length of sweet bamboo was 3.11 mm (2.2-4.0 mm); (Figure 2, (B)). It was as long as softwood fiber and longer than hardwood fiber. For example fiber length of softwoods black spruce, *P.* radiata, and southern pine were 3.5, 3.0, and 4.6 mm, respectively and fiber length of hardwood, *E. camaldulensis* fiber was 1.1 mm [1,9].

The fiber width and cell lumen measurement was measured by high capacity light microscope and used a standard micrometer for fiber calculation. The resulted of fiber width and cell lumen of sweet bamboo were18.0 mm (16-23 μm) and cell lumen 4.4 mm (4-5 μm). Its fibers were slender and cell lumen was smaller than fiber from other softwoods (Figure 2, (C)). Sweet bamboo cell wall thickness was 6.98 μm (6.0-9.4 μm) which is comparable to softwood cell wall thickness. It was demonstrated by black spruce and southern pine, which were averaged 6.5 μm and 9.5 μm [1]. thus sweet bamboo cell wall is very thick.

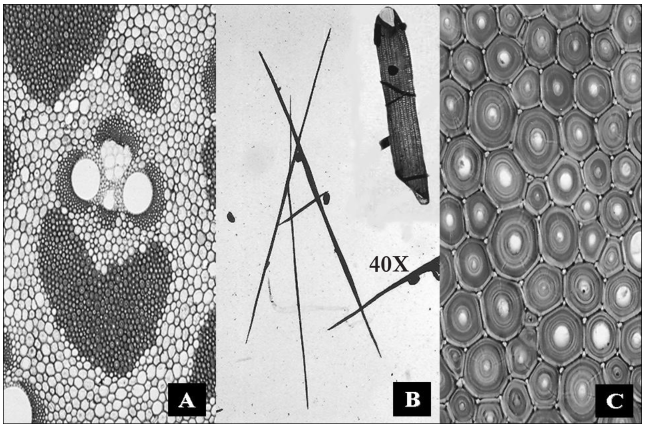


Figure 2. The anatomy of sweet bamboo
(A) Vascular bundle of sweet bamboo (20X)
(B) Vessel (40X) and fiber (20X) of sweet bamboo
(C) Cell wall and cell lumen of sweet bamboo (40X).

Table 3 illustrates the chemical compositions of sweet bamboo and they were 76.3%; holocellulose, 68.1%; alpha-cellulose, and 28.7 %; lignin. All of those chemical contents in sweet bamboo affect pulped yield, pulp strength and they use to estimate pulping and bleaching conditions for appropriate pulp application. Generally bamboo holocellulose and alpha-cellulose is as high as wood fiber. Dransfield and Widjaja indicated bamboo holocellulose was 61 -71% [6]. The 3 years old tropical bamboo (*Gigantochloa scortechinii*) had high holocellulose and alpha-cellulose content 72.9% and 70.8%, [10]. Considering the amount of lignin in sweet bamboo relative to general bamboo lignin was 26 – 43 % [11].

Table 3. The chemical compositions of sweet bamboo.

Chemical compositions (%)	Results	SD.
Holocelllose	76.3	0.64
Alpha-cellulose	68.1	0.94
Lignin	28.7	1.84
Ash	1.4	0.55
Alocohol + Benzene Solubility	5.9	1.19
Hot Water Solubility	8.0	1.09
Cold Water Solubility	7.0	3.40
1%NaOH Solubility	24.9	1.17

Sweet bamboo ash content was 1.4% and it can also be referred to as the silica content. Lises found that silica content varied on an average from 0.5-4%, increasing from bottom to top [12]. The amount of sweet bamboo ash content investigated by Satrakhom was 4.1% [13]. The solubility of sweet bamboo were alcohol and benzene solubility 5.1%, hot water solubility 8.4%, cold water solubility 7.0% and 1% NaOH solubility 24.9%.

3.2 Pulping Processes

The cooking results of sweet bamboo AS-AQ pulping are presented in Table 4. The investigation into the effect of AQ addition in AS pulping on pulped yield and kappa number at 25-35% chemical charge. Consequently, pulping process was modified by 0.1% AQ and increased chemical charge about 5%. The pulping chemical had mainly affect screen yield and kappa number of AS-AQ pulping. The increment of chemical charge in AS-pulping change in screened yield after 0.1% AQ was added. It was reduced about 0.9%. On another hand the effect of chemical charge and 0.1 % AQ addition on lignin content in AS-AQ pulp had more influence and it demonstrated by kappa number reduction which was decreased about 2.9 points The experiment found that AS-AQ screened yield was 55.57 to 56.67% and its reject was 0.53 between 1.43 %. Kappa number indicated delignification rate and decreased from 12.53 to 9.60.

Table 4. The results of sweet bamboo AS-AQ pulping**.**

Process	Pulping condition						Screen Yield (%)	Reject (%)	Kappa number
	Chemical charge (%)	Na_2SO_3/ NaOH	Total time (min)	Temp. (C^o)	L:W	AQ (%)			
AS-AQ	25	70:30	180	170	4:1	0.1	55.8	1.4	12.5
	30						56.7	1.2	11.4
	35						56.3	0.5	9.6

The modification pulping process by AQ addition has more investigated and pulped by other raw materials and different pulping processes. Ingruber, Miller and Gounder reported the addition of AQ to AS pulping can raise the delignification rate and protected cellulose degradation which was demonstrated by quantity of screened yield [2,3]. The AQ addition could adjust pulping condition for screened yield development and it was traded for greater reduction in kappa number with a greater pulp yield increased [4].The delignification rates of pulping processes were ranked as following: kraft-AQ > kraft e” AS-AQ > NS-AQ [14]. Thus the results of sweet bamboo AS-AQ pulping were similar when it compared with all pulping references such as pulping chemicals effect and pulped yield development. The lowest chemical charge of sweet bamboo AS-AQ pulping and highest kappa number (12.5) was selected to evaluate unbleached AS-AQ pulp properties.

3.3 Pulp Properties

Table 5 illustrates the pulp properties of unbleached sweet bamboo AS-AQ pulp after pulp was beaten by PFI-mill. The unbleached pulp test found that the effect of beating revolution on pulp properties related to drainability of sweet bamboo AS-AQ pulp and it continued to decrease when beating revel continued to increase. The beating revolutions had strongly affected pulp strength and slightly influenced optical properties such as brightness. The strength of paper increased with pulp beating or refining since it relied on fiber-to-fiber bonding [15]. However the strength development of unbleached sweet bamboo dropped when the maximum strength occurred.

Table 5. Unbleached sweet bamboo AS-AQ pulp properties.

Pulp Properties	Beating revs. by PFI mill							
	0	1000	2000	3000	4000	5000	6000	7000
Freeness (ml, CSF)	750	700	609	573	455	335	273	240
Basis weight (g/m^2)	59.53	57.22	57.24	59.95	58.53	58.11	59.95	56.83
Thickness (mm)	0.18	0.17	0.15	0.15	0.15	0.14	0.14	0.14
Density (g/cm^3)	0.34	0.35	0.38	0.40	0.40	0.41	0.42	0.42
Bulk (cm^3/g)	2.90	2.82	2.62	2.49	2.49	2.43	2.39	2.38
Tensile Index (Nm/g)	20.76	30.28	44.66	51.71	60.10	54.34	37.95	36.12
Tear Index (mN.m^2/g)	9.36	25.01	26.92	27.50	27.87	24.52	22.29	21.92
Burst Index (kPa.m^2/g)	0.81	2.18	2.52	2.80	3.10	3.34	3.25	3.21
Folding endurance	3	29	75	158	269	371	381	405
Brightness (%ISO)	26.62	25.57	25.89	25.42	25.02	25.28	25.41	25.21

3.3.1 Beatability and Drainability Development

The influence of beating level on drainability of unbleached sweet bamboo AS-AQ pulp is presented in Figure 3. The drainability of sweet bamboo AS-AQ was reported by freeness value development and it was referred the "degree of beating". The important effects of beating on the drainage of pulps are to shorten the fiber, and to bruise, crush or internally fibrillate the fiber which greatly affects their drainability. Therefore the drainability development of AS-AQ pulp depends on the beating revolution and its freeness values continued to decreased when beating levels increased. Smook reported that unbleached pulps were more difficult to beat than bleached pulp [1]. Aspen AS-AQ pulp with kappa number.25.8 was slightly harder to beat than kraft pulp with kappa number 17.7 [16].The beating revolution result of unbleached AS-AQ pulp with 12.5 kappa number was 0 – 7000 revs. and freeness value was 240- 750 ml, CSF.

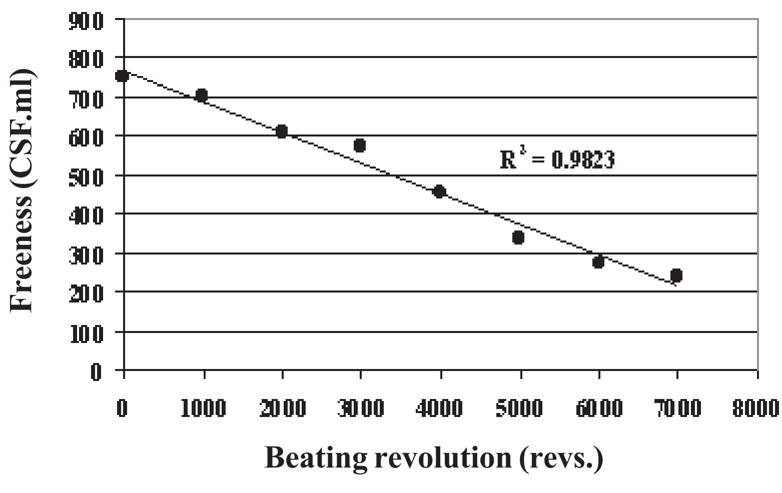


Figure 3. The relationship between freeness and beating level of unbleached sweet bamboo AS-AQ pulp.

Biermann presented the action of beating or refining on fibrillation, exposure of cellulose fibrils to increase the surface area of fiber [15]. The beating level increases the surface area and it is essentially to the pulp strength properties. The beating process is mainly to increase fiber to fiber bonding and decrease fiber to fiber bonding also at high beating revolution. The experiment the highest mechanical strength of unbleached sweet bamboo AS-AQ unbleached pulp at 4000 revs. Hence the relationship between beating level and freeness can predict at 4000 revs. this has higher fibrillation and lower fiber degradation than 7000 revs, because of the unbleached sweet bamboo AS-AQ freeness value at 7000 revs. is less than 4000 revs and it refers at 7000 revs, the sweet bamboo length of this beating revolution is shorter. The beating experiment indicates sweet bamboo AS-AQ pulp requires more energy requirement. Yusoff. *et al.* reported the unbleached tropical bamboo (*Gigantochloa scortechinii*) soda pulp could be beat at 0 -10,000 revs, and its freeness values were about 250 – 770 ml, CSF [10].

3.3.2 Density

The effect on beating on handsheet density showed in figure 4. The density of unbleached sweet bamboo AS-AQ handsheet continued to increase from 0.35 to 0.40 g/cm^3 at 0 – 30000 revs, and then it slightly rises from 0.40 to 0.42 g/cm^3 at 4000 – 7000 revs. (Table 5). At the beginning, the fibers are relatively long, thick and the sheet bulky. The cohesion of unbeaten fibers is often too low to enable them effectively to resist the applied tensile and tearing forces. The beating proceeds, the handsheet density and the cohesiveness of the fiber increase and it means that the paper strengths are developed. The beating not only increases the handsheet density with its adverse effects on tear, but also reduces the length of the fibers.

3.3.3 Tensile Strength

Tensile index of all unbleached sweet bamboo AS-AQ pulps were 20.76 – 61.10 Nm/g (Table 5). The highest tensile index was 61.1 Nm/g at 4000 revs, beating levels and 455 ml.CSF, freeness value in the Table 5. Figure 5 shows the relationship between tensile

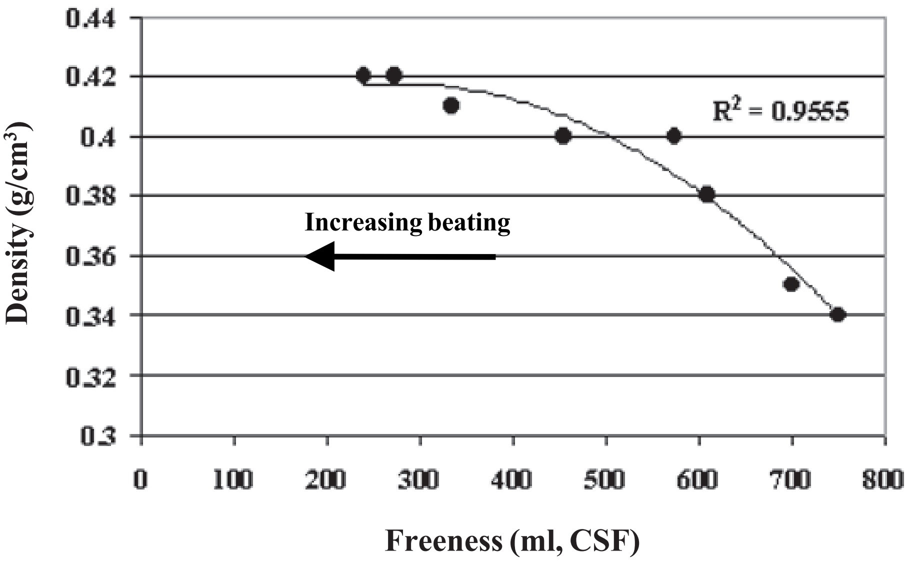


Figure 4. The relationship between density and freeness of unbleached sweet bamboo AS-AQ pulp.

index and freeness it demonstrates the trend of tensile strength development after beating of unbleached AS-AQ pulps rises. Maximum tensile index is reach and thereafter freeness continues to decrease, resulting from increasing beating revolution, tensile index will drop if beating levels are extended. Hong Man reported, the tensile strength of bleached bamboo soda-AQ pulp was high 68.7 Nm/g, with 5000 revs [17].

3.3.4 Tear Strength

The range of tear index of all unbleached sweet bamboo AS-AQ pulp was 9.36-27.87 mN.m^2/g (Table 5). Figure 6 indicates the trend of tear strength development against freeness of unbleached sweet bamboo AS-AQ pulps which was almost similar to tensile strength. The highest tear strength of unbleached sweet bamboo AS-AQ presented at 4000 revs, and it was 27.87 mN.m^2/g, freeness value 455 ml, CSF. The tear strength of 3 – years old unbleached tropical bamboo (*Gigantochloa scortechinii*) soda pulp was 22.1 mN.m^2/g at 7000 revs, beating levels and 430 ml.CSF, freeness value [10]. Considering the tear strength of unbleached mix hardwood AS-AQ pulps was measured by Miller and Gounder. The tear index was 9.7 mN.m^2/g at 440 ml, CSF, freeness value [3].

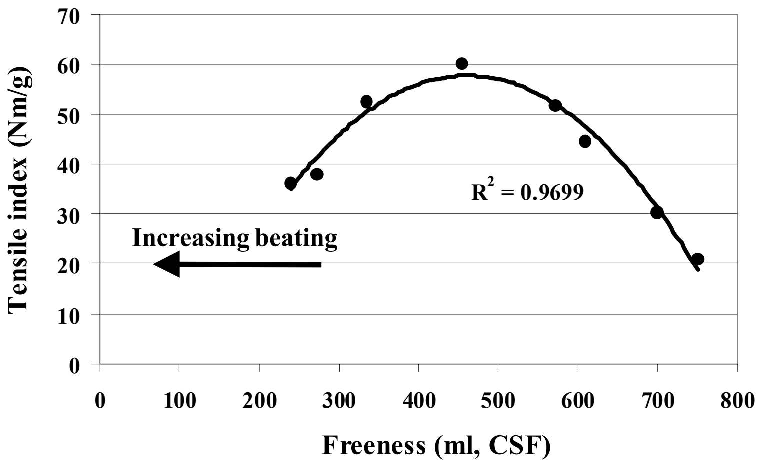


Figure 5. The relationship between tensile index and freeness of unbleached sweet bamboo AS-AQ pulp.

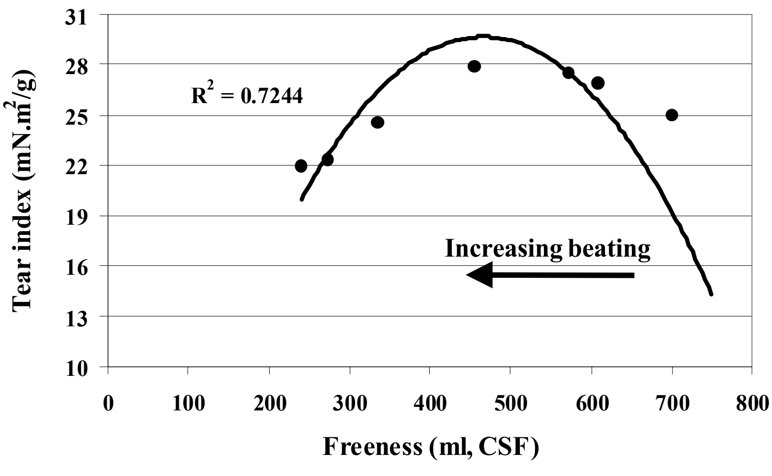


Figure 6. The relationship between tear index and freeness of unbleached sweet bamboo AS-AQ pulp.

3.3.5 Tear and Tensile Strength Relationship

Tear strength of unbleached sweet bamboo AS-AQ pulp is plotted against their tensile strength and it is showed in Figure 7. The relationship between tear and tensile strength presents both strengths trend to rise when beating level continues to increase. The highest of tear and tensile strengths illustrated at similar beating level and freeness values. Generally, the two most important fiber characteristics are fiber length and cell wall thickness which affect paper properties. Sweet bamboo fiber is long and very thick cell wall and its fiber morphology will be related with paper properties. The thicker wall fibers trend to produce an open, absorbent, bulky sheet with low burst/tensile strength and high tearing resistance [1]. The long fibers can make high tensile strength paper. Not only fiber morphology can develop paper strength but beating process can improve handsheet properties as well. The tear and tensile strengths can increase at appropriate beating revolution.

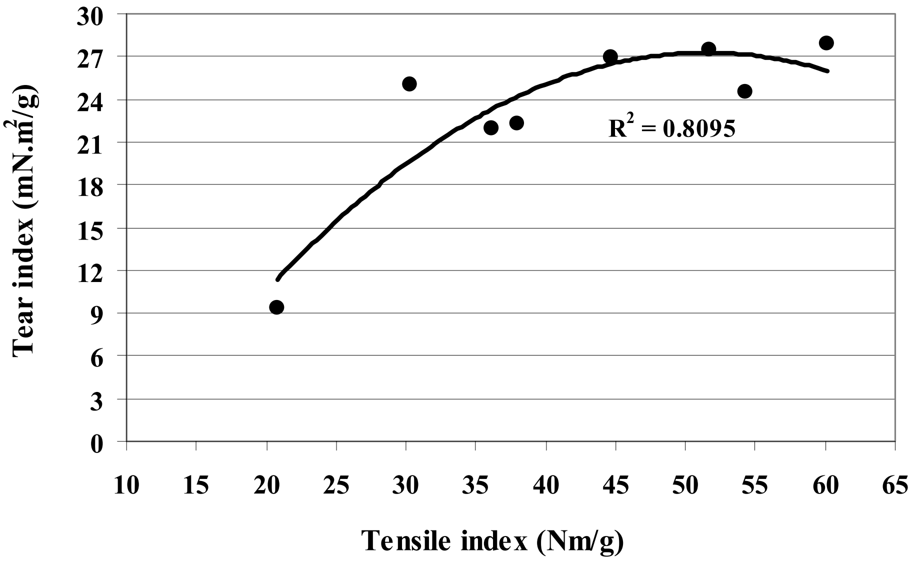


Figure 7. The relationship between tear and tensile strength of unbleached sweet bamboo AS-AQ pulp.

3.3.6 Burst Strength and Folding Endurance

The burst index and folding endurance of unbleached sweet bamboo AS-AQ pulp are presented in figure 8 and 9. The curve of both properties was similar when compared with other sweet bamboo pulp properties graphs. The refining reaction affects bursting index and folding endurance. However, burst strength continued to increase until beating level was 5000 revs. and freeness was 335 ml, CSF. At this beating level, the highest burst index was 3.34 kPa.m^2/g. Next the burst strength continued to decrease together with freeness dropped. In contrast, the folding endurance data was highest at lower freeness value and more beating revolution. It was 405 at 7000 revs. beating level and 240 CSF; ml; freeness.

3.3.7 Optical Property

The experiment presented the optical property such as unbleached AS-AQ brightness it had low brightness values (25.02 – 26.62 %ISO.) and it was slightly change by beating revolution. Generally brightness value of unbleached pulps is lower than bleached pulp. The brightness value depends on pulping processes and pulping condition and they can reduce and remove lignin content in wood and non- wood fiber. The residual lignin remains in unbleached pulp it has major effect on brightness value. This study indicates that AS-AQ pulping has high delignification rate and it reveals by lower kappa number. Kappa number is the value of residue lignin content that remains in unbleached pulp. Thus the optical property can develop particularly in bleaching process.

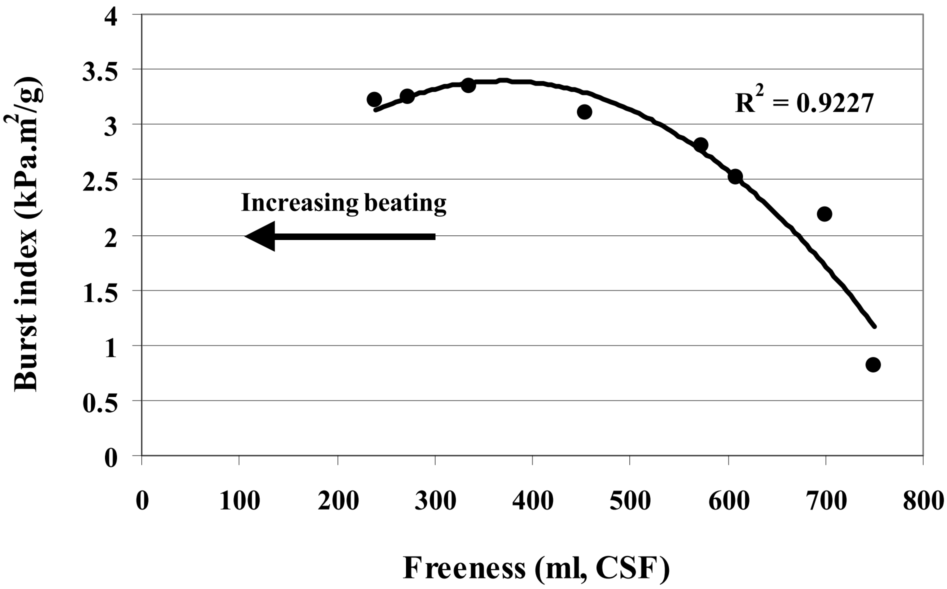


Figure 8. The relationship between burst index and freeness of unbleached sweet bamboo AS-AQ pulp.

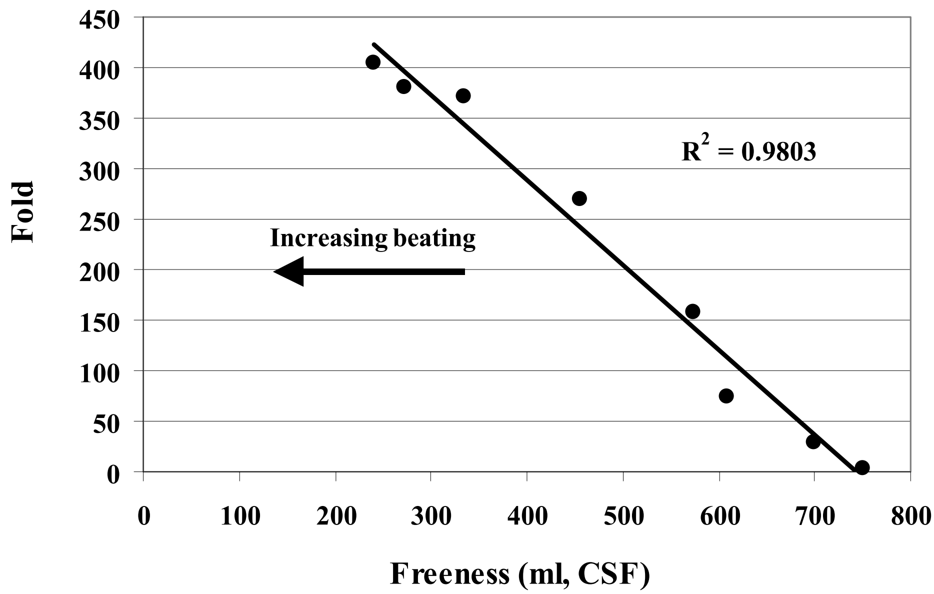


Figure 9. The relationship between folding endurance and freeness of unbleached sweet bamboo AS-AQ pulp.

4. Conclusions

The results of this investigation demonstrate the principle physical properties such as basic density and moisture along the sweet bamboo culm are averaged 725 kg/m^3 and 60.2% respectively. The sweet bamboo morphologies such as fiber length, fiber width, cell wall thickness and cell lumen are 3.1 mm, 18.0 mm, 4.4 mm and 6.9 mm, respectively. Analysis of bamboo fiber morphology is long fiber, thick cell wall and narrow cell lumen.

Sweet bamboo has high holocellulose, alpha-cellulose, lignin and low ash content, which are 76.3%, 68.1%, 28.7% and 1.4%, respectively. The solubility of sweet bamboo present by the alcohol-benzene solubility, hot and cold water solubility and 1% NaOH solubility and they are 5.9%, 8.0%, 7.0% and 24.9%, respectively.

The addition of 0.1% AQ in sweet bamboo pulping as AS-AQ pulping has a tendency to improve pulping process at 25 - 35% chemical charges. The experiment shows AS-AQ screened yield is 55.8 - 56.7% and its reject is 0.5 - 1.4 %. Kappa number indicates delignification rate and it decreases from 12.5 to 9.6 when chemical charge is increased. Thus the preliminary of modified AS pulping process by AQ addition reveals AS-AQ pulping process can produce high pulped yield and low kappa number.

Unbleached sweet bamboo AS-AQ pulp (12.5 kappa number) strengths increase by beating process and they relate with sweet bamboo pulp drainability. The result illustrates the beating level mainly affect all pulp strengths and slightly influences optical properties such as brightness. At 4000 revs. and freeness 455 ml, CSF, the highest tensile and tear strength are 60.10 Nm/g and 27.87 mN.m^2/g, respectively. For the highest burst strength and fold endurance indicate at 5000 revs., 335 freeness ml, CSF and 7000 revs., freeness 240 ml, CSF, respectively. They are 3.34 kPa.m^2/g. and 405.

Acknowledgements

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