

EFFECTS OF TOTAL CHLORINE FREE (TCF) BLEACHING ON THE CHARACTERISTICS OF CHEMI-MECHANICAL (CMP) PULP AND PAPER FROM MALAYSIAN DURIAN (*DURIO ZIBETHINUS MURR.*) RIND

Shaiful Rizal Masrol^{a,b*}, Mohd Halim Irwan Ibrahim^{b,c}, Sharmiza Adnan^d, Muhammad Syauqi Asyraf Ahmad Tajudin^c, Radhi Abdul Raub^c, Siti Nurul Aqma Abdul Razak^c, Siti Nur Faeza Md Zain^c

^aFaculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia (UTHM), Malaysia

^bAdvanced Manufacturing and Materials Center (AMMC), ORICC, Universiti Tun Hussein Onn Malaysia (UTHM), Malaysia

^cFaculty of Mechanical and Manufacturing, Universiti Tun Hussein Onn Malaysia (UTHM), Malaysia

^dPulp and Paper Laboratory, Biomass Technology Programme, Forest Products Division, Forest Research Institute Malaysia (FRIM)

Article history

Received

20 October 2016

Received in revised form

26 February 2017

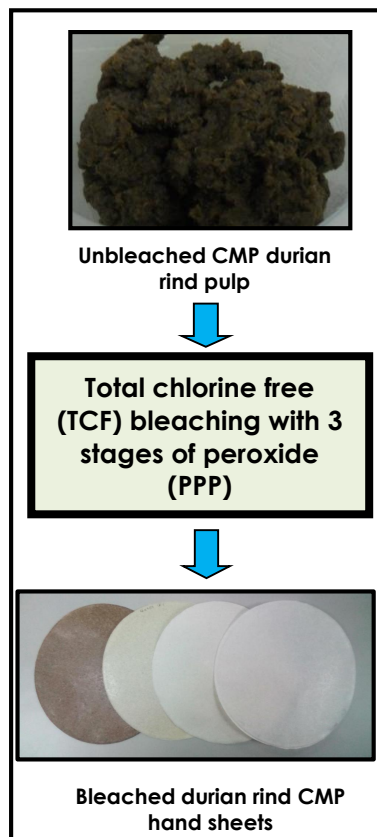
Accepted

10 March 2017

*Corresponding author

rizal@uthm.edu.my

Graphical abstract



Abstract

The effects of bleaching process on the characteristics of pulp and paper produced from durian rind under chemi-mechanical pulping (CMP) method were investigated. All process and characteristic tests were conducted according to Malaysian International Organisation for Standardization (MS ISO) and Technical Association of the Pulp and Paper Industry (TAPPI). Three (3) stages of peroxide (P-P-P) bleaching sequence through the Total Chlorine Free (TCF) bleaching process were applied to the unbleached and unbleached durian rind CMP pulp. Bleached CMP durian rind pulp drainage time (32s) decreased (faster) and CSF freeness level (172.50ml) increased as compared to a control pulp. It was obtained that overall optical (brightness (66.36 %)) and mechanical characteristics (tensile index (38.33 Nm/g), tearing index (7.56 mN.m²/g), bursting index (2.42 kPa.m²/g), and number of folds (43)) of durian rind CMP 60 gsm paper sheet improved as the TCF bleaching process was applied to the unbleached CMP durian rind pulp.

Keywords: Bleaching, total chlorine free, peroxide, durian, durian rind, pulp, paper

Abstrak

Kesan proses pelunturan terhadap ciri-ciri pulpa dan kertas yang dihasilkan daripada pulpa kulit durian menggunakan kaedah pempulpaan kimia-mekanikal (CMP) telah dikaji. Semua proses dan ujikaji yang terlibat dalam kajian ini telah dijalankan dengan merujuk kepada Organisasi Piawai Antarabangsa Malaysia (MS ISO) dan piawai Persatuan Teknikal Industri Pulpa dan Kertas (TAPPI). Tiga (3) peringkat rawatan peroksida (P-P-P) melalui proses pelunturan bebas klorin (TCF) telah dijalankan ke atas pulpa kulit durian kimia-mekanikal yang masih tidak dikenakan proses pelunturan dan pemukulan. Masa saliran pulpa kulit durian CMP terluntur menurun (lebih cepat) dan tahap kebebasan CSF meningkat berbanding dengan pulpa kawalan. Secara keseluruhannya, ciri-ciri optikal (kecerahan (66.36 %)) dan mekanikal (indeks tegangan (38.33 Nm/g), indeks koyak (7.56 mN.m²/g), indeks pecahan (2.42 kPa.m²/g) dan bilangan lipatan (43)) kertas 60 gsm kulit durian telah meningkat setelah proses pelunturan bebas klorin dilakukan ke atas pulpa kulit durian CMP tanpa kesan pelunturan.

Kata kunci: Pelunturan, bebas klorin, peroksida, durian, kulit durian, pulpa, kertas

© 2017 Penerbit UTM Press. All rights reserved

1.0 INTRODUCTION

Nowadays, non-wood based raw materials for pulp and paper industry has gained a big interest. From 1970, the non-wood plant fibre pulping capacity has increased on a global basis two to three times as fast as the wood pulping capacity [1]. Non-woods have been used as the main raw materials for paper productions in many countries, including China and India [2]. Hence, research and developments of several non-wood-based raw materials for pulp and paper have been undertaken rapidly by researchers in Malaysia. Several studies have utilised Malaysia's huge oil palm industry residues such as empty fruit bunch (EFB) [3–5], oil palm fronds [6–9] and oil palm male flower spikes (OPMFS) [10, 11] as potential non-wood based papermaking material. Adnan *et al.*, Mosello *et al.* and Ibrahim *et al.* developed pulp and paper from kenaf [12–16]. Main *et al.* and Mohamad Jani *et al.* investigated the suitability of coconut coir [17–19] as non-wood based raw material for pulp and paper industry. *Gigantochloa scortechinii* (Semantan bamboo) pulp and paper have been successfully developed by Mohd Hassan *et al.* [20–22]. Daud *et al.* explored the suitability of several Malaysia's agricultural industry residues such as pineapple leaf [23,24], corn stalk [23], and Napier grass [23, 24] as substitution materials for papermaking industry. However, to the best of the author's knowledge, there is lack of studies and published works focusing on the use of durian rind as a raw material for pulp and paper.

Durian is the most popular fruit in Malaysia and Southeast Asia and also known as the "King of Fruits". There are a lot of durian species but only *Durio zibethinus* is of economically importance and commercially grown [25]. As reported, durian trees have a lifespan of 80–150 years or more [26]. The Department of Agriculture Malaysia (DOA) [27] stated that there are 13 popular durian varieties in Malaysia, which are D24, Kop Kecil (D99), D123, Beserah (D145), Kan Yau (D158), Mon Thong (D159), Hajjah Hasmah (D168), Tok Litok (D169), Udang Merah (D175), MDUR 78 (D188), MDUR 79 (D189), MDUR 88 (D190), and Musang King (D197). According to the statistics provided by the Ministry of Agriculture and Agro-Based Industry Malaysia (MOA) [28], 75,370-hectare areas were planted with durian contributing to 373,565 metric tons of durian fruits production in 2014.

The durian fruit is ovoid or ovoid-oblong to nearly round shaped, with an average size weighing between 2 and 4.5 kg depending on their varieties [29]. Durian rind is a biomass waste of durian fruit consumption [30]. A significant percentage of the planted durian fruit crop is wasted each year. Only one-third of durian is edible, whereas the seeds (20–25%) and the shell are usually discarded [31, 32]. Durian flesh constitutes only about 30% of the nett fruit weight while another 70% of it are non-edible components [33]. The amount of mass that the aril contributes to the entire fruit was recorded only from 15% to 30% [34]. Durian only has 20–35% parts that can be eaten, and the peels (60–75%) are dumped

as trashes [35, 36]. Due to the high consumption of durians, massive amounts of the peels (as waste products) are disposed, causing a severe problem in the community [32]. In a common practice, durian residues are burned or sent to the landfills, without consideration of the surrounding environment, nor consideration on any precautions to prevent the percolation of contaminants into the underlying water channels [37]. Thus, to overcome this problem, durian rind (Figure 1) was proposed as a newly explored raw material for pulp and paper industry.



Figure 1 Durian Rind

As a new source of natural fibre, durian skin fibre (DSF) is renewable, biodegradable, and cheap. These characteristics make it suitable for packaging, such as for food packaging applications [38]. Author's previous study by Masrol, Ibrahim, and Adnan [39] revealed that unbleached durian rind pulp produced via chemi-mechanical pulping process has great potentials to be applied as a newly explored raw material for pulp and paper industry. Unfortunately, the optical characteristics of the virgin CMP pulp, especially its brightness, are low. Thus, bleaching process was proposed in our previous study [39] to improve the optical characteristics of CMP durian rind pulp, especially its brightness.

There are two types of bleaching methods that receive growing attention nowadays, which are Elemental Chlorine Free (ECF) and Totally Chlorine Free (TCF). TCF bleaching is widely used in the world due to a concern for environmental protection [40]. TCF-bleached pulps also have higher brightness and viscosity [40]. Roncero *et al.* [41] proposed a bleaching sequence that provides increased brightness and, like all TCF sequences, it is environmental friendly and causes less pollution. The TCF is the most commonly used bleaching method for mechanical and chemi-mechanical pulps with the purpose of removing any chromophores present.

In this study, the hydrogen peroxide bleaching of CMP durian rind pulp produced via chemi-mechanical pulping (CMP) process was investigated. The objective of this study was to investigate the effects of TCF bleaching process to the physical, mechanical, and optical characteristics of the unbleached CMP durian rind pulp and paper produced during our previous study [39]. The three stages of peroxide (P-P-P) sequences were adopted for the bleaching process.

The physical, mechanical, and optical characteristics of TCF bleached CMP durian rind pulp were compared with the unbleached pulp produced during our previous study [39]. Therefore, the findings of this study are expected to improve the quality of durian rind as an alternate non-wood-based material for pulp and paper.

2.0 METHODOLOGY

2.1 Raw Material Preparations

In this study, the durian rinds waste was collected from a local farm in Batu Pahat, Johor, Malaysia after the arils were taken away. The dried durian rind preparation process was referred to our recent study by Masrol *et al.* [39]. First, fresh durian rinds were cleaned and washed from any dirt and residual aril under running water. The center vertical wall that separates the arils was removed away from the rinds using a sharp knife. Next, durian rinds were sliced to the thickness of 5–10 mm. Then, the durian rind spikes were removed using a cutter. After that, the durian rind slices were cut into small cubes with an approximate size of 5–10 mm for width, length, and depth. Finally, the durian rind cubes were naturally dried under direct sunlight for about 3–5 days to remove the moisture. The dried durian rinds were stored inside a closed air-tight container at room temperature to prevent fungus infestation.

2.2 Chemi-mechanical Pulping (CMP) Process

In this research, unbleached durian rind pulp was produced by a CMP process, as according to Masrol *et al.* [39]. The naturally dried durian rinds were treated with 10% sodium hydroxide (NaOH) based on durian rind oven-dry (o.d.) weight for two hours with liquor to the material ratio of 6:1. Next, the treated durian rinds

were washed under running water and refined using Sprout-Waldron model D2A505 refiner mechanical pulping (RMP) machine to produce the CMP pulp. Then, the CMP durian rind pulp was screened using Frank-PTI Somerville Fractionators according to TAPPI T 275 standard with a slot size of 0.15 mm to screen out the oversized debris. Then, the screened pulp was spin-dried using Neng Shin extractor to remove excess water and dispersed using the Hobart Mixer. Finally, the durian rind CMP pulp was stored inside chillers at 6°C.

2.3 Total Chlorine Free (TCF) Bleaching Process

TCF bleaching method with three stages of Peroxide (P-P-P) was applied to the unbleached chemi-mechanical durian rind pulp produced according to the process suggested by Masrol *et al.* [39]. Before the bleaching sequence was applied, unbleached CMP durian rind pulp was disintegrated to break down the lumpy pulp and to achieve pH level of 2–6. First, 100 grams of o.d. unbleached CMP durian rind pulp were weighted and poured inside the disintegrator tank.

Next, two litres of hot water (distilled water) with 0.2 grams of Diethylenetriaminepentaacetic acid (DTPA) were poured into the pulp inside the disintegrator tank. As reported, DTPA is more effective than Ethylenediaminetetraacetic acid (EDTA) in chelating and effectively removing the metal content [2]. Hot water was used to remove the pulp latency and straighten the fibres, which were twisted during the refining process. Then, sulphuric acid (H_2SO_4) was slowly dripped into the pulp slurry until a stable pH level of 2–6 was achieved. After that, the durian rind pulp slurry was disintegrated for 20 minutes. Finally, the disintegrated CMP durian rind pulp was washed under running water and spin-dried for three times using Neng Shin extractor to remove excess water before proceeding with multi-stage bleaching sequences.

Table 1 Details of the Bleaching Process

Stage	Stage 1 (P)	Stage 2 (P)	Stage 3 (P)
Chemical and charges	- NaOH = 5% (based on o.d. pulp) - H_2O_2 = calculated based on NaOH/ H_2O_2 ratio : 0.35 - Na_2O_3Si = 5% (based on o.d. pulp) - DTPA = 0.2%(based on o.d pulp)		
Time and water bath temperature	90 min, 70°C	120 min, 70°C	120 min, 70°C
Kneading and washing	- Pulp kneaded every 15min. - Pulp washed thoroughly after each bleaching stage.		
Moisture content, yield, and sheet making	- Determination of the o.d. weight content and yield for every bleaching stage - Continued with hand sheet making		
DTPA = Diethylenetriaminepentaacetic acid; H_2O_2 = Hydrogen peroxide; NaOH = Sodium hydroxide; Na_2O_3Si = Sodium silicate; o.d. = oven dried weight			

For every bleaching stage, the pulp's moisture content was measured and recorded to measure the correct o.d. weight of the pulp and the final bleaching

yield. Figure 2(a–i) shows the overall procedures for TCF bleaching process conducted in this study. For Stage 1, the chemical ingredients as shown in Table 1 were

prepared. Firstly, water bath was heated to 70°C. Secondly, all the chemical ingredients were dissolved with distilled water using a magnetic stirrer. Thirdly, the chemicals were mixed with the durian pulp obtained from Stage 1 and adjusted to 10% consistency with distilled water. Next, the mixture was sealed inside a polyethylene bag and it was then immersed in the water bath at 70°C for 90 minutes. During the bleaching process, the pulp was manually kneaded for every 15 minutes. Afterwards, the bleached durian rind pulp was

washed thoroughly using running water and spin-dried using a Neng Shin extractor to remove excess water. Finally, the bleached CMP durian rind pulp was dispersed using a Hobart mixer and stored inside chillers at 6°C before proceeding with the laboratory hand sheets preparation. The percentage of pulp yield for each stage was calculated and recorded. The overall processes were repeated for the second and third stages of peroxide bleaching with chemical charges, reaction time, and temperature as shown in Table 1.

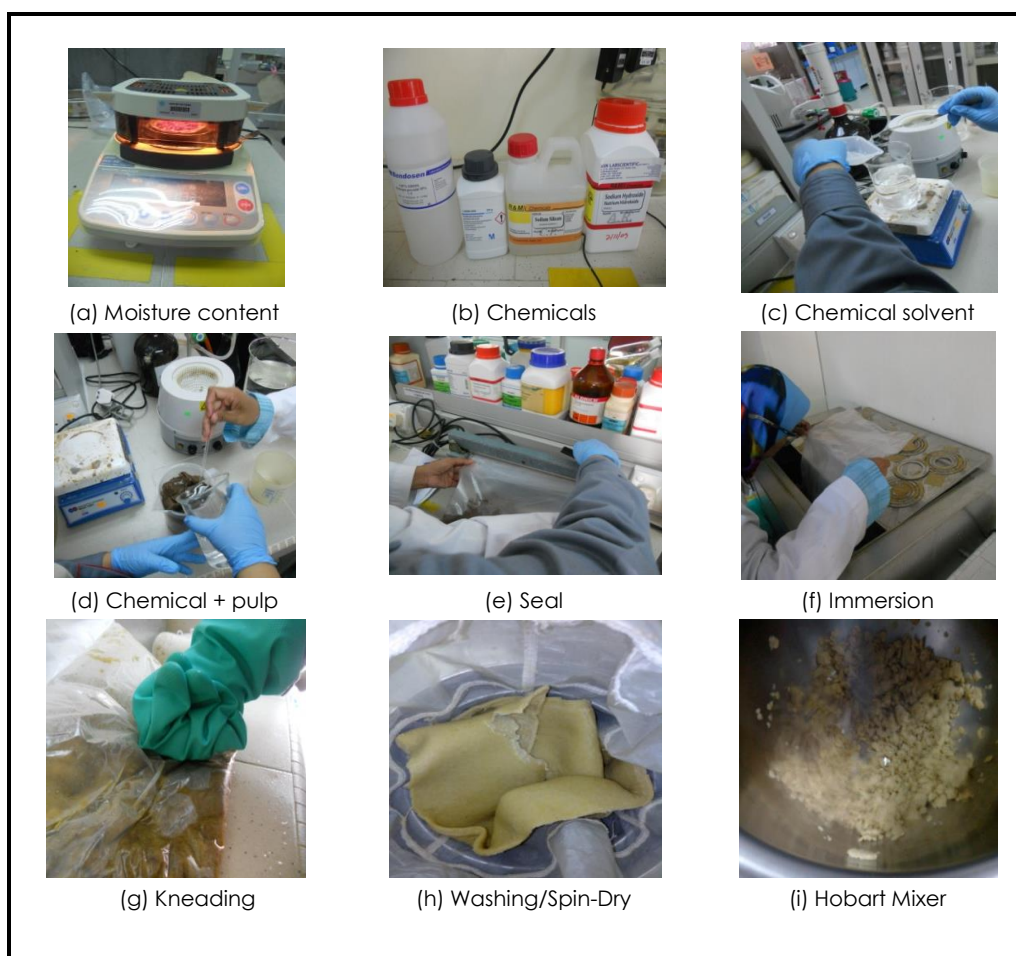


Figure 2 TCF Bleaching Process Procedure

2.4 Laboratory Hand Sheets Preparation

The 60 ± 3 gsm laboratory hand sheets were prepared using semi-automatic sheet machine (British Hand-sheet Machine) according to guidelines by TAPPI T 205 sp-02: Forming Hand-sheets for Physical Tests of Pulp and MS ISO 5269-1:2007: Pulps — Preparation of Laboratory Sheets for Physical Testing — Part 1: Conventional Sheet-Former Method (ISO 5269-1, 2005, IDT). Two sets of correction test were performed during the stock preparation process before proceeding with hand sheets formation in order to obtain the correct grammage of 60 ± 3 gsm. The freeness test was conducted according to TAPPI T 227 om-99: Freeness of

Pulp (Canadian Standard Method). The drainage time of pulp was evaluated according to TAPPI T221-cm 99: Drainage Time of Pulp. The hand sheets were dried and conditioned at $23 \pm 1^\circ\text{C}$ and $50 \pm 2.0\%$ RH as stated in TAPPI T 402 sp-03: Standard Conditioning and Testing Atmospheres for Paper, Board, Pulp Handsheets and Related Products and MS ISO 187: 2001: Paper, Board and Pulps — Standard Atmosphere for Conditioning and Testing and Procedure for Monitoring the Atmosphere and Conditioning of Samples (ISO 187:1990, IDT) for at least 24 hours before the characteristics test. Detailed hand sheets formation procedures are explained in our previous study [39].

2.5 Characteristics Test

The characteristics tests (a-i) listed in Table 2 were conducted according to ISO 5270: 2012 Pulps — Laboratory Sheets Determination of Physical Properties. The characteristics tests were performed inside a control room with controlled temperature and humidity environment as stipulated in TAPPI T 402 sp-03: Standard Conditioning and Testing Atmospheres for Paper, Board, Pulp Handsheets and Related Products and MS ISO 187: 2001: Paper, Board and Pulps — Standard Atmosphere for Conditioning and Testing and Procedure for Monitoring the Atmosphere and Conditioning of Samples (ISO 187:1990, IDT). The

sampling was conducted according to MS ISO 186: 2003: Paper and Board — Sampling to Determine Average Quality (ISO 186:2002, IDT). The weight of each 60 gsm durian rind CMP hand sheet sample was recorded. From the weight obtained, hand sheets with the highest and lowest weight were excluded from the test. The best eight hand sheets were selected for testing. For grammage test, the overall specimen after the tear test (16 pieces) were placed into the oven for not less than 30 minutes at a temperature of 105°C as stated in MS ISO 287: 2010: Paper and Board — Determination of the Moisture Content of a Lot — Oven-drying.

Table 2 Characteristics Test

No.	Test	Standard
a.	Grammage	MS ISO 536: 2001: Paper and Board — Determination of Grammage
b.	Moisture Content	MS ISO 287: 2010: Paper and Board — Determination of Moisture Content of a Lot — Oven Drying Method (ISO 287: 2009, IDT)
c.	Thickness	MS ISO 534: 2007: Paper and Board — Determination of Thickness, Density, and Specific Volume (ISO 534:2005, IDT)
d.	Brightness	MS ISO 2470-1: 2010: Paper, Board and Pulps — Measurement of Diffuse Blue Reflectance Factor — Part 1: Indoor Daylight Conditions — ISO Brightness — First revision (ISO 2470-1: 2009, IDT)
e.	Opacity	MS ISO 2471: 2010: Paper, Board and Pulps — Determination of Opacity (Paper Backing) — Diffuse Reflectance Method — First revision (ISO 2471: 2008, IDT)
f.	Tensile	MS ISO 1924-2: 2010: Paper and Board — Determination of Tensile Properties — Part 2: Constant Rate of Elongation Method — 20 mm/min — First revision (ISO 1924-2: 2008, IDT)
g.	Tearing	MS ISO 1974: 1999: Paper — Determination of Tearing Resistance — Elmendorf Method — Second Revision (ISO 1974:1990, IDT)
h.	Bursting	MS ISO 2758: 2007: Paper — Determination of Bursting Strength (ISO 2758: 2001, IDT)
i.	Folding	MS ISO 5626:1999: Paper — Determination of Folding Endurance

3.0 RESULTS AND DISCUSSION

3.1 Pulp Characteristics

Table 3 shows the characteristics of hydrogen peroxide bleached CMP durian rind pulp as compared to the unbleached durian rind pulp reported in our previous study [39]. The yield was reduced by about 29.4% as the hydrogen peroxide bleaching sequences were applied to the unbleached pulp. The pulp yield decreased to 70.6% at Stage 3 of peroxide bleaching. Previous research by Chen *et al.* [42] reported that the yield of de-inked old newspaper pulp (ONP) decreased with the increment of hydrogen peroxide content. The pulp yield continuously decreased as peroxide charge increased due to the loss of soluble fines, filler,

alkaline-soluble wood components, and contaminants during the hydrogen peroxide bleaching [42]. Pulp yield data reported by other researchers indicated that, when the bleaching conditions become more intense, the loss of pulp increases [43].

Freeness level for bleached CMP durian rind pulp after P-P-P bleaching sequence shows an increasing trend up to 172.50mL as compared to the unbleached pulps with 89.0mL. The drainage time also decreased from 74s to 32s as the peroxide bleaching was applied to the unbleached pulp. This means the drainage of the pulp improved by the bleaching process, resulting in a faster paper sheet formation process. Figure 3 shows a clearer view of the P-P-P bleaching sequence effects on the characteristics of chemi-mechanical (CMP) durian rind pulp.

Table 3 The Characteristics of CMP Durian Rind TCF Bleached Pulp

Pulp	Stage 0[39]		Stage 1		Stage 2		Stage 3	
	Unbleached	STDV	P	STDV	P	STDV	P	STDV
Yield (%)	100%	-	82.06%	-	74.30%	-	70.60%	-
Loss (%)	0%	-	17.94%	-	25.70%	-	29.40%	-
Moisture Content (%)	82%	-	84.27%	-	83.40%	-	82.67%	-
Oven dry (%)	18%	-	15.73%	-	16.60%	-	17.33%	-
CSF Freeness (mL)	89.00	0.71	-	-	-	-	172.50	6.36
Drainage time (s)	74	3.96	-	-	-	-	32	1.77

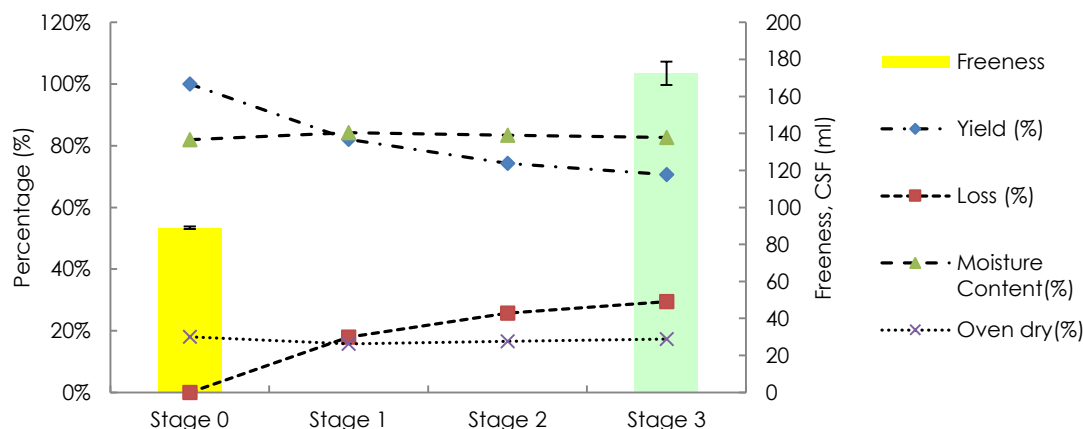


Figure 3 Effects of TCF Bleaching on the Characteristics of CMP Durian Rind Bleached Pulp

3.2 Physical Characteristics

Table 4 shows the physical characteristics of bleached CMP durian rind paper that indicate a minimum difference as compared to a control pulp from our previous study [39]. Laboratory 60±3 gsm CMP durian rind paper sheets show that bleached pulp depicts an acceptable grammage of 59.48 g/m² as compared to the unbleached pulp with the grammage of 58.87 g/m². Meanwhile, bleached pulp shows 134.55µm of

bulk thickness as compared to 128.59µm for the unbleached pulp. The paper bulk density from bleached pulp shows the value of 0.44 g/cm³ as compared to 0.46 g/cm³. The bulk of peroxide bleached pulp decreased as the peroxide charge increased due to the dissolution of hydrophobic material (such as extractives and low molecular weight lignin) and the introduction of more carboxylic groups into the fibre structure [44].

Table 4 Physical Characteristics of Bleached CMP Durian Rind 60 gsm Laboratory Hand Sheet

Pulp Condition	Grammage (g/m ²)	Bulk Thickness (µm)		Paper bulk density (g/cm ³)	
		Mean	STDV	Mean	STDV
Unbleached[39]	58.87	128.59	1.99	0.46	0.007
Bleached(PPP)	59.48	134.55	1.19	0.44	0.004

3.3 Mechanical Characteristics

Table 5 shows that TCF P-P-P bleaching sequence significantly enhances the mechanical characteristics of CMP durian rind paper. Tensile index of the bleached pulp shows a value of 38.33 Nm/g, which is an increment of 10.6% from the unbleached pulp (34.67 Nm/g). Meanwhile, tearing index increased by 53.7% (bleached pulp showed a value of 7.56 mN.m²/g while the value for unbleached pulp was 4.92 mN.m²/g). Tear index results for bleached CMP durian rind paper show a similar pattern with a study by Liu *et al.* [44], which reported that for low-freeness thermo-mechanical pulp (TMP), the tear index of the bleached pulp is always

higher than the unbleached pulp. For burst index, bleached CMP durian rind paper recorded a value of 2.42 kPa.m²/g, which is 30.1% higher as compared to the value shown by the unbleached CMP durian rind pulp, which is 1.86 kPa.m²/g. The number of the fold for bleached durian rind CMP paper shows an increment of 186.7%, with 43 folds while unbleached pulp recorded 15 folds. These results show that three-stages TCF peroxide bleaching improves the mechanical characteristics of CMP durian rind pulp. A study by Chen *et al.* [42] showed that the strength properties of ONP pulp also has an evident improvement after peroxide bleaching.

Table 5 The Mechanical Characteristics of Bleached CMP Durian Rind 60 gsm Laboratory Hand Sheet

CMP Pulp Properties	Unbleached[39]		Bleached(PPP)		Increment (%)
	Value	STDV	Value	STDV	
Tensile Index (Nm/g)	34.67	1.40	38.33	0.57	10.6
Tear index (mN.m ² /g)	4.92	0.36	7.56	0.34	53.7
Burst Index (kPa.m ² /g)	1.86	0.16	2.42	0.14	30.1
Folding No.	15	1.00	43	3.54	186.7

3.4 Optical Characteristics

Figure 4(a–d) shows the bleached pulp obtained after every stage of peroxide treatment. The effectiveness of the three stages of peroxide TCF bleaching process was

observed and it can be seen that the durian rind pulp's original dark brown colour at Stage 0 (unbleached) changed to a brighter colour after each peroxide treatment. Figure 5(a–d) shows the paper sheets samples for every stage of bleaching.

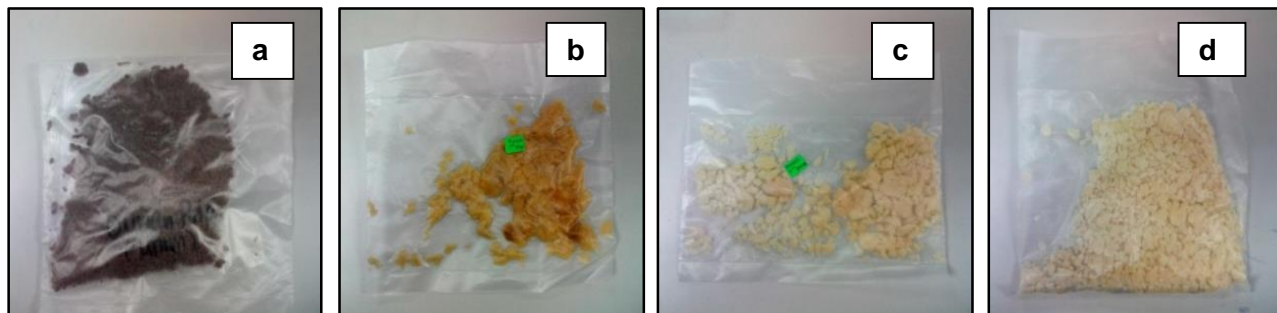


Figure 4 CMP Durian Rind Pulps: (a) Unbleached[39]; (b) Bleached after Stage 1-P; (c) Bleached after Stage 2-P; and (d) Bleached after Stage 3-P

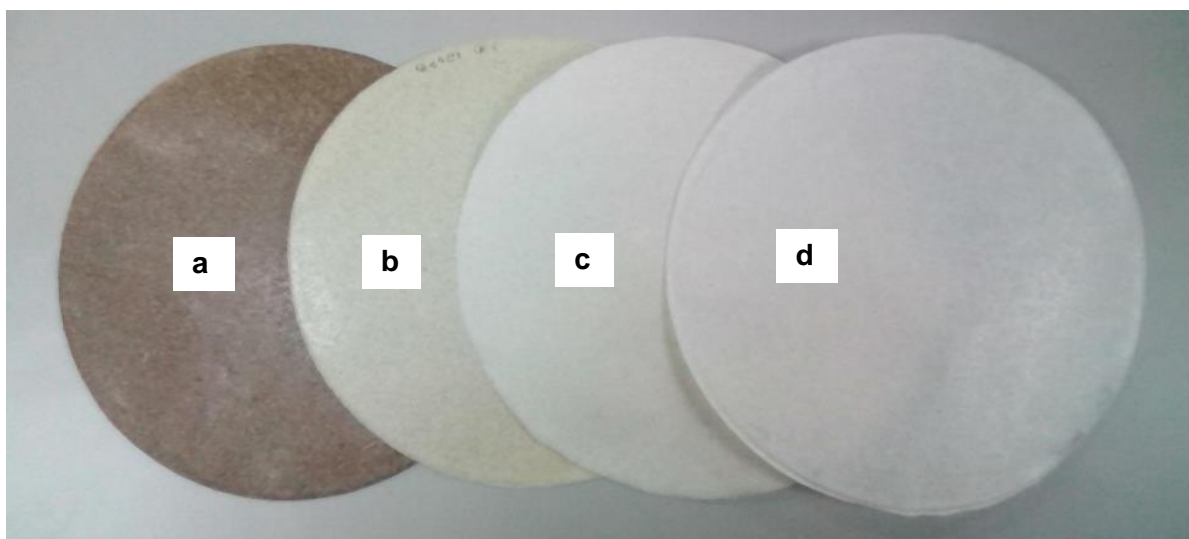


Figure 5 CMP Durian Rind 60 gsm Paper Sheets: (a) Unbleached[39]; (b) Bleached after Stage 1-P; (c) Bleached after Stage 2-P; and (d) Bleached after Stage 3-P

Table 6 shows the effectiveness of TCF bleaching sequences with three stages peroxide (P-P-P) on optical characteristics of CMP durian rind pulp and paper. After Stage 3 of peroxide bleaching, bleached CMP durian rind pulp shows 402.7% increment on the ISO brightness with a value of 66.36% as compared to the unbleached pulp with the value of 13.20%. Chen *et al.* [42] in his study also showed that brightness and fibre charge of de-inked ONP increases with the increment of hydrogen peroxide. As the hydrogen peroxide charge increases, as expected, the brightness increases [45]. The ISO opacity percentage of bleached CMP durian rind pulp decreased by 27.6% with the value of 70.75% as compared to 97.73%, recorded by the unbleached pulp. In this study, both brightness and opacity of CMP

durian rind pulp significantly changed after the three-stages of peroxide bleaching. A similar result was shown by Mohamad Jani and Rushdan [19] in their study, in which bleaching coir fibre pulp produced paper with better brightness properties and lower opacity. The opacity reduction may partly due to the removal of chromophores from cellulose fibres as a result of hydrogen peroxide bleaching [2]. Lignin were dissolved out during the bleaching and resulted in the collapse of fibre lumens, while alkaline swelling made the fibres more flexible and softer resulted in an increase of fibre contact area and causing the reduction of light scattering coefficient of paper sheet, which caused the decrease of opacity [46].

Table 6 Optical Characteristics of CMP Durian Rind 60 gsm Bleached Paper

Pulp Condition	ISO Brightness (%)				ISO Opacity (%)			
	Mean	STDV	COV	%	Mean	STDV	COV	%
Unbleached[39]	13.20	0.80	6.03	-	97.73	1.09	1.12	-
Stage 1-P	41.34	0.41	0.98	213.2	-	-	-	-
Stage 2-P	59.12	0.22	0.38	347.9	-	-	-	-
Stage 3-P	66.36	0.50	0.75	402.7	70.75	0.76	1.07	-27.6

3.5 SEM Image Analysis

Fibre surface morphologies of control pulp and peroxide bleaching pulp were observed using the scanning electron microscopy (SEM) as illustrated in Figures 6 and 7, respectively. The control unbleached CMP durian rind hand sheet in Figure 5 shows smoother surface than bleached CMP durian rind paper in Figure 6. The control pulp fibres were mostly intact, there were more long fibres, and the fibre surface of control pulp was smoother [42]. Bleached pulp surface shows rougher and fibres are no more intact, with more fibrils and longitudinal tearing could be observed on the fibre surface, which demonstrated that the delignification of the peroxide bleaching occurred on the fibre surface, releasing fibrils which led to better bonding between fibres in hand sheets, hence in an increase of paper strength [42]. The fibre to fibre bonding can also be improved by the removal of hydrophobic substances, such as lignin and extractives, under the peroxide bleaching conditions which renders the fibres to become more hydrophilic and the oxidative environment during the course of the reaction leads to the introduction of more carboxyl groups into the lignin structures that largely remain as part of the bleached pulp [44]. It shows peroxide bleaching has a positive effect on the fibre to fibre bonding of CMP durian rind pulp and it supports the increment of physical and mechanical characteristics.

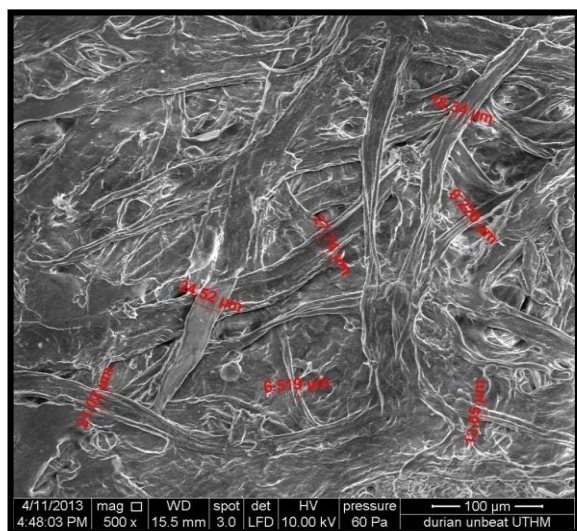


Figure 6 Top SEM Image of Unbleached Durian Rind Paper (500x magnifications) [39]

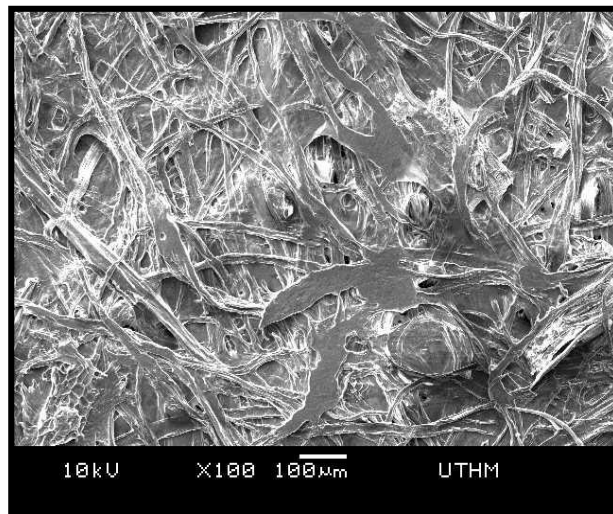


Figure 7 Top SEM Image of Bleached CMP Durian Rind Paper after Stage 3 of Peroxide Bleaching (100x magnifications)

4.0 CONCLUSION

Total chlorine free (TCF) bleaching process with three stages of peroxide (P-P-P) was successfully conducted to unbleached chemi-mechanical pulping (CMP) durian rind pulp. Research findings show that CMP durian rind pulp freeness level increased and drainage time decreased (faster) as P-P-P bleaching sequence was applied. This condition improves the drainage of the pulp and resulting faster paper sheets formation as compared to unbleached CMP durian rind pulp. Mechanical characteristics such as tensile index, tearing index, bursting index, and the number of folds show increment patterns as the P-P-P bleaching sequence was applied to the CMP durian rind pulp. As expected, optical characteristics, especially the brightness of bleached CMP durian rind pulp, increased up to 66.36% (402.7% increment) but the opacity value (70.75%) decreased by 27.6% as the P-P-P bleaching sequence was complete. In future, other improved TCF bleaching process technique and sequence should be taken into consideration as a way to improve the CMP bleached durian rind pulp characteristics. To conclude, this preliminary work indicates that durian rind offers a great potential to be applied as a newly explored material for the pulp and paper industry.

Acknowledgements

The authors would like to thank Universiti Tun Hussein Onn Malaysia (UTHM) for funding this project under UTHM Short Term Grant (STG Vot. 1333) and the Ministry of Higher Education Malaysia under SLAI scheme. The authors would also like to acknowledge Pulp and Paper Laboratory, Biomass Technology Programme, Forest Products Division, Forest Research Institute Malaysia for research facilities and support.

References

- [1] Hedjazi, S., Kordsachia, O., Patt, R., Latibari, A. J. and Tschirner, U. 2009. Alkaline Sulfite-anthraquinone (AS/AQ) Pulping of Wheat Straw and Totally Chlorine Free (TCF) Bleaching of Pulps. *Industrial Crops and Products*. 29(1): 27-36.
- [2] Hosseinpour, R., Latibari, A. J. and Fatehi, P. 2014. Hydrogen Peroxide Bleaching of Canola Straw Chemimechanical Pulp. *BioResources*. 9(1): 1201-1211.
- [3] Ibrahim, R. 2003. Structural, Mechanical and Optical Properties of Recycled Paper Blended with Oil Palm Empty Fruit Bunch. *Journal of Oil Palm Research*. 15(2): 28-34.
- [4] Rushdan, I. Latifah, J. Hoi, W. K. and Mohd Nor, M. Y. 2007. Commercial-scale Production of Soda Pulp and Medium Paper from Oil Palm Empty Fruit Bunches. *Journal of Tropical Forest Science*. 19(3): 121-126.
- [5] Mohd Zukeri, M. R. H., Ghazali, A., Wan Daud, W. R., Ibrahim, R., Ahmad, T. and Ahmad Khan, Z. 2013. Fiber Morphological Transition for Extraordinary EFB Pulp Network: Effects of Extended Beating of EFB Alkaline Peroxide Pulp. *Journal of Industrial Research & Technology*. 3(1): 47-52.
- [6] Wan Rosli, W. D., Mazlan, I., Mohd Asro, R. and Law, K.-N. 2012. Interactions of Oil Palm Fibres with Wood Pulps. *Wood Research*. 57(1): 143-150.
- [7] Zainuddin, Z., Wan Daud, W. R., Ong, P. and Shafie, A. 2011. Wavelet Neural Networks Applied to Pulping of Oil Palm Fronds. *Bioresource Technology*. 102(23): 10978-10986.
- [8] Zainuddin, Z., Wan Daud, W. R., Ong, P. and Shafie, A. 2012. Pulp and Paper from Oil Palm Fronds: Wavelet Neural Networks Modeling of Soda-ethanol Pulping. *BioResources*. 7(4): 5781-5793.
- [9] Wan Rosli, W. D., Mazlan, I., Law, K. N. and Nasrullah, R. 2011. Influences of the Operating Variables of Acetosolv Pulping on Pulp Properties of Oil Palm Frond Fibres. *Maderas. Ciencia y Tecnología*. 13(2): 193-202.
- [10] Masrol, S. R., Ibrahim, M. H. I. Adnan, S. Amir Shah, M. S. S. Main, N. M. Esa, M. F. and Othman, M. H. 2015. Effect of Beating Process to Soda Anthraquinone Pulp of Oil Palm Male Flower Spikes Fibre. *Applied Mechanics and Materials*, 773-774: 158-162.
- [11] Masrol, S. R., Ibrahim, M. H. I., Adnan, S., Amir Shah, M. S. S., Main, N. M., Esa, M. F. and Othman, M. H. 2014. Soda Anthraquinone Pulping of Oil Palm Male Flower Spikes. *Applied Mechanics and Materials*. 660: 373-377.
- [12] Adnan, S., Jasmani, L., Saleh, M. and Mohd Yusoff, M. N. 2004. Suitability of locally Planted Kenaf for Pulp and Paper Applications. *Proceeding of 3rd USM-JIRCAS International Symposium: Lignocellulose: Materials for the Future from the Tropics*. In Cheng L. H. & Tanaka R. (eds.). Penang, Malaysia: Universiti Sains Malaysia. 9-11 March 2004. 54-57.
- [13] Mossello, A. A., Harun, J., Resalati, H., Ibrahim, R., Fallah Shamsi, S. R. and Md Tahir, P. 2010. New Approach to Use of Kenaf for Paper and Paperboard Production. *BioResources*. 5(4): 2112-2122.
- [14] Mossello, A. A., Harun, J., Resalati, H., Ibrahim, R., Md Tahir, P., Fallah Shamsi, S. R. and Mohamed, A. Z. 2010. Soda-anthraquinone Pulp from Malaysian Cultivated Kenaf for Linerboard Production. *BioResources*. 5(3): 1542-1553.
- [15] Mossello, A. A., Harun, J., Ibrahim, R., Resalati, H., Fallah Shamsi, S. R., Md Tahir, P. and Mohad Yusof, M. N. 2010. Evaluation of linerboard Properties from Malaysian Cultivated Kenaf Soda-anthraquinone Pulps Versus Commercial Pulps. *BioResources*. 5(3): 1595-1604.
- [16] Ibrahim, M., Wan Daud, W. R. and Law, K.-N. 2011. Comparative Properties of Soda Pulps from Stalk, Bast and Core of Malaysian Grown Kenaf. *BioResources*. 6(4): 5074-5085.
- [17] Main, N. M., A Talib, R., Ibrahim, R., Abdul Rahman, R. and Mohamed, A. Z. 2014. Suitability of Coir Fibers as Pulp and Paper. *Agriculture and Agricultural Science Procedia*. 2: 304-311.
- [18] Main, N. M., A Talib, R., Ibrahim, R., Abdul Rahman, R. and Mohamed, A. Z. 2015. Linerboard made from Soda-anthraquinone (Soda-AQ) treated Coconut Coir Fiber and Effect of Pulp Beating. *BioResources*. 10(4): 6975-6992.
- [19] Mohamad Jani, S. and Rushdan, I. 2014. Effect of Bleaching on Coir Fibre Pulp and Paper Properties. *Journal of Tropical Agriculture and Food Science*. 42(1): 51-61.
- [20] Mohd Hassan, N. H., Muhammed, S. and Ibrahim, R. 2013. Effect of Soda-anthraquinone Pulping Conditions and Beating Revolution on the Mechanical Properties of Paper made from *Gigantochloa scortechinii* (Semantan bamboo). *The Malaysian Journal of Analytical Sciences*. 17(1): 75-84.
- [21] Mohd Hassan, N. H., Muhammed, S. and Ibrahim, R. 2014. Properties of *Gigantochloa scortechinii* Paper Enhancement by Beating Revolution. *Journal of Tropical Resources and Sustainable Science*. 2: 59-67.
- [22] Mohd Hassan, N. H. Muhammed, S. and Ibrahim, R. 2015. Properties of Corrugated Paper from Recycled Paper Blended with Semantan bamboo. *Australian Journal of Basic and Applied Sciences*. 8(9): 113-117.
- [23] Daud, Z., Mohd Hatta, M. Z., Mohd Kassim, A. S., Awang, H. and Aripin Mohd, A. 2014. Exploring of Agro Waste (Pineapple Leaf, Corn Stalk, and Napier Grass) By Chemical Composition And Morphological Study. *BioResources*. 9(1): 872-880.
- [24] Daud, Z., Mohd Hatta, M. Z., Mohd Kassim, A. S. and Aripin Mohd, A. 2013. Suitability of Malaysia's Pineapple Leaf and Napier Grass as a Fiber Substitution for Paper Making Industry. *EnCon 2013, 6th Engineering Conference, "Energy and Environment"*. Kuching, Sarawak. 2-4 July 2013. 1-4.
- [25] Jun, T. Y., Arumugam, S. D., Abdul Latip, N. H., Abdullah, A. M. and Abdul Latif, P. 2010. Effect of Activation Temperature and Heating Duration on Physical Characteristics of Activated Carbon Prepared From Agriculture Waste. *EnvironmentAsia*. 3(Special Issue): 143-148.
- [26] Chung, F. Botany of the Common Durian: Durian Tree. *Durian Information - A Durian Blog Devoted to 'The King of Fruits'*. [Online]. From: <http://durianinfo.blogspot.my/p/origin-and-botany-of-durian.html>. [Accessed on 3 January 2016].
- [27] Department of Agriculture Malaysia (DOA). Varieti Durian Popular. *Mengenal Varieti Durian Popular di Malaysia*. [Online]. From: <http://www.doa.gov.my/documents/10157/bf38cd7a-cca9-401c-beec-ad4c4887414c> [Accessed on 3 January 2016].
- [28] Ministry of Agriculture and Agro-Based Industry Malaysia (MOA). 2015. *Agrofood Statistics 2014*. Putrajaya: Information Management and Statistics Section, Policy and Strategic Planning Division.
- [29] Hokputsa, S., Gerddit, W., Pongsamart, S., Inngjerdigen, K., Heinze, T., Koschella, A., Harding, S. E. and Paulsen, B. S. 2004. Water-soluble Polysaccharides with Pharmaceutical Importance from Durian Rinds (*Durio zibethinus* Murr.): Isolation, Fractionation, Characterisation and Bioactivity. *Carbohydrate Polymers*. 56(4): 471-481.
- [30] Penjumras, P., Abdul Rahman, R. B., A Talib, R. and Abdan, K. 2014. Extraction and Characterization of Cellulose from Durian Rind. *Agriculture and Agricultural Science Procedia*, 2: 237-243.

- [31] Mat Amin, A., Ahmad, A. S., Yin Yin, Y., Yahya, N. and Ibrahim, N. 2007. Extraction, Purification and Characterization of Durian (*Durio zibethinus*) Seed Gum. *Food Hydrocolloids*. 21: 273-279.
- [32] Hameed, B. H. and Hakimi, H. 2008. Utilization of Durian (*Durio zibethinus* Murray) Peel as Low Cost Sorbent for the Removal of Acid Dye from Aqueous Solutions. *Biochemical Engineering Journal*. 39(2): 338-343.
- [33] Zddin, Z. and Risby, M. 2010. Durian Husk As Potential Source For Particleboard Industry. *AIP Conference Proceedings*. 1217: 546-553.
- [34] Brown, M. J. 1997. *Durio - A Bibliographic Review*. New Delhi, India: International Plant Genetic Resources Institute Office for South East Asia.
- [35] Linda Jana, S. Nurcahyani Oktavia, H. and Dewi, W. 2010. *The Using of Durian Peels Trashes as a Potential Source of Fiber to Prevent Colorectal Cancer*. Surakarta: Medical Faculty, Sebelas Maret University.
- [36] Ismail, I., Mohd Nor, A. B., Hamid, M. F. and Ismail, A. R. 2015. The Impact of Durian Rind in Water-based Mud in Combating Lost Circulation. *Jurnal Teknologi*. 74(1): 51-56.
- [37] Foo, K. Y. and Hameed, B. H. 2011. Transformation of Durian Biomass Into a Highly Valuable End Commodity: Trends and Opportunities. *Biomass and Bioenergy*. 35(7): 2470-478.
- [38] Nur Aimi, N., Anuar, H., Manshor, M. R., Wan Nazri, W. B. and Sapuan, S. M. 2014. Optimizing the Parameters in Durian Skin Fiber Reinforced Polypropylene Composites by Response Surface Methodology. *Industrial Crops and Products*. 54: 291-295.
- [39] Masrol, S. R., Ibrahim, M. H. I. and Adnan, S. 2015. Chemi-Mechanical Pulping Of Durian Rinds. *Procedia Manufacturing*. 2: 171-180.
- [40] Wang, X., Hu, J., Liang, Y. and Zeng, J. 2012. TCF Bleaching Characteristics of Soda-Anthraquinone Pulp from Oil Palm Frond. *BioResources*. 7(1): 275-282.
- [41] Roncero, M. B., Torres, A. L., Colom, J. F. and Vidal, T. 2005. The Effect of Xylanase on Lignocellulosic Components During The Bleaching of Wood Pulp. *Bioresource Technology*. 96: 21-30.
- [42] Chen, Y., Wan, J., Dong, X., Wang, Y. and Huang, M. 2015. Fiber Properties of De-inked Old Newspaper Pulp After Bleaching with Hydrogen Peroxide. *BioResources*. 10(1): 1857-1868.
- [43] Zeinaly, F., Shakhesh, J. and Zeinali, N. 2013. Multi Stage Peroxide and Activated Peroxide Bleaching of Kenaf Bast Pulp. *Carbohydrate Polymers*. 92(2): 976-981.
- [44] Liu, Z., Ni, Y., Li, Z. and Court, G. 2005. Peroxide of Low-freeness TMP. *Pulp & Paper Canada*. 106(3): 63-66.
- [45] El-Sakhawy, M. 2005. Effect of Bleaching Sequence on Paper Ageing. *Polymer Degradation and Stability*. 87(3): 419-423.
- [46] Li, L., Lee, S., Lee, H. L. and Youn, H. J. 2011. Hydrogen Peroxide Bleaching of Hardwood Kraft Pulp with Adsorbed Birch Xylan and Its Effect on Paper Properties. *BioResources*. 6(1): 721-736.