Atmospheric Soda Pulping of Banana Stem

Nurul Amal Nadhirah Mohamad, Junaidah Jai

Abstract*: Banana stem is one of the most explored non-wood lignocellulose due to its high cellulose content with small amount of lignin. The conventional pulping processes efficiently remove the lignin, but there is potential to reduce the energy and chemical consumptions due to the low lignin content of banana stem. In this work, soda pulping was carried out for 60-120 minutes using 16-20% w/v alkali charge at boiling temperature of 105°C. The efficiency of lignin removal at low temperature was evaluated using kappa number analysis. The effects of pulping time and alkali charge on pulp properties were investigated using fourier transform infrared spectrometry (FTIR), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). Soda pulping using 18% w/v alkali charge at 10 liquid-to-solid ratio for 90 minutes under atmospheric pressure efficiently removed lignin with minimal cellulose degradation. Extended pulping time and concentrated alkali charge would induce cellulose degradation. FTIR analysis verified that alkaline pulping caused depolymerization on both lignin and cellulose. SEM images of banana stem showed ordered structure cellulose fibrils arrangement. Removal of lignin and hemicellulose was observed through smoother surface of the banana pulp. However, TGA analysis suggested that a better thermal stability could be achieved through pulping using 16% w/v alkali charge.

***Keywords* : Banana stem, cellulose degradation, soda pulping, thermal stability.**

I. INTRODUCTION

Agricultural residues from banana plantation have created a waste disposal problem to the local farmers. The annual production of banana fruits in Malaysia was more than 500,000 tons with four times of waste was generated after the harvesting process [1]. In recent years, there has been initiative towards efficient utilization of agricultural residues including the banana stem. Few approaches were considered to convert the residues into valuable products such as biogas [2]-[4], nanofiber composite [5]-[7] as well as pulp and papermaking [8]-[10].

In pulp and papermaking, cellulose was separated from lignin and other lignocellulosic components through acidic or alkaline pulping. Sulfite pulping using sulfurous acid was normally used during acidic pulping, but the process released sulfur dioxide as the major pollutant. Kraft pulping was the most utilized method in the pulp and paper industry. The process used mixture of sodium hydroxide and sodium sulfide which contributed to the release of hydrogen sulfide and other odorous compounds. Soda pulping using high temperature sodium hydroxide was preferable for non-wood lignocellulose due to lower lignin content as compared to wood.

The high temperature was important for efficient lignin removal due to the high thermal stability of lignin [11]. Pulping process was normally performed at temperature range of 170-180°C and pressure range of 660-925 kPa. In order to achieve the high temperature, the process was carried out in pressurized vessel to withstand the high pressure and temperature. Atmospheric pulping was explored to reduce the pulping temperature as well as the energy consumption. However, pulping at lower temperature required concentrated alkali solution to achieve high delignification rate, but excess alkali can cause cellulose degradation [12]. Therefore, modification of each operating parameter should be considered for atmospheric pulping to obtain pulp with comparable properties to conventional pulp.

In this study, soda pulping of banana stem was carried out at atmospheric pressure with varied pulping time and alkali charge to evaluate the process efficiency and the effect of the pulping conditions toward pulp properties.

II. MATERIALS AND METHODS

A. Raw Material Preparation

Banana stem from *Musa paradisiaca* species was collected from cultivation area located at Sungai Buloh, Selangor, Malaysia, after fruit harvesting process. The banana stem was separated from its foliage, cleaned with tap water to remove all contaminants and further cut into approximately 3 cm x 3 cm dimensions. By following standard TAPPI methods T257 cm-02 [13] and T264 cm-97 [14], the banana stem was dried at 105°C until all of its moisture content was removed before ground to pass a 0.4 mm screen. This sample was then used in the pulping process.

B. Atmospheric Soda Pulping

The pulping process was carried out in a beaker under constant stirring and heating using laboratory hot plate. Banana stem was added to sodium hydroxide solution at liquid-to-solid ratio of 10 after the solution reached its boiling point (~105°C) and the level was marked. Continuous heating would evaporate some water from the solution and therefore distilled water was added in a small volume up to the marked level throughout the process in order to maintain the concentration with minimal temperature changes [15]. Alkali charge and pulping time were the pulping parameters studied, with their ranges between 16-20% w/v and 60-120 minutes, respectively. The resulting banana pulp was then rinsed under running tap water until all residual chemicals was removed and oven dried at fixed temperature of 105°C to remove its moisture content for

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further analyses.

C. Pulp Characterization

Pulp yield was determined by measuring the weight difference between the initial sample weight, m_i, and the obtained moisture-free pulp, m_f, as in (1). Lignin removal was evaluated using kappa number analysis following TAPPI method T236 om-99 [16]. FTIR spectra were recorded in the range of 4000-500 cm^{-1} to support the analysis on lignin removal. Thermal stability was determined using TGA from 25-550°C at heating rate of 10°C/min under a nitrogen atmosphere. Finally, surface morphology of untreated banana stem and banana pulp produced at the best pulping conditions were captured using SEM at 800x magnification and compared.

$$\text{Pulp yield (\% w/w)} = (m_i - m_f)/m_i \times 100 \qquad (1)$$

III. RESULTS AND DISCUSSIONS

A. Pulping Efficiency

Efficiency of the atmospheric soda pulping was evaluated based on the pulp yield and kappa number. The amount of residual lignin was then estimated from the kappa number. Properties of each pulp produced at their respective conditions are shown in Table I.

Fig. 1 shows the effect of pulping variables on atmospheric soda pulping of banana stem. The changes in pulping time only caused significant effect on the pulp yield. Based on Fig. 1(a), the pulp yield has increased from 36.1 to 46.1% w/w as the pulping time was extended from 60 to 90 minutes, suggesting a better separation of cellulose from lignin. This might be related to the slow degradation rate of lignin [17]. More lignin was able to be dissolved at longer pulping time as can be observed through the reduction in kappa number. Although the difference in kappa number for pulping at 60 and 90 minutes was small, but the separation of cellulose from lignin has significantly improved the pulp yield. However, relatively low pulp yield was observed after pulping for 120 minutes which associated with depolymerization occurred on both lignin and cellulose chains. This finding has been supported by Wan Rosli *et al.* [18] who previously reported that depolymerization of lignin occurred before cellulose degradation. Another previous work by Cordeiro *et al.* [8] also found that longer pulping time would lead to cellulose degradation. Therefore, pulping at the conditions used in this study should not be performed for more than 90 minutes in order to minimize cellulose degradation.

Further study was carried out to evaluate the effect of alkali charge on lignin removal and cellulose degradation by increasing the concentration of sodium hydroxide from 16 to 20% w/v at constant pulping time of 90 minutes. Based on Fig. 1(b), the kappa number has decreased from 33.5 to 29.7 with proportional increase in alkali charge, suggesting a better removal of lignin at higher concentration of sodium hydroxide. Paananen and Sixta [12] also agreed that high alkali charge was important for effective delignification during low temperature pulping. On the other hand, the pulp yield has slightly reduced from 46.1 to 45.2% w/w when the alkali charge was increased from 16 to 18% w/v. Further increased to 20% w/v alkali charge has resulted in great loss of pulp yield, probably due to the simultaneous degradation of cellulose. Previously, the cellulosic degradation was also observed by Cordeiro *et al.* [8] for pulping above 18% w/v alkali charge. Banana pulp produced by Arafat *et al.* [19] has resulted in banana pulp with kappa number of 28. Therefore, the kappa number achieved from this study was considered as satisfactory. The best condition for maximum lignin removal without inducing the cellulose degradation was using 18% w/v alkali charge for 90 minutes pulping at atmospheric boiling temperature.

Table- I: Pulp Properties

Alkali Charge (% w/v)	Pulping Time (minutes)	Pulp Yield (% w/w)	Kappa Number
16	60	36.1	35.3
16	90	46.1	33.5
16	120	34.4	33.3
18	90	45.2	31.4
20	90	36.7	29.7

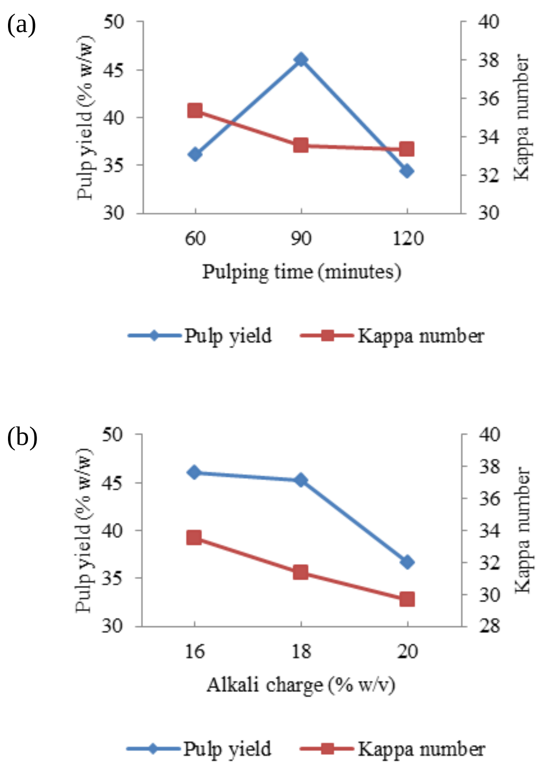

Fig. 1. Effects of (a) pulping time at constant 16% w/v alkali charge and (b) alkali charge at constant 90 minutes pulping time on pulp yield and lignin removal.

B. FTIR Analysis

The removal of lignin can also be observed from FTIR spectrum as illustrated in Fig. 2. The bands around 3300 cm^{-1} were assigned to O–H stretch in cellulose, hemicellulose and lignin. The bands around 2900 cm^{-1} and 1600 cm^{-1} were assigned to C–H and C=O stretch in lignin, respectively. The bands around 1300 cm^{-1} were assigned to aromatic skeletal vibrations combined with $-OCH_3$ in hemicellulose. The bands around 1000 cm^{-1} and 800 cm^{-1} were assigned to C–O stretch and glycosidic bonds in both cellulose and hemicellulose [11]. This analysis further confirmed the finding from kappa number analysis where the lowest absorption bands of lignin was recorded from sample after 90 minutes of pulping. The almost overlapping bands for pulp produced at 60 and 120 minutes indicated that extended pulping time was insignificant. The spectra also verified that alkaline pulping caused depolymerization of both lignin and cellulose.

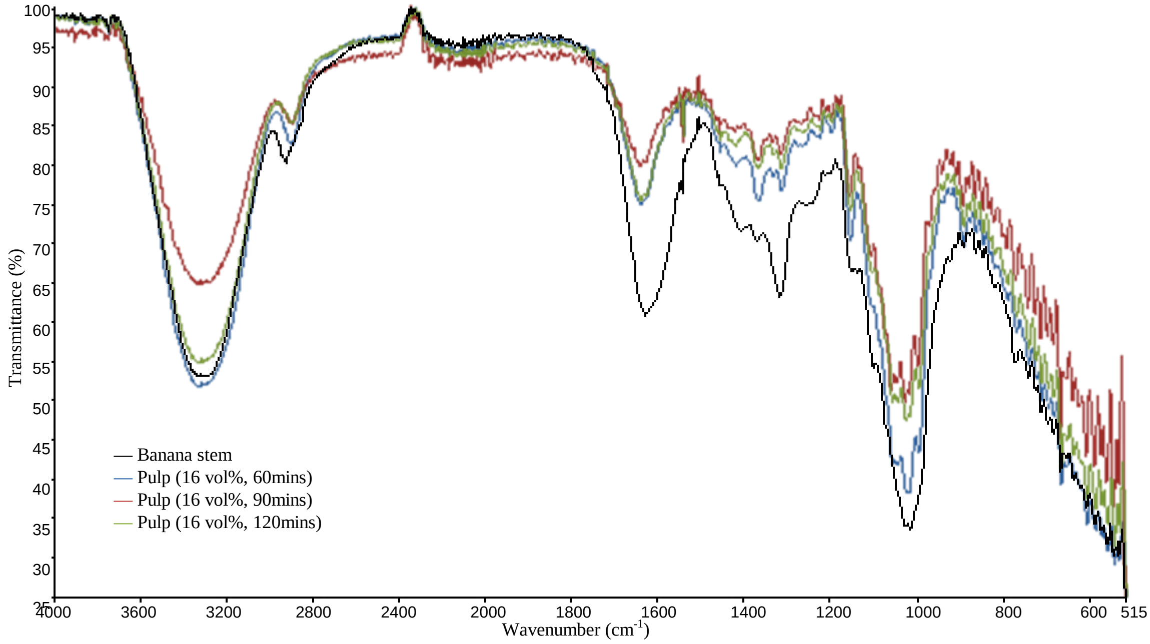

Fig. 2. FTIR spectra of banana stem and the produced pulps.

C. Thermal Stability

Fig. 3 shows the effect of pulping variables on thermal decomposition of banana pulp. Analysis on the mass loss was carried out between 25-550°C and two decomposition steps were observed for each sample. Initial mass loss that occurred at temperature less than 200°C was attributed to evaporation of adsorbed moisture [20]-[22]. Based on Fig. 3(a), the initial mass loss of pulp samples produced using 16% w/v alkali charge at all three different pulping times begin at lower temperature compared to the banana stem. This was probably due to the exposed fiber surface which allowed for evaporation at lower temperature. Thermal stability was justified based on the temperature for maximum mass loss during the second decomposition step. Mass loss during this step was mainly due to cellulose decomposition. Hemicellulose decomposition started at lower temperature around 200°C, while lignin has wide decomposition range between 200-600°C and therefore its contribution to the mass loss was difficult to distinguish [23], [24]. The maximum mass loss for banana stem and pulps produced at 60, 90 and 120 minutes was 355, 356, 356, and 334°C, respectively. The findings indicated that thermal stability has slightly improved after the pulping process. It was believed that removal of hemicellulose and lignin during the pulping process has increased the crystallinity of the pulp as well as the heat resistance towards thermal degradation [25]. The lower temperature recorded for pulp produced at 120 minutes further supported the findings from previous analyses that cellulose degradation occurred at extended pulping time. Other than that, the banana pulps also produced lower char residue than banana stem at the end of pyrolysis, except for pulp produced at 90 minutes. This was clearly observed from Fig. 3(a) where banana pulp at 90 minutes produced the highest residue of approximately 72%. Banana stem was expected to produce high residue due to the higher lignin content which has slow decomposition rate [17], but the higher residue recorded for pulp produced at 90 minutes might be associated with the cellulose structure. There was also huge difference in the amount of residues between pulp samples in despite of the small difference in their residual lignin content, indicating that the influence of cellulose structure toward formation of residue is greater than the residual lignin content. Further investigation was required to validate this finding.

Fig. 3(b) shows the effect of alkali charge on thermal decomposition of banana pulp during 90 minutes of pulping time. Maximum mass loss for banana pulps produced using 16, 18 and 20% w/v alkali charge occurred at 356, 336, and 305°C, respectively. Although higher alkali charge would remove greater amount of lignin, but pulping using high concentration of alkali would result in thermally less stable pulp. Therefore, pulping using 16% w/v alkali charge for 90 minutes was the best conditions to obtain pulp with a good thermal stability.

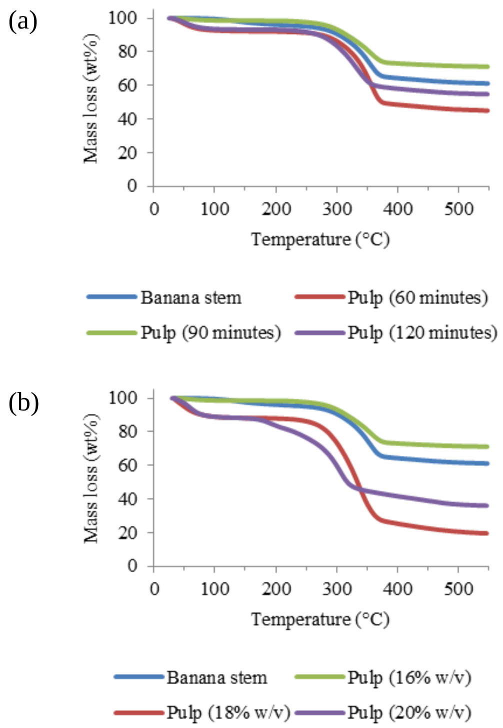

Fig. 3. Effects of (a) pulping time at constant 16% w/v alkali charge and (b) alkali charge at constant 90 minutes pulping time on thermal stability of banana pulp.

D. Surface Morphology

SEM image in Fig. 4 revealed that the banana stem was made up of hollow fibers, similar to the previous finding reported by Bilba *et al.* [11]. The surface was quite rough with cellulose fibrils structured parallel to each other. After 90 minutes pulping using 16% w/v alkali charge, the surface turned out to be smoother probably due to the partial removal of hemicellulose and lignin that initially embedded on the cellulose fibrils. Some ruptures were also observed on the fiber surface of banana pulp which might be related to the degradative action of sodium hydroxide.

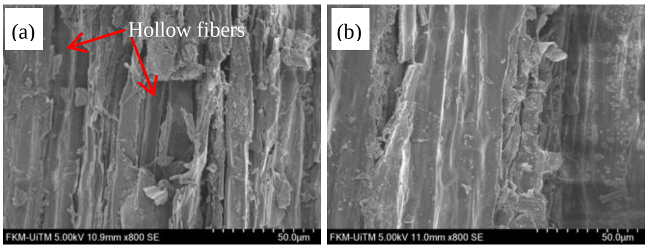

Fig. 4. Surface morphology of (a) untreated banana stem and (b) banana pulp produced through pulping using 16% alkali charge for 90 minutes captured at 800x magnification.

IV. CONCLUSION

Banana stem was suitable for atmospheric soda pulping due to the high cellulose and low lignin content. The pulping time has insignificant effect on pulp properties, while the alkali charge significantly affects the delignification process and thermal stability of the pulp. The best condition to maximize lignin removal without causing great loss of cellulose was using 18% w/v alkali charge for 90 minutes pulping. However, a better thermal stability could be achieved through pulping using 16% w/v alkali charge.

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