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Chemical Composition and Morphological of Cocoa Pod Husks and Cassava Peels for Pulp and Paper Production

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Abstract: Non-wood materials which are cassava peels and cocoa pod husks are potential fibre sources of pulp and paper production. These materials were used as pulp for paper production industries to promote the concept "from waste to wealth" and "recyclable material to available product" for reducing the environmental issues. In order to maximize the utilization of non-wood fibres for pulp and paper production, a more complete understanding of its chemistry is required. In this context, the main objective of this work is to improve and investigate the chemical composition of different material fibers used for pulp and papermaking. All the determinations of chemical compositions were in accordance with relevant Technical Association of the Pulp and Paper Industry (TAPPI) Test Method, Kurscher-Hoffner approach and Chlorite method. The holocellulose, cellulose, hemicellulose, lignin, hot water and 1% NaOH solubility, ash and moisture content are parameters that involved in chemical characteristics determination. The scanning electron microscopy (SEM) was used to visualize the surface morphological of materials. In order to propose the suitability of the studied plant as alternative fibre resources in pulp and paper making, the obtained result is compared to other literatures especially wood sources. Results indicated the amount of holocellulose contents in cassava peel (66%) is lower than wood plants. But, cocoa pod husks (74%) are higher than that Pine pinaster (70%) in holocellulose content. Besides that, lignin content (7.5 – 14.7%) of alternative fibre is lower than those wood species (19.9-26.22%). From SEM images, cassava peels contained abundance fibre rather than cocoa pod husks. Cassava peels have impurities in white colour on surface fibre. Besides that, cocoa pod husks have a rough surface to protect their fibre. In conclusion, chemical properties and morphological characteristics of cassava peels and cocoa pod husks indicated that they a promising to be used as an alternative fibre sources for pulp and paper making.

Key words: Chemical composition, Cassava peels, Cocoa pod husk, Green technology, Surface morphology.

INTRODUCTION

The steady increase in Malaysia's paper consumption is creating a large and constant demand on the supply of fibres for pulp and paper production (Jean & Santosh, 2006). Due to increasing of pulp and paper demand consumption in Malaysia has inevitably caused the depletion in wood resources. Non-wood fibres offer several advantages including its abundance volume, a short cycle growth and environmentally friendly (Jahan *et al.,* 2007). The rapid increasing of environmental problems; global warming, soil erosion and climate change occur globally could be due to the massive scale deforestation of wood sources for purpose of pulp and paper production.

Agricultural waste residue is one type of non-wood resources that is used as an alternative fibre in pulp and paper production (Han, 1998). Generally, agricultural waste residue is generated from processing for example, cocoa fruits and cassava tuberous root produce important product such as cocoa powder and cassava flour respectively. The concept of "waste to wealth" and "recyclable material" is important to build a sustainable and sound material-cycle society through the effective use of these waste resources.

Generally, cassava (*Manihot esculenta Crantz*), a member of the *Euphorbiaceae* is a perennial shrub whose centre of origin is the Amazon basin. Cassava cultivation has now spread throughout the humid tropics from Latin America to Africa and Asia, where it grows principally for its large tuberous root (Buschmann *et al.,* 2002). Cassava peels is one of the wastes that are obtained from the processing cassava tuberous root (Adesehinwa *et al.,* 2011). The thickness of cassava peels varies between 1 to 4 mm and may accounts for 10 to 13% of the root dry matter (Adesehinwa *et al.,* 2011; Ezekiel *et al.,* 2010). Malaysia has large cassava plantations (42,000 ha in 2009) which yield about 440,000 tonnes of roots during harvesting season (FOA,

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2012). Therefore, the waste of cassava peels produced in 2009 is estimated at 44,000 to 57,200 tonnes. The explosive development of cassava plantation in this country has generated massive amounts of cassava peels as waste materials that was dump in landfills and could create great environmental problems in the long run (Reddy *et al.*, 2005).

Cocoa (*Theobroma cacao L*.) fruits are important commodity in Malaysia because of the economic value of its seeds or beans to produce high demand products such as cocoa powder, butter and chocolate. The processing of cocoa fruits generates a large amount of cocoa pod husk discard as wastes (Alemawor et al., 2009). Cocoa pod husk represents between 70 to 75% of the whole cocoa fruit weight where each ton of cocoa fruit will produce between 700 to 750 kg of cocoa pod husks (Cruz *et al.,* 2012). In Malaysia, the plantation of cocoa is over 20,643 ha (Malaysia Koko Board, 2011). Hence, it can be estimated at least 320,000 kg of cocoa pod husk is generated after processing. Conventionally, these organic wastes is shipped away for processing or disposed to landfill. These large quantities of cassava peel and cocoa pod husk could yield a large quantity of fibrous materials which might be suitable as alternative resources especially in pulp and paper making industries.

In order to maximize the utilization of organic wastes or non-wood fibres for pulp and paper production, a complete study of its chemical and morphological properties is required. In this context, the main objective of this work is to investigate the chemical compositions of cassava peels and cocoa pod husks fibre used for pulp and papermaking industry. In addition, characterization of surface morphology in both non-wood fibres was also determined. The results obtained in this study could be utilised in assessing the agriculture wastes potential as raw materials for pulp and paper production industries.

MATERIALS AND METHODS

Materials:

For this study, cassava peels and cocoa pod husks were collected from Salleh Food Industry and Pusat Pembangunan Komoditi, Parit Botak, Jabatan Pertanian Malaysia respectively. Before air-dried, these wastes were cut into 2-5 cm and thoroughly washed to eliminate sand and other contaminants. Representative parts of sample were ground to 0.40 - 0.45 mm and stored in air tight container for further chemical and morphological analyses**.**

Chemical Characterization:

Chemical composition of cassava peels and cocoa pod husks were performed according to Technical Association of the Pulp and Paper Industry (TAPPI) Test Method. The samples were first submitted to soxhlet extraction for 6 hours according to method T 264 om-88. The evaluation of extractive substances was carried out in different liquids according to experimental parameters: hot water (T 207 cm-08) and 1% sodium hydroxide solution (T 212 om-07). The ash content (T 211 om-07) also was determined. The amount of lignin, holocellulose, hemicelluloses and cellulose were assessed by using the following respective standard methods: T 222 om-06, Chlorite Method and Kurschner-Hoffner approach. All the experiments were done in triplicate of samples.

Surface Morphology Characterization:

The surface morphology of the cassava peels and cocoa pod husks were visualized in a JEOL JSM-6380LA analytical Scanning Electron Microscopy (SEM). The materials were treated with 8% NaOH solubility to remove impurities and placed in vacuum dry oven at 60^{o}C for overnight. A small piece of specimen (0.5 cm^2) was placed into double-sided tape of the specimen stub. The specimen was lightly pressed by release paper and coated with a thin layer of gold-palladium film before submitted to SEM for visualization the surface morphology characteristic of the sample.

Statistical Analysis:

Data collected was subjected to analysis of variance (ANOVA, $p \leq 0.05$) and the treatment means were checked by Duncan's test. All the statistical analyses were conducted by using SPSS 19 software.

RESULTS AND DISCUSSIONS

Chemical Characterization:

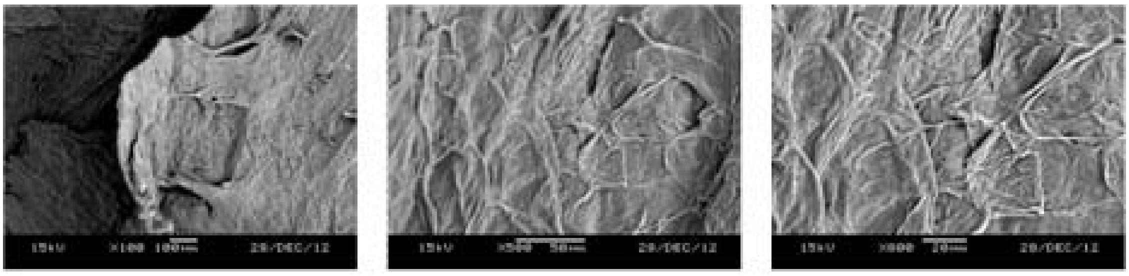
Table 1 shows the overall mean of the results for the compositions of the cassava peel and cocoa pod husk fibres. The holocellulose content of cocoa pod husks is higher than cassava peels in this study. In additions, higher amount of cellulose content in cassava peels (37.9%) rather than cocoa pod husks (35.4%) was identified. On contrast, in hemicelluloses content, cassava peels (23.9%) represents lower amount compared to the cocoa pod husks (37%). In general, cassava peels are characterized by a low lignin (7.5%), hot water solubility (7.6%) and ash contents (4.5%), but higher in 1% NaOH solubility (27.5%) than that of cocoa pod husks. Finally, moisture content determined in cassava peels and cocoa pod husks are quite similar, however, the moisture content could depends markedly on the harvesting time, local climate and storage conditions, therefore it lacks relevance to the characterization of raw materials. The cocoa pod husk presents the lower cellulose content and the higher lignin content (14.1%). Based on analysis of variance and treatment means show that there is significant difference ($p \leq 0.05$) between chemical compositions in cassava peel and cocoa pod husk fibres.

Table 1: Chemical composition of cassava peels and cocoa pod husks (%, w/w oven dried materials).

Properties	Cassava peels, % (w/w)	Cocoa pod husks, %(w/w)
Holocellulose	66.0±0.71*	74.0±0.81*
Cellulose	37.9±0.33*	35.4±0.33*
Hemicelluloses	23.9±0.49*	37.0±0.50*
Lignin	7.5±0.40*	14.7±0.35*
Hot water solubility	7.6±0.15*	17.6±0.67*
1% NaOH solubility	27.5±0.37*	20.2±0.59*
Ash content	4.5±0.02*	12.3±0.23*
Moisture content	14±0.01*	14.1±0.05*

* $p \leq 0.05$, statistically significant difference

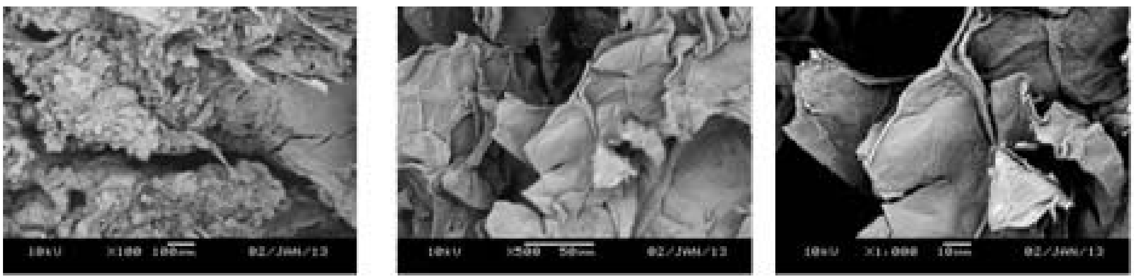
The surface morphology analysis was carried out by Scanning Electron Microscopy (SEM). **Figure 1** and 2 display the SEM images of cassava peels and cocoa pod husks observed under different magnification level. The study on surface morphology was significant in understanding the distribution and fibre arrangement of the agriculture wastes. The surface morphology of cassava peels shows major structure of micro pores (**Figure 1 (a)**) and consist of abundant and long fibres **Figure 1 (b)** and **(c).** Slight impurities indicate by the white speckles were present on the surface as seen in **Figure 1(a)**.



(a) **(b)** **(c)**

Fig. 1: SEM image of cassava peels on difference magnification level; **(a)** 100x, **(b)** 500x and **(c)** 800x.

SEM image for cocoa pod husk shows the lamella-shaped particles on the surface **Figure 2(a)**. The fibre produces a rough and thick layer of surface as shown in **Figure 2(b)** to protect the lignocellulosic content in this fibre. Cocoa pod husk also indicated high content of lignocellulosic with linear fibrillar arrangements as shown in **Figure** 2**(c)**. This characteristic enhances the strength properties of pulp and paper produced.



(a) **(b)** **(c)**

Fig. 2: SEM image of cocoa pod husks on difference magnification level; **(a)** 100x, **(b)** 500x and **(c)** 1000x

***Discussions*:**

Chemical Characterization:

In general, all plant cell walls consist primarily of sugar-based polymers (carbohydrates) that are bounded with lignin with lesser amounts of extractives, protein, starch and inorganics. In addition, the chemical compositions in plant matters are different depending on its geographic location, climate, ages and soil condition. Moreover, the compositions are also varies in different parts of same plants (Rowell *et al.,* 2000; Han *et al.,* 1997).

Holocellulose is the total content of cellulose and hemicelluloses in dry materials (Rowell *et al.*, 2000) and usually accounts for 65-70% of the plant dry weight (Han *et al.,* 1997). Based on **Table 2**, cassava peels (66%) shows the lower holocellulose content rather than cocoa pod husks (74%) and wood plants species (70 - 80.5%). The lower content in holocellulose indicates a less interesting candidate for pulp and paper making industry. Therefore, cassava peels might provide a lower quality performance in paper produced. On the other hand, cocoa pod husks and Eucalyptus globules in non-wood and wood plants respectively contained high amount of holocellulose could be due to high account in sugar polymers.

Cellulose is natural organic material and is found in abundance throughout the plant kingdom, hence it could be manipulated for the benefit of mankind (Kontturi *et al.,* 2005). In pulp and paper industry, cellulose is an important constituent in paper making because the higher content of cellulose produces a higher quality and strength properties of a paper. High cellulose content is considered advantageous for the pulp and paper industry because it yield higher pulp content after cooking process (Shakhes *et al.*, 2011). From **Table 2**, it was identified that the wood species (53 – 55.9%) contain the higher amount of cellulose content rather than that non-wood species (35.4 – 37.9%), therefore the amount of pulp yield produced is expected to be higher. The difference in cellulose content of non-wood and wood plants depends on their cell wall content, which varies in different plant species and varieties. However, the content of hemicelluloses is higher in non-wood than in wood sources (13.7-27.7%) as shown in **Table 2**. The content of hemicelluloses could contribute to the strength of paper pulp.

Lignin is a one of the component in plants structural that binds the cellulose fibres together. Prior to paper making process, the lignin must be removed from the pulp because it affects the performance and decreases the paper quality (Akpakpan *et al.,* 2011; Abdul Khalil *et al.,* 2006). Based on **Table 2**, the lignin content found in cassava peel (7.5%) was lower than cocoa pod husk (14.7%) and wood fibre (19.9-26.2%). Lignin is considered to be an undesirable polymer that is removed during pulping process (Rodríquez *et al.,* 2008). In addition, lower lignin content could be advantageous for use in pulp and paper making manufacturing, as fewer amounts of chemicals needed during pulping and bleaching process (Marques *et al.,* 2010) and ultimately reducing hazard release to environment.

The solubility in different solvents pointed to the extractives contents, which were not cell wall components (Shakhes *et al.*, 2011). Generally, the water solubility estimates a part of extraneous components such as inorganic compounds, tannis, gums, sugars, colouring matter, starch and protein which could affect the pulping process as a whole (Shakhes *et la.,* 2011; Rodríquez *et al.,* 2008; Sridach, 2010). As shown in **Table 2**, cocoa pod husk contains higher amount of hot water than wood fibres. High content of hot water will yield in low pulp content after the pulping process. Cassava peels show a higher amount of 1% NaOH solubility rather than coca pod husk and wood fibres. The consequence of high solubility will indicate the extent of fibre degradation during the chemical pulping process and thus the pulp yield would be low (Hosseinpour *et al.,* 2010; Sridach, 2010). Therefore, from the chemical composition analysis, the pulp yield of cassava peel is expected to less than those of cocoa pod husk and wood species.

The ash qualification defined as the mineral component of lignocellolsic material that is found in plant fibre (Shakhes *et al.,* 2011; Jun and Ulrike, 2010). Like other organic wastes fibre, ash content of cassava peels and cocoa pod husk were markedly higher than that of the wood fibre (0.5-0.6%) as seen in **Table 2**. High content of ash in cocoa pod husk does not only contribute to low pulp yield but also might generate processing problem since it could cause severe scaling problems during pulping and subsequent chemical recovery (Jun and Ulrike, 2010).

Table 2: Chemical compositions of non-wood and comparison with wood sources plants (%, w/w oven dried materials).

Materials	Non-wood, (%, w/w oven dried)		Wood, (%, w/w oven dried)	
Components	Cassava peels [This study]	Cocoa pod husks [This study]	Pine pinaster (Jiménez et al., 2008)	Eucalyptus globules (Jiménez et al., 2008)
Holocellullose	66.0	74.0	70.0	80.5
Cellulose	37.9	35.4	55.9	53
Hemicellulose	37.0	37.0	13.7	27.7
Lignin	7.5	14.7	26.2	19.9
1% NaOH	27.5	20.2	7.9	12.4
Hot water	7.6	17.6	2.0	2.8
Ash	4.5	12.3	0.5	0.6

Surface Morphology Characterization:

Changes in physical properties can be due to the differences in fibre morphology (Rowell *et al.,* 2000). As seen in **Figure 1 and 2**, the different in structure in the two plant types that is cassava peels and cocoa pod husks are a few of the vast display of fibre structures that exist in the plant kingdom (Rowell *et al.,* 2000) and Cruz *et al.* (2012) stated that the micro pores presence on the surface produce the low pores size of structure as in cassava peels (**Figure 1(a)**). Meanwhile, white speckles as identified in **Figure 1(a)** was due to the improper cleaning of material (Boopathi *et al.,* 2012).

In their natural state and before chemical extraction, Rowell *et al.* (2000) stated that fibre surfaces have waxes and other encrusting substances such as hemicelluloses, lignin and pectin that form a thick layer to protect the important substances, i.e. the cellulose inside as shown in **Figure 2(b).** Besides that, the presence of encrusting substances causes the fibre to have an irregular appearance as shown in **Figure 2(c)**. In addition, **Figure 1(c)** and **2(c)** shows the fibrillar arrangements are linear. There are irregular void spaces between the fibrilles and enhance the strength properties of paper produced (Goswani *et al.,* 2008).

Conclusion:

The holocellulose content of non-wood; cassava peels and cocoa pod husks are comparable to wood plants. Meanwhile, the cellulose content presents in cassava peels were higher than that cocoa pod husks, but lower than Pine pinaster and Eucalyptus gobulus (wood). Moreover, the lignin content obtained in cassava peels is lower in cocoa pod husks and wood plants, which is desirable in the pulp and paper production. Non-wood had higher water and 1% NaOH solubility than that of wood which could yield lower pulp. The results of SEM indicated different morphological structure were identifiend for both cassava peels and cocoa pod husks. Regardless, both of the plant surfaces show high content of fibre arrangement. In conclusion, the chemical compositions and surface morphological studies indicated both agriculture wastes would yield comparable pulp as in wood resources. Overall analaysis indicates coca pod husk would be a more suitable candidate for alternative fibre resources to be used as pulp in papermaking industries.

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