

## THESIS

# ALKALINE SULFITE PULPING AND ECF-BLEACHING OF SWEET BAMBOO

(Dendrocalamus asper Backer)

SUPHAT KAMTHAI

GRADUATE SCHOOL, KASETSART UNIVERSITY 2003

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โครงการพัฒนาองค์ความรู้และศึกษานโยบายการจัดการทรัพยากรชิวภาพในประเทศไทย c/o ศูนย์พันธุวิศวกรรมและเทคโนโลยีชีวภาพแห่งชาติ อาคารสำนักงานพัฒนาวิทยาศาสตร์และเทคโนโลยีแห่งชาติ 73/1 ถนนพระรามที่ 6 เขตราชเทวี กรุงเทพฯ 10400



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## **THESIS**

## ALKALINE SULFITE PULPING AND ECF-BLEACHING OF SWEET BAMBOO (Dendrocalamus asper Backer)

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In this study, the morphological, physical and chemical properties of the 3 year-old sweet bamboo were investigated. The sweet bamboo chips were pulped using alkaline sulfite (AS), alkaline sulfite with anthraquinone (AS-AQ) processes. Conventional kraft pulping was performed as reference. The selected pulps were subsequently ECF bleached with DoED EP sequence. The papermaking properties of unbleached and bleached pulps were evaluated. The results demonstrated that sweet bamboo is an appropriated raw material for pulp production due to its morphological, physical and chemical properties, and also pulp and papermaking properties. The basic density and moisture content of sweet bamboo were 725 kg/m<sup>3</sup> and 60.24% respectively. The important chemical compositions were holocellulose 76.31%, lignin 28.70% and ash 1.46%. Data were collected in part of fiber morphology which indicated its fiber dimensions as follows: fiber length 3.11 mm, fiber width 18.03 µm, cell lumen 4.35  $\mu$ m, cell wall thickness 6.98  $\mu$ m and Runkel ratio 3.2. Sweet bamboo fiber was long, fair narrow, thick wall and had blunt or end point. The pulping results indicated that pulp yield and kappa number of AS pulping were approximately 10% and 17 points higher than those of kraft pulping. The addition of anthraquinone (AQ) in AS pulping resulted in better delignification while the pulp yield was unchanged. Thus kappa numbers of AS-AQ pulps were approximately 20 points lower than those of AS pulps. The results of ECF-bleaching with DoED, EP sequence presented that the AS-AQ pulp required less bleaching chemicals than kraft pulp to reach target brightness at 88 %ISO. Consideration on papermaking properties indicated that beatability and strength of AS-AQ pulp were lower than those of kraft pulp. After bleaching, tensile strength of both pulps decreased while tear and burst strength, and folding endurance of AS-AQ pulp increased. The unbleached AS-AQ pulp had higher density and lower thickness than kraft pulp. The advantages of AS-AQ pulping over kraft pulping were higher pulp yield at the same delignification rate, higher brightness of unbleached pulp and better bleachability. However, strength and beatability of kraft pulp was superior than AS-AO pulp.

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#### LIST OF ABBREVIATIONS

AA = Active alkali

AOX = Absorbable organic halide

AQ = Anthraquinone

AS = Alkaline sulfite pulping

AS-AQ = Alkaline sulfite pulping with anthraquinone

BOD = Biological oxygen demand

CC = Chemical charge

COD = Chemical oxygen demand

D = Chlorine dioxide

E = Extraction

ECF = Elementally chlorine-free

K = Kraft

P = Hydrogen peroxide

TAPPI = Technical Association of Pulp and Paper

Industry

TCF = Totally chlorine-free

## ALKALINE SULFITE PULPING AND ECF BLECAHING OF SWEET BAMBOO (Dendrocalamus asper Backer)

#### INTRODUCTION

Pulp and paper industries have been intense developed since it was introduced in the mid-1800s. Recently they have the world's highest growth rates in Asia. In 2000, the world's total paper and paperboard consumption was 327 million tons. In Asia-Pacific this consumption was about 102 million tons, or one third of global consumption. During the present decade between 2000 to 2010, annual paper consumption in Asia increased and is predicted to grow totally ca. 50 million tons (Malinen, 2001).

Throughout 2001, overall consumption of pulp and paper in Thailand was 2,920,000 tons consisting of 896,000 tons for pulp and 2,024,000 tons for paper. Only short fiber pulp could be produced in Thailand whereas long fiber pulp would be 100% imported, mainly from Canada, Chile, USA and South Africa. In 2001, long fiber pulp demand was 205,000 tons, 2% raised from last year. The prediction of pulp and paper demand in next four years was expected to grow by 4% per annum from 896,000 tons in 2001 to 1,043,000 tons in 2005. Particularly long fiber pulp was demanded from 205,000 tons in 2001 to 237,000 tons in 2005 (Thai Pulp and Paper Industries Association, 2001).

The non-wood fiber will play an important role in the world's pulp and paper industries. In could be made available and more grown if necessary to sustain the increasing pulp and paper requirement. In this study, the new long fiber resource such as non-wood fiber from bamboo will be investigated. The driving force behind the interest in non-wood fiber is the lack of softwood which is the important raw material for the long fiber production. Moreover, bamboo is an indigenous species in Thailand.

In this research the morphological and chemical properties of sweet bamboo will be studied. The pulping and bleaching process with low pollution will be carried out. The full chemical pulping process, alkaline sulfite using sodium hydroxide (NaOH) and sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) as pulping chemicals, is selected in the study. Because it dominates the

pulping process in the world, kraft pulping is used as a reference. After pulping, the bleachability of the obtained pulps with ECF (Elementally Chlorine-Free Bleaching) will be investigated. The physical and chemical properties of the bleached pulps will be evaluated.

The objectives of this study are:

- 1. To investigate morphological, physical and chemical properties of sweet bamboo
  - 2. To optimize pulping and bleaching processes with low pollution.
  - 3. To investigate papermaking quality of the obtained pulps.

The expected outputs of this study are:

- 1. Pulp yield and quality from bamboo will be improved for pulp and paper manufacture.
- 2. The use of alkaline sulfite pulping and ECF-bleaching will decrease the pollution from the paper mill.
- 3. The cultivation and utilization of bamboo will be promoted for the new long fiber resource in Thailand.

#### LITERATURE REVIEW

#### Bamboo

#### Bamboo as a raw material in papermaking

Bamboo is one of the socio-economically plant species in Thailand. It has found in the mixed deciduous, tropical evergreen forest and plantation such as sweet bamboo or Pai Tong. Bamboo is a perennial lignified plant which belongs to Bambusoideae, a subfamily of Gramineae. There are 15 genera and 82 species in Thailand (Pattanaviboon *et al.*, 2001). In 1996, the total bamboo area in natural forest of Thailand was 32,827,971 rai (ca. 5,252,475 ha). The sweet bamboo plantation area in 1998 was 153,227 rai (ca. 24,516 ha) (Pungbun Na Ayudhya, 2000).

Bamboo is a common non-wood plant in most of Asia. It is one of the most important minor forest products for utilization. They were used for many purposes such as food, household construction, furniture and pulp production. It is considered the advantages of bamboo for pulp and paper are: (a) it is very fast growing, (b) it is a raw material which does not require debarking, (c) the yield is quite high for kraft pulps, (d) the chemical consumption is low, (e) pulps are easily bleached and (f) the pulp is stronger than most tropical hardwood pulps. The disadvantages of bamboo included: (a) gregarious and sporadic flowering which upset and disrupts regular supply, (b) difficult to chip because of hollow stem, (c) difficult to handle mechanically because of variable diameter and crookedness of stems, (d) dense nodes which are highly lignified and difficult to pulp, (e) high silica which causes scale formation and problems with lime mud reburning, and (f) high percentage of parenchyma cells. Bamboo genera used for papermaking are Bambusa, Dendrocalamus, Melocanna and Phyllostachys (Bhragava, 1987; Atchison, 1987).

#### Morphology of Bamboo

The properties of bamboo culm are determined by its anatomical structures. The culm consists of internodes and nodes. At the internodes, the cells are axially oriented

whereas at the nodes, cells provide the transverse interconnection. At the peripheral zone of the culm, the vascular bundles are smaller and more numerous in the outerpart but in the innerpart are larger. Within the culm wall the total number of vascular bundle decrease from bottom toward the top, while their density and specific gravity increase at the same time. The culm tissue is mostly parenchyma and vascular bundles which are composed of vessels, sieve tube with companion cell and fiber. The number of cell in culm tissue may be variance in another species (Liese, 1995; Liese and Weiner, 1997).

The important cell tissues of bamboo are fibers, which have effect to pulp and paper strength. The fiber constitutes the sclerenchymatous tissue and occurs in the node and internode as cap of vascular bundles and in some species additionally as isolated stands. They contribute to 40-50% of the total culm tissue and 60-70% by weight (Liese, 1995; Liese and Grosser, 2000).

Identification of bamboo fiber is long fair narrow, thick wall and has blunt or pointed end. There are also wide, thin-walled pitted fibers, which are fair long and have tapering ends (Ilvessalo-Pfäffli, 1995). The fiber length of bamboo varies from species to species and often varies across the culm wall in a characteristic pattern. In some species, it varies from bottom to top, outer to inner part and some cases they vary with internode length (Yulong and Liese, 1997).

The bamboo fibers are shortest at the outer part, longer at the center and decrease again in length towards the inner part. This pattern is presented in both internodes and nodes. However, in the nodal region the fibers are generally considerably shorter than those in the internodes (Yulong and Liese, 1997). Average length of fiber ranges from 1.5 to 4.4 mm and fiber width varies widely from 7 to 27  $\mu$ m, with an average of 14  $\mu$ m (Casey, 1979). The approximate fiber dimensions of sweet bamboo are: length 3.78  $\mu$ m, diameter 19  $\mu$ m, lumen width 7  $\mu$ m and cell wall thickness 6  $\mu$ m (Dransfield and Widjaja, 1995)

#### **Chemical Properties**

The main chemical compositions of bamboo are cellulose, hemicellulose and lignin, which are in cell wall. The minors are extractives such as resins, tannins, waxes and inorganic salts, which are not chemical components of cell wall (Liese, 1995). Considerable variation in compositions occurs among bamboo of different species. These differences are due to a number of factors, such as soil, climatic condition, growth rate and species. The chemical compositions of sweet bamboo culm are approximately: holocellulose 53%, pentosan 19%, lignin 25%, ash 3%, the solubility in cold water 4.5%, in hot water 6%, in alcohol-benzene 1% and in 1% NaOH solution 22% (Dransfield and Widjaja, 1995).

#### Cellulose and Hemicellulose

Bamboo cellulose is likewise in wood-fiber or another non-wood plant fiber. The strength of bamboo fiber depended on cellulose molecule, linear and moderately crystalline. Hemicellulose content in bamboo is the most abundant renewable organic material next to cellulose. More than 90% of bamboo hemicellulose consists of a xylan but appears to be different from the xylan found in wood. Bamboo xylan has about 6.7% of native acetyl group. Bamboo cellulose and hemicellulose are changed when bamboo age increased. Cellulose and hemicellulose content in internode are always much more than node (Bhargava, 1987; Liese, 1995).

#### Lignin

Bamboo lignin is a typical grass lignin composed of mixed dehydrogenation polymers of coniferyl, sinaply and p-coumaryl alcohol. The order of basic building units is as follow: syringyl > guaiacyl > p-hydroxyphenyl. The lignin also contains 1-(4-hydroxy-3-methoxyphenyl)-3-hydroxypropane-1-one structure (Bhargava, 1987). The lignification within every internode process downward from top to bottom, whereas transversely it proceeds from inside to outside (Itoh, 1990). The quantitative results for lignin content clearly increased with maturation of culm but no clear trend in lignin content with internode height was detected at these sampling time (Murphy and Alvin, 1997).

#### **Sulfite Pulping**

#### The Sulfite Systems

Unlike the kraft process, which based on sodium at a pH of the fresh cooling liquor of about 13.5, the sulfite process is characterized by covering the whole range of pH from below one for sulfur dioxide solution in water, to above 13 for sodium sulfite solutions with free sodium hydroxide added. Within this range lies the versatility of process of producing pulp of different yield and properties covering all commercial requirements when it is compared with kraft pulping (Ingruber, 1985; Smook, 1997).

From a chemical standpoint sulfite pulping liquors vary with respect to the possible forms of sulfur dioxide in aqueous solution and the type of base added to this system (Ingruber, 1985; Fengle and Wegener, 1989). Biermann (1993) explained that the cooking chemicals all start out with SO<sub>2</sub>. The reaction of sulfur dioxide with water principally yields are: dissolved SO<sub>2</sub> and/or sulfurous acid (H<sub>2</sub>SO<sub>3</sub>), bisulfite (hydrogen sulfite (HSO<sub>3</sub>)) and monosulfite (SO<sub>3</sub>).

The type of base used in the cooking liquor additionally influences the pH values. The following bases are normally used in sulfite pulping for example calcium, magnesium, sodium and ammonia. Calcium is the traditional base used in sulfite pulping. It is the classical base in acidic sulfite pulping. When limestone (CaCO<sub>3</sub>) reacts with H<sub>2</sub>SO<sub>3</sub> in pressurized towers to produce the pulping liquor. The liquor is used at a pH of 1-2 (maintained with excess SO<sub>2</sub>); at higher pH values, calcium sulfite precipitates. The cooking temperature is 140°C. The advantages are the low price and the good availability of limestone as the dominant raw material. The drawbacks are the limited solubility of calcium sulfite, scaling problems and the lack of suitable recovery system. Pulping is characterized relative to the other bases by-intermediate pulping rate (Ingruber, 1985; Biermann, 1993).

A much better solubility is obtained with magnesium as a base. In magnesium base sulfite pulping is carried out as a pH below 5 and is characterized relative to the other bases by intermediate pulping rate, moderate scaling and screening, and relatively simple

chemical recovery. There are two major processes: acid bisufite at pH below 2 and bisulfite pulping at pH 4.5. Due to limited solubility of magnesium sulfite, magnesium based sulfite pulping must be carried out below pH 5. The outstanding advantage of magnesium-base sulfite pulping is the possibility of combusting the waste liquor to yield magnesium oxide and sulfur dioxide for producing fresh cooking liquor (Ingruber, 1985; Biermann, 1993).

Sodium sulfite and sodium bisulfite are soluble under condition applied in sulfite pulping. It is a highly attractive base. NaOH or Na<sub>2</sub>CO<sub>3</sub> may be formed the cooking liquor from H<sub>2</sub>SO<sub>3</sub>. When the sulfite pulping process used NaOH and Na<sub>2</sub>SO<sub>3</sub>, the pH range up to about 10-13. The process is characterized by a slow pulping rate, low amounts of screenings and low scaling and complex chemical recovery. The sodium recovery was a drawback of this base as compared to magnesium, but there were several commercial recovery systems available today (Ingruber, 1985; Biermann, 1993).

Ammonium based sulfite pulping is very similar to sodium based pulping except for two important differences. (1) The cooking rate is faster than the three bases mentioned and, (2) the ammonium ion is lost in chemical recovery by combustion. However, the use of fresh ammonia (which reacts as ammonium hydroxide) allows the sulfur to be recovered in relatively simple process. The appearance practical pH limit is about 9, above this pH free ammonia begin to be significant. Ammonium was recovered from the spent liquor by distillation with lime (Ingruber, 1985; Biermann, 1993).

#### **Sulfite Process**

The cooking liquor of sulfite pulping is usually prepared by burning sulfur to produce SO<sub>2</sub> gas and the absorbing the SO<sub>2</sub> in alkaline base solution. The sulfite cooking operation is usually carried out batchwise in a pressure vessel (digester). It can be continuously or a discontinuous batch process. In the process chip is filled in the digester. After this the absorption reaction will be start by hot cooking liquor. The liquor is heated by direct steam injection or by indirect heating using a heat exchanger to reach the maximal cooking temperature, which varies between 125-180°C depending on special process and the desired pulp type. The cooking pressure varies between 5-7 bar and cooking time between 3-8 hours. When the cooking is finished, the digester is discharged in to blow

tank and reduces pressure of about 2 bar. When the spent liquor is being removed, wash water is introduced. The ready washed pulp is screened and cleaned to select the reject, and finally thickened. The spent liquor may be used for the recovery of by-products or combusted after evaporation to yield heat and to recover the base. The advantages of sulfite pulping process over kraft pulping as followings (Fengel and Wegener, 1989):

- higher pulp yield at a given-kappa number, resulting in lower wood consumption
- higher brightness of unbleached pulps
- higher flexibility of bleaching and bleaching without chlorine
- fewer pollution problem
- lower installation capacity cost

Whereas formerly sulfite pulping was mainly represented by the acid calcium bisulfite process, today a number of different and modified sulfite processes are known. Sulfite processes are characterized by the composition of cooking liquor, which influences the pH and the choice of the base. They can be grouped into five principal types:

The acid sulfite process uses a cooking liquor that is strongly acidic (pH 1.5-2) with a pulping temperature of 125-145°C and a cooking time up to 7 hours. A long heating time (time to maximum temperature about 3 hours) is necessary to prevent diffusion of SO<sub>2</sub> ahead of the base that causes lignin to condense at high temperature in the center of the chip causing a "black cook". The base is usually calcium. Due to acid hydrolysis, the result is a weak pulp, with low hemicellulose content suitable for dissolving pulp, tissue paper, and glassine (Biermann, 1993).

Bisulfite process is a full chemical pulping process with higher liquor pH (3-4) and nearly equal amounts of free and combined  $SO_2$  in the liquor. The temperature is  $160-180^{\circ}$ C with a cooking time of 0.25-3 hours giving yield of 55-75%. The Arbisco process uses sodium as the base; the magnefite process uses magnesium. Ammonia is also a suitable base. This pulp is suited for medium grades of paper such as newsprint and writing paper (Biermann, 1993). The bisulfite pulp has higher brightness values and

bleaching advantage. The yields of unbleached bisulfite pulps were up to 6% higher than those of comparable kraft pulps (Fengel and Wegener, 1989).

Neutral sulfite with a small excess of alkali is mainly applied in the production of semichemical pulp with sodium as the predominate base, but recently considerable interest has arisen in the AQ-catalyzed neutral sulfite process, applying cooking pH values between 8-10 (Fengel and Wegener, 1989).

The alkaline sulfite, full chemical pulping process uses a chemical charge containing approximately equal amounts of NaOH and Na<sub>2</sub>SO<sub>3</sub> at temperature of 160°-180°C and 3-5 hours at the maximum temperature. Ingruber (1985) presented the pH range for alkaline sulfite pulping was 10-13. This process produces pulps fairly similar in quality to kraft pulps in terms of yield, brightness, bleachability and strength (Biermann, 1993).

#### **Influencing Factors in Sulfite Pulping**

Pulping conditions vary widely in sulfite pulping. Therefore the number of variables is much higher and more complex than in kraft pulping. Sulfite pulping is influenced by the following main factors (Fengel and Wegener, 1989; Smook, 1997):

#### Wood

The effects of wood in sulfite pulping are wood species, general chip quality (size distribution, freedom form contaminant) and moisture content. Sulfite processes, acidic process in particular, are much more sensitive to wood species than the alkaline kraft process. In the calcium-based acidic sulfite process only small amounts of pine heartwood and bark can tolerated because otherwise phenolic components condense with lignin under the acidic conditions. This prevents the lignification reactions. If the soluble base are applied in acidic sulfite pulping the raw material basis can be expanded to some extent, but an essential improvement was made possible by the bisulfite processes, and the multi-stage processes starting with a high pH level.

#### Impregnation conditions

The impregnation of wood chips is a combined effect of liquor penetration and diffusion of the dissolved cooking chemicals in the soaked chips. The penetration is mainly affected by the applied pressure and to a lesser extent by the temperature. The diffusion rate is mainly determined by concentration of chemicals and the accessible total cross-section pore area. The types of wood or non-wood plant and the chip size additionally influence the penetration. The liquor-to-wood ratio is important in the impregnation phase, normally about 5:1.

#### Cooking liquor composition

The chemical composition of the cooking liquor is characterized by the pH value and the amounts of free, combine and total sulfur dioxide and the four base factors, which are depended on each other. The pH is the dominant variable influencing the pulping rate and the pulp yield and quality as well. The pH level is especially important in bisulfite pulping because of the hydrogen concentration, which determines the hydrolysis reaction is low and must be compensated by increased temperature. The increase of the combine sulfur dioxide charge in the range from 4-9% based on wood results in higher yields at a given kappa number, increased brightness, increased breaking length but decreased tear strength. The control of the total SO<sub>2</sub>-concentration is more significant in bisulfite pulping than acid sulfite pulping, where the excess free sulfur dioxide maintains a high hydrogen ion concentration.

#### **Anthraquinone Reaction**

In 1972/73 AQ (anthraquinone) was used in soda and kraft pulping. It accelerated the delignification and protected carbohydrates. AQ is an organic substance with aromatic molecules. Its characteristics are a pale yellow powder of low toxicity, and not an alkaline and acidic substance. It is insoluble in water or pulping solutions but becomes soluble in alkaline solution when in contact with reducing substances such as sugar and carbohydrate released from the wood into the liquor. The Figure 1 demonstrates the reaction of AQ with reducing substances (reduction reaction). The reduced compound, anthrahydroquinone

(AHQ), is formed which dissolves as the anion, anthraquinone dianion (AHQ-ion), after the ionization reaction (Ingruber, 1985; Dimmel, 1996).

Figure 1 Transferred forms of anthraquinone in alkaline medium.

Source: Ingruber (1985)

AQ and AHQ oxidizes reducing end groups of polysaccharides to aldonic acids, thereby reducing the extent of carbohydrate degradation caused by peeling off reaction. It is called "carbohydrate stabilization". AHQ-ion is formed in this process. Then AHQ-ion reacts with lignin resulting in fragmentation of the lignin (delignification rate increase) and oxidation of AHQ-ion back to AQ or AHQ. Figure 2 indicates the reaction mechanism of AQ (Dimmel, 1996; Lab, 1999).

AQ has maximum effect on degradation of lignin and stabilization of carbohydrate in the pulping process. AQ-reaction doesn't different in type of pulping processes but it is depended on the pulping conditions and quality of AQ. Blain (1998) reported that changing in AQ's kraft pulping acceleration occurred as sulfidity is increased. This work showed that care must be taken to optimize the kraft processes at each sulfidity studied. It was also demonstrated that AQ induced a delignification acceleration at sulfidity from 15 to 35%. AQ can be applied in different pulping processed such as soda-AQ, kraft-AQ, sulfite-AQ and alkaline sulfite with anthraquinone (AS-AQ).

## **Acceleration of delignification**

### Carbohydrates oxidation and....

....reduction of lignin

Figure 2 Reaction mechanism of anthraquinone proposed.

Source: Lab (1999)

#### Alkaline Sulfite Pulping with Anthraquinone

The use of AQ in pulping has received a great deal attention in the last decade. The most dramatic effect of AQ in pulping has been shown in studies using in neutral sulfite and alkaline sulfite pulping. The advantages of sulfite pulping with AQ claimed are: increase delignification rate, high yield, easier to refine and give strong pulp than sulfite pulps produced without AQ (Miller and Gounder, 1997).

Compared to kraft pulping, the AS-AQ process required either higher temperature or more time for an equal kappa number. The advantages of AS-AQ for the cooking over kraft process could be concluded (Ingruber, 1985; Miller and Gounder, 1997; Blain, 1998):

- accelerate delignification rate
- reduce kappa number
- protect cellulose degradation
- increase pulp yield
- much more easier to beat and reach higher levels of mechanical strength
- higher brightness and easier to bleach
- reduce sulfur pollution into the air

The modification of AS-AQ pulping by the addition of methanol and ethanol was improved the pulping rate and pulp strength. In 1987 AS-AQ pulping of bagasses with ethanol was investigated by Wang et al. (1987). The AS-AQ process results in good yield and good in unbleached pulps with high brightness (48-59.7%ISO) and excellent strength properties. Delignification can be performed to extremely low kappa without pulp degradation, which renders possible an easy bleaching. The pulping process of eucalyptus by alkaline sulfite pulping with anthraquinone and methanol (ASAM) was presented in 1997 (Puthson et al., 1997). Compare to kraft pulping, ASAM pulping gave better delignification with higher pulp yield above 50% and lower kappa number.

#### **Bleaching of Pulp**

#### **Bleaching Principles and Chemicals**

Bleaching is the treatment of wood and other lignocellulose pulps with chemical agents. It used for bleaching of chemical and mechanical pulps but the bleaching of chemical pulp involves a much different strategy than mechanical pulp (Smook, 1997). Regard to environmental aspect from bleaching chemicals such as chlorine and hypochlorite, the use of chlorine for bleaching is decreasing at present. Its decline can be concerns about the formation of chlorinated organic compounds, so-called "dioxin". Chlorinated organic compounds is mainly fragment of degraded lignin as by-products of chlorination (Dence and Reeve, 1996). Some important new or modified technologies for manufacturing bleached pulp with low environment impact included extended delignification, oxygen delignification, "elementally chlorine-free" (ECF) bleaching with chlorine dioxide and "totally chlorine-free" (TCF) bleaching with oxygen, ozone and hydrogen peroxide (Khanh, 1999).

The principal aim of pulp bleaching is to increase brightness. As the light-absorbing chromophoric components in unbleached pulps are predominantly functional group of degraded and altered residual lignin, bleaching can be performed either by converting and stabilizing chromophoric groups without loss of substance or by removing the lignin in pulps (Fengel and Wegener, 1989). Table 1 summarizes the chemicals used in pulp bleaching, their functions, advantages and disadvantages (Dence and Reeve, 1996; Khanh, 1999)

#### Parameters in Bleaching Process

The bleaching of pulp is performed through chemical reactions of bleaching agents with lignin and colored matter of the pulp. Due to the numerous bleaching chemicals and sequences the influencing factors in pulp bleaching process are very different, but all processes have six basic parameters. They are including type of bleaching agents, charge of chemicals, time, temperature, consistency and pH, which govern the extent and efficiency of bleaching reaction, and also strongly influence selectivity (Dence and Reeve, 1996).

Table 1 Functions, advantages and disadvantages of bleaching chemicals

Chemicals	Formulas	Stage	Function	Advantages	Disadvantages
Chlorine	Cl <sub>2</sub>	С	Oxidize and	Effective, economical	Organochlorinated
			chlorinate lignin.	delignification.	formation.
				Good particle removal.	Highly corrosive.
Hypochlorite	NaOCl	Н	Oxidize, decolorize	Easy to make and use.	Loss of pulp strength.
			and solubilize lignin.	Low cost.	Chloroform formation.
Chlorine	$ClO_2$	D	Oxidize, decolorize	Achieves high	Must be made on-site;
dioxide			and solubilize lignin.	brightness without loss	cost.
			In small amounts	of pulp strength.	Highly corrosive.
			with Cl <sub>2</sub> , protects	Good particle	Some organochlorine
			against cellulose	bleaching.	formation.
			degradation.		
Oxygen	$O_2$	О	Oxidize lignin.	Low cost; provides	Requires significant
				chloride-free effluent	capital equipment when
				for recovery.	used in large amounts.
					Loss of pulp strength.
Hydrogen	$H_2O_2$	P	Oxidize and	Easy to use.	High chemicals cost.
peroxide			decolorize lignin.	Low capital cost.	Poor particle
					bleaching.
					Loss of pulp strength.
Ozone	$O_3$	Z	Oxidize and	Effective; provides	Must be made on-site.
			decolorize lignin.	chloride-free effluent	Cost.
				for recovery.	Poor particle bleaching
					and pulp strength.
Hydrosulfite	$Na_2S_2O_4$	Y	Reduce and	Easy to use.	Decomposes readily.
			decolorize lignin in	Low capital cost.	Limited brightness
			high yield pulps.		gain.
Xylanase		X	Catalyze xylan	Easy to use.	Limited effectiveness.
			hydrolysis and aid in	Low capital cost.	Cost.
			lignin removal.		
Sodium	NaOH	Е	Hydrolyze	Effective and	Darken pulp.
hydroxide			chlorolignin and	economical.	
		<u> </u>	solubilize lignin.		
EDTA or		Q	Remove metal ions.	Improves peroxide	Cost.
DTPA				selectivity and	
				efficiency.	

Source: Dence and Reeve (1996); Khanh (1999)

Bleaching agents: Types of agents used in bleaching depend on type of unbleached pulp, the sequence of bleaching process, kappa number in pulps and particularly brightness gain to achieve. Each of bleaching chemicals provides benefit and negative effects in bleaching process (Table 1). In a typical delignification sequence, the residual lignin is solubilized by single and combination of oxidants such as chlorine, chlorine dioxide, oxygen, hydrogen peroxide and ozone in conjunction with joint or sequential alkali treatments.

Chemical charge: Charge of chemicals or chemical consumption, which is based on brightness target levels, is the most important parameter. The extent of applying chemicals also depends on the kinetics of the chemical reaction and the reaction time.

Time: Time required for pulp exposed to bleaching chemicals is normally depended on bleaching chemicals in each sequence. It is different and varies from 5 minutes to 240 minutes.

Temperature: Temperature during bleaching increases bleaching reaction rate, but it is limited by economic factor. It requires the use of steam and partly by equipment design. Temperature in each stage can vary from 60°C to 90°C.

Consistency: Consistency of stock in bleaching process increases reaction rate and efficiency of bleaching chemicals. However, it is normally fixed by original equipment design. Some stages of bleaching, such as oxygen and ozone, are optionally provided opportunity in choosing the level of stock consistency as medium, or high compatible with the whole bleaching sequence.

pH-Value: pH is very important in controlling chemical agents and rate of chemical reactions during bleaching. The adjustment of pH can be done by addition of alkali or acid before or with the bleaching chemicals. The pH values need to be monitored and controlled to achieve completed bleaching reaction. It is may different in each sequence or stage of bleaching process.

#### **Bleaching of Chemical Pulps**

The aim of bleaching chemical pulps is to remove the residual lignin after the cooking process to obtain so-called "full-bleached" pulps with brightness levels above 90% or "semi-bleached" qualities with brightness values in the range of 60-70%. The bleachability of chemical pulps can be determined by residual lignin content, which effected to brightness value. Lignin-removing bleaching is predominantly carried out today in multi-stage procedures with oxidative stages combined with normally at least one alkaline extraction step. Generally sulfite and bisulfite pulps are easier to bleach than kraft pulps. The multi-stage processes for sulfite pulps are usable for pulps form softwood and hardwood. In the case of alkaline pulps, hardwood pulps generally require fewer stages than softwood pulps (Fengel and Wegener, 1989).

#### **Chlorine Dioxide Bleaching**

Chlorine dioxide has long been known to be an excellent delignifying and bleaching agent. It is one of the most important chemicals used for bleaching chemical pulp because chlorine dioxide reacts readily with lignin and does not react to with carbohydrate. However, using of chlorine dioxide in large-size industrial processes is also difficult due to its high reactivity in the gas phase and its toxicity. Nevertheless chlorine dioxide is gradually displacing chlorine in the first stage. This development is the result of several advantages of chlorine dioxide, e.g. higher brightness, improved strength properties, lower chemical consumption and a substantial decrease in the BOD of the effluents. Chlorine dioxide bleaching is generally performed at low to medium consistency, at pH values of 3-5, at low temperature in the first stage or at about 70°C in intermediate or final stages for 3-5 hours (Fengel and Wegener, 1989; Dence and Reeve, 1996).

#### Alkaline Extraction

The sodium hydroxide applied in the alkaline extraction stage is not a bleaching agent as such. Its main effects are the removal of lignin degradation products in combination with a neutralization of acidic components formed during the pre-bleaching step. In normal pulp bleaching 1-2% alkaline (based on pulp) is used at 50-60°C for

30-60 min at medium-consistency level (10-18%). In dissolving pulp production most of the residual polyoses (hemicellulose) must also be extracted at this stage. Therefore higher concentrations of sodium hydroxide (up to 5%) are applied at considerably higher temperatures up to 100°C (hot alkali treatment) and higher consistency up to 35% for 3-5 hours (Fengel and Wegener, 1989; Dence and Reeve, 1996).

#### Hydrogen Peroxide Bleaching

Hydrogen peroxide is one of bleaching chemicals used in bleaching mechanical pulps. It is also established today in several industrial bleaching sequences for chemical pulps. Hydrogen peroxide is used in final stage such as DEOP and DEHP. The addition of a final hydrogen peroxide stage can increase brightness gain and improve brightness stability while preserving high viscosity and pulp strength. More recently an alkaline peroxide stage (P/E) combining bleaching and extraction in one stage sometimes replace the traditional sodium hydroxide extraction (E). By increasing the application of hydrogen peroxide the amounts of chlorine bleaching chemicals are reduced, resulting in decreased chloride load of the effluents. Drawbacks are still the high price of hydrogen peroxide and the necessary additives for stabilization. Peroxide bleaching is usually performed at medium to high consistency at 60-80°C for 2-4 hours and peroxide charge 1.5-2.5% (Dence and Reeve, 1996).

#### Oxygen Bleaching

Oxygen bleaching (or oxygen delignification) is one of the most thoroughly investigated processes in the field of pulping and bleaching of the last twenty years. Oxygen delignification is usually conducted under pressure and delignification is normally applied to kraft wood pulps but can be also used for sulfite pulps. As oxidation is the essential in lignin-removing bleaching it is quite reasonable to aim at using oxygen as the cheapest oxidizing agent for bleaching. The disadvantage of oxygen bleaching is the low selectivity for lignin degradation. Therefore the chemical pulps cannot be bleached to high brightness exclusively with oxygen without considerable attack on the polysaccharides, resulting in rather poor strength properties. Thus the common practice in mill-scale bleaching today is to remove about one-half of the residual lignin in unbleached pulp by oxygen. The main

benefits of oxygen delignification are environmental. The effluent from oxygen stage can be recycled to the recovery system that decreases the potential environmental impact of bleach plant. Not only the chlorinated organic by-products are reduced, but also other environmental parameters associated with bleach effluents, including BOD, COD and color. The decrease in color is larger than expected on the basis of lignin removed in oxygen stage. Oxygen bleaching can use in the first stage for bleaching process; to replace chlorine bleaching. The conditions in oxygen bleaching are not established yet. In principle oxygen bleaching is a gas-phase process at pressures usually between 4-8 bar and 0.4-0.8 MPa performed at high consistency of 10-12% or 20-30%, temperature of 90-110°C, 2-3% NaOH, pH 10-12 and 0.3-1.0 hours retention time (Dence and Reeve, 1996).

#### **Ozone Bleaching**

A patent tracing the application of ozone in the bleaching of fibrous substances used to make paper was issued in 1890. Interest in ozone as a replacement for chlorine in pulp bleaching has been accelerated by the progression toward minimizing discharges of chlorinated compounds and by market demands for TCF pulps. Ozone is a powerful oxidizing agent, which reacts readily with most organic materials, including lignocelluloses. It's used in commercial oxidation process to bleach textiles, waxes, and starches, and to disinfect air and water. Although ozone itself is highly reactive, its application is restricted. It was toxic in small amount but its odor can detect at only 0.01-0.015 ppm. The other disadvantage of ozone is gas-form thus it is generated in low concentration diluted with a carrier gas, usually oxygen or air, and low solubility in water. This limits its reactivity in aqueous systems where ozone must transfer from the gas phase into water to react. Because of limitations in pulp mixing equipment, the most efficient delignification for ozone bleaching occur near pH 2-3 and temperature of 25-30°C for high, medium and low consistency ozonation. Ozone is currently being applied in both elementally chlorine-free (ECF) and totally chlorine-free (TCF) processes (Dence and Reeve, 1996).

#### **Elementally-Chlorine Free Bleaching**

Recently, the environment concerns related to use of element chlorine gave birth to ECF-bleaching. Basic bleaching sequence of ECF-bleaching was D-E-D (E-D). This

sequence can be modified depended on target brightness. The modifications for specific conditions can include oxygen delignification, reinforcement of extraction with oxygen or peroxide, and peroxide in final bleaching stage. The modifications are also needed in the cases of limited production capacity of chlorine dioxide or COD/AOX minimization (Dence and Reeve, 1996).

The important kinetics of ECF-bleaching is pointed in the chlorine dioxide and extraction stage because these sequences effectively reduced kappa number or increased delignification rate. Alkaline extraction stage is to remove as much of the residual lignin as possible with smallest pulp damage and yield loss. The bleaching agents used in the final stage are depending on accepted brightness values which can be improved by the selective bleaching chemicals such as hydrogen peroxide and chlorine dioxide (Dence and Reeve, 1996).

#### **ECF-Bleaching of Bamboo**

The ECF-bleaching process applied for unbleached bamboo pulp can produce bleached pulp with high final brightness. Lab (1999) investigated ECF-bleaching sequence (D<sub>0</sub>ED<sub>1</sub>D<sub>2</sub>) of bamboo kraft, bamboo soda and bamboo soda-AQ pulps. The highest brightness value obtained came from bamboo kraft pulp (82-83%ISO) and the lowest brightness value came from bamboo soda pulp (80%ISO). This was a result of the higher initial kappa number of bamboo soda pulp. The bamboo soda pulp had clearly highest bleaching chemical consumption and poorest bleachability.

Khanh (1999) investigated ECF-bleaching of mixed bamboo: eucalyptus (70:30) kraft pulp using  $D_0$ -E/O- $D_1$  and  $D_0$ -E/O- $D_1$ - $D_2$  bleaching sequences. He reported that the three-stage sequence resulted in brightness of about 85-87%ISO and by using a four-stage sequence the brightness of 85-90%ISO can be reached with good quality of bleached pulps. Man (1999) modified the ECF-bleaching sequence of bamboo soda-AQ by using five-stage sequence (D- $E_0$ - $D_1$ -E- $D_2$ ). The results showed that the final brightness of bamboo soda-AQ pulp was 83-89%ISO.

#### MATERIALS AND METHODS

#### **Materials**

- 1. Chipper
- 2. Screener
- 3. Batch Digester
- 4. Soxhlet Apparatus
- 5. Light Microscope
- 6. PFI Mill
- 7. Canadian Standard Freeness Tester
- 8. Sheet Former
- 9. Brightness Tester
- 10. Tensile Strength Tester
- 11. Tear Strength Tester
- 12. Folding Endurance Tester
- 13. Burst Strength Tester

#### Methods

The experimental part was divided into five phases. The first was raw material preparation. The second was analysis of sweet bamboo properties, consisting of physical properties, fiber morphology and chemical properties. The third was focused on pulping processes. The fourth was investigation of ECF-bleaching and the last was testing of papermaking properties.

#### Raw Material Preparation

Sweet bamboo, 3 years old from bamboo plantation in Prachinburi province, was used in this study. The sweet bamboo culms were selected and cut at 0.30 m above ground (Figure 3), for (I): analysis of physical, chemical properties and fiber morphology, and for (II): pulping and bleaching. For pulping experiment, sweet bamboo culms were chipped. The chips were then screened in 19-25 mm hole screener. The accepted chips

were remained on the 22 mm hole screen and under 19 mm hole screen. The moisture content of screened chip was determined using TAPPI T208 om-98.

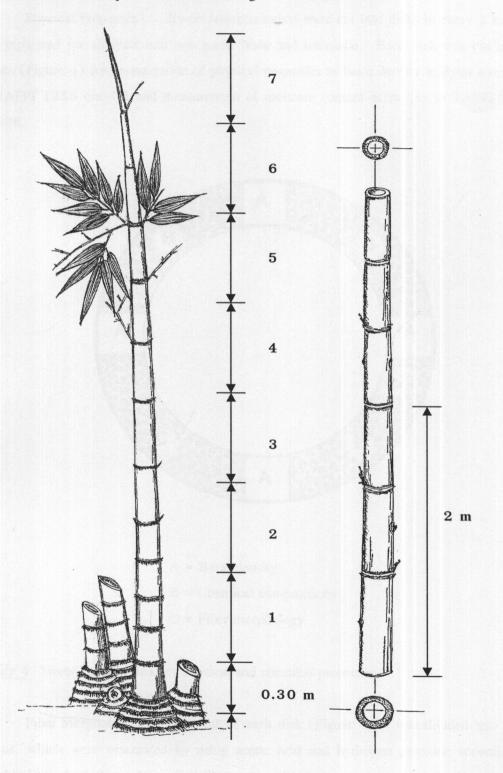
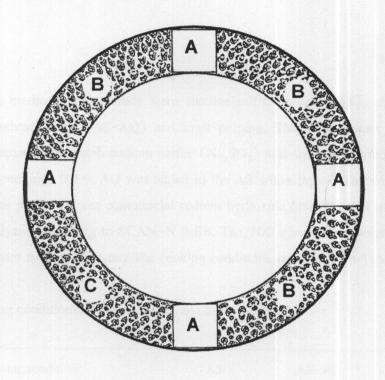


Figure 3 The various parts of bamboo culm cuttings.

#### **Analysis of Bamboo Properties**

Physical Properties Sweet bamboo culms were cut into disks in every 2 m long and separated for analysis into two parts: node and internode. Each disk was cut into 4 pieces (Figure 4) for investigation of physical properties as basic density analysis according to TAPPI T258 om-02 and measurement of moisture content according to TAPPI T208 om-98.



A = Basic density

B = Chemical compositions

C = Fiber morphology

Figure 4 Sweet bamboo disk for physical and chemical properties.

Fiber Morphology The rest of each disk (Figure 4,C) was divided into small pieces, which were macerated by using acetic acid and hydrogen peroxide according to Franklin's method. Then delignified fibers were liberated and measured their characteristics such as fiber length, fiber width and cell lumen.

Chemical Properties The rest of each disk (Figure 4,B) was chipped into small pieces and milled to be wood meal with laboratory mill. Then the wood particles were screened through the 40- and 60- mesh screen. The wood meal under 40 mesh and over 60 mesh was collected for chemical analysis such as holocellulose (Wise method), ash content (TAPPI T212 om-98), alpha cellulose content (TAPPI T203 om-99), 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), alcohol-benzene and alcohol solubility (TAPPI T204 cm-97).

#### **Pulping**

Cooking methods in this study were alkaline sulfite pulping (AS), alkaline sulfite pulping with anthraquinone (AS-AQ) and kraft pulping. The white liquor used in AS cooking was prepared from fresh sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) and sodium hydroxide (NaOH). In the AS-AQ cooking, 0.1% AQ was added in the AS white liquor. The white liquor of kraft pulping was prepared from commercial sodium hydroxide (NaOH) and sodium sulfide (Na<sub>2</sub>S) and analyzed according to SCAN-N 2:88. The 700 g oven-dry weight chips were cooked in a 7-liter rotating digester. The cooking conditions were listed in Table 2.

Table 2 Cooking conditions of AS, AS-AQ and kraft pulping.

Cooking conditions	AS	AS-AQ	Kraft
Chemical charge (%)*	25 - 30	25 - 30	_
Na <sub>2</sub> SO <sub>3</sub> /NaOH	70:30	70:30	_
Active alkaline (%)*	-	-	14 - 22
Sulfidity	-	-	30
AQ (%)*	-	0.1	_
Liquor to wood ratio	4:1	4:1	4:1
Time to max. temperature (min)	90	90	60
Time at max. temperature (min)	90	90	90
Max. temperature (°C)	170	170	170

<sup>\*</sup>based on oven-dry weight of sweet bamboo chips

After each cooking, brown stock was washed with excess tap water and then mechanically disintegrated for 2 minutes in disintegrator at about 5% consistency. The pulps were screened with screen slots of 0.15 mm according to TAPPI T275- SP-98, by which screened pulps and reject were separated. The screened pulps were continuously dewatered in a centrifuge for 10 minutes. Kappa number of screened pulps was evaluated according to TAPPI T236 om-99, and dry matter content of screened pulps and reject were determined according to TAPPI T208 om-98. The pulp yield and reject content, as percentages on an oven-dry basis, were calculated.

#### **Bleaching**

In this experiment, ECF-bleaching process was used for evaluation of the bleachability of obtained pulps. The unbleached AS-AQ and kraft pulps were selected on the appropriated pulping conditions that resulted in high pulp yield and low kappa number. The pulps were subjected to five-stage bleaching (D<sub>0</sub>-E-D<sub>1</sub>-E-P) in order to achieve a final target brightness of 88-90%ISO. After each bleaching stage, the final pH was measured at room temperature; bleached pulp was washed with distilled water and then dewatered in a centrifuge for 10 minutes. Then moisture contents of bleached pulps were determined. The bleaching conditions were given in Table 3.

Table 3 Conditions in bleaching stages.

Bleaching stages	$\mathbf{D_0}$	E	$D_1$	Е	P
Temperature, °C	70	70	70	70	80
Time, min	60	60	180	60	120
Consistency, %	10	10	10	10	10
Final pH (target)	1-3	11	3-4	11	10.5-11
NaOH, %	_	1	-	0.5	0.5
MgSO <sub>4</sub> , %		-	-	_	0.1
Chemical charge, %	3.8-5.0*	1.0	1.0-3.0	0.5	0.25-0.50**

<sup>\*</sup> as % active chlorine at kappa factor 0.3-0.5

<sup>\*\*</sup> as % H<sub>2</sub>O<sub>2</sub>

#### Chlorine Dioxide Bleaching

The chlorine dioxide stage was carried out in sealed polyethylene bag in a hot water bath. The amount of unbleached pulp used in the initial chlorine dioxide  $(D_0)$  stage was about 400 g oven-dry weight. After  $D_0$ -stage, bleached pulp was divided for the next stage as extraction stage (E). The active chlorine concentration of chlorine dioxide solution can be determined by the procedure as following:

D stage (ClO<sub>2</sub>) bleaching (in terms of active chlorine)

- Add to the erlenmeyer flask 10 ml KI solution (100 g/l) and 20 ml  $H_2SO_4$  (1M or 2N)
- Add 2 ml ClO<sub>2</sub> into the flask. The tip of the pipette must be below the surface of liquor.
- Titrate with 1N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (standardized).
- Add starch indicator when color is straw yellow (add enough starch to get very dark blue color)
- Titrate with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to the inflexion point (when light blue just disappears)

Calculation :  $C = (a \times N \times E)/b$ 

Where,

C - concentration of active chlorine in g/l

a - consumption of standardized thiosulphate in ml

N - normality of standardized thiosulphate solution

E - equivalent weight of chlorine

b - volume of the sample in ml

In all chlorine dioxide stages, the pH was adjusted with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) or sodium hydroxide (NaOH) at the beginning of the reaction so that final pH target was obtained.

#### Alkaline Extraction

The extraction stages were carried out 2 phases, after  $D_0$  with 1% alkaline concentration and after  $D_1$  with 0.5% alkaline concentration. The amounts of bleached pulp from D-stage used in the first and second E-stage were 400 g and 50 g oven-dry weight, respectively. Only after the first E-stage, kappa number and brightness were determined.

### Hydrogen Peroxide Bleaching

Hydrogen peroxide was used in the last stage of bleaching. It was carried out in sealed polyethylene bags in a hot water bath that kept the temperature about 80°C. The amount of bleached pulp was used in final stages about 20 g oven-dry weight. The brightness was determined after last stage. Procedure for determining the hydrogen peroxide concentration was explained following:

## Hydrogen Peroxide Concentration:

- Pipette 2 ml of hydrogen peroxide solution into 100 ml of distilled water
- Add 10-15 ml of 4N H<sub>2</sub>SO<sub>4</sub>, 10 ml KI solution and 3 drops of ammonium molybdate solution
- Titrate with 0.1 N thiosulphate (standardized) to a pale yellow color, add 10 ml of starch solution and continue titration until blue color disappear.

Calculation: Gram per liter = 
$$0.1 \text{ (norm, thio)} \times 17 \text{ (equiv, } H_2O_2) \times \text{ml, thio}$$
  
2 ml (sample size)

## **Testing of Papermaking Properties**

The unbleached and bleached pulps were 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 beated pulps was measured according to TAPPI T227 om-99. The handsheet for testing of papermaking properties was formed according to TAPPI T205 sp-02. The handsheet of each beating condition was measured 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-96), tearing strength (TAPPI T414 om-98), bursting strength (TAPPI T407 om-97) and folding endurance (TAPPI T511 om-02).

#### **RESULTS AND DISCUSSION**

### **Analysis of Sweet Bamboo Properties**

### **Physical Properties**

The principle physical properties as basic density and moisture content were presented in Table 4. Moisture content was influenced road transport cost. For a given position, the moisture contents of nodes were higher than those of internodes. They tended to increase from top to base of sweet bamboo culm, reaching maximum of 65.44 and 69.71% for internode and node respectively. The average moisture content was 60.24%.

Basic density was an important factor in the assessment of pulpwood quality. It affected transport cost, the pulp wood production capacity of the digester, and the relationship between wood volume and pulp production rate. For a given position, the basic densities of nodes were higher than those of internodes and increased from base to top of sweet bamboo culm. They were inversely related to moisture content. The basis density of sweet bamboo was 610–870 kg/m³ and the average was 725 kg/m³. This result was not different from the work of Parkkeeree (1997) who reported that average basic density of sweet bamboo was 730 kg/m³.

Table 4 Moisture content and basic density of sweet bamboo.

Bamboo disk	Basic density (kg/m³)	Moisture content (%)
Node (top)	870	52.70
Internode (top)	830	47.30
Node (middle)	740	64.07
Internode (middle)	660	62.19
Node (base)	640	69.71
Internode (base)	610	65.44
Average	725	60.24

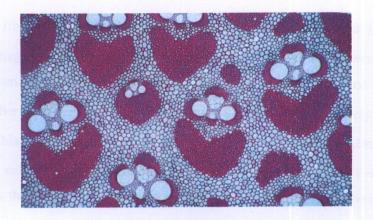
#### Fiber Morphology

The anatomy of sweet bamboo is shown in Figure 5. Liese and Grosser (2000) found that the vascular bundle of sweet bamboo consists generally of the phloem, two metaxylem vessels, and the protoxylem with attached sclerenchyma sheaths (fiber sheaths; fiber cap) and depending on the species, additional fiber strands (Figure 5 A).

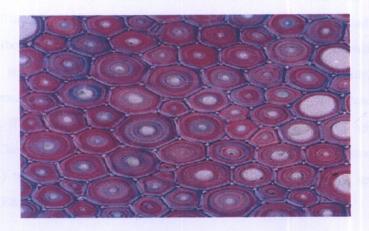
Table 5 summarizes the fiber dimensions of macerated sweet bamboo fibers. The increasing of fiber length was normally being good for strength of paper but also increased the tendency for fiber to flocculate rapidly. It was found from this experiment that the average fiber length of sweet bamboo was 3.11 mm (2.15-3.99 mm), which was comparable with softwood. For comparative purpose, the fiber length of black spruce, *P. radiata*, southern pine and *E. camaldulensis* were 3.5, 3.0, 4.6 and 1.1 mm respectively (Smook, 1997; Patanopast, 1995). For a given position, the fibers in the nodal region were considerably shorter than those in the internode. This result was similar to the study of Yulong and Liese (1997), which the fibers from bamboo (*Phyllostachys edulis*) were measured.

<u>Table 5</u> Fiber dimensions of sweet bamboo fibers.

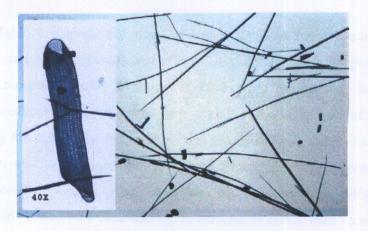
Bamboo disk	Fiber length	Fiber width	Lumen	Cell wall thickness	Runkel ratio
	(mm)	(µm)	$(\mu m)$	(µm)	
Node (top)	2.24	19.43	4.29	7.57	3.53
Internode (top)	3.50	16.37	3.94	6.22	3.15
Node (middle)	2.15	23.52	4.76	9.38	3.94
Internode (middle)	4.54	16.27	4.19	6.04	2.88
Node (base)	2.23	17.39	4.79	6.30	2.63
Internode (base)	3.99	16.87	4.14	6.37	3.07
Average	3.11	18.03	4.35	6.98	3.20



(A) Vascular bundles of sweet bamboo (20X).



(B) Cell walls and cell lumens of sweet bamboo (40X).



(C) Vessel (40X) and fibers (10X) of sweet bamboo.

Figure 5 Anatomy of sweet bamboo.

The fiber width and cell lumen of sweet bamboo was  $16-23~\mu m$  and  $4-5~\mu m$  with the average  $18.03~\mu m$  and  $4.35~\mu m$  respectively. Its fibers were slender and cell lumen were smaller than fiber from other softwood, such as black spruce and southern pine, which the fiber diameter was  $25-30~\mu m$  and  $35-45~\mu m$ , respectively. For the cell wall thickness of black spruce and southern pine were  $3-7~\mu m$  and  $5-11~\mu m$  (Smook, 1997). The average cell wall thickness of sweet bamboo was  $6.98~\mu m$  ( $6.04-9.38~\mu m$ ). It can be seen from the Figure 5 (B) that the cell wall of sweet bamboo was very thick.

The important data, Runkel ratio, was calculated by cell wall thickness and cell lumen. The Runkel ratio was indicated characteristics of fiber cell wall thickness. It was effected to fiber bonding, pulp strength and paper properties. Fiber with thick cell wall, especially if only slightly fibrillated, was resisted and did not contribute to interfiber bonding. It tended to produce an open, absorbent, bulky sheet with low burst and tensile strength, but if it was also long and sufficiently bonded, it had a relative high tearing resistance (Clark, 1978). The average Runkel ratio of sweet bamboo fiber was 3.14 (2.63-3.94) which was higher than those of southern pine and black spruce (0.40-0.96 and 0.31-0.88, respectively) (Smook, 1997).

# **Chemical Properties**

Table 6 presents the chemical compositions of sweet bamboo. The chemical compositions were very important and affected to pulp and paper properties. The average holocellulose content of sweet bamboo was 76.31%. It can be seen from the table that holocellulose contents of the internodes were slightly higher than those of the nodes and not different along the culm. The results show that the average of alpha cellulose content was 68.11% and tended to increase from top to base. The average lignin content was 28.70%, which was closed to wood's lignin. Therefore, bamboo was more difficult to pulp than other non-wood. It was very clear that lignin contents of nodes were about 3% higher than those of internodes. The results were contrast to the work of Liese (1995) who reported that the nodes contained less lignin than the internodes. In this study, the difference of lignin content along the culm was not found. The average of ash content of sweet bamboo

Table 6 Chemical compositions of sweet bamboo.

				Bamboo disks			
Chemical compositions	Node	Internode	Node	Internode	Node	Internode	Average
(%)	(top)	(top)	(middle)	(middle)	(base)	(base)	
Holocellulose	75.65	76.72	76.36	77.36	75.59	76.31	76.31
Alpha-cellulose	67.07	67.33	68.53	67.67	68.39	69.64	68.11
Lignin	30.08	26.47	30.86	27.19	30.41	27.20	28.70
Ash	2.29	1.04	1.95	0.95	1.59	0.92	1.46
Alcohol+Benzene solubility	5.55	7.44	6.67	6.37	3.75	5.85	5.93
Alcohol solubility	5.10	6.91	5.55	5.95	3.83	6.10	5.57
Hot water solubility	7.39	9.63	7.51	8.36	6.47	8.86	8.04
Cold water solubility	5.10	6.87	5.43	14.05	4.23	6.50	7.03
1% NaOH solubility	26.72	25.82	24.38	23.40	24.99	24.07	24.89

was 1.46%. The ash contents of the nodes were higher than those of the internodes and decreased from top to base. Silica was the important part of ash content in bamboo. Liese (1995) found that silica content varied on an average from 0.5-4%, increasing from bottom to top. Satrakhom (1972) reported that the silica content of sweet bamboo was 4.16%. Most silica was deposited in the epidermis, whereas the nodes contained little silica and the tissues of the internodes almost none. Silica content affected the pulping properties of bamboo (Dransfield and Widjaja, 1995).

The solubility in different solvents indicated the extractive contents, which were not the cell wall component. The average of solubility of sweet bamboo were the follows: alcohol+benzene solubility 5.93%, alcohol solubility 5.57%, hot-water solubility 8.04%, cold-water solubility 7.03% and 1% NaOH solubility 24.89%.

### **Pulping**

The effect of chemical charges and pulping processes were investigated in this study. The cooking results and pictures of sweet bamboo unbleached pulps are presented in Table 7 and Figure 6, respectively. Figure 7 shows the relationship between screened yield and kappa number of unbleached pulps. It can be seen that all screened yields of kraft pulping were lower than 50% and decreased from 48.83 to 39.53% when active alkali increased from 14 to 25%, while kappa number decreased from 17.8 to 8.1. The kraft pulping gave a very slightly amount of reject.

In contrast with kraft pulping, the results show that all screened yields of AS and AS-AQ pulping were more than 50%. In AS pulping, no effect of chemical charges on screened yield (55.73 to 56.33%) was found, but kappa number decreased from 34.7 to 23.6 and reject decreased from 2.58 to 0.79% when chemical charges increased from 20 to 35%. The effect of chemical charges on screened yield, reject and kappa number was found in AS-AQ pulping. The AS-AQ screened yields increased slightly from 53.79 to 56.67%, whereas kappa numbers decreased from 13.7 to 9.6 and reject decreased from 1.45 to 0.53 when chemical charges increased.

Table 7 Cooking results of sweet bamboo pulping.

Process	Conditions	Screened yield (%)	Reject	Kappa number
Kraft	K14	48.83	0.20	17.8
	K16	46.32	0.01	12.5
	K18	43.25	0.02	10.6
	K20	42.66	0.01	8.4
	K22	41.10	0.01	8.5
	K25	39.53	0.01	8.1
Alkaline sulfite (AS)	AS20	56.33	2.58	34.7
	AS25	55.93	1.88	32.5
	AS30	55.96	1.54	31.0
	AS35	55.73	0.79	23.6
Alkaline sulfite with AQ	AS-AQ20	53.79	1.45	13.7
(AS-AQ)	AS-AQ25	55.57	1.44	12.5
	AS-AQ30	56.67	1.18	11.4
	AS-AQ35	56.26	0.53	9.6

Compared to kraft pulping, the screened yield and reject of AS and AS-AQ pulping were substantially higher. Kappa numbers of AS pulps were higher than those of kraft and AS-AQ pulps. Both screened yield and reject were slightly different between AS and AS-AQ pulping, but kappa numbers of AS-AQ pulping were much lower than those of AS pulping. Ingruber (1985) and Miller and Gounder (1997) mentioned that the addition of AQ to alkali sulfite cook raised the rate of delignification while protecting cellulose components against degradation. In this study, the effect of AQ on delignification rate was larger than cellulose protection. This result was similar to the study of Blain (1998) who reported that by adjusting pulping conditions after AQ addition, the yield advantage can be traded for greater reduction in kappa number or conversely a smaller kappa number reduction with a grater pulp yield increase.



(A) Alkaline sulfite pulp



(B) Alkaline sulfite with anthraquinone pulp



(C) Kraft pulp
Figure 6 Unbleached pulps of sweet bamboo (A-C).

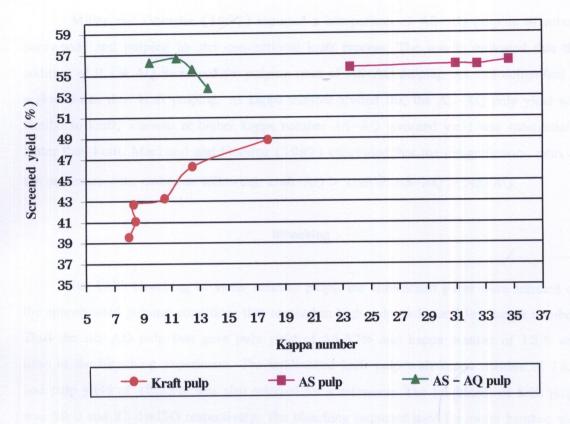


Figure 7 Kappa number and screened yield of sweet bamboo pulps.

Ingruber (1985) reported a comparison of spruce-type pulps at 50% yield prepared with strongly alkaline sulfite liquors without and with AQ, and regular kraft pulping. It was seen that the addition of AQ to the AS cook abruptly increases the delignification rate that was presented by decreasing of kappa number from 72 points in AS pulping to 36 points in AS-AQ pulping. A similar comparison of liner pulp cooks of southern pine at equal time at temperature and similar pulp yield (55%) shows again the great improvement in cooking rate due to adding 0.1% AQ to strongly AS cook.

In contrast with Ingruber (1985), MacLeod (1997) indicated that the delignification of trembling aspen (*Populus tremuloides*) pulped in AS liquor containing AQ was slow but screened yield increased to approximately 65%. This was about 10% above the normal yield in kraft pulping.

Miller and Gounder (1997) reported a comparison of AS-AQ pulping of mixed hardwoods and pulping by the conventional kraft process. The results indicated that the addition of 0.1% AQ increased the pulping rates of AS-AQ pulping but still delignified at a slower rate than kraft pulping. At kappa number around 30, the AS-AQ pulp yield was similar to kraft, whereas at higher kappa number AS-AQ screened yield was substantially better than kraft. MacLeod and Fleming (1997) concluded that the delignification rates of the processes were ranked as following: kraft-AQ > kraft ≥ AS-AQ > NS-AQ.

#### Bleaching

For ECF-bleaching of sweet bamboo pulps, the unbleached pulps were selected on the appropriated pulping conditions that resulted in high pulp yield and low kappa number. Thus the AS-AQ pulp that gave pulp yield of 55.57% and kappa number of 12.5 was used in the bleaching experiment. The unbleached kraft pulp with kappa number of 12.5 and pulp yield of 46.32% was also selected for a reference. The brightness of both pulps was 20.0 and 25.6%ISO respectively. The bleaching sequence used for sweet bamboo was  $D_0ED_1EP$ .

The bleaching results of sweet bamboo AS-AQ and kraft pulps are summarized in Table 8 and 9. Figure 8 and 9 show the effect of kappa factor in the first stage of chlorine dioxide (D<sub>o</sub>) on kappa number and brightness of the pulps. The results show that an increase of kappa factor from 0.3 to 0.4 resulted in decreased kappa number from 12.5 to 2.7 and increased brightness after D<sub>o</sub>E stage. The brightness gain was about 23 to 30%ISO. At the same kappa factor, the kappa number and brightness gains of both pulps were similar. However, the brightness of AS-AQ pulp after D<sub>o</sub>E stage was higher than that of kraft pulp. This resulted from the higher initial brightness around 5%ISO of unbleached AS-AQ pulp over kraft pulp.

Table 8 Bleaching results of unbleached sweet bamboo AS-AQ pulp (brightness 25.6%ISO and kappa number 12.5)

Pulp	Kappa	D <sub>o</sub> Charge	D <sub>1</sub> Charge	P Charge	Total NaOH	D <sub>0</sub> E Kappa	D <sub>0</sub> E Brightness	D <sub>0</sub> ED <sub>1</sub> EP
	factor	% active Cl	% active Cl	% as $H_2O_2$	charge	number	OSI %	Brightness
					% as NaOH			OSI %
			1.00	0.25				83.26
			1.00	0.50				84.94
Bamboo	0.30	3.80	2.00	0.25	1.50	3.1	48.7	87.26
AS - AQ			2.00	0.50			(brightness gain 23.1% ISO)	88.17
			3.00	0.25			ł	88.56
			3.00	0.50				89.00
			1.00	0.25				85.20
		,	1.00	0.50				86.50
Bamboo	0.35	4.40	2.00	0.25	1.50	3.0	50.7	87.49
AS - AQ		•	2.00	0.50			(brightness gain 25.1% ISO)	88.82
			3.00	0.25			I	88.54
			3.00	0.50				89.05
			1.00	0.25				87.42
		•	1.00	0.50				88.14
Bamboo	0.40	5.00	2.00	0.25	1.50	2.7	55.6	89.71
AS - AQ		•	2.00	0.50			(brightness gain 30.0% ISO)	90.63
			3.00	0.25				90.39
			3.00	0.50				91.04

Table 9 Bleaching results of unbleached sweet bamboo kraft pulp (brightness 20.0%ISO and kappa number 12.5)

Pulp	Kappa	D <sub>o</sub> Charge	D <sub>1</sub> Charge	P Charge	Total NaOHc	D <sub>o</sub> E Kappa	D <sub>0</sub> E Brightness	D <sub>0</sub> ED <sub>1</sub> EP
	factor	% active Cl	% active Cl	% as $H_2O_2$	charge	number	OSI %	Brightness
					% as NaOH	:		OSI %
			1.00	0.25				77.26
			1.00	0.50				80.66
Bamboo	0.30	3.80	2.00	0.25	1.50	3.2	43.6	83.62
Kraft		·	2.00	0.50			(brightness gain 23.6% ISO)	84.35
			3.00	0.25			l	84.79
			3.00	0.50				85.62
			1.00	0.25				80.24
		•	1.00	0.50				82.46
Bamboo	0.35	4.40	2.00	0.25	1.50	3.0	45.6	86.19
Kraft			2.00	0.50			(brightness gain 25.6% ISO)	87.28
			3.00	0.25			I	87.44
			3.00	0.50				88.20
			1.00	0.25				84.44
		,	1.00	0.50				86.53
Bamboo	0.40	5.00	2.00	0.25	1.50	2.7	49.8	88.48
Kraft		'	2.00	0.50			(brightness gain 29.8% ISO)	89.10
			3.00	0.25				88.60
			3.00	0.50				89.77

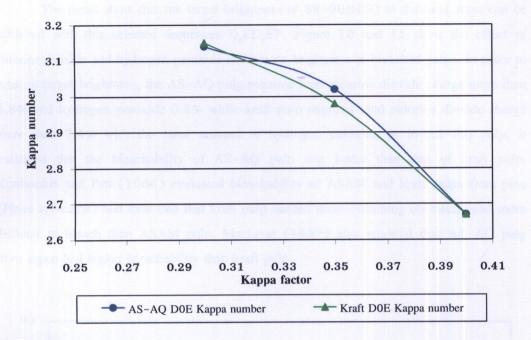


Figure 8 Effect of kappa factor on D<sub>0</sub>E kappa number of sweet bamboo AS-AQ and kraft pulps.

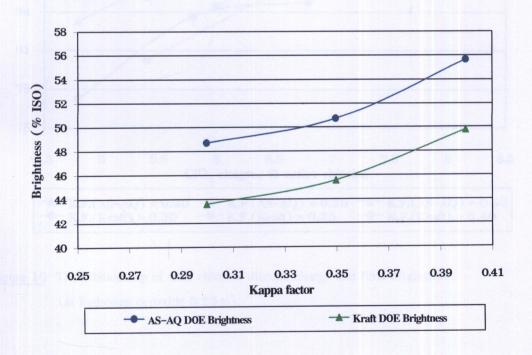


Figure 9 Effect of kappa factor on  $D_0E$  brightness of sweet bamboo AS-AQ and kraft pulps.

The result show that the target brightness of 88-90%ISO in the final stage can be achieved with this selected sequences D<sub>o</sub>ED<sub>1</sub>EP. Figure 10 and 11 show the effect of chlorine dioxide and hydrogen peroxide charges on brightness of bleached pulps. In order to achieve target brightness, the AS-AQ pulp required total chlorine dioxide charge more than 5.8% and hydrogen peroxide 0.5% while kraft pulp required total chlorine dioxide charge more than 7.4% with the same amount of hydrogen peroxide as in AS-AQ pulp. It indicated that the bleachability of AS-AQ pulp was better than that of kraft pulp. Kordsachia and Patt (1988) evaluated bleachability of ASAM and kraft pulps from pine (*Pinus sylvestris*) and indicated that kraft pulp needed more bleaching chemicals and more difficult to bleach than ASAM pulp. MacLeod (1997) also reported that AS-AQ pulp from aspen had higher bleachability than kraft pulp.

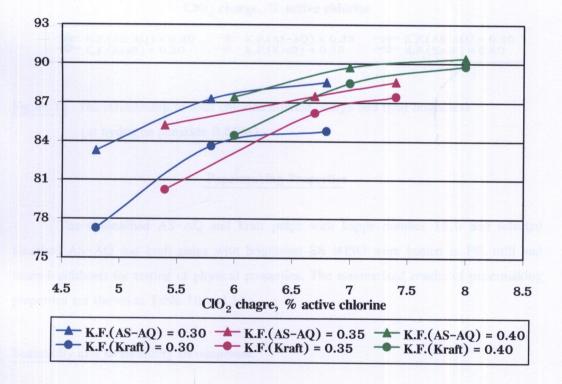


Figure 10 The relationship of total chlorine dioxide charge and final brightness (at hydrogen peroxide 0.25%).

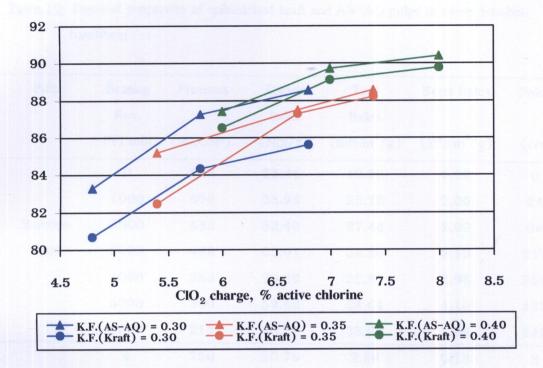


Figure 11 The relationship of total chlorine dioxide charge and final brightness (at hydrogen peroxide 0.50%).

#### **Papermaking Properties**

The unbleached AS-AQ and kraft pulps with kappa number 12.5 and selected bleached AS-AQ and kraft pulps with brightness 88 %ISO were beaten in PFI mill and made handsheets for testing of physical properties. The summarized results of papermaking properties are shown in Table 10 and 11.

#### **Beatability and Drainability Development**

The influence of the beating level on drainability of these pulps is presented in Figure 12. which demonstrates that the response of both AS-AQ and kraft pulps to beating was similar. Freeness of the beaten pulps decreased when the beating revolution increased. The cooking method had a major effect on beatability of pulps. The AS-AQ pulps were slightly harder to beat than kraft pulps. The kraft pulps required beating revolution about

<u>Table 10</u> Physical properties of unbleached kraft and AS-AQ pulps of sweet bamboo handsheet.

Pulp	Beating	Freeness	Tensile	Tear	Burst Index	Folds
	Rev.		Index	Index		
	PFI mill	(ml,CSF)	(Nm/g)	$(mN.m^2/g)$	$(kPa.m^2/g)$	(r/c)
	0	743	22.44	10.29	0.62	0
	1000	670	33.96	25.76	2.05	24
Bamboo	2000	582	52.49	27.44	2.09	66
kraft	3000	488	63.01	34.20	3.19	217
	4000	388	70.20	35.82	3.96	358
	5000	300	59.68	34.64	4.10	492
	6000	212	40.41	33.60	3.98	349
	0	750	20.76	9.36	0.18	3
	1000	700	30.28	25.01	2.18	29
	2000	609	44.66	26.92	2.52	75
Bamboo	3000	573	51.71	27.50	2.80	158
AS - AQ	4000	455	60.10	27.87	3.10	269
	5000	335	54.34	24.52	3.34	371
	6000	273	37.95	22.29	3.25	381
	7000	240	36.12	21.92	3.21	405

<u>Table 11</u> Physical properties of bleached kraft and AS-AQ pulps of sweet bamboo handsheet.

Pulp	Beating	Freeness	Tensile	Tear	Burst Index	Folds
	Rev.		Index	Index		
	PFI mill	(ml,CSF)	(Nm/g)	$(mN.m^2/g)$	$(kPa.m^2/g)$	(r/c)
	0	740	16.43	7.20	0.60	0.00
	1000	685	27.12	20.64	2.18	15
Bamboo	2000	580	40.53	28.20	2.47	36
kraft	3000	492	43.43	29.66	2.69	71
	4000	380	53.98	32.12	3.62	169
	5000	315	60.57	34.29	3.94	520
	6000	210	33.18	27.56	3.26	373
	0	743	11.92	12.57	0.56	0
	1000	677	25.72	28.04	1.97	23
	2000	597	33.30	30.63	2.51	81
	3000	530	36.97	32.69	3.07	147
Bamboo	4000	483	39.67	33.32	3.26	198
AS - AQ	5000	418	41.54	33.12	3.50	257
	6000	370	51.13	32.91	3.87	777
	7000	317	42.05	29.41	4.11	534
	8000	290	38.43	29.02	3.45	471
	9000	252	34.08	26.83	3.30	319

4000 rpm to reach certain freeness 400 ml,CSF while AS-AQ pulps required more beating revolution than kraft pulps. This result was contrast with Smook (1997) who indicated that generally, kraft pulps were more difficult to beat (i.e. require more energy) than sulfite pulps.

The bleaching process had no effect on beatability development of kraft pulps. However, the beatability of unbleached AS-AQ pulp increased faster than that of bleached AS-AQ pulp. This result was contrast to Smook (1997) who reported that unbleached pulps were more difficult to beat than comparable bleached pulps. Pulps with higher lignin content are less responsive to the beating because the lignin does not absorb water, and therefore the fibers do not swell as much. MacLeod (1997) found that aspen AS-AQ pulps with kappa number 25.8 was slightly harder to beat than its kraft counterpart (kappa number 17.7)

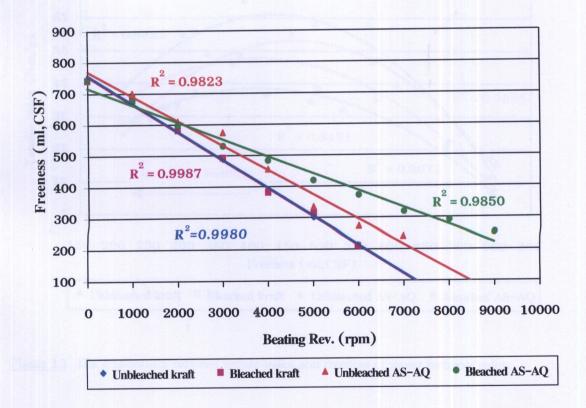


Figure 12 The relationship between freeness and beating levels of sweet bamboo pulps.

### **Tensile Strength**

The tensile index of all sweet bamboo pulps were 11.9 to 70.2 Nm/g (Table 10 and 11). Figure 13 shows the relationship between tensile index and freeness. It can be seen that the trend of tensile strength development after beating of both AS-AQ and kraft pulps was identical. When freeness decreased (resulting from increasing beating revolution), tensile index increased until the maximum tensile index was reached, and then decreased if the pulps were continuously longer beaten. The pulping and bleaching processes had effect on tensile strength of sweet bamboo pulps. Obviously, kraft pulps gave the higher tensile strength than the AS-AQ pulps. A comparison to the unbleached pulps, the tensile strength of both pulps decreased after bleaching.

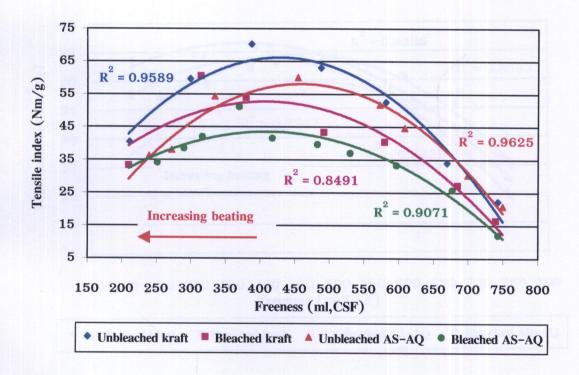


Figure 13 The relationship between tensile index and freeness of sweet bamboo pulps.

## **Tear Strength**

The range of tear index of all sweet bamboo pulps was 7.2 to 35.8 mN.m²/g, as shown in Table 10 and 11. Figure 14 indicates that the trend of tear strength development against freeness of all sweet bamboo pulps was almost similar to tensile strength. The effect of pulping and bleaching processes on tear strength of pulps were obviously. Depending on pulp types bleaching had an effect on tear strength in different ways. For kraft pulps tear index decreased after bleaching. However, bleached AS-AQ pulp gave higher tear index than the unbleached. The increase of tear index after bleached process was occurred in the research of MacLeod (1997) who found that tear index from aspen AS-AQ pulp was raised after CEDED bleaching sequence.

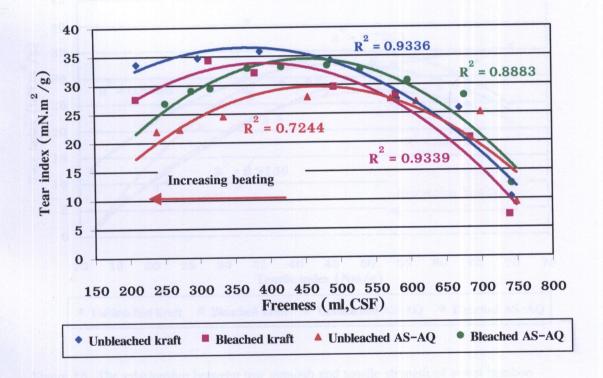


Figure 14 The relationship between tear index and freeness of sweet bamboo pulps.

# Tensile and Tear Strength Relationship

Figure 15 show the relationship between tensile and tear strength of sweet bamboo pulps. Generally, tear-tensile strength was depended on fiber morphology as fiber length, cell wall thickness and fiber strength. It was seen that development of tensile-tear strength curve of the pulps was similar. The pulp types had no distinct effect on these curves but bleaching process had. At a given tensile index both bleached pulps gave higher tear index than the unbleached pulps. McLeod (1997) also investigated tensile-tear strength of aspen AS-AQ and kraft pulps and found that unbleached AS-AQ pulp had less tearing resistance than the kraft pulp, but bleaching eliminated the difference.

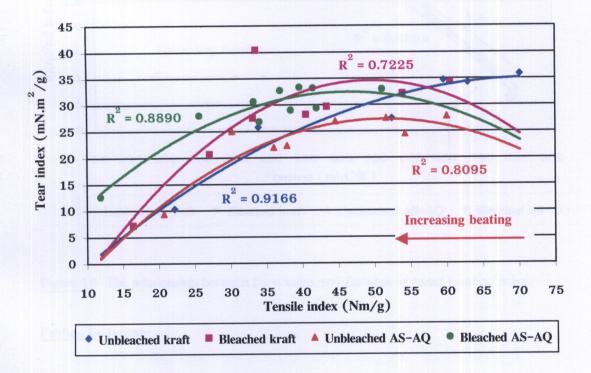


Figure 15 The relationship between tear strength and tensile strength of sweet bamboo pulps.

### **Bursting Strength**

The burst index of sweet bamboo pulps was 0.6 to 4.1 kPa.m<sup>2</sup>/g (Table 10 and 11). The relationship between bursting strength and freeness was shown in Figure 16, which indicates that pulping and bleaching had slightly effect on burst strength of all pulps.

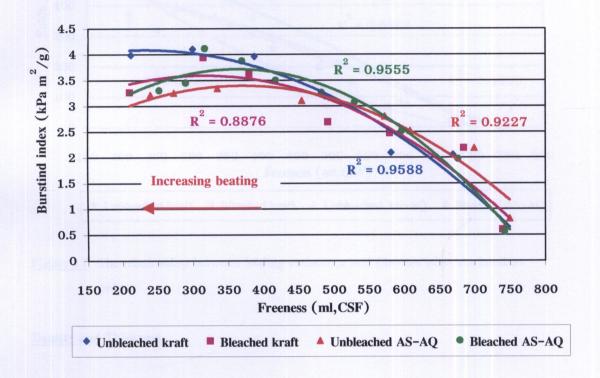


Figure 16 The relationship between burst index and freeness of sweet bamboo pulps.

#### **Folding Endurance**

The fold number of the sweet bamboo pulps was 0 to 777 r/c (Table 10 and 11). Figure 17 indicates the relationship between fold number and freeness. As expected, beating revolution had effect on folding endurance. The fold endurance increased when freeness of the pulp decreased. The pulping process had no effect on fold endurance. The unbleached kraft and AS-AQ pulps were virtually identical in folding endurance. However, the bleached kraft pulps gave less fold number than the unbleached kraft pulps. The bleached AS-AQ pulps responded conversely.

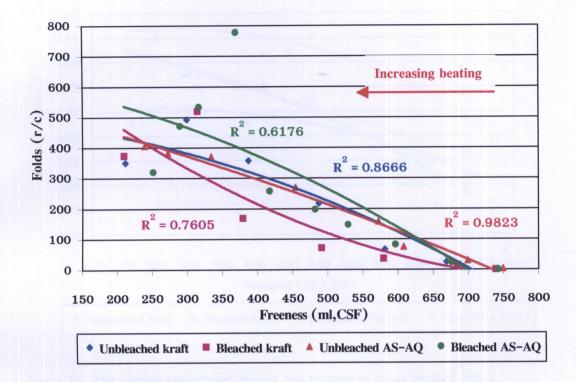


Figure 17 The relationship between folding endurance and freeness of sweet bamboo pulps.

## **Density and Thickness**

Figure 18 and 19 show density and thickness of sweet bamboo pulps. The density of the sweet bamboo handsheet was 0.27 to 0.42 g/m³, while the thickness was 0.13 to 0.22 mm. The results indicate that density of such pulps increased with increasing beating revolution, but thickness performed conversely. The unbleached AS-AQ pulp gave highest density and lowest thickness, while the unbleached kraft pulp gave lowest density and highest thickness. Density and thickness of the both bleached kraft and AS-AQ pulps were slightly

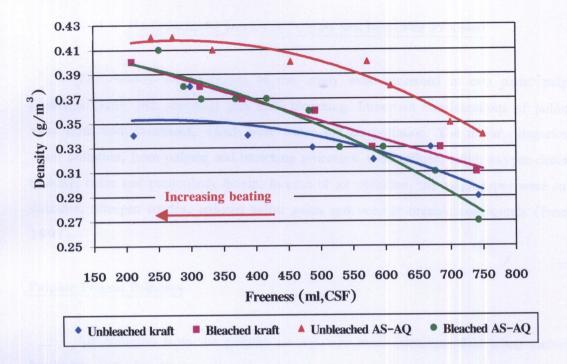


Figure 18 The relationship between density and freeness of sweet bamboo pulps.

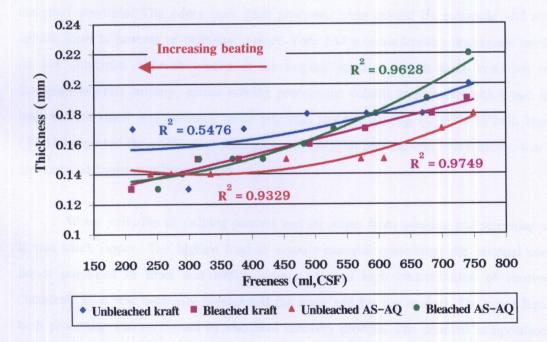


Figure 19 The relationship between thickness and freeness of sweet bamboo pulps.

# **Environmental Impact of Pulping and Bleaching Processes**

The environmental aspects of this study were presented in two parts: pulping processes (kraft and AS-AQ) and ECF bleaching. Important considerations of pollution were from both processes, which were water and air pollution. The major categories of water pollution, from pulping and bleaching processes, were effluent solid, oxygen demand, toxicity, color and particularly dioxin. In case of air pollution, the major types were sulfur dioxides, nitrogen oxides, reduced sulfur gases and volatile organic compounds (Smook, 1997).

### **Pulping Process Pollution**

Air emission from the pulping process was more interested than water emission. Particulate and odorous are pollutants, which had an environmental impact in the vicinity of pulping part. Smook (1997) was concluded that kraft pulping odor was principally due to four reduced sulfur gases such as hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide. The odors from kraft processes were caused by inorganic and organic sulfide form in process or recovery system. They had a characteristic, unpleasant smell but do not constitute a heath hazard at the tropical level at which these emission occur. Compare to kraft pulping, sulfite pulping process the volatile compounds which had strong odor but the smell was normally much less than in kraft pulping (UNEP, 1996). Ingruber (1985) reported the addition of anthraquinone (AQ) in pulping was low toxicity, low odor and reduced kappa number reported

Water pollution of pulping process was an output from washing and screening steps. It was black liquor. The highest load of organic material came from the residual cooking liquor produced in kraft and sulfite pulping. It had high concentration of recoverable chemicals so it was normally regenerated for reuse and for use as fuel. The spent liquor of both processes was recovered by chemical recovery process. The detailed composition and the environmental impact of the liquor depended on fiber raw material, the pulping yield and process condition (UNEP, 1996). Blain (1998) reported that problems were the formation of AQ deposits in evaporation. However, in this study the amount of AQ was 0.1% use it was very less and suitable for pulping conditions.

### **Bleaching Process Pollution**

Emission of water from bleaching process was the first previously aspect. It depended on the bleaching process used such as conventional bleaching, ECF bleaching and TCF bleaching. The effluent from bleaching operation in chemical pulps was much lower in organic content than those from pulping, but bleaching with chlorine compounds, particularly chlorine (Cl<sub>2</sub>) and hypochlorite (HOCl) posed a specific environmental problem. Another bleach effluents also contributed to the COD, BOD, toxicity and color. The conventional bleaching or bleaching with high charges of chlorine caused the formation of toxic polychlorinated compounds such as polychlorinated phenols, dioxin and furan. They could be formed in chlorination stage (Dence and UNEP, 1996).

After the replacement of ECF bleaching by using chlorine dioxide (ClO<sub>2</sub>) in bleaching sequence. Numerous reported indicated that, as ClO<sub>2</sub> was substituted for Cl<sub>2</sub> the amount of chlorinated organic matter in the effluent was decreased. For example the chlorinated compounds were reduced to below approximately 0.15, the formation of 2,3,7,8-tetrachlorodibenzene-p-dioxin (TCDD) and its furan (TCDF) was eliminated. Similar study when only ClO<sub>2</sub> in bleaching, the amount of Absorbable Organic Halides (AOX) form was low (Dence, 1996). UNEP (1996) reported the impact from conventional bleaching contained a complex mixture of chlorinated organic compounds corresponding to 4-10 kg/t AOX. In case of BOD decreased very slightly ClO<sub>2</sub> substitution and effluent COD decreased approximately 10% as ClO<sub>2</sub> substitution increased from 0-100% (Dence, 1996).

The results could be compared with pervious reference. At 88%ISO brightness achievement, it was found that the total ClO<sub>2</sub> consumption of unbleached kraft pulp (7.4%) was higher than unbleached AS-AQ pulp (5.8%) about 1.6% total ClO<sub>2</sub> or 16 kg/t. It could predict the amount of AOX and BOD after kraft bleaching was higher than AS-AQ bleaching. The kraft pulp was more difficult, more bleaching requirement and more AOX loading in water than AS-AQ pulp. It was same effect in case air emission by pulping process.

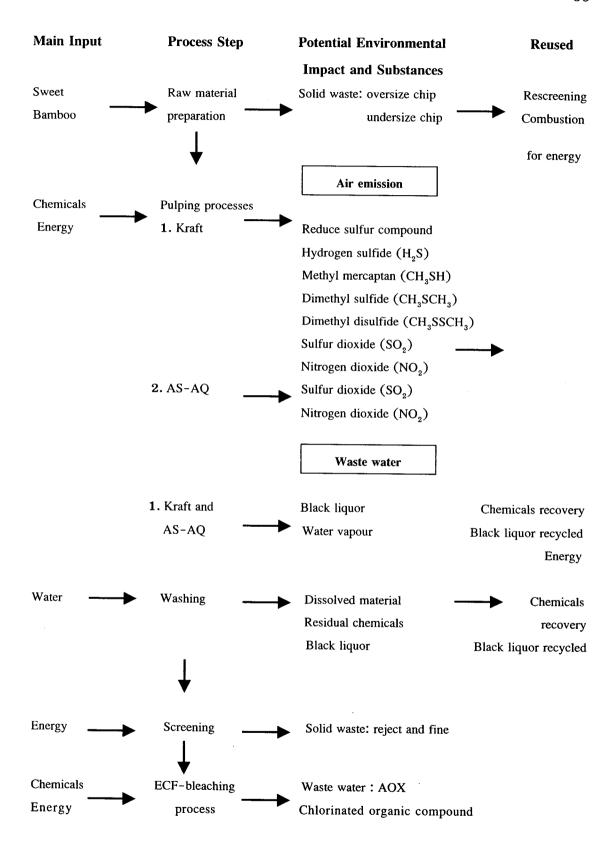


Figure 20 The potential environmental impact and substances in pulping and bleaching processes of sweet bamboo.

#### **CONCLUSION**

The results of this investigation demonstrated that the principle physical properties as basic density and moisture content along the culm were  $725~kg/m^3$  and 60.24% respectively. The important chemical compositions of sweet bamboo were holocellulose 76.31%, lignin 28.70% and ash 1.46%. The dimensions of sweet bamboo fiber were as follows: fiber length 3.11~mm, fiber width  $18.03~\mu m$ , cell lumen  $4.35~\mu m$ , cell wall thickness  $6.98~\mu m$  and Runkel ratio 3.2. The fibers in the internode were much longer than those in the node region. The fiber morphology of sweet bamboo was long, fair narrow, thick wall and had blunt or end point.

The pulping results of alkaline sulfite process and kraft process were different. The alkaline sulfite pulps (AS and AS-AQ) gave higher pulp yield than kraft pulps. The effect of AQ in sulfite cooking was mainly on increasing of delignification rate. Therefore, kappa number of AS-AQ pulp at the same pulp yield was approximately 20 points lower than that of AS pulp. The best cooking result was obtained from AS-AQ process with pulp yield 55.57% and kappa number 12.53, while kraft reference gave pulp yield 46.32% at the same kappa number.

At 88 %ISO of final brightness of ECF bleaching with  $D_0ED_1EP$  sequence was indicated the bleachability of the sweet bamboo pulps. The AS-AQ pulp was easier to bleach. It required less bleaching chemicals than unbleached kraft pulp to reach the target brightness. The AS-AQ pulp required chlorine dioxide 5.8% and hydrogen peroxide 0.5%, while the kraft pulp required 7.4% and 0.5% respectively

The results of papermaking properties indicated that the AS-AQ pulp was slightly harder to beat than the kraft pulp. The kraft pulp gave higher tensile strength than AS-AQ pulp and tensile strength of both unbleached pulps decreased after bleaching. Surprising, tear and burst strength, and folding endurance of AS-AQ pulps increased after bleaching. The unbleached AS-AQ pulp gave highest density and lowest thickness, while the unbleached kraft pulp gave lowest density and highest thickness. Density and thickness of both pulps were slightly different after bleaching.

#### RECOMMENDATION

For the further study of bamboo pulping it should be related this area, some suggestions might be considered as follows:

The optimal pulping process and pulp properties from different bamboo species should be investigated

Comparison of different bamboo species in pulping processes and bleaching processes, as TCF bleaching in order to reduce chlorine compound should be investigated.

Investigation of the possibility to producing fully brightness bamboo pulps with shorter bleaching sequence should be experimented.

Optimization the oxygen delignification stages in order to decreased bleaching chemicals and still maintains bamboo pulp quality should be used.

Evaluation of the viscosity bamboo pulp after pulping and bleaching processes in order to optimize the condition in each process should be tested.

Environmental parameters should be measured and environmental analysis should be done to evaluate the environmental benefit of bleaching process.

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