Effects of Alkaline Sulfite Anthraquinone and Methanol Pulping Conditions on the Mechanical and Optical Paper Properties of Bamboo (Gigantochloa scortechinii)

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The objective of this study was to evaluate the mechanical and optical properties of paper made from alkaline sulfite anthraquinone and methanol (ASAM) unbleached pulp from bamboo (Gigantochloa scortechinii). The bamboo pulps were beaten using a PFI mill at 10,000 revolutions. To determine the properties of unbleached bamboo ASAM paper, handsheets with a density of 60 g/m² were formed with 14 to 18% NaOH, 80/20 Na₂SO₃/NaOH, 0.1% AQ, 0.5% EDTA, and 15% methanol pulping conditions. Pulping at 18% NaOH for 120 min cooking time produced paper with properties of 24.8 Nm/g and 43.02% for the tensile index and ISO brightness, respectively. Cooking at 16% sodium hydroxide for 90 min rendered the best results for mechanical and optical properties, with results of 20.86 Nm/g, 22.64 mN.m²/g, and 39.32% ISO value for the tensile, tear indices, and brightness, respectively. High quality bamboo paper produced by the ASAM pulping process was beneficial for producing highly durable paper and paperboard.

Keywords: ASAM pulp; Bamboo; Brightness; Burst index; Tensile index

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INTRODUCTION

Sodium sulfite and sodium hydroxide are ingredients of the alkaline sulfite process (Casey 1951; Clark 1985; Smook 1992). In this process, kraft and sulfite processes have the finished product specification. For example, the mechanical strength of the paper is similar to the kraft process. On the other hand, this process resembles sulfite in that no significant odor is generated at the digester, and bleached pulp is also made easily (Patt and Kordsachia 1986; Patt et al. 1991; Young and Akhtar 1998).

The process of ASAM, using the ratio of sodium carbonate to sodium peroxide, generates pulp with the strongest tensile index, highest pulp yield, and highest brightness. Also, by increasing the ratio of sodium carbonate to sodium peroxide, pulp de-lignification will increase. Therefore, if the amount of initial high yield pulp with high brightness is considered, the sodium carbonate can be used as a source of alkaline additives (Young and Akhtar 1998; Shukry et al. 1999; Muurine 2000; Sridach 2010).

On the other hand, the use of alkaline sodium sulfite as an additive in the ASAM process, can produce a low kappa number pulp in high yield and high brightness. In addition, low production cost is the most significant benefit of using sodium sulfite as a
source of alkaline additives because by using this add-on, the total alkali consumption becomes less (Young and Akhtar 1998; Shukry et al. 1999; Khristova et al. 2002; Sarwar Jahan et al. 2007; Mertoglu-Elmas et al. 2012).

More lignin is eliminated in the period of bulk de-lignification. This elimination occurs much more quickly from the third stage (residual de-lignification) and carbohydrates removal (Clark 1985; Smook 1992). As a result, the proportion of lignin removal to polysaccharides removal happens slowly. Thus, this is only true when a sufficient amount of alkali charge is available. Thereupon, by adding AQ to the cooking liquid, more alkaliinity can be stored for the bulk de-lignification volume, and more lignin can be removed (Young and Akhtar 1998; Muurine 2000; Fišerová et al. 2006; Hart and Rudie 2014).

The initial piercing will be greater by discharging air from the chips. Tiny air bubbles trapped within the chips prevents the transfer of liquor into the chips. A common method used to remove the air is using pre-steam chips before entering the digester (Young and Akhtar 1998).

Due to the use of methanol in the cooking liquor, more penetration of chemicals into the chips occurs. Raising pressure of the digester and more air removal of chips are the two most important ways of improving the penetration of chemical materials into wood or non-wood chips. Therefore, adding methanol while an ASAM cooking liquor is in the process of penetrating the leads to a higher pressure of the digester. As a result, the entrapped air of the chips is displaced, and chemical materials can penetrate both wood and non-wood chips. Consequently, more de-lignification occurs and fibers can be easily separated (Patt and Kordsachia 1988; Paik et al. 1988; Young and Akhtar 1998).

In the ASAM process, the use of methanol is preferred over ethanol because of the lower boiling point that results in lower energy consumption for recovery. Methanol has less viscosity, polarity, and surface tension but the partial pressure is greater than water. The low surface tension and increased pressure, together with the ability of methanol to dissolve resins have a positive impact on the penetration of chemicals into the chips (Enqvist 2006; Sridach 2010).

At the time of de-lignification, methanol increases the solubility of lignin, produces a uniform (homogeneous) chemical performance in the cooking time, and also suppresses the dissociation of the inorganic pulping chemicals. Nakano et al. (1981) found that cellulose stability was improved in alkaline systems in the presence of methanol. They concluded that the peeling reaction is suppressed by the acceleration of stopping the reaction and/or a slower transformation of the cellulose aldehydic end groups into keto groups that initiate the peeling reaction.

Few studies have considered the application of alkaline sulfite anthraquinone and methanol (ASAM) in the pulping process of wood and non-wood materials. Khider et al. (2012b) studied Acacia mellifera from Sudan that had been pulped by three alkaline pulping conditions, namely, soda-AQ, AS-AQ, and ASAM. ASAM pulping produced a higher pulp yield, better mechanical properties, and a low kappa number. The mechanical properties, such as burst and tensile indices, were related to fiber-to-fiber bonding. The structure of Acacia mellifera fiber after ASAM pulping is more flexible than after soda-AQ and AS-AQ pulping. In addition, the brightness of unbleached Acacia mellifera ASAM pulp was 37.6% ISO, which is an outstanding brightness value for unbleached pulp.

In another study, Khristova et al. (2002, 2004) investigated the optical and mechanical properties of whole kenaf stalks by using four different alkaline cooking methods-soda, soda-AQ, AS-AQ, and ASAM. At 17% active alkali and a pulping
temperature of 175 °C, ASAM pulping resulted in the highest tensile and burst indices of 101.9 Nm/g and 10.1 kPa.m²/g, respectively. This result may be due to more delignification, which releases more cellulose and hemicelluloses. The cited authors also studied Acacia seyal from Sudan using five types of chemical pulping, including kraft, kraft-AQ, soda-AQ, alkaline sulphite anthraquinone (ASA), and ASAM processes. They found that under conditions of 18.5% active alkali and 175 °C, ASAM pulping produced higher burst and tensile indices (4.9 kPa.m²/g and 72 Nm/g, respectively) than other pulping methods. This result was attributed to the methanol and AQ in the pulping system. The addition of methanol and AQ in the white ASAM pulping liquor increased the delignification rate. Incremental delignification may cause more carbohydrates to be released on the fiber surface. As a result, the fiber bonding was improved, enhancing the mechanical properties of paper made from ASAM pulp.

Hassan et al. (2013) studied the effect of soda-AQ pulping and beating revolutions on the paper properties of Gigantochloa scortechinii. In this study, handsheets from bamboo pulp produced higher paper properties, with tensile and burst indices of 42.04 Nm/g and 7.1 kPa.m²/g, respectively. Bamboo pulp can be used to produce high durability properties using more ecofriendly pulping processes, similar to the kraft process.

Compared with kraft pulp, poplar ASAM pulp results in better properties, with up to 10% enhancements. In addition, ASAM pulping rendered a higher poplar pulp yield and was easily bleached, unlike kraft pulping (Patt et al. 1989). Patt et al. (1991) studied ASAM pulps and methanol sulfite (MS) pulps from pine. Hydrogen peroxide, alkali/oxygen, and ozone were used as chemical materials for bleaching both pulps. The results showed that ASAM pulp contributes to higher paper properties and is easily bleached.

Hassan et al. (2014) studied the effect of different portions and beating revolutions on the paper properties of Gigantochloa scortechinii soda-AQ. The results showed that handsheets of beaten pulp can have higher strength compared with unbeaten pulp. The tensile and tear indices of beaten pulp were 41.23 Nm/g and 16.64 mN.m²/g, respectively. It seems that bamboo culms can be applied to produce paper with suitable properties without adding any additives, which may reduce the manufacturing cost. The alkaline sulfite anthraquinone with methanol (ASAM) pulping process is an alternative to the kraft and soda pulping processes. The biometrics characteristics, chemical compassion, pulp yield, and kappa number of the unbleached bamboo ASAM pulp have been presented in a previous study (Moradbak et al. 2016). This work offers a brief outline of the papermaking process and describes the mechanical and optical paper properties associated with the tested processes. In addition, there is little or no information available about producing paper using the ASAM pulping in bamboo. Therefore, the objective of this study was to evaluate the effects of ASAM pulping in manufacturing unbleached paper from bamboo.

**EXPERIMENTAL**

**Material**

Bamboo culms (Gigantochloa scortechinii) aged 3 to 4 years old were harvested from Pahang, Malaysia, and transported to the Institute of Tropical Forestry and Forest Products (INTROP), Selangor, Malaysia. The culms were converted to chips (with sizes ranging from 2 to 2.5 cm) by a mini-chipper. The chip moisture content was determined after air-drying the chips. The pulping conditions of unbleached bamboo ASAM pulp are shown in Table 1 (Moradbak et al. 2016).
Table 1. Conditions for Producing Unbleached Bamboo ASAM Pulp

<table>
<thead>
<tr>
<th>Cooking Code</th>
<th>Chemical Materials (%)</th>
<th>L/W</th>
<th>Temp (°C)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>NaOH</td>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>A2</td>
<td>14</td>
<td></td>
<td></td>
<td>90</td>
</tr>
<tr>
<td>A3</td>
<td></td>
<td></td>
<td></td>
<td>120</td>
</tr>
<tr>
<td>A4</td>
<td></td>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>A5</td>
<td>16</td>
<td>80/20</td>
<td>0.1</td>
<td>15</td>
</tr>
<tr>
<td>A6</td>
<td></td>
<td></td>
<td></td>
<td>120</td>
</tr>
<tr>
<td>A7</td>
<td></td>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>A8</td>
<td>18</td>
<td></td>
<td></td>
<td>90</td>
</tr>
<tr>
<td>A9</td>
<td></td>
<td></td>
<td></td>
<td>120</td>
</tr>
</tbody>
</table>

NaOH, sodium hydroxide; Na$_2$SO$_3$, sodium sulfite; AQ, anthraquinone; EDTA, ethylene diamine tetraacetic acid; L/W, liquor to wood ratio; Temp, temperature

Method

Disintegrating and beating

The unbleached bamboo ASAM pulp was beaten according to TAPPI T 200 sp-96 (1997). Briefly, 24 g of oven-dried (o.d.) unbleached bamboo ASAM pulp was weighed and soaked in 2 L of distilled water for 4 h. The pulp was then disintegrated with a British disintegrator (DSG-2000, Regmed, Brazil) for 75,000 revolutions. The pulp was then beaten for 10,000 revolutions. The freeness of unbleached bamboo ASAM pulp was determined in accordance with TAPPI T 227 om-99 (1999).

Handsheet formation

Prior to handsheet formation, the unbleached pulps were disintegrated in a British disintegrator for 3,000 revolutions. Handsheets were formed in a sheet machine in accordance with the TAPPI T 205-sp-95 (1995) to make sheets with a basis weight of 60 g/m². These handsheets were conditioned at 23 ± 1 °C and 50% relative humidity.

Mechanical and optical tests

Unbleached bamboo ASAM paper was tested according to TAPPI standard methods. Five replications were tested for each test. The tensile index, burst index, tear index, folding endurance, brightness, and opacity were determined according to TAPPI T 494 om-96 (1996), TAPPI T 403 om-97 (1997), TAPPI T 414 om-98 (1998), TAPPI T 423 cm-98 (1998), TAPPI T 452 om-98 (1998), and TAPPI T 425 om-96 (1996), respectively.

RESULTS AND DISCUSSION

Three types of testing were conducted: pulp freeness, paper mechanical, and optical properties. The tensile, burst, tear indices, and folding endurance for mechanical part and brightness and opacity for optical part were determined.

Effect of Pulping Conditions on Pulp Freeness and Energy Consumption
Table 2 shows the initial and final pulp freeness as well as the energy consumed during beating for all samples. The initial pulp freeness decreased after enhancing the pulping conditions, namely, the alkali charge and pulping time.

This result is supported by Rosli et al. (2009), who found that pulping conditions affect the chemical and physical properties of pulp fibers. The incremental enhancement of pulping conditions provides greater delignification, and more polysaccharides, such as cellulose and hemicellulose, are released.

An important factor affecting fibrillation, both external and internal, is the presence of lignin and hemicellulose between the cellulose crystallites and the various lamina of the fiber. In general, if the yield of pulp is greater than about 75%, then the various cellulose elements are still intact and closely bound together with lignin as well as hemicellulose. Accordingly, the body of the fiber is inflexible so that it cannot produce fine fibrils (Smook 1992). Thus, with an increasing cooking parameter at severe pulping conditions, more delignification happens and more polysaccharides such as cellulose and hemicellulose are released. Therefore, the energy needed to beat and fibrillate these fibers is reduced, as shown in Table 2. The difference in energy consumption of A1 and A9 is 33.33%. This result showed that pulping conditions are crucial in producing pulp. The data in Table 2 also demonstrated that the high pulping condition had the least pulp freeness. For example, sample A9 exhibited a 45.83% decrease in pulp freeness from initial to final freeness values.

### Table 2. Initial and Final Freeness of Unbleached Bamboo ASAM Pulp

<table>
<thead>
<tr>
<th>Cooking Code</th>
<th>Initial CSF (mL)</th>
<th>Revolutions</th>
<th>Final CSF (mL)</th>
<th>Energy Consumption (kWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>749.33</td>
<td></td>
<td>455</td>
<td>0.087</td>
</tr>
<tr>
<td>A2</td>
<td>745.67</td>
<td></td>
<td>452</td>
<td>0.081</td>
</tr>
<tr>
<td>A3</td>
<td>741.67</td>
<td></td>
<td>442</td>
<td>0.076</td>
</tr>
<tr>
<td>A4</td>
<td>740.33</td>
<td></td>
<td>435</td>
<td>0.074</td>
</tr>
<tr>
<td>A5</td>
<td>737.67</td>
<td></td>
<td>427</td>
<td>0.072</td>
</tr>
<tr>
<td>A6</td>
<td>735.00</td>
<td>10,000</td>
<td>419</td>
<td>0.069</td>
</tr>
<tr>
<td>A7</td>
<td>732.67</td>
<td></td>
<td>405</td>
<td>0.068</td>
</tr>
<tr>
<td>A8</td>
<td>730.33</td>
<td></td>
<td>400</td>
<td>0.065</td>
</tr>
<tr>
<td>A9</td>
<td>727.33</td>
<td></td>
<td>391</td>
<td>0.058</td>
</tr>
</tbody>
</table>

*Energy is a measure of how much fuel is used over a specific period of time, as measured in kWh; CSF, Canadian Standard Freeness.

### Effect of Pulping Conditions on Tensile Indices

According to Fig. 1, at more severe pulping conditions the tensile indices increased quite distinctly. During pulping, the fiber cell wall became swollen greatly due to the high charge of alkaline pulping liquors. Most of the lignin is removed from the fibers; as a result, internal splitting and fiber interior swelling proceed easily (Vainio and Paulapuro 2007). The reduction of lignin was evident by the low kappa number recorded for pulps that were subjected to much more severe conditions (Mordabak et al. 2016).

Consequently, increasing both the alkali charge and pulping time can enhance the amount of fibrils, cellulose, and hemicellulose present in the fibers. The physical properties of the fibers changed, while the mechanical properties simultaneously improved (Vainio and Paulapuro 2007; Koubaa and Koran 2008). The fiber-to-fiber bonds were greater, which led to better strength in terms of the tensile index.
Fig. 1. The effect of condition and duration of cooking on paper tensile indices

Fig. 2. The effect of condition and duration of cooking on paper tear indices

**Effect of Pulping Condition on Tear Indices**

Incremental increases in the duration of pulping increased the value of the tear indices (Fig. 2). This result may reflect the higher ability of alkaline charges, which attacked the lignin and carbohydrate molecules. The main reaction of alkaline charges with polysaccharides, such as carbohydrates, that occurred during the pulping process reduced the chain’s end group. This effect is referred to as a peeling reaction due to its removal of the terminal end group (Smook 1992). Thus, the fiber length decreased, and the tear index also decreased.

**Effect of Pulping Condition on Burst Indices**

According to Fig. 3, increasing the duration of pulp conditioning increased the burst indices value at 10,000 beating revolutions. In this study, the addition of AQ and methanol in the white pulping liquor exacerbated the loss of carbohydrates, hemicelluloses, and
celluloses from the pulp fibers (Khider et al. 2012a; Moradbak et al. 2016). Therefore, more fiber-to-fiber bonding was developed during papermaking. Fibers with high hemicellulose content possessed good cohesiveness because the beating allowed for the formation of more fibrillations. As stated by Sixta (2006), hemicellulose within the fibers constitutes weak zones that encourage internal fibrillation via the beating process.

![Graph showing the effect of condition and duration of cooking on paper burst indices.](image)

**Fig. 3.** The effect of condition and duration of cooking on paper burst indices

**Effect of Pulping Condition on Folding Endurance**

Folding endurance testing determines the resistance of paper towards folding action. High pulping conditions (A9) produced better folding endurance (Fig. 4). During the alkaline pulping process, cell walls are swollen, and the middle lamella of the cell walls is removed. Hence, these fibers are easily separated. By increasing the pulping conditions in terms of alkaline white liquor charges, the fibers are easily collapsed, and more fiber-to-fiber bonding can be produced during papermaking (Wai et al. 1985; Feria et al. 2012).

![Graph showing the effect of condition and duration of cooking on paper folding endurance.](image)

**Fig. 4.** The effect of condition and duration of cooking on paper folding endurance
The folding endurance improved because the folding property was influenced by fiber-to-fiber bonding. In addition, by beating these pulp fibers, the pulp flexibility was improved. The swelling of the cell walls becomes greater after beating, which results in increased pulp cohesiveness (Kamthai and Puthson 2005; Hassan et al. 2014). The increased alkaline charge also allows for easier beating, and it softens the pulp by forming splits in the fibrous structure (Maddern and French 1989; Seth 2001).

**Effect of Pulping Condition on Paper Brightness**

As shown in previous results, the paper brightness also increased in proportion to the pulping conditions. This result may reflect the use of sodium hydroxide, methanol, and AQ. Sodium hydroxide influences the pH of the alkaline charges white liquor. Methanol causes higher pressure in the pulp digester, which releases air trapped in the bamboo chips and permits the penetration of chemicals, while AQ accelerates lignin dissolution (Shukry et al. 1999; Khristova et al. 2004; Sixta 2006; Sridach 2010; Moradbak et al. 2016). As a result, the kappa number of unbleached bamboo ASAM pulp was relatively low, 19.18 to 10.38 (Moradbak et al. 2016).

![Brightness vs Time Graph](image)

**Fig. 5.** The effect of condition and duration of cooking on paper brightness

These combinations of chemicals and release of the lignin in the unbleached bamboo pulp may have reduced the chromophore content of the produced pulp. Such reduction is instrumental for the low kappa number as chromophores add color to the fibers.

**Effect of Pulping Condition on Paper Opacity**

Opacity is an important aspect of paper appearance. The opacity properties of ASAM papers showed the same trend as paper brightness (Fig. 6). The removal of lignin during pulping is crucial to release hemicellulose on the fiber surfaces. The influence of hemicellulose is significant due to its effect on fiber-to-fiber bonding. Moreover, less voids would becoming better which light scattering occur at fiber-air and pigment-air interfaces (Rance 1982; Schild et al. 2010).
Increases in refining, wet pressing, and calendaring at high moisture content are the main factors that affect opacity property. These factors have one effect: all enhanced fiber-to-fiber bonding decreased the free fiber surface that is available for light scattering (Rance 1982).

The scattering of light in essentially all opaque grades of paper occurs at fiber-air and pigment-air interface. Normally, when particle sizes are made smaller, less light is absorbed during passage through each particle and, at same time, total particle surface becomes greater. Therefore, the increase of particle surface leads to increased light scattering or diffusion (Harold 1987).

CONCLUSIONS

1. Both pulping conditions (alkali charge and cooking time) had significant effects on the paper strength. High tensile and burst indices of 24.80 Nm/g and 10.83 kPa.m²/g, respectively, were produced by the high NaOH 18% and high cooking time 120 min; the pulping conditions, such as alkaline chemicals, had great effects on loosening and swelling the cell walls. The swelling created more fibrils, microfibrils, nanofibrils, cellulose, and hemicellulose molecules on the fiber surface, which enhanced fiber-to-fiber bonding.

2. The highest tear index was 26.33 mN.m²/g, which occurred during the low cooking condition (14% NaOH and 60 min cooking time) of ASAM pulping. A high tear index is usually attributed to the peeling reaction. The prime reaction of polysaccharides is highlighted because it erases and eliminates these terminal end groups one at a time. Consequently, the fiber length, which is the most important factor of pulp, is decreased in the final product.
3. ASAM pulp with 16% NaOH and 90 min cooking time produced paper with the acceptable values of 20.86 Nm/g, 22.64 mN.m²/g, 10.05 kPa.m²/g, 39.32%, and 97.1% for the tensile, tear, and burst indices, brightness, and opacity, respectively.

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