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Research Journal of Food Science and Nutrition
Volume 4(2), pages 37-47, April 2019
Article Number: FE102C481
ISSN: 2536-7080
https://doi.org/10.31248/RJFSN2018.058
http://integrityresjournals.org/journal/RJFSN

Full Length Research

Effect of processing methods and storage time on chemical properties of palm oil

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Received 17th December, 2018; Accepted 15th February, 2019

ABSTRACT: The effect of four processing methods and the storage time on the chemical properties of palm oil were determined. The palm oil samples were extracted using hot extraction (HEPO), Cold extraction (CEPO), hot extraction with Sand (HSEPO) and Mechanized extraction (MEPO). Processing methods had no significant effect on the iodine value (45.94±0.68 to 47.06±2.25 wijis) whereas there were significant (p≤0.05) variations in saponification value (250.89±4.84 to 260.50±3.35mgKOH/g), peroxide value (8.59±4.14 to 12.08±4.70 mEq/kg), free fatty acid value (1.80±1.01 to 3.94±1.03%, mgKOH/g), acid value (3.77±1.91 to 7.90±2.08%, mgKOH/g) and carotenoids level (301.12±13.38 to 311.21±12.59 mg/kg) due to the processing methods. Storage time (months) caused no significant (p≤0.05) effect in iodine value (45.93±1.55 to 47.91±0.83 wijis) of palm oil samples stored for 0 to 3 month(s) but caused significant (p≤0.05) decrease in the carotenoids content (321.72±5.68 to 287.15±5.19 mg/kg). Storage time caused significant (p≤0.05) increase in saponification value (250.41±4.30 to 260.96±3.61 mgKOH/g), peroxide value (4.56±1.36 to 14.93±1.61%, mgKOH/g), free fatty acid value (1.83±0.84 to 3.77±1.32%, mgKOH/g) and acid value (2.45±1.74 to 7.54±1.80). Hot extraction method of palm oil was observed as the best method because its palm oil had the better quality parameter than other methods such as saponification value (252.20±4.00 mgKOH/g), iodine value (47.03±0.94 wijis), peroxide value (8.59±4.14 mEq/kg), free fatty acid (2.03±0.96%, mgKOH/g), acid value (3.94 ± 2.04%, mgKOH/g) and carotenoids level (302.90±13.46 mg/kg). Crude palm oil should not be stored for more than two months. It is recommendable to study the effect of storage conditions on the chemical properties of palm oil.

Keywords: Iodine value, fatty acids, oxidation, saponification value, peroxide value.

INTRODUCTION

Palm oil plant (*Elaeis guineensis*) is the highest oil producing plant (Ngando et al., 2011; Madubuike et al., 2015) with an average yield of 3.5 tons of oil/ha/year of which has an increasing consumer interest in tropical West. Since 2006, palm oil has become the world's most important edible oil with about 37 million tons produced that year, representing 25% of the total oils and fats production (Riris and Silalahi, 2017). The palm oil industry in Nigeria is very important and vital for the Nigerian economy, which represents 3% of the world production in 2010, thus increasing its cultivation in many parts of Nigeria especially the Niger Delta (Ihenetu et al., 2018).

Palm oil is edible oil referred to by the FAO/WHO Codex Alimentarius as being derived from the fleshy mesocarp of the oil palm fruit and Palm kernel oil is derived from the kernel of the fruit of the oil palm (FAO/WHO, 2013). Extracted from the mess carp of the fruit, crude palm oil (usually referred to as CPO) represents 95% of the total oil production of the oil palm which also provides palm kernel oil. The fruit is reddish and each fruit is made up of an oily, fleshy outer layer (pericarp), with a single seed and palm kernel oil from the seeds both of which are important in the world trade. Palm oil contains approximately 50% saturated fats and 40% unsaturated fat. Meanwhile, the light yellow to orange red of palm oil is due to the fat soluble carotenoids in terms of retinol which are responsible for

the high vitamin A content (Ugwu et al., 2002). Industrially, palm oil could be refined to give a light product which could be used in the manufacturing of margarine, biscuits, ice-cream, shortenings, cooking fats as well as cooking oils (Madubuike et al., 2015).

The quality of crude palm oil (CPO) is essential in determining its applications. The quality is associated with the method of processing. In Nigeria, there are three types of oil palm processing methods: traditional (mostly manual), semi-mechanized and mechanized methods. To a larger extent, smallholder/traditional processor dominate the sector accounting for about 80% (Ohimain et al., 2012a, b; 2013), the semi-mechanized processors 16% (Ohimain and Izah, 2013a) and mechanized processor of the remaining 4%. Smallholders use rudimentary/ manual/traditional equipment for processing (Ohimain and Izah, 2013a; 2014). Smallholder processors maintain low level of hygiene in the processing mills (Okechalu et al., 2011). These have resulted to low quality of CPO.

CPO consists of glycerides (i.e. tri, di and mono) of fatty acids like other vegetable oil from other sources. CPO contains other lipids such as phosphatides, unsaponifiable constituents and free fatty acids (FFA) (Chabiri et al., 2009). CPO is orange red to brownish or yellow-red in color (Akinola et al*.,* 2010), semi-solid at room temperature and is highly saturated. CPO is insoluble in universal solvent like water and soluble in organic solvents like trichloromethane and alcohol. The quality of CPO is influenced by deterioration due to microbial infestation that occurs in the palm fruit via bruises that may have occur before processing. These often manifest in the taste and odor of the CPO over a period of time, thereby increasing its rancidity. The rancidity of CPO could be associated with FFA increase due to atmospheric oxidation (Chabiri et al., 2009). Parameters affecting the quality of CPO include FFA, peroxide value, moisture content, iodine value, saponification value, impurity level etc (Onwuka and Akaerue, 2006; Udensi and Iroegbu, 2007; Akubor and Ogu, 2012; Enemuor et al., 2012).

Authors have reported the physicochemical and microbial properties of CPO processed traditionally to be of poor quality. The semi-mechanized processor share about 50% of smallholder characteristics. The major processing activities irrespective of kind of processing that could affect the quality of CPO produced include bruises during transportation, fermentation prior to threshing, clarification and storage (Ohimain et al., 2012a-d; Ohimain et al., 2013a; b; Ohimain and Izah, 2013a; b; 2014). Like other vegetable oil sources such as coconut, cotton seed, groundnut, maize germ, mustard seed, palm nut, sesame seed, soya beans, and sunflower seed (Chabiri et al., 2009), CPO have found application in food and industries (Izah and Ohimain, 2013a, b). The major application of CPO includes biodiesel production (Pleanjai et al., 2007; Ohimain, 2010), pharmaceutical, cosmetics, polish, detergents, shampoo, lipstick (Embrandiri et al*.,* 2012; Aghalino, 2000; Basiron and Weng, 2004). In food industries, CPO is an ingredient in soup cooking, margarine and confectionaries (Ohimain et al., 2013a, b). They are important food source for man, and are also extensively used for nutritional, cosmetic, drug dispersant in therapeutics and industrial purposes and are used for supplying essential fatty acids such as linoleic and arachidonic acids (Goudoum et al., 2015).

The quality of palm oil could be affected by various factors ranging from improper postharvest handling, processing and storage. Recently, there has been wide spread speculation that palm oil is adulterated in order to maximize profit (Ohimain, et al., 2013; Madubuike et al., 2015). The various methods for palm oil processing have been complied in a bulletin by Food and Agriculture Organization (FAO, 2000) of the United Nations. The compilation explains that batch processes is often employed by small-scale facilities, which process two or less tones of fresh fruit bunch per hour. The small-scale factories make use of manual skilled labourers. On the other hand, large-scale plants process more than ten and often up to sixty tones of fresh fruit bunches per hour (Enyoh et al., 2017a). The level of oil extraction varies wildly, mainly due to the different methods. In Imo state, in the traditional/local channel most of the palm oil is produced by women using manual traditional method namely mortar and pestle. Oil extracted usually reaches only 25% of the available oil in the fruit (Enyoh et al., 2017b). The major processing activities irrespective of kind of processing that could affect the quality of CPO produced include bruises during transportation, fermentation prior to threshing, clarification and storage (Ohimain, et al., 2013). However, the consumption of CPO can also be detrimental to human beings, as CPO contains some components which are likely to enhance numerous reactions (hydrolysis, oxidation, etc.) involved in the degradation of this product (Nwosu-Obieogu et al., 2017). Moreover, these degradation reactions can also be initiated and/or accentuated by poor transportation and storage conditions (Tagoe et al., 2012) of the product as it is generally the case among small holders. The most effective degradation process of CPO is acidification which was already mentioned by Desassis in 1957 (Ngando-Ebongue et al., 2013). Previous studies tend to demonstrate that, there was a problem with the consumption of CPO with respect to food safety. Based on the determination of the physicochemical parameters studied by Ngando et al. (2011), CPO from small holders' extraction sites was of lesser quality compared to that from industrial oil mills in term of food safety. Agbaire (2012) reported on the quality assessment of palm oil sold in some major markets in Delta State, Southern Nigeria. Result revealed that the investigated parameters where all within the SON/NIS standard, indicating that the palm oil is of good quality with no evidence of adulteration (SON, 2000).

This paper looks at the effect of four different processing methods and storage time on the chemical properties of palm oil. Peasant farmers in Nigeria depend on palm oil for

their source of income. This work helped in determining the optimum processing technique and storage time to be employed to maintain the quality of palm oil.

MATERIAL AND METHOD

Source of sample

The palm fruits were obtained from Umuoparaozara, Olokoro, Umuahia South Local Government Area, Abia State, Nigeria and the palm oil samples used for the analysis were obtained from four different processing methods. The various processing methods for the production of the palm oil samples were employed.

Process of cold extraction sample

This process involved cleaning and pounding of fresh fruits and then the nuts removed and low heated to facilitate the fluidity of the oil. The pulps were hand pressed manually. The oil was filtered and the result was clear oil. The process of heating does not involve addition of water and only low heating temperature (50^{o}C) is allowed to prevent bleaching. The flavor of the oil was strong and of fine aroma (Nwakodo et al., 2018). The flow chart is shown in Figure 1.

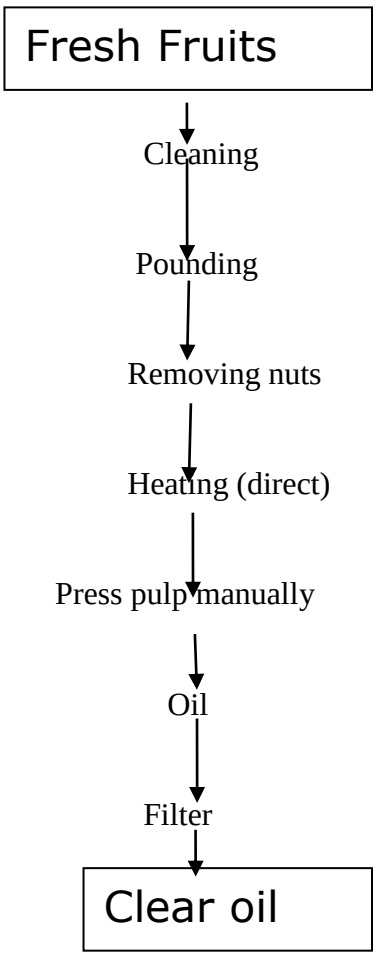

Figure 1. Flow chart for cold extraction of palm oil sample.

Method of hot extraction of palm oil sample

The process involved cutting the bunch, keeping it for two to three days to facilitate the removal of the fruit from the bunch, after which the fruits were cleaned and heated at 100^{o}C with small amount of water until soft. The fruits were placed in a pounder and pounded. After pounding, the nuts were separated from the pulp by sorting them out and kept in a pot and cold water was added to aid in scooping out the oil which floats on the surface of the water. Thereafter the oil was heated to separate oil from water. After the nuts removal, the pulp was placed in a bag and the oil pressed out using a locally made pressing machine. The locally made pressing machine facilitated oil extraction. The product got after pressing was mainly oil and some water. The mixture was then heated to separate oil from water. The oil floats on the surface of the water which was scooped out (Nwakodo et al., 2018). The flow chart is shown in Figure 2.

Process of hot extraction of palm oil sample with red sand

The process of hot extraction using red sand involved cutting the bunch, keeping it for two or three days to enhance removal of the fruits from the bunch, the fruits were cleaned and heated with small water until soft. The fruits were placed in pounder and red sand added, before pounding. The red sand was to add friction needed to bruise the fruits well prior to oil extraction. After pounding, the fibre was separated from the nuts. This was followed by pressing of the oil using a manual pressing machine (locally made) to extract the oil. The locally made pressing machine facilitated oil extraction. The product got after pressing was mainly oil and some water. Heating (100^{o}C) was employed to separate oil from water. The oil floated on the surface of the water because water is denser than oil. The floating oil was scooped out (Nwakodo et al., 2018). The flow chart is shown in Figure 3.

Mechanized processing method

The mechanized palm oil processing adopted for the purpose of this study was obtained from Itaja Olokoro in Umuahia, Abia State, Nigeria. In this very process, there is a very big pot used in boiling of the palm fruits after which it was transferred to the machine that pounds, separate the

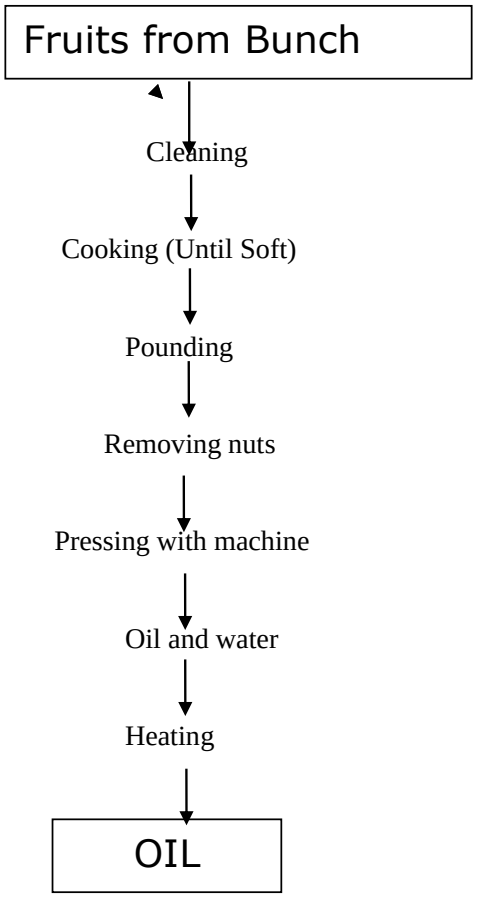

Figure 2. Flow chart for hot extraction of palm oil sample.

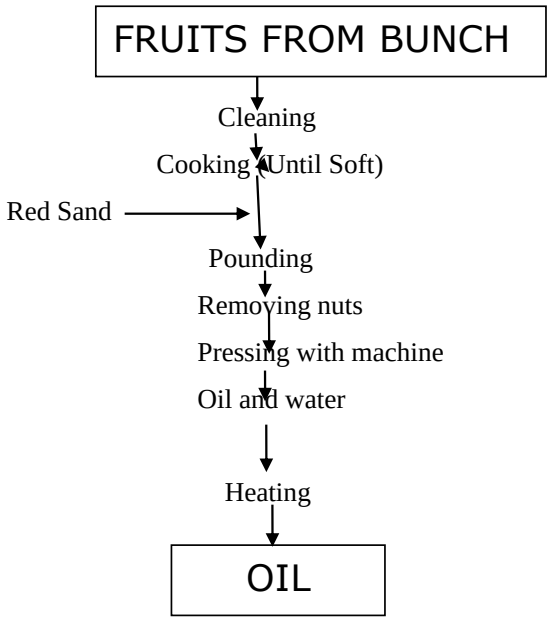

Figure 3. Flow chart for hot extraction of palm oil sample with red sand.

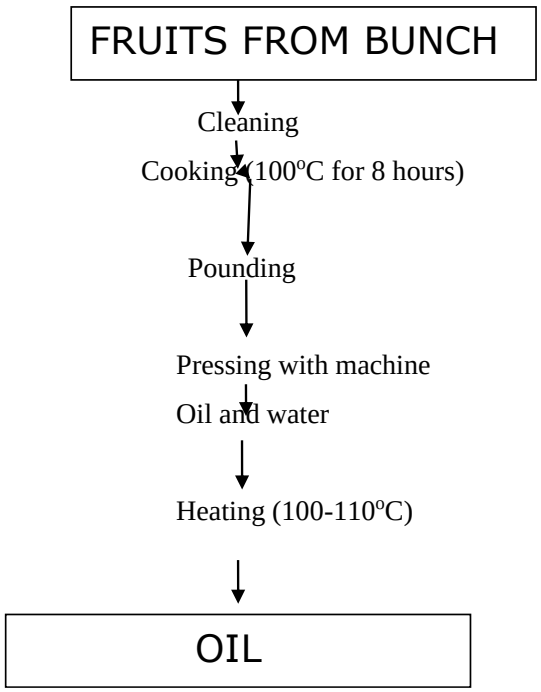

Figure 4. Flow chart for mechanized extraction of palm oil sample.

pulp from the nuts and extracts the oil (Nwakodo et al., 2018). The method of palm oil processing involved the use of locally made machines in processing of the fresh fruits to retain good quality and quantity of oil (Figure 4).

Analysis of chemical properties of palm oil samples

The chemical properties of palm oil samples were determined according to Nielsen (2010) and Onwuka (2018). Triplicate samples of CPO were collected in sampling containers for chemical analysis.

Saponification value determination

Saponification value is the amount of alkali necessary to saponify a definite quantity of the sample (oil). It is expressed as the number of milligrams of potassium hydroxide (KOH) required for saponifying 1 g of the sample. The smaller the saponification number, the larger the average molecular weight of the tricylglycerol present in the oil. The saponification value was determined using the guide provided by Pike (2003) and Odoh et al. (2017). About 2 g of CPO were weighed into excess 0.5 M alcoholic KOH of about 25 ml (Akinola et al., 2010). Heat was applied while swirling to saponification of the fat. The treated CPO samples were titrated with 0.5 M HCl using 1% phenolphthalein as indicator. A blank titration was also carried out. The weight of sample and titration values of the blank and samples were calculated as:

$$\text{Saponification value} = \frac{(S-B)xN \text{ x } 56.1}{\text{weight of Sample (g)}} \quad \text{Eqn. 1}$$

Where, S = Sample titre value, B =Blank titre value, N = Normal titration of the HCl and 56.1 = The Molar weight of KOH.

Iodine value determination

Iodine value is the quantity of iodine absorbed by one gram of the oil to saturate the sigma bond. It is an indication of the level of unsaturation and susceptibility of oil to oxidation and rancidity (Agbaire, 2012). The iodine value was determined by the Wijs' method using the guide provided by Pike (2003) and Odoh et al. (2017). A moderate mixture of iodine monochloride and acetic acid were added to the CPO samples. The mixture was allowed to stand for 30 minutes in dark. About 15 ml of 10% potassium iodide was added to the mixture (Akinola et al., 2010). The solution was titrated with 0.1 ml sodium thiosulphate solution using starch indicator to a colourless end point (S). Analysis of blank (B) was also carried out. Therefore,

$$\text{Iodine value} = \frac{(S-B)xN \text{ x } 12.69}{\text{weight of Sample (g)}} \quad \text{Eqn. 2}$$

Where: B = Blank titre value, S = Sample titre value, N = Normality of $Na_2S_2O_3$, 12.69 is used to convert from mEq thiosulphate to g iodine and molecular weight of iodine = 126.9.

Peroxide value determination

The peroxide value was determined by titrating chloroform/glacial acetic acid/potassium iodide solution of the oil with an aqueous solution of sodium thiosulphate using starch as indicator (Odoh et al., 2017). About 5 g of oil was weighed into the 250 ml conical flask. A mixture of glacial acetic acid and tri chloromethane chloroform (30 ml) was added in a ratio of 3:2. About 0.5 ml of saturated potassium iodide solution was also added. The mixture was properly shaken. 30 ml of water was added. The solution was filtrated with 0.01 M sodium thiosulphate, while slowly adding the titrant with a continuous shaking until a yellow colour is shown. About 5 ml of starch indicator was added to the titration process while shaking vigorously until a blue-black color is discharged. A blank sample devoid of CPO was also analyzed using the same procedure. The peroxide value is expressed mathematically as follows:

$$\text{Peroxide value (meq Peroxide/kg)} = \frac{(S-B)xM \text{ x } 1000}{\text{weight of Sample (g)}} \quad \text{Eqn. 3}$$

Where: B = Blank titre value, S = Sample titre value and M = Molarity of sodium thiosulphate.

Determination of acid value (AV) and free fatty acid content (FFA) of palm oil

The acid value and FFA were determined using titrimetry method as described by Enyoh et al. (2017a,b). About 5 g of palm oil sample was weighed in a dry conical flask and 25 ml of absolute ethanol and 2 to 3 drops of phenolphthalein were added. Heat was applied with continuous shaking in a water bath till the content of the flask started boiling. The content was allowed to cool and then tritrated with 0.1 N NaOH until pink color was achieved. The volume of NaOH used was recorded and the AV and %FFA of the palm oil was calculated using the formulae below:

$$\%\text{FFA} = \text{AV x } 0.503 \quad \text{Eqn. 4}$$

Determination of total carotenoids

Palm oil sample of 2.5 g was weighed into a conical flask, 30 ml hexane, 20 ml ethanol, 2 ml of 2% NaCl were added to the sample, and the solution was mixed and transferred into a separating funnel for about ten minutes to allow extraction of carotenoid. Total carotenoid was determined spectrometrically at 436 nm using the below relationship according to AOAC (2005) and Adetola et al. (2016).

$$\text{Total Carotenoids} = \frac{Abs*454*22}{196*L*W} \quad \text{Eqn. 5}$$

Where: L = Cell length (1cm), W = Weight of sample and Abs = Absorbed value.

Statistical analysis

Triplicate data obtained were subjected to statistical analysis using SPSS software of version 21. Mean values were determined and ANOVA was done as well as Fisher's Least Significant Difference (Pallant, 2004) was used for the separation of the means at ($p \leq 0.05$).

RESULTS AND DISCUSSION

Saponification value

Table 1 showed that the storage period had significant effect on the saponification value of the palm oil ($p<0.05$). The Saponification value of the freshly palm oil was 250.41±4.30 mgKOH/g and increased to 260.96±3.61 mgKOH/g after three months storage. Table 2 showed that the processing method had significant ($p \leq 0.05$) effect on the saponification value of the palm oil. The mechanized processing method (MEPO) had 260.50±3.35 mg KOH/g followed by cold processing method (CEPO) had 256.36±4.44 mg KOH/g and hot extraction of palm oil

Table 1. Mean values of effect of storage time on the chemical properties of palm oil.

Storage Time (Month)	Parameters					
	SV (mgKOH/g)	IV (wijis)	PV (mEq/kg)	FFA (%, mgKOH/g)	AV (%, mgKOH/g)	Carotenoids (mg/kg)
0	250.41 ± 4.30^{c}	46.31 ± 1.42^{a}	4.56 ± 1.36^{d}	1.28 ± 0.84^{d}	2.45 ± 1.74^{d}	321.72 ± 5.68^{a}
1	252.27 ± 4.42^{c}	46.65 ± 0.56^{a}	6.30 ± 1.14^{c}	1.83± 0.84^{c}	3.85 ± 1.52^{c}	316.42 ± 2.69^{a}
2	256.31 ± 3.22^{b}	45.93 ± 1.55^{a}	13.55 ± 1.47^{b}	3.27 ± 0.82^{b}	6.57 ± 1.61^{b}	296.26 ± 4.68^{b}
3	260.96 ± 3.61^{a}	47.91 ± 0.83^{a}	14.93 ± 1.61^{a}	3.77 ± 1.32^{a}	7.54 ± 1.80^{a}	287.15 ± 5.19^{c}
$LSD_{0.05}$	2.274	2.282	0.7545	0.248	0.452	5.76

Mean ± Standard deviation of triplicate. Means with the same superscript within a column are not significantly different from each other (p≤0.05).
KEY: SV = Saponification Value; IV = Iodine Value; PV = Peroxide Value; FFA = Free Fatty Acid; AV = Acid Value; $LSD_{0.05}$ = Least Significant Difference at p≤0.05.

Table 2. Mean values of effect of processing method on the chemical properties of palm oil.

Processing Method	Parameters					
	SV (mgKOH/g)	IV (wijis)	PV (mEq/kg)	FFA (%, mgKOH/g)	AV (%, mgKOH/g)	Carotenoids (mg/kg)
HEPO	252.20 ± 4.00^{c}	47.03± 0.94^{a}	8.59 ± 4.14^{c}	2.03 ± 0.96^{c}	3.94 ± 2.04^{c}	302.90 ± 13.46^{b}
CEPO	256.36 ± 4.44^{b}	45.94± 0.68^{a}	8.92 ± 4.72^{c}	1.80± 1.01^{c}	3.77 ± 1.91^{c}	301.12 ± 13.38^{b}
HSEPO	250.89 ± 4.84^{c}	46.77± 0.62^{a}	9.77 ± 4.38^{b}	2.38 ± 1.10^{b}	4.80 ± 2.18^{b}	306.31 ± 17.73^{ab}
MEPO	260.50 ± 3.35^{a}	47.06± 2.25^{a}	12.08± 4.70^{a}	3.94 ± 1.03^{a}	7.90 ± 2.08^{a}	311.21 ± 12.59^{a}
$LSD_{0.05}$	2.274	2.282	0.7545	0.248	0.452	5.76

Mean ± Standard deviation of triplicate. Means with the same superscript within a column are not significantly different from each other (p≤0.05).
KEY: SV = Saponification Value; IV = Iodine Value; PV = Peroxide Value; FFA = Free Fatty Acid; AV = Acid Value; $LSD_{0.05}$ = Least Significant Difference at p≤0.05; HEPO = Hot Extraction Method of Palm Oil; CEPO = Cold Extraction Method of Palm Oil; HSEPO = Hot Extraction with Red Sand of Palm Oil; MEPO = Mechanized Extraction Method of Palm Oils.

(HEPO) had 252.20±4.00 mg KOH/g; then, hot extraction with sand (HSEPO) had 250.89±4.84 mg KOH/g. Saponification value is an indication of the molecular weights of triglycerides of oils. High saponification value indicates high proportion of low fatty acids since saponification value is inversely proportional to the average molecular weight or length of fatty acids (Muhammad et al., 2011; Riris and Silalahi, 2017). The saponification value gives information with regard to the solubility in water and soap formation (Akinola et al., 2010). Adetola et al. (2016) showed that the saponification value of the palm oil increased with time and this indicates that the quantity of potassium hydroxide needed to turn the palm oil into soap increases with time of storage. The research carried out by other researchers on the quality assessment of palm oil sold in major markets in Abia State, Nigeria is in compliance with this result (Udensi and Iroegbu, 2007). Therefore, the shorter the average chain length (C_4-C_{12}) the higher the saponification value.

Iodine value

Iodine value is the quantity of iodine absorbed by one gram of the oil to saturate the sigma bond. It is an indication of the level of unsaturation and susceptibility of oil to oxidation and rancidity (Agbaire, 2012). Iodine value determines the stability and shelf life of oil. High iodine value makes the oil to be unstable thereby influencing other downstream application beside food (Enyoh et al., 2017a,b). Table 1 showed that the iodine value (45.93±1.55 to 47.91±0.83) of crude palm oil was not significantly (p≤0.05) affected by storage time (0 to 3 months). The freshly produced palm oil had iodine value of 46.31±1.42 wijis, while 3 months stored palm oil sample had the highest

iodine value of 47.91±0.83 wijis. The palm oil stored for 1 and 2 month(s) had 46.65±0.56 wijis and 45.93±1.55 wijis respectively. Table 2 illustrated that the effect of processing method on the iodine value of the palm oil was not significant at p≤0.05. The mechanized processing method (MEPO) had the highest iodine value of 47.06±2.25 wijis followed by the hot extraction method (HEPO) which had 47.03 ± 0.94 wijis.The cold extraction method (CEPO) produced palm oil sample with 45.94±0.68 wijis and the hot extraction with sand (HSEPO) also produced palm oil sample with an iodine value of 46.77±0.62 wijis. The iodine values obtained in this study were at the standard range of 45 to 53 wijis as recommended by SON (2000). These values suggest that the palm oil samples had low level of unsaturation and might not be susceptible to oxidation. The iodine value of CPO from this study is lower than 51.17±1.775 obtained by Riris and Silalahi (2017) and 52.61 to 53.48 reported by Udensi and Iroegbu (2007) as the iodine value of CPO sold in major markets of Abia state, Nigeria.

Peroxide value

Peroxide value is a measure of oxidation during storage and the freshness of the lipid matrix. Thus, it is the reactive oxygen that combined with the double bonds of the fatty acids in the triglycerides. During oxidation, the bonds are broken, resulting to short chain volatile compounds and residues of oxidized glycerides. Furthermore, it is a useful indicator of the early stages of rancidity (Ijeh et al., 2011; Riris and Silalahi, 2017). Table 1 showed that there were significant (p≤0.05) differences in peroxide values of the palm oil samples due to the storage time. The freshly produced palm oil had peroxide value of 4.56±1.36 mEq/kg which increased to 6.30±1.14 mEq/kg after 1 month storage at ambient temperature. After 2 months storage at ambient temperature, the peroxide value also increased to 13.55±1.47 mEq/kg and later increased to 14.93±1.61 mEq/kg in the palm oil sample stored for 3 months at ambient temperature. Peroxide value of the produced samples increased significantly over storage time (Zaeroomali et al., 2014; Goudoum et al., 2015).

The Peroxide value of an oil or fat is used as a measurement of the extent to which oxidation reactions have occurred during processing and storage. The best test for autoxidation (oxidative rancidity) is determination of the peroxide value, as peroxides are intermediates in the autoxidation reaction. Autoxidation is a reaction involving oxygen that leads to deterioration of fats and oils which form off-flavours and off-odours. Peroxide value, which is the concentration of peroxide in an oil or fat, is useful for assessing the extent to which spoilage has occurred (Alhibshi et al., 2016). Peroxide values of fresh oils are less than 10 milliequivalents/kg, when the peroxide value is between 30 and 40 milliequivalents/kg, a rancid taste is noticeable. High peroxide values are a definite indication of a rancid fat, but moderate values may be the result of depletion of peroxides after reaching high concentrations (Alhibshi et al., 2016).

The processing method caused significant (p≤0.05) variation in the peroxide value of the palm oil samples produced. There was no significant difference between the peroxide values of palm oil samples produced by HEPO (8.59±4.14 mEq/kg) and CEPO (8.92±4.72 mEq/kg) but HSEPO (9.77±4.38 mEq/kg) was significantly different from CEPO and MEPO (12.08±4.70 mEq/kg) was also significantly different from HSEPO. The peroxide values recorded in this study were close to the 10 MeqO2/kg limit recommended by World Health Organization (SON, 2000). The results of this study are within the range of other authors' findings on peroxide value of CPO produced and used in Nigeria (Akubor and Ogu, 2012; Okechalu et al., 2011). Amata and Ozuor (2013) reported peroxide value of CPO produced from Delta North Agricultural Zone of Delta State via different processing methods as 11.3 to 15.00 meqO_2/kg (traditional), 7.33 to 11.00 meqO_2/kg (semi-mechanized), 6.67 to 8.33 meqO_2/kg (mechanized). Peroxide value is a critical factor for examining the quality and stability of fats and oils, stages of oxidation and spoilage extent (Ohimain et al., 2013a). Because of this, the oil could become harmful to human health due to the free radical that is generated during processing (Tagoe et al., 2012).

Free fatty acids

Deterioration of a fat leads to the liberation of free fatty acids (FFA) from triglycerides. The amount of free fatty acid (FFA) in a fat or oil is indicative of its level of spoilage (Ekwenye, 2006; Constant et al., 2017). The storage time caused significant (p≤0.05) difference in the FFA values of the palm oil samples produced (Table 1). The freshly produced palm oil sample had the FFA of 1.28±0.84%, mgKOH/g which increased significantly to 1.83±0.84%, mgKOH/g after 1 month storage. The 2 months palm oil sample had 3.27±0.82%, mgKOH/g FFA which increased significantly to 3.77±1.32%, mgKOH/g after 3 months storage. SON recommended a maximum value of 3.5 mg KOH/g (SON, 2000). The free fatty acid value of palm oil increased with time irrespective of the storage container except that the increment was more rapid in a transparent container compared to an opaque container. Adetola et al. (2016) reported that, in both samples, the free fatty acid at day 21 was less than the maximum recommended value of free fatty acid of palm oil which is 5.00 with good quality which means that at day 21, the palm oil was still able to preserve its quality. Tagoe et al. (2012) reported that the FFA of the processed CPO increases with the duration of storage.

Table 2 illustrated the significant (p≤0.05) variation in the FFA of the palm oil samples caused by the processing methods. There was no significant difference between the

FFA of HEPO (2.03±0.96%, mgKOH/g) and FFA of CEPO (1.80±1.01%, mgKOH/g). The FFA of HSEPO (2.38±1.10%, mgKOH/g) was also significantly different from the FFA of HEPO and FFA of MEPO (3.94±1.03%, mgKOH/g). The FFA values of this study are within the recommended maximum value of SON/NIS. Enyoh et al. (2017a) reported that the maximum acceptable limit for FFA is 5%. Amata and Ozuor (2013) reported %FFA of CPO produced from Delta North via different processing methods as 15.1 to 17.6% (traditional), 12.80 to 15.40% (semi-mechanized) and 11.27 to 12.53% (mechanized). Ngando et al. (2011) reported %FFA of CPO produced by semi-mechanized approach in Cameroun as 5.00 to 10.26% whereas traditional and mechanized approach were 6.39 and 4.71% respectively. Zu et al. (2012) reported %FFA of 13.77 to 18.67 in Ghana which is higher than the result of this study. The result of this study is also different from that of other authors (Akinola et al., 2010; Okechalu et al., 2011; Akubor and Ogu, 2012; Enemuor et al., 2012). The CPO produced by semi mechanized mill in Bayelsa state could be regarded as hard oil because their FFA content is greater than 5% (Ohimain et al., 2012a). Riris and Silalahi (2017) reported that the high FFA reported in this study could be attributed to the level of exposure to sunlight (Ohimain et al.,2013a). The FFA content could serve as an indicator for a good harvest and a good method of extraction. Their presence in palm oil indicates the level of oil degradation during the extraction process. If the FFA content is high, this indicates that the fruits were damaged between harvest and extraction or harvested fruits were rotten (De Almeida et al., 2013; Constant et al., 2017). Without refining, such oil may be unsuitable for human consumption.

Acid value

Table 1 showed that the storage time caused significant (p≤0.05) increase in the acid values (AV) of palm oil samples stored for 0 to 3 months at ambient temperature. There was significant (p≤0.05) difference between the AV (2.45±1.74%, mgKOH/g) of freshly prepared palm oil sample and the AV (3.85±1.52%, mgKOH/g) of the palm oil sample stored for 1 month. The AV (6.57±1.61%, mgKOH/g) of palm oil sample stored for 2 months significantly (p≤0.05) increased to 7.54±1.80%, mgKOH/g after 3 months storage. International standards recommended 0.60%, mgKOH/g which is the maximum allowable limit in palm oil. The measure of the free fatty acids in oil is the acid value. Fatty acids are usually in the triglyceride form but during processing, they tend to get hydrolyzed into free fatty acids. Therefore, there is a direct relationship between acid value and the free fatty acid content. These mean that higher acid value will cause higher free fatty acid and thereby decreasing the oil quality (Enyoh et al., 2017a,b; Odoh et al., 2017).

Table 2 illustrated that the processing methods significantly (p≤0.05) varied the acid values (AV) of the palm oil samples. There was no significant difference between the AV (3.94±2.04%, mg KOH/g) of HEPO sample and AV (3.77±1.91%, mg KOH/g) of CEPO sample. However, there was significant difference between the AV (4.80±2.18%, mgKOH/g) of HSEPO sample and the AV (7.90±2.08%, mgKOH/g) of MEPO sample. The acid value obtained in this study (Table 2) ranges from 3.77±1.91%, mgKOH/g to 7.90±2.08%, mg KOH/g with palm oil from CEPO having the lowest value and palm oil from MEPO had the highest value. The acid value is an indirect measure of free fatty acid (FFA) contents present in oil/fat. It is an index of freshness. Exposure of oil to humidity and temperature results in increased acid value due to hydrolysis of glycerides. Acid value does not directly measure the rate of oxidation; it merely measures the by-product of oxidation (Ngassapa et al., 2012). Oils, on decomposition-due to chemical or physical factors, yield free fatty acids. Usually, acid number is used to determine the quality of oils, where it shows the amount of free fatty acid present in the oil samples (Alhibshi et al., 2016). Higher acid value gives indication of increased susceptibility of oils to rancidity. The oils intended for human dietary purposes should not contain high free fatty acids. Presence of free fatty acids in oils/fat renders unpleasant odor and deteriorate the quality of the product (Akinyeye et al., 2011).

Carotenoids

Carotenoids are located within the internal membranes of chloroplasts which they are surrounded by a double membrane. These carotenoids are fat-soluble, very sensitive to heat, but susceptible to enzymatic oxidation, chemical and photochemical (Goudoum et al., 2015). The carotenoids content of the palm oil significantly (p≤0.05) reduced from 321.72±5.68 to 287.15±5.19 mg/kg after 0 to 3 month(s) storage (Table 1). There was no significant different between the carotenoids content (321.72±5.68 mg/kg) of the freshly produced palm oil and the carotenoids content (316.42±2.69 mg/kg) of the palm oil stored for 1 month. The carotenoids (296.26±4.68 mg/kg) of palm oil stored for 2 months significantly reduced to 287.15±5.19 mg/kg after 3 months. Adetola, et al. (2016) reported that the concentration of total carotenoids decreased significantly with time because high temperature accelerates reactions. This reaction occurred more slowly at room temperature which was why the rate of decrease was slow. The carotene content values obtained were below the recommended carotene content values recommended by SON and NIS (500 to 2000 mg\kg) which shows a good quality palm oil. Also, the decrease in the carotene content value throughout the storage duration does not have significant effect on the oil quality or cause any reduction on its value (Adetola, et al. (2016).

Table 2 exhibited that there was significant ($p \leq 0.05$) variations in the carotenoids of the palm oil samples produced by the four different processing methods. There was no significant difference amongst the carotenoids levels of the palm oil samples from HEPO (302.90±13.46 mg/kg), CEPO (301.12±13.38 mg/kg) and HSEPO (306.31±17.73 mg/kg). However, there was significant difference between the carotenoids level of MEPO (311.21±12.59 mg/kg) and CEPO (301.12±13.38 mg/kg) but no significant difference existed between the carotenoids level of MEPO and HSEPO. During storage, these carotenoids oxidize and give rise to oxidation products. These oxidation products are difficult to remove during refining. In addition, during refining, they polymerize under the action of high temperatures and make the dark refined oil (Goudoum et al., 2015).

Crude palm oil is a complex mixture consisting principally glycerides that represent the major component while carotenoids, tocopherols, tocotrienols, phytosterols and phosphatides represent the minor components. Red palm oil is produced from crude palm oil through a milder refining process that enables the retention of most of the carotenes and vitamins in the refined oil. Thus, red palm oil is considered as one of the richest plant source of carotenes which are precursor of vitamin A and vitamin E. Therefore, carotenes and vitamin E play important roles as antioxidants that may provide oxidative stability to the oil. The stability of oil depends partly on the extent of deterioration during heating or storage (Akinola et al., 2010).

Conclusion

The result of the effects of processing methods and storage time on the chemical properties of palm oil were determined. Storage time caused no significant effect on the iodine values of the palm oil samples while it caused significant increase in the following chemical properties of the palm oil samples: saponification value, peroxide value, free fatty acid value and acid value. Palm oil stored for 3 months had significant increase in the chemical properties which might lead to deterioration of the palm oil. However, storage time caused significant decrease only in the carotenoids content of palm oil samples. Also, the processing methods had no significant effect only on iodine value whereas it caused significant variations in saponification value, peroxide value, free fatty acid value, acid value and carotenoids level. The best processing method discovered was HEPO because it produced palm oil sample that was moderately low in most of the chemical properties.

Recommendation

Effort should be made in proper processing, packaging and storage conditions of palm oil as well as the reduction of the chemical parameter which might cause an adverse effect on the quality of palm oil and health of the consumers. It is recommendable to study the effect of storage conditions on the chemical properties of palm oil.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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