Chemical pulping of waste pineapple leaves fiber for kraft paper production

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1. Introduction

Pulp and paper industries have been considered the main consumers of natural resources (wood) and energy (electricity), including water, and significant contributors of pollutant discharges to the environment. The demand for paper and the unacceptable large ecological footprint of current paper production requires the need for alternatives. It was reported in 2004 that the annual paper consumption is 52.45 kg per person and was 16.32% greater than in 1991. The use of printing and writing paper grew by more than 10% from 1980 to 2000 [1]. In many parts of the world, local supplies of wood cannot support the demand for pulp. As a result, the search for non-wood raw materials in papermaking industry has been given more attention due to the rising consumption of wood resource for the paper production. From 1970 to present time, the non-wood plant fiber pulping capacity has increased on a global basis two to three times as fast as the wood pulping capacity. It was also forecasted that during the next decade, the non-wood pulp production will annually grow at an average of 6%, which is three times as fast as the production of pulp on wood basis [2]. Initially, non-wood fiber pulping occurred in regions where wood supply had been reduced to levels insufficient to sustain papermaking, and an alternative source of fiber feedstock was mandatory. Non-wood fiber resources have the potential to complement conventional wood supplies. This is because, they are abundant, have short cycles
and rapid regeneration, and are of comparatively low price. Therefore, non-wood fiber will play important roles in papermaking as substitutes or complements to wood. Examples of non-wood fiber resources available for paper production are wheat-straw [3-5], rice-straw [6,7], sugarcane straw [8], reeds [9], bamboo [10], bagasse [11,12], kenaf [13], palm oil [14], and jute [15]. Non-wood material, particularly wheat straw, was successfully exploited as the main raw material for papermaking in China because of the limited wood resource with forest coverage of only 13.94% [16]. By a wide margin, the leading non-wood plant fiber presently in use is straw, followed by bagasse and bamboo. However, pineapple leaf fiber (PALF) is another alternative non-wood fiber that can be used for paper production. There have been numerous studies carried out by researchers on various aspects of PALF. PALF obtained from plants bearing edible fruits were examined for textile purposes, and blends of PALF with silk and polyester fibers were studied [17]. PALF have also been incorporated into thermoplastic materials such as polypropylene and polyethylene to produce biocomposite materials. The use of non-wood raw materials provides several interesting advantages; specifically, it allows wood raw materials to be saved for other more decent uses and hence deforestation and replanting to be alleviated. It can also reduce wood and cellulose fiber imports in countries with a shortage of wood raw materials. Besides, users are increasingly demanding papers that are obtained by using clean technologies or made from recycled or non-wood fiber. The current challenges of the pulp and paper industry are the achievement of affordable quality pulp while preserving the environment by using increasingly smaller amounts of water and energy and gradually fewer raw materials [4]. It is also important to minimize pollution from residual effluents that results from cooking and bleaching of the raw materials. The increasing concern with the environment and its preservation have exposed the need to replace the classical pulping process such as kraft and sulfite pulping which use sulfur containing reagents. This is due to the fact that the release of sulfur to the environment can cause serious pollution problem [6]. The new pulping processes using less polluting chemicals known as the "organosolv" processes have been developed by the researchers to resolve the problem. During the last years, this large progress of process technology has been reported to reduce the sulfur emissions by the pulp mills. Even though the ability to obtain pulp by using the organic solvents has been known for some time, pilot plants and small-scale industrial plants exploiting them have only recently come into operation. This has been the result of the shortage of alternatives to traditional procedures, which leads to the expenditure of substantial efforts in new processes. In fact, some processes that use organic solvents are being reconsidered in response to the new economic and environmental order.

2. Methodology

2.1. Raw material

Pineapple leaves were obtained from the plantation of Malaysian Pineapple Industry Board (MPIB), Johor, Malaysia. Industrial grade acetone with 65% purity was purchased from Krass Instrument and Services.

2.2. Sample preparation

Dried pineapple leaves were immersed in mixtures of acetone/water of 1%, 3%, 5%, 7%, and 10% (v/v) for 3 days to study the effect of acetone concentration on paper quality and to optimize the best mixture content for farther preparation. The effect of soaking time was studied at interval times of 3, 7, 21 and 28 days. Mixture of 3% acetone was used to investigate the effect of cooking time on paper properties at 118 °C under applied pressure of 80 kPa. The pineapple leaf pulp was washed with water and disintegrated in a laboratory blender. The pulp was molded using mold and deckle. The paper was dried in the oven at 60 °C until the pulp was fully dried. Finally, the paper was pressed using the compression molding machine at 100 °C and pressure of 10 MPa to get even thickness of paper sheet.

2.3. Testing

The turbidity of spent liquor from pulping process was determined using HACH Ratio/XR Turbidimeter. Thermogravimetric analysis (TGA) was performed by using Mettler Toledo TGA/SDTA851 at heating rate 10 °C/min with the temperature range between 30 °C and 800 °C. TGA was used to determine the thermal stability of cellulose and lignin in pineapple leaves and the paper sheet. The tearing resistance test or Elmendorf tear test was used to measure the internal tearing resistance of the paper rather than the edge-tear strength of paper. The test was carried out according to ASTM D1922 using the HT-8181 Elmendorf Tearing Strength Tester. The tearing resistance (expressed in grams-force, gf) of the paper was determined from the average tearing force and the number of sheets comprising the test piece using following equation:

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\text{Tearing resistance, } \text{gf} = \frac{16 \times 9.81 \times \text{average scale reading } \times \text{gf capacity}}{n \times 1600 \text{gf}}
\]

where gf capacity = 3200 g and number of plies, \(n = 1\).

Inverted Microscope LEICA DMIRM equipped with a digital camera was used to study the morphology of the paper at 200× magnification. Morphological study was used to observe the fibers structure and their coarseness in the paper.

3. Results and discussion

3.1. Turbidity

Pulp quality is identified by the good strength, bleach ability, high cellulose and hemicellulose content and low lignin content. Therefore, it is desirable to have a pulp process that gave the highest delignification efficiency and good quality of cellulose and hemicellulose [18]. The effect of acetone concentration on the pineapple leaves pulping was first observed by the turbidity of the spent liquor after the pulping process. In organic solvent pulping process, the removal of lignin
Fig. 1 – The turbidity of spent liquor for various acetone concentrations at specified soaking time. The turbidity of soaking liquor for 3% acetone concentration at various soaking times. The turbidity of cooking liquor for 3% acetone concentration at various cooking times, at temperature of 118°C.

depends not only on the cleavage of ether bonds in lignin macromolecules, but also on the ability of the aqueous solvent solution to dissolve lignin fragments [19]. The result in Fig. 1 indicated that when the acetone concentration is increased from 1% to 3% (v/v), the turbidity also increases dramatically, which means a large amount of lignin was precipitated at 3% acetone concentration. Below 3% acetone concentration, the turbidity was low, which is an indication of low content of lignin dissolved [19]. On the other hand, the turbidity of the solution decreases with the increase of the acetone concentration in the solution. Higher amount of acetone concentration that is above 3% is not effective for delignification due to highly evaporated and low boiling point of acetone, which is 56.2°C.

Fig. 1 illustrates the effect of soaking time on the turbidity of spent liquor. It can be seen that when the pineapple leaves were soaked for a longer period of time, the turbidity increases dramatically, which indicates that a significant amount of lignin dissolves in the solvent. The effect of cooking time at high temperature of 118°C under applied pressure on turbidity of spent liquor also shows the same trend as illustrated in Fig. 1. From the results, delignification without any applied pressure and temperature requires much longer time.

Fig. 1 indicates that the turbidity for cooking liquor at higher temperature is higher than the soaking liquor. This is because of the precipitation of lignin on the surface of the fibers due to the presence of most of spent liquor between the fibers and the fiber walls [19].

3.2. Thermogravimetric analysis (TGA)

Fig. 2 shows the thermogravimetric (TG) curve for pineapple leaves paper produced from pulping with various acetone concentrations. Thermal decomposition of the samples takes place in a programmed temperature range of 30–800°C. Dehydration as well as degradation of lignin for pineapple leaves occurs in the temperature range 90–230°C. The cellulose component starts to decompose at the temperature above 230°C and most of it already decomposed at a temperature of 350°C. The paper being produced shifts toward higher values compared to pineapple leaves indicating their increasing thermal stability. Thermal stability increased corresponds to the
Fig. 3 – TG analysis for paper produced from pulping with 3% acetone concentration at various soaking times.

Fig. 4 – TG analysis for paper produced from pulping with 3% acetone concentration at 118 °C and various cooking times.
amount of lignin presence in the paper. The higher the lignin the least stable the paper is thermally. Paper soaked in 10% acetone contains the highest lignin amounting to 27.7% compared to the pineapple leaves that consist of about 30% lignin. The paper produced from pulping with 3% acetone concentration shows the highest thermal stability, with the least amount of lignin. Major decomposition of cellulose component in the resultant paper occurred at a temperature of approximately 370°C [17].

Thermal stability of the paper sheets pulped with 3% acetone is slightly increased with soaking time as shown in Fig. 3. Thermal stability increases with the decrement of lignin in the paper. The amount of lignin has been slightly decreased in conjunction with the increase in delignification time. Reduction of lignin with delignification time indicates that the time of soaking is an important factor in determining the quality of paper, which means a good quality paper with good thermal stability and low lignin content is produced at long soaking time. Twenty-eight days of delignification time at room temperature results in full removal of lignin; therefore, the paper had the highest thermal stability.

Fig. 4 indicates that the time was reduced initially when temperature and pressure increased. When the cooking time extended to 180 min, the thermal stability was the highest and the amount of lignin in the paper was reduced to the lowest level. However, as the cooking time was further prolonged, the thermal stability reduced at which after 450 min, the paper being produced shows the lowest thermal stability.
with high content of lignin. However, the amount of remaining lignin in the paper sheet did not show any significant changes above 360 min, which is similar to that at 90 min. Even though the turbidity of the cooking liquor has been increased with time, higher amount of lignin was observed in the paper produced after 450 min of cooking. This is due to the fact that the dissolved lignin was precipitated back onto the fibers [19].

3.3. Tearing resistance

The result in Fig. 5 indicates that the strength of paper was reduced at acetone concentration above 3% (v/v). It is therefore equivalent to the turbidity test, where less lignin has been dissolved in the solvent. As a consequence, higher amount of lignin remaining in the paper sheet causes the paper to become brittle and hence constitutes to lower strength properties.

When the pineapple leaves was soaked in the acetone/water mixture at 3% acetone concentration (v/v) for a longer period of time, the paper strength increased as shown in Fig. 5. The improvement in paper strength is a result of low lignin content at longer soaking time. The results in Fig. 5 show that the temperature and pressure have positive effect on paper strength and more lignin was removed from pineapple leaves. Applying pressure during the cooking increases the boiling point of cooking solvent up to higher temperature of 118 °C and enhances the lignin removal. These conclude that the tearing strength of the paper is dependent upon the lignin content, where the reduction of lignin increases the tearing resistance and produced better paper quality. In order to produce chemical-grade pulps, high temperature and long cooking time are the main factors [20].

3.4. Morphological analysis

The fibers structure and coarseness of the pineapple leaves fiber using various acetone concentrations in the acetone/water mixture pulping were observed by using the microscope, as shown in Fig. 6. The results showed that there were large fiber bundles in the paper sheets, being orientated in various orientations. The large fiber bundles were made of a number of technical fibers that were made of even finer elementary fibers of below 10 μm diameters [17] as shown in Fig. 7. However in Fig. 6(b), larger portion of elementary fibers was distributed throughout the paper sheets, hence introducing to the paper strength. This is because, the fiber extraction from dried leaves proved difficult with more tissues present on the surface and fine fibers torn from the bundles [17]. Drying the leaves also made it almost impossible to remove the technical fibers from the bottom face of the leaves. Besides, delamination of elementary fibers in the solvent containing more than 3% acetone concentration did not adequately occur due to acetone evaporation or due to dilution of the acetone concentration in the spent liquor during washing [19].

![Fig. 7 – Micrograph of pineapple leaves fiber bundles.](image1)

![Fig. 8 – Light microscopic images at 200x magnification of pineapple leaves acetone/water mixture pulp fibers: (a) 3 days; (b) 7 days; (c) 21 days; and (d) 28 days soaking time, at 3% acetone concentration.](image2)
When the soaking time was prolonged, more elementary fibers have been delaminated from the technical fibers as shown in Fig. 8. Fig. 9 also shows the same result when the pineapple leaves were cooked under pressure for up to 450 min. However, the delamination of the elementary fibers was improved when temperature and pressure were applied during the cooking. From the color of the fibers as observed in all Figs. 6–8, in addition to the brown color of lignin particles on the fibers, many other parts of the paper appear brownish. This indicates that some lignin, although not in particle form or not being observed by the light microscope, exists in the fiber wall [19]. For instance, the acetone is not nearly as strong as caustic, which can shorten the fiber lengths and lead to poor surface appearance of the paper sheets as can be seen from the micrographs in all figures.

4. Conclusions

The 3% acetone concentration shows the highest lignin solubility, the best tear properties, better delamination and distribution of technical fibers, hence producing the most acceptable properties of paper. The pineapple leaves with 3% acetone concentration must be soaked for a longer period of time to achieve the optimum delignification. Cooking the pineapple leaves at high temperature and applied pressure for more than 450 min reduced delignification time. Acetone/water mixtures can be used as alternative-pulping media due to low polluted spent liquor as a result of low consumption of acetone during the pulping process. Besides, pineapple leaves constitute an effective alternative pulping raw material, where paper sheets with good properties can be produced based on pineapple leaves fibers.

Conflicts of interest

The authors declare no conflicts of interest.

References


