The Physicochemical Characteristics of Residual Oil and Fibers from Oil Palm Empty Fruit Bunches

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Abundant oil palm empty fruit bunches (OPEFB) generated from the palm oil mill industry create huge problems for the environment and the palm oil mill itself. Despite the importance of determining the amount of oil left in the OPEFB, little research of that nature has been reported. This study describes the oil content and physicochemical characteristics of OPEFB fibers, detection of oil attachment on the fiber's surface using sudan red dye, contact angle values, and also the quality of the residual oil. The OPEFB fibers, which are normally used as mulch for the palm oil mill, have been found to be a rich source of lignocellulosic materials, especially cellulose, which constitutes 33.70 to 35.10% for a press-shredded fiber. Residual oil (3 to 7% on dry basis) extracted from the OPEFB exhibits good quality parameters such as deterioration of bleachability index (DOBI), free fatty acid (FFA), and peroxide value (PV). The DOBI values were still in the acceptable range, which is from 1.94 to 2.43, while the PV results are within the range of about 1.84 to 2.80 meq/kg. The major fatty acids of the residual fiber oil were palmitic and oleic acids, at 39.77% to 39.89% and 39.55% to 42.60%, respectively. There were no significant changes in the macronutrients and quality of the OPEFB residual oil. Therefore, the residual oil from the OPEFB should be recovered and reused as a raw material for industrial applications, boosting the oil extraction rate (OER) in the palm oil industry.

Keywords: Crude palm oil; Oil palm empty fruit bunches; Physicochemical characterization; Crude palm oil quality; Oil extraction rate

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INTRODUCTION

Malaysia, as one of the biggest exporters of palm oil, contributes about 51% of the world's edible crude palm oil and accounts for 62% of world exports. In the processing of palm oil, there are two types of products: crude palm oil (CPO) and palm kernel oil (PKO). However, the major problem with this process is the huge amount of wastes produced in the form of oil palm empty fruit bunches (OPEFB), mesocarp fiber (MS), decanter cake (DC), and palm oil mill effluent (POME) solids (Baharuddin *et al.* 2009; Sulaiman 2009; Baharuddin *et al.* 2010; Baharuddin *et al.* 2011). From this biomass, the mill generates about 1.5 t of oil palm empty fruit bunches per hectare of oil palm annually (Abd Majid *et al.* 2012). The OPEFB is generated after the stripping process, in which the sterilized fruits are separated from the bunch stalks. As the major waste of oil palm industry, OPEFB is currently being applied as a wood composite, fiberboard, soil mulching material in the oil palm estate, and as a composting material (Baharuddin *et al.* 2009; Kheong *et al.* 2010; Ibrahim *et al.* 2009). OPEFB is made up of two component parts, which are present in the proportions of 20 to 25% of spikelet and 75 to 80% of stalk (Han and May 2012). Each of these components can be regarded as lignocellulosic biomass, which is composed of lignin, hemicellulose, and cellulose (Siti Aisyah *et al.* 2014). A study conducted by Ngan 2005 shows that OPEFB does contain a significant amount of oil. Total oil (residual oil) ranged from 0.28 to 1.38% with a mean of 0.75% relative to dry OPEFB. The presence of residual oil on the surface of OPEFB is a result of the stripping and threshing process in the mill. In general, the lignocellulosic material of OPEFB has the ability to adsorb and retain certain amount of oil inside and on the surface of its matrix fiber through an adsorption process. The residual oil diffuse to the external surfaces of the fibers, then the migration of oil from the external surface of material to the pores within the fibers, and lastly the oil will remain on the surface of the pores (Karan *et al.* 2011). The amount of oil entrapped on the fiber depends on the consequence of sterilization on the fruit (Abd Majid *et al.* 2012).

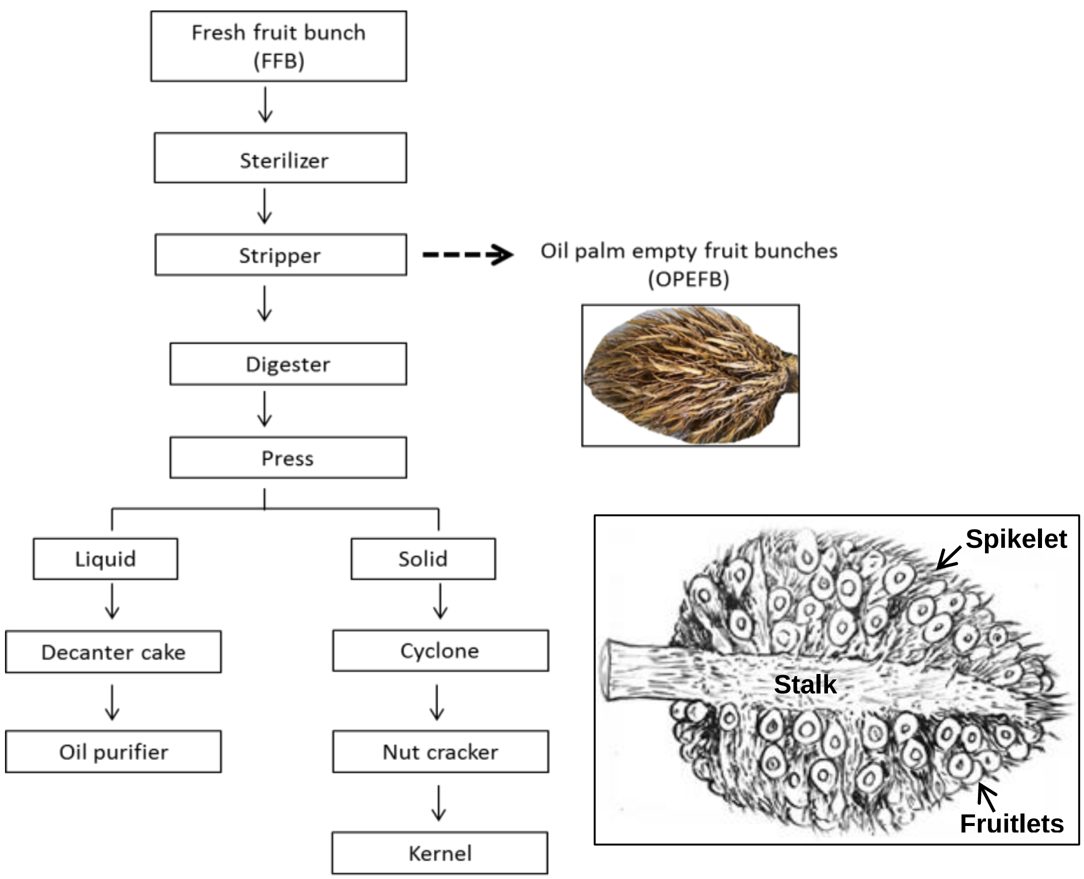

Fig. 1. Material flow chart of a palm oil mill and components of FFB (re-drawn from Simarani *et al*. 2009).

To date, there has been very little research conducted on recovery of residual oil from OPEFB. Detailed study on the exact location of mainly residual oil entrapped had never been conducted, either on the spikelet or stalk. The current technology applied to recover the remaining oil from OPEFB is through the pressing and shredding processes. The OPEFB is transported into a pressing machine, where it is screw pressed, and then it is shredded for easier handling. The capacity of this process can be up to 5 tons OPEFB per hour (Jorgensen 1985). The product generated from this process is known as press-shredded OPEFB. The oil retained on the OPEFB, which translates as oil losses, has a negative impact on the total oil extraction rate (OER) of palm oil mill industry. The loss of oils from OPEFB is a course of concern for the palm oil industry, as it reflected the overall efficiency of the mill (Sahad *et al*. 2014). It is believed that the amount of residual oil that could be recovered from the OPEFB could potentially increase the OER. Therefore, this paper aimed to study the quantity and qualities of oil recovered by individual spikelet and stalk in comparison to the oil from press-shredded OPEFB. In addition, the physico-chemical properties of the spikelet and stalk were evaluated. Then, the analysis using contact angle measurement was conducted to give information regarding surface area, contact angle, and wetting behavior between spikelet and press-shredded OPEFB. This could give better understanding on mechanisms of adsorption process of residual oil and OPEFB fiber of both spikelet and press-shredded.

EXPERIMENTAL

Materials

OPEFB samples were collected from Besout Palm Oil Mill, Felda Besout, Perak, Malaysia. Two types of samples were taken in the form of whole bunches and press-shredded fibers. The OPEFB were taken directly from the conveyer after stripping process, brought back and stored in a freezer at -20 °C. The bunches were separated into two parts, namely: stalk and spikelet and dried at 90 °C for 24 h for the purpose of analyses. A grinder with a screen size of 1.0 mm was used to reduce the size of samples. Crude Palm oil (CPO) and press-shredded oil samples were taken from Besout Palm Oil Mill, Felda Besout, Perak. Meanwhile, spikelet oil was collected by washing using a high pressure jet process with water and steam.

Methods

Analysis of lignocellulosic content

The compositions of cellulose, hemicellulose, and lignin of OPEFB were analyzed via acid detergent fiber (ADF), neutral detergent fiber (NDF), and acid detergent lignin (ADL) methods (Baharuddin *et al*. 2012). The percentage of cellulose, hemicellulose, and lignin were then calculated using the equations below:

$$\text{Cellulose (\%)} = \text{ADF} - \text{ADL} \quad (1)$$

$$\text{Hemicellulose (\%)} = \text{NDF} - \text{ADF} \quad (2)$$

$$\text{Lignin (\%)} = \text{ADL} \quad (3)$$

Inorganic element analysis

The composition of press-shredded, stalk and spikelet of OPEFB samples were analyzed using CNHS analyzer to determine the contents of nutrients. Contents of heavy metal elements were measured using an inductively coupled plasma-optical emission spectrometer (ICP-OES) (Perkin Elmer, USA).

Oil palm empty fruit bunches (OPEFB) oil content

A Soxhlet extraction method was performed in this experiment. Approximately 1 g of samples were weighed and placed into an extraction thimble for each extraction process. Hexane solvent was used to extract the oil residues of OPEFB fibers. The extraction was carried out for 8 h to allow complete extraction. Then, the collected liquid mixture was placed in the rotary vapor at 70 °C to complete the evaporation of hexane. Then, the remaining oil was placed in the oven for 3 h for complete removal of hexane. The oil content is taking account of the weight loss from the difference between initial and final weight. This study was conducted in triplicate.

$$\text{Oil content (\%)} = \frac{Thimble\ with\ oil\ (g) - Thimble\ (g)}{Sample\ (g)} \times 100\% \tag{4}$$

Characterization of residual oil

The oil samples were analyzed for determination of the deterioration bleachability index (DOBI), FFA, PV, total carotene content, moisture, and impurities (MPOB Test Method 2004). The derivatives of fatty acid were analyzed by Gas Chromatography (GC). The separation was performed using capillary column BPX 70: 30 m L x 0.25 µm x 0.32 µm ID (equivalent column to stabile wax-Crossbond Carbowax PEG, Agilent) with programmed temperature as follows: oven temperature: 100 ºC; initial temperature: 100 ºC; final temperature: 230 ºC; injector temperature: 250 ºC; detector temperature: 250 ºC; carrier gas: helium.

Contact angle measurement

A contact angle goniometer (Data Physics OCA15ES, Germany) was employed to measure the contact angle and absorption rate of CPO with OPEFB fibers. Prior to the analysis, the OPEFB fibers were categorized into two different parts: spikelets of OPEFB and press-shredded OPEFB.

The materials were injected using a syringe at a dosing volume of 1 µL onto the samples surface as sessile drop. Once the droplet was stable, the contact angle was measured. The measurement was repeated three times.

Oil observation on OPEFB fibers by sudan red

Lipophilic sudan red g (sigma) was prepared according to Brundrett *et al.* (1991) to observe the oil attachment on OPEFB fibers. Three categories of OPEFB were used: spikelet, stalk, and press-shredded.

Each sample was immersed with a few drops of Sudan red dye solution. Sudan dye is used due to its lipophilic (lipid- loving) nature, where it will move into the oil and color it red so that it can be observed under the fluorescence light.

RESULTS AND DISCUSSION

Properties of Oil Palm Empty Fruit Bunches (OPEFB)

The proximate analysis encompasses the quantitative determination of nitrogen content, cellulose, hemicellulose, lignin, nutrients, and metal elements between types of fiber from OPEFB; press-shredded, spikelet, and stalk, as shown in Table 1. The proximate analysis reveals that the press-shredded OPEFB fibers contained the highest percentage of cellulose and hemicellulose, accounting for 33.70% to 35.10% and 26.50% to 26.90%, respectively. This was expected, since press-shredded OPEFB is a mixture of two types of fibers, those from spikelet and stalk. The bunch is made up of a main stem called stalk and numerous spikelets on its surface. The fruitlets, which were attached onto the spikelets, were detached from the bunch during the threshing process. It can be seen clearly that the spikelets contained relatively high amounts of lignin ranging from 23.50% to 23.60%. Meanwhile, cellulose and hemicellulose were within the range of 20.60% to 20.70% and 23.90% to 25.10% respectively. On the other hand, stalk was found to have a high cellulose content ranging from 26.90% to 28.80% but a low lignin content ranging from 11.50% to 12.10%. A comparison of this value was in agreement with the previous study conducted by Zaharah and Lim (2000). It is apparent that the percentage of lignin in the stalk fibers was half of the amount of cellulose composition in the material, except for the spikelet fibers. Low lignin content is an advantage, since the recovering of almost completely total cellulose make it economical feasible for future usages (Piarpuzan *et al.* 2011).

Nonetheless, inadequate studies have been paid related to the composition of lignocellulosic compounds from stalk and spikelet. The stalk, which is rich in cellulose, has the potential to be utilized in the production of value-added products such as biosugar and bioethanol. Mat Som *et al.* (2012) have carried out a study on conversion of cellulose into a high value product, cellulose ether, which can contribute towards the growth of the oil-palm based specialty chemicals industry. Cellulose, hemicellulose, and lignin, which are associated with each other, are three different types of polymers. Some pretreatment should be conducted to recover oil, as well as to remove the hemicellulose and lignin, to enhance the effective extraction of cellulose. Since both stalk and spikelet have valuable cellulose, the removal of oil from OPEFB might make the process much easier, as the oil hinders the extraction process of cellulose. The residual oil from the fibers can be routed back to the mill, where it will increase the oil extraction rate (OER), which is very crucial in the palm oil industry. OER is an indicator to measure the actual amount of oil obtained from a known amount of fresh fruit bunch (FFB) that is processed.

The ultimate analysis of press-shredded, spikelets, and stalk fibers showed a carbon and nitrogen content in the ranges of 43.62% to 52.68% and 0.69% to 0.96%, respectively. These values are within the range to those previously determined (Baharuddin *et al.* 2013). A higher carbon content tends to increase the calorific value of the OPEFB, making it very suitable for gas fuel production (Mohammed *et al.* 2012). The most abundant metal element found in these three fibers was Ca, which was 0.16 to 0.17% for press-shredded, 2.41% for spikelet, and 0.27% for stalk. Sources of C, N, nutrients, and metal elements are important for the bioconversion purposes in composting, mulching, and animal feed processing. All these elements can contribute towards the enhancement of soil fertility and plants. However, if the oil is still retained in the fibers, then it may affect the soil and cause another pollutant. Thus, the remaining oil retained on the OPEFB fibers should be recovered before it can be used for other purposes. If the industries realize the profit that can be generated from the OPEFB, then they would fully utilize both the residual oil and the fibers.

Table 1. Mass Fraction Composition of Raw Press-shredded, Spikelet, and Stalk of the OPEFB

Main fraction	Composition (%)					
	Press-shredded (This study)	Press-shredded (Literature)	Spikelet (This study)	Spikelet (Literature)	Stalk (This study)	Stalk (Literature)
Cellulose	33.70-35.10	38.10-63.00[a,b,c,d]	20.60-20.70	-	26.90-28.80	-
Hemicellulose	26.50-26.90	20.10-35.30[a,b,c,d]	23.90-25.10	28.90[e]	24.00-28.80	28.70[e]
Lignin	12.00-12.90	10.50-36.60[a,c,d]	23.50-23.60	29.10[e]	11.50-12.10	28.10[e]
Ash	4.70-5.00	-	8.11-10.80	6.80[e]	5.05-6.30	18.60[e]
Others (extractives)	21.70-21.80	-	23.19-25.23	-	28.30-28.40	-
Nitrogen	0.69-0.72	0.44-0.80[d]	0.91-0.96	0.50[e]	0.70-0.71	0.70[e]
Carbon	50.67-52.68	44.30–48.79[c,d,f]	50.23-51.67	51.10[e]	43.62-45.01	48.60[e]
Ca	0.16-0.17	0.34[d]	2.41	2.0[e]	0.27	0.27[e]
P	0.03-0.06	0.06[d]	0.05	0.19[e]	0.07-0.10	0.30[e]
Cu	0.0001	-	0.00006	-	0.00006	-
Mg	0.008-0.09	0.10[d]	0.12	0.17[e]	0.13-0.14	0.15[e]

References: [a]Mohd Zainudin *et al.* (2012), [b]Law *et al.* (2007), [c]Kelly-Yong *et al.* (2007), [d]Baharuddin *et al.* (2013), [e]Zaharah & Lim (2000), [f]Mohammed *et al.* (2012).
*Each parameter was analyzed in duplicate.

Comparison of Oil Content Analysis Among Press-Shredded, Stalk, and Spikelet of the OPEFB

The oil content in press-shredded, spikelet, and stalk of the OPEFB are shown in Table 2. Oil content indicates that oil still remained on the fibers after the milling process. The oil content for spikelet, stalk, and press-shredded ranged from 7.39%, 2.04%, and 3.61%, respectively. The oil content in the spikelet was higher than that of the stalk and the press-shredded. Interestingly, this data is supported by the results shown in Fig. 2. The localization of oil on the surface detected by red sudan dye under the fluorescent light in Fig. 2 indicates that the most significant oil attachment is on the surface of the spikelet, followed by press-shredded and then stalk. Sudan dye, which has a lipophilic (oil loving) characteristic, was used to detect the presence of oil or lipid on the fibers (Brundrett *et al.* 1991). This can be clearly seen from the retained oil on the outer layer of the fiber due to the adsorption process between oil and fibers. Karan *et al.* (2011) reported in their study that the oil sorption by raw cotton fiber is due to the hydrophobic interactions and Van der Waals forces between the hydrocarbon elements. The Van der Waals interaction is a weak bonding and can be easily broken with a physical disruption. Since spikelet fiber is located at the outer layer of the bunches and nearest to the fruitlets, it retained the most of oil from the mesocarp of the fruitlets.

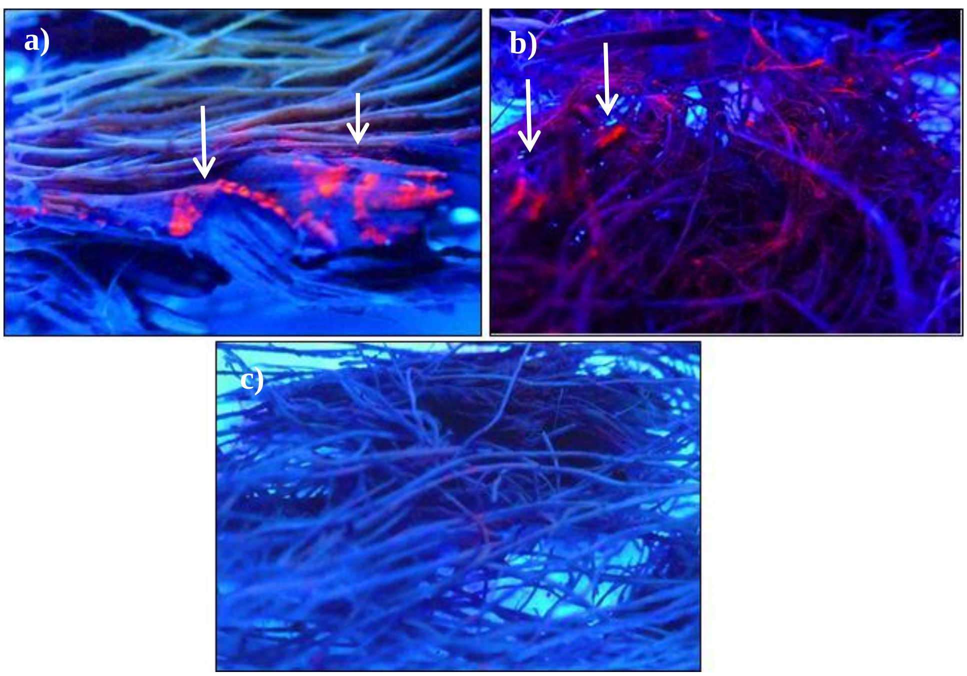

Fig. 2. Morphological picture under fluorescence light of a) spikelet, b) press- shredded, and c) stalk of the OPEFB. The arrow indicates the presence of oil on the surface of fibers.

Table 2. Oil Content in Press-shredded, Spikelet, and Stalk of the OPEFB

Materials	Weight sample dry (kg)	Weight oil (kg)	Total oil (%)
Spikelet	1.24±1.04	0.11±0.08	7.39±3.45
Stalk	1.03±0.85	0.01±0.009	2.04±2.31
Press-shredded	0.02	0.0007	3.61±0.34

These results differ from the published data (Ngan 2005), in which the oil content obtained was in the range of 3.5% to 12.0% for dry OPEFB with a mean of 8.6% for a mixture of spikelet and stalk. It also had been stated that the accepted ranges of oil content in the OPEFB waste generated from the palm oil mill industry is 0.4% to 0.5% or about 5.0% for dried OPEFB (Ngan 2005). The value of oil content for stalk and press-shredded OPEFB were within the accepted range as required by the oil palm industry, but the oil content was a bit higher for the spikelet. Oil content in spikelet indicates potential of oil losses in the process. It is crucial to ensure that the oil loss from the OPEFB is kept to a minimum. Therefore, higher oil content of spikelet is considered not good. Most of the OPEFB that contains significant amounts of oil has been neglected by the industry without realizing the potential that can be generated. If most of the oil can be recovered from these wastes, it may contribute to the increasing of OER and bring additional income to the palm oil industry.

Contact Angle Measurement

The contact angle provides a measure of the degree of wetting when a solid and liquid interact with each other. Images of static contact angle between two types of liquid in contact with press-shredded and spikelet OPEFB fibers are shown in Fig. 3. The contact angle test was not performed for the stalk due to its low content of oil. In this study, the presence of waxy material on the fibers can also be detected with the contact angle test by observing the shape of droplets, in addition to the contact angle value. The images taken during the first contact of the target liquid with the surface of material show that the oil droplet formed a cylindrical shape on the surface of the spikelet, but not on the surface of press-shredded samples. It can be seen that the contact angle value for spikelet was higher compared to those of the press-shredded when in contact with oil. The contact angles measured for the images of spikelet and press-shredded fibers were 64.60° and 48.90°, respectively.

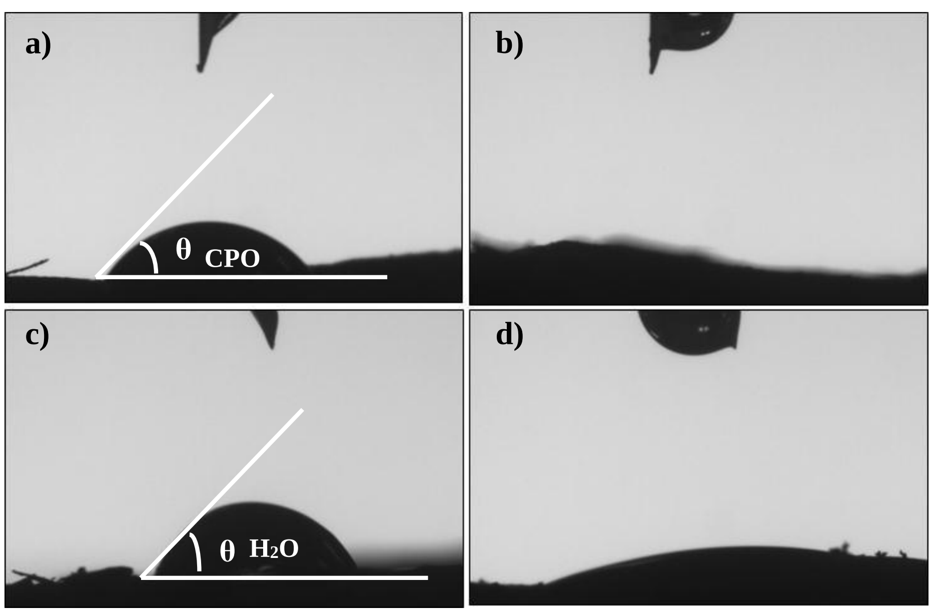

Fig. 3. Static contact angle of CPO with a) spikelet with CPO, b) Press-shredded with CPO, c) spikelet with water, and d) press-shredded with water. θ indicates the value of contact angle

After a few seconds, the values of contact angles for spikelet and press-shredded fibers with CPO were reduced to 19.77° and 0°. The profile of this phenomenon is shown in Fig. 4. In another study, Carmody *et al.* (2007) found that the changes of contact angles show the degree of 'spreading' of the liquid on the material's surface. The CPO spreads on the surface of the fibers, thus lowering its contact angle value. The CPO on the surface had penetrated into the inner parts of the fiber

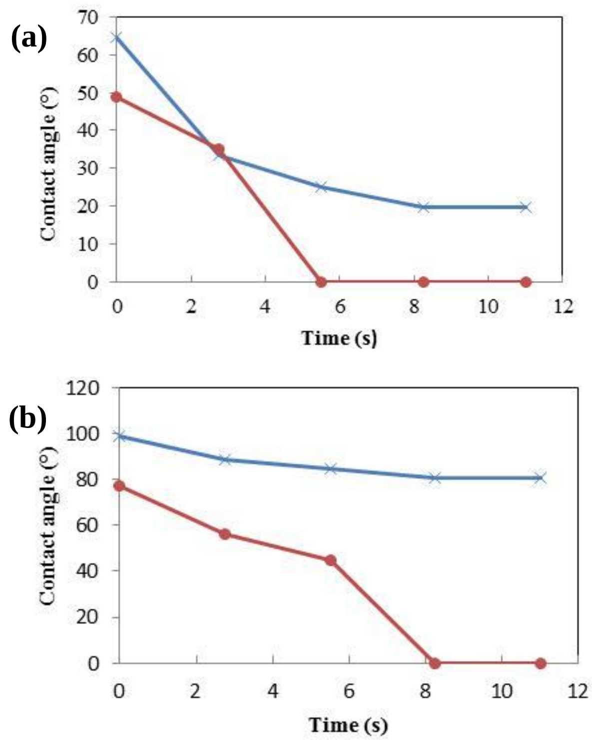

Fig. 4. Measured contact angles over time for spikelet and press-shredded of the OPEFB with a) contact of water and b) contact of CPO. Blue colour indicates spikelet fibers and red colour for press-shredded fibers.

According to Carmody *et al.* (2007), there are two main adsorption mechanisms that take place on the fiber's surface, which are face adsorption where the oil is coating the fibers and uptake of oil by interfiber capillaries. The fibers with low contact angle value will have more interaction with the oil. The value of the contact angles for the spikelet is much higher than those of the press-shredded due to the wax coating that covers on its surface. Initially, the oil was adsorbed on the fibers surface, due to the capillary action and van der Waals forces between the oil and the wax that exist on the fiber's surface (Lim and Huang 2007). The spikelet allowed oil to be retained on its surface due to compatibility, because both the spikelet and oil are hydrocarbons. However, the samples of press-shredded were in the form of loosened fibers and allowed the penetration of oil through the internal capillary structure and therefore absorb more oil. According to Karan *et al.* (2011), the fibers which have a higher porosity will have higher initial pick up but poor retention capacity. This finding is also supported by a study done by Huang and Lim (2006), which stated that the fibers with water repellent and waxy surface characteristics will contribute to the higher oil removal efficiencies. Thus, the oil adsorbed on the spikelet fibers can be easily recovered, while an additional method should be applied for better recovery of press-shredded oil.

On the other hand, it can be observed that the water tended to remain in the shape of spherical droplets on the surface of spikelet fibers, but not on the press-shredded fibers. The contact angle value for the spikelet with water was 99.13° and for press-shredded was 77.03°. Generally, the liquid tends to form droplets on the surface if $\theta > 90°$. Then if the $\theta < 90°$, the liquid tends to spread out over the surface. Lastly, if it gave values of $\theta \approx 0$, then the liquid forms a thin film (Carmody *et al.* 2007). It is expected that the water will form spherical droplets on spikelets because of the high surface tension of water and the relatively low energy of the spikelet's surface. The water did not spread on the spikelet's surface, which means that the material is relatively hydrophobic (water repelling) (Carmody *et al*. 2007). Karan *et al.* (2011) stated, in their study related to kapok fibers, that water cannot easily penetrate through the fibers due to the presence of negative capillary entry pressure arising from the high value of contact angle (> 90°). After a few seconds, the contact angle values for spikelet and press-shredded fibers were reduced to 80.80° and 0°. The contact angle obtained at steady-state conditions for spikelet indicates that the water still remains on the surface and it cannot easily penetrate into the fibers. This was due to the existence of waxy materials on the fibers surfaces, which make them have water repellent properties. After a period of equilibration, if the liquid still remains on the surface, that means that the material is relatively hydrophobic. Press-shredded OPEFB exhibited a lower contact angle, which must be due to the conditions of the fibers itself. Even though the fibers did not absorb the water, the diffusion of water through the space between the fibers had occurred and transferred the liquid into the interior of the fibrous mass. Karan *et al.* (2011) reported that oil with low viscosity will quickly move into the fibrous materials as well as on the surface, but it desorbs easily during the drainage period. It is apparent that the value of contact angles for the spikelet was much higher compared to the press-shredded. Contact angles between oil at the solid surfaces indicated that spikelet has less attraction with the oil compared to the press-shredded. It follows that the recovery of residual oil from spikelet will be much easier.

Physicochemical Quality Parameters of Crude Palm Oil (CPO)

Table 4 shows the physicochemical quality parameters of the samples of CPO from the mills, both the press-shredded and the spikelet. The quality of CPO is essential in determining its suitability for further applications. The basic tests that were performed for characterization of oil include the determination of free fatty acids (FFA), deterioration of bleach ability index (DOBI), peroxide value (PV), carotene content, moisture, impurities, and fatty acid compositions. In the palm oil mill industry, the information of FFA and DOBI are required during the trading of oil (Abd Wafti *et al.* 2011). Table 4 shows that the value of FFA for spikelet residual oil was higher compared to those of CPO from mill and press-shredded sources. For this study, CPO from mill, the residual oil from press-shredded, and spikelet OPEFB exhibited FFA of 4.12%, 5.67%, and 6.36%, respectively. The general value for FFA in the mill must not exceed 5% of standard level, since it is the most important parameter of crude oil quality. A high concentration of FFA in the residual oil of press-shredded and spikelet could be associated with the duration of storage (Ohimain *et al.* 2013), the handling practiced during processing, and the exposure with a large amount of water.

In order to control the quality of oil, all samples were quickly dried to remove the moisture within the fibers before analysis. Moisture will allow the growth of the microorganisms and acts as a source of water molecules for undesired chemical reactions (Ariffin 2000). The FFA occurs due to the fat-splitting reactions in which glyceride molecules combine with water to yield diglyceride, monoglyceride, and free glycerol.

The DOBI values of the residual oil from both spikelet (2.43) and press-shredded (2.42) was comparable with the CPO from the mill (2.45). The DOBI is used to determine the ease of bleaching of crude palm oil during refining and can be easily obtained by simple spectrometric measurement. CPO samples with a DOBI values between 3 to 4 are easily bleached to lighter colour oil, while a value less than 2 implies that the oil is difficult to refine (Siew 2000). A CPO with a high value of DOBI is higher in quality. The residual oil from spikelet was still within the recommended limits and can be categorized as good oil, but the residual oil from press-shredded required further treatment to increase the DOBI level.

The peroxide value (PV) for the residual oil from spikelet recorded in this study (2.80 meq/kg) was higher than the residual oil from the press-shredded (1.84 meq/kg). The PV value for residual oil of press-shredded was not too far from the value of commercial CPO (1.80 meq/kg) of the mill. Aletor *et al.* (1990) reported that the acceptable limit for PV in the application of palm oil is 0 to 5 meq/kg. This indicates that both residual oils were still in the accepted range of good quality oil. The PV indicates the extent of primary oxidation and measures the amount of oxygen uptake by the unsaturated sites in the oil, resulting in the formation of hydroperoxides and peroxides. In addition, PV value can be used as an indicator of the early stages of rancidity (Ohmain *et al.* 2013).

It was found that the total carotene content for residual oil from both press-shredded and spikelet were comparable (409.02 ppm and 405.37 ppm). These values were quite far from the value of carotene content for CPO of the mill, which is 480.05 ppm. The value of carotene content is much higher for the original CPO because it was extracted directly from the fruitlets which are the rich source of carotene. According to Ahmad *et al.* (2008), the concentration of carotene in the crude palm oil is within the ranges of 400 to 3500 ppm. In the present study, both of the residual oils confirmed the presence of carotenes due to the colour of deep red similar to the CPO from the mill. The carotenes are important minor constituents as they are known to have provitamin A and also possess certain anti-carcinogenic properties. According to Abd Majid *et al.* (2012), CPO contains 15 to 300 times more provitamin A compared to carrot, leafy green vegetables, and tomato.

The moisture content and impurity level for both residual oil from press-shredded and spikelet were higher than the standard levels of 0.01 to 0.04% and 0.1% for moisture and impurities content. Generally, CPO had the lowest moisture content (0.01%) with the lowest impurities (0.1%), whereas the moisture content for residual oil from spikelet and press-shredded was 0.39% and 4.91%. The high moisture content was directly proportional to the high water activity that later support the growth of microorganisms in the oil samples. Microorganisms present in the oil attack the material, leading to the hydrolysis of the oil, hence increasing the value of FFA (Ariffin 2000). The residual oil from press-shredded had an impurity value of 0.78%, similar to the residual oil from spikelet, while CPO had a value of 0.10%.

Table 4. Physicochemical Quality Characteristics of Crude Palm Oil (CPO) from the Mill, and Residual Oil from Press-shredded and Spikelet

Parameter	CPO from mill (This study)	Residual oil from press-shredded OPEFB (This study)	Residual oil from spikelet OPEFB (This study)
FFA (%)	4.12	5.67	6.36
DOBI	2.45	2.42	2.43
PV (meq/kg)	1.80	1.84	2.80
Carotene (ppm)	480.05	409.02	405.37
Moisture (%)	0.01	0.39	4.91
Impurity (%)	0.10	0.78	0.78
Fatty acid (%)			
C10:0 caprylic	0.01	ND	ND
C12:0 lauric	0.10	0.07	ND
C14:0 myristic	0.94	0.84	0.91
C16:0 palmitic	42.84	39.77	39.89
C16:1 palmitoleic	0.19	0.25	ND
C18:0 stearic	4.39	3.99	4.14
C18:1 oleic	40.23	42.60	39.55
C18:2 linoleic	10.47	11.49	10.68
C18:3 linolineic	0.31	0.33	0.31
C20 arachidic	0.37	0.36	0.43
C22 behenic	0.07	0.07	ND
C24 lignoceric	0.10	ND	4.09

Each parameter was analyzed in duplicate. ND=not detected

The higher moisture and impurity content for both residual oils would appear to be related to the method of extraction during the experimental work. The processing operation to recover CPO is automatically controlled to ensure smooth and efficient operation, leaving behind any impurities at the bottom during the skimming process. The moisture and impurities are the most important quality parameters, as both will affect the crude and any finished products. This is because the excessive impurities present in the oil, especially iron, will catalyze the oxidation process of the oil. Meanwhile, if unnecessary moisture is present, it will hydrolyze the oil and cause an increase value of FFA. Therefore, in this study, the high value of FFA was higher in the press-shredded and spikelet oil. It is speculated that this may be related to the high value of moisture content

In this study, the fatty acid composition of residual oil from press-shredded and spikelet were compared with the CPO from the same mill. The major fatty acids in residual oil of press-shredded and spikelet sample were palmitic acid (39.77%, 39.89%), and oleic acid (42.60%, 39.55%). Generally, the fatty acids compositions for both residual oil were quite similar to the original CPO. The percentages of palmitic acid (C16:0) of the residual oil of press-shredded were slightly higher than the residual oil of spikelet but a bit lower than the CPO. On the other hand, the oleic acid (C18:1) content was higher than that of residual oil of spikelet and also the CPO. According to Tan *et al.* (2009), the ratio of palmitic/stearic content in the CPO varies due to the geographical influences. Palmitic acid increases in palm oil are mostly associated with oil produced from over-ripe, bruised, and crushed fruits, fruits subjected to severe impact from loading, off-loading bunches, and oil stored for a long period (Tagoe *et al.* 2012).

CONCLUSIONS

1. Most of the residual oil was mainly located on the surfaces of spikelet, about 7.39% compared to the stalk (2.04%) and press-shredded (3.61%). Lower contact angle values of spikelet showed that it has less attraction with the oil and indicates that it is a preferable raw material for OPEFB oil recovery.
2. The results indicate that the residual oil from OPEFB contains a higher amount of valuable carotenes, comparable values of DOBI, PV, and fatty acid compositions in comparison to the original CPO from the mill.

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