QUALITY ASSESSMENT OF CRUDE PALM OIL AVAILABLE IN BENIN-CITY, NIGERIA

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ABSTRACT

The degree of oxidative and hydrolytic rancidification and total carotene content are important quality criteria of crude palm oil (CPO). Handling, harvesting, processing and extraction techniques of CPO affect its quality. This study aims at assessing the standard of CPO available in Benin City, Nigeria. Ten samples of CPO were purchased from wholesalers, twelve samples from retailers and a sample from a manufacturer. The peroxide value, free fatty acid (FFA) value, Thiobarbituric acid (TBA) value, total carotene content and density of the CPO samples were assessed according to standard procedures. The results showed that peroxide values ranged from 0.83 to 5.35 meqO₂/kg, FFA values ranged from 6.33% to 21.33%, TBA values ranged from 0.014 to 0.24 mg malonaldehyde/kg, total carotene content ranged from 574.04 to 1523.07 mg/kg and density ranged from 0.9142 to 0.9346 g/cm³. The peroxide values, TBA values, total carotene content and densities of the CPO samples are within limits recommended by the standard organization of Nigeria (SON). However the FFA values of the CPO samples is lower than SON recommendation. Since a high FFA value is not a health issue but an industrial issue, CPO sold in major markets in Benin City is suitable for domestic use but may require some refinement before they can be used as pharmaceutical excipients.

Keywords: Palm oil, Quality control, Pharmaceutical, Carotene, Tocopherol.

INTRODUCTION

The oil palm (*Elaeis guineensis*) is an important oil producing plant in Africa (Vickery and Vicky, 1979). The fruit from the palm tree produces two types of oils namely, palm oil which is extracted from the pericarp of the fruit and palm kernel oil, obtained from the seed (FAO, 2002). Palm oil contains high proportion of fatty acid especially palmitic acid. It is rich in β -carotene and lycopene (Ngando *et al*; 2013). Palm oil also contains tocopherols, tocotrienols, phytosterols and glycolipids (Ping, 2000). Tocotrienols has demonstrated neuro-protective properties in brain tissues (Khanna *et al*, 2005). Palm oil derived tocotrienols supplements result in significant protective effects against end-stage liver failure (Patel, 2012). According to Tagoe et *al.*, 2012, the major factors determining the free fatty acid value of crude palm oil are the length and conditions of storage of the oil after processing. Work done by Odunfa (1989) on the storage of palm oil, showed that microbial attack results in the hydrolysis of the oil and subsequently, the formation of free fatty acids. β -carotene is responsible for the high vitamin A content of palm oil (Ugwu *et al.*, 2002) and its value decreases with storage time (Udensi. and Iroegbu, 2007). β -carotene are susceptible to degradation by oxidation on exposure to atmospheric oxygen and in the presence of free radicals (Caitlin *et al.*, 2010).

There is widespread speculation that palm oil is being adulterated for the sole purpose of profit maximization. The adulteration ranges from the use of azo dyes, artificial food colourants and other addictives which could affect the quality of palm oil with respect to its nutritive value, wholesomeness, utilization, safety, and shelf life. Arising from these issues is the need to assess the quality of palm oil in Benin City and determine their suitability for domestic and pharmaceutical use. The aim of the study is to assess the quality of crude palm oil sold in major markets of Benin City, Nigeria.

MATERIALS AND METHOD

Collection of Palm Oil Samples

Thirteen samples of palm oil were collected from different wholesalers and retailers in four major markets in Benin City namely Uselu market, Oba market, New Benin market and Oregbeni market. Markets selected reflect the different regions of the city.

A sample of fresh palm oil (milled within 24 hours from sampling) was obtained from Nigerian Institute for Oil palm Research (NIFOR).

Analysis of the samples was carried out within two weeks after sampling.

Reagents

All reagents used for the study were of analytical grade. They were purchased from local suppliers and were used without further purification.

Peroxide value

Peroxide value was determined by weighing 5 g of oil sample into a clean conical flask and dissolving in 10 ml of chloroform and 15 ml acetic acid. 1 ml of a freshly prepared saturated solution of potassium iodide was added and the flask was shaken for one minute before incubating at room temperature for 5 minutes. 25 ml distilled water was added and 0.5 ml starch solution was added as indicator before titrating with 0.01 N solution of sodium thiosulphate (Na₂S₂SO₃) shaking vigorously until the blue grey color disappeared in the aqueous layer (upper layer) and a milky color appeared. The procedure was repeated for blank (AOCS, 2011). Triplicate determinations were carried out.

Expression of results:

Peroxide value expressed as meqO₂/kg = $S-B \times N \times F \times 1000/mass$ (g)

Where: S = Titer volume for sample,

B = Titer volume of blank,

F = Factor of 0.01N sodium thiosulphate

N = Normality of sodium thiosulphate (Na₂S₂SO₃).

FREE FATTY ACID VALUE

A neutralizing solvent was prepared by adding 0.5 ml phenolphthalein into 25 ml of ethanol. Palm oil (5 g) and 25 ml neutralizing solvent were weighed into a conical flask. The solution was heated before titrating with 0.1N sodium hydroxide until a permanent pink color was obtained. The color persisted for at least 30 seconds (MPOB, 2004). Triplicate determinations were carried out.

Expression of results:

Free fatty acid (FFA) (%) = $25.6 \times M \times F \times V/m$

Where,

M = Molarity of the standard sodium hydroxide.

V = Volume in millimeters of sodium hydroxide used

m = Mass in grams of the sample

F = Factor of 0.1N sodium hydroxide

THIOBARBITURIC ACID VALUE (TBA Value)

TBA value was obtained by weighing 50 - 200 mg of sample into a clean, dry conical flask and dissolving in 5 ml of 1-butanol. 5 ml of sample solution was added. 5 ml of 0.2 % w/v solution of 2-thiobarbituric acid in 1-butanol (TBA reagent) was added. The test tube was mixed and placed in a Thermostated water bath at 95 ± 5 °C for 120 minutes before cooling it under running tap water for about 10 minutes until it reaches room temperature. The absorbance of the test solution was determined in a 10 mm cuvette at 530 nm using butan-1ol as the reference standard (IUPAC, 1989). The determinations were carried out in triplicate. Expression of results:

Results are calculated as follows;

TBA value expressed in mg of malonaldehyde/kg = $50 \times (A-B)/m$

Where: A = Absorbance of the test solution

B = Absorbance of the blank solution

m = Mass of the test portion

Total Carotene content

Total carotene content was measured by dissolving 0.1g of oil sample in 25 ml of n-hexane and the absorbance at a wavelength of 446 nm was measured in a 10 mm cuvette using n-hexane in the reference cuvette (MPOB, 2004). Triplicate determinations were carried out. Expression of results:

Total carotene content of palm oil as b-carotene, in $mg/kg = 383 \times E/l \times c$ Where:

E = absorbance of the sample solution at 446 nm

- L = path length of the cell in cm
- C = concentration used for absorption measurement (in gram per 100 ml)

Density

Density was determined by a simple gravimetric method. The weight of the density bottle with cap was measured before adding the sample and determining the weight of the bottle with cap and sample (Pike, 2003). Triplicate determinations were carried out.

Expression of results:

Specific gravity in $g/cm^3 = W_1 - W_0/25$ ml Where:

 W_1 = weight of bottle + cap + oil

 $W_0 = Weight of bottle + cap$

Volume of the density bottle = 25 ml.

STATISTICAL ANALYSIS

The results of this study were subjected to statistical analysis using IBMTMSPSSTM statistics version 20. Comparison of the means was done with the Welch's T- test and one-way analysis of variance (ANOVA).

RESULTS

Table 1. Physicochemical properties of pain on from wholesalers in Benni City	Table 1: Ph	ysicochemical	properties of	palm oil from	wholesalers in	n Benin City
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Samples	Peroxide value	TBA value	FFA value	Total Carotene	Density
	(MeqO ₂ /kg)	(mg/kg)	(%)	content (mg/kg)	(g/cm^3)
	Mean \pm SD	Mean \pm SD	Mean± SD	Mean \pm SD	Mean ±SD
Wholeseller1	1.5800 ± 0.13	0.0948±0.0136	15.7300±0.1300	880.9000±30.98	0.9314 ± 0.0005
Wholeseller2	1.4700 ± 0.19	0.1760 ± 0.0010	13.4900±0.1200	1523.0700±49.43	0.9292 ± 0.0001
Wholeseller3	2.4100 ± 0.19	0.0996 ± 0.0011	9.5200 ± 0.0300	859.5200±22.30	0.9246 ± 0.0008
Wholeseller4	1.9500 ± 0.21	0.1921±0.0046	18.5100 ± 0.3100	968.9900±19.79	0.9346 ± 0.0059
Wholeseller5	4.2000 ± 0.29	0.2423 ± 0.0014	6.3300±0.0600	1047.8300±15.03	0.9229 ± 0.0026
Wholeseller6	1.5900 ± 0.10	0.0842 ± 0.0146	12.5500 ± 0.1800	861.1100±63.30	0.9255 ± 0.0007
Wholeseller7	1.5900 ± 0.10	0.0817 ± 0.0002	17.5200 ± 0.2400	788.0200±23.55	0.9344±0.0012
Wholeseller8	0.9800 ± 0.10	0.0802 ± 0.0025	13.6900±0.1200	574.0400±25.41	0.9294 ± 0.0015
Wholeseller9	1.1600 ± 0.10	0.1150 ± 0.0006	16.0700±0.0400	1353.2700±20.23	0.9286 ± 0.0002
Wholeseller10	0.9300 ± 0.10	0.1005 ± 0.0002	21.3300 ± 0.1800	895.2700±16.78	0.9271 ± 0.0016

SD = standard deviation

Analysis of the oil samples collected from the various wholesalers shows that the oil palm marketed by wholesaler 5 is different from that from other wholesalers as the peroxide value, Thiobarbituric acid value and the Total carotene content were significantly higher than oils from other wholesalers.

 Table 2: Physicochemical properties of palm oil from retailers in Uselu market

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Samples	Peroxide value	TBA value	FFA value	Total Carotene	Density
	(MeqO ₂ /kg)	(mg/kg)	(%)	content	(g/cm^3)
				(mg/kg)	
	Mean \pm SD	Mean \pm SD	Mean \pm SD	Mean \pm SD	Mean \pm SD
Retailer1	1.0000 ± 0.2000	0.0680 ± 0.0000	10.1600 ± 0.1300	765.2400±15.1500	0.9282±0.0023
Retailer2	0.8300 ± 0.0000	0.1075 ± 0.0120	16.6300±0.0900	741.7400±30.2000	0.9282 ± 0.0011
Retailer3	0.7900 ± 0.0000	0.0990 ± 0.0028	10.0900 ± 0.2300	685.5700±7.8400	0.9239 ± 0.0008

SD = standard deviation

The peroxide values, Thiobarbituric acid value, Total carotene content and density of all oil samples from the different retailers in Uselu market, Benin city were not statistically different from each oil. However, the free fatty acid of samples from retailer 2 was statistically different from other samples.

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Samples	Peroxide value	TBA value	FFA value	Total Carotene	Density
	(MeqO ₂ /kg)	(mg/kg)	(%)	content	(g/cm^3)
				(mg/kg)	
	Mean \pm SD	Mean \pm SD	Mean \pm SD	Mean \pm SD	Mean \pm SD
Retailer1	1.1800 ± 0.0000	0.0880 ± 0.0085	9.8300±0.1400	768.5500 ± 10.5000	0.9246±0.0011
Retailer2	0.9100±0.1200	0.1840 ± 0.0071	10.2000±0.1300	981.1200±13.2100	0.9246±0.0018
Retailer3	1 1200+0 1200	0 1420+0 0000	13 9000+0 4600	856 3300+6 5200	0 9219+0 0013
Retuiters	1.1200±0.1200	0.1120±0.0000	15.9000±0.1000	050.5500±0.5200	0.9219±0.0015

SD = standard deviation

Oil samples from retailers in Oba market were not statistically different from one another except that retailer 3 oil sample had higher free fatty acid than the others.

Table 4: Physicochemical	properties of	palm oil from	retailers in N	New Benin market
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Samples	Peroxide value	TBA value	FFA value	Total Carotene	Density
	(MeqO ₂ /kg)	(mg/kg)	(%)	content	(g/cm^3)
				(mg/kg)	
	Mean \pm SD	Mean \pm SD	Mean \pm SD	Mean \pm SD	Mean \pm SD
Retailer1	1.2500 ± 0.1200	0.1220 ± 0.0014	14.0100 ± 0.0200	1306.3500±32.1300	0.9319 ± 0.0008
Retailer2	0.9200 ± 0.1200	0.0340 ± 0.0014	14.9700±0.0900	906.1100±29.3600	0.9183 ± 0.0003
Retailer3	1.1800 ± 0.2000	0.0170 ± 0.0000	11.0100 ± 0.0900	942.8200±32.7800	0.9231 ± 0.0005

SD = standard deviation

The Total carotene content in oil samples from Retailer 1 was statistically higher than those from the other retailers in New Benin market. Other parameters were not statistically different from each other.

Table 5: Physicochemical properties of palm oil from retailers in Oregbeni market

Samples	Peroxide value	TBA value	FFA value	Total Carotene	Density
Samples	(MeqO ₂ /kg)	(mg/kg)	(%)	content (mg/kg)	(g/cm^3)
	$Mean \pm SD$	Mean \pm SD	$Mean \pm SD$	Mean \pm SD	Mean \pm SD
Retailer1	0.8500 ± 0.1200	0.0140 ± 0.0014	14.0500±0.0900	942.8200 ± 28.0200	0.9276 ± 0.0034
Retailer2	1.5200 ± 0.1200	0.0805 ± 0.0021	15.7900 ± 0.2000	1229.1100 ± 18.8200	0.9232 ± 0.0023
Retailer3	1.3300 ± 0.1200	0.1335 ± 0.0007	17.3700 ± 0.1800	833.3500 ± 14.6600	0.9142 ± 0.0014

SD = standard deviation

The peroxide value and Thiobarbituric acid values of samples from Retailer 1 in Oregbeni market, Benin City were statistically different from those of other retailers from the same market; whereas the total carotene content of oil from Retailer 2 was higher and statistically different from the other retailers.



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Samples	Peroxide value	TBA value	FFA value	Total Carotene	Density
	(MeqO ₂ /kg)	(mg/kg)	(%)	content	(g/cm^3)
				(mg/kg)	
	$M_{POD} + SD$	Mean + SD	Mean + SD	Mean + SD	Mean + SD
	Mean ± SD				
NIFOR	5.3500±0.2000	0.0962±0.0021	6.8800±	637.8700 ± 4.3800	0.9244±0.0006

	Table 6: phys	sicochemical	properties of	palm oil	from NIFOF
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SD= standard deviation

The Peroxide value of the oil from NIFOR was higher statistically different from the values from the oil from the wholesalers and retailers from all the market in the City. The free fatty oil of NIFOR oil was however lower than all the other oil sampled.

DISCUSSION

The peroxide values of crude palm oil (CPO) samples from wholesalers was significantly difference from those obtained from retailers (p<0.05); but among retailers, there was no significant difference (p<0.05). The peroxide values of all samples range from 0.83 meq.O₂/kg - 5.35 meq.O₂/kg which is lower than the 10 meq.O₂/kg limit recommended by the standard organization of Nigeria (SON, 2000). The low level of peroxides in the crude oil samples shows that the CPO samples are stable to oxidation and it also shows that the extent of oxidative rancidification in the samples is minimal. This is likely as a result of the antioxidant properties of the β -carotenes present in the crude oil samples at significantly high quantities. Palm olein, one of the liquid fraction of palm oil contains higher levels of both monounsaturated free fatty acids (oleic acid) and poly unsaturated free fatty acids (linoleic acid). Palm stearin is the heavier fraction of crude palm oil. It contains higher levels of saturated free fatty acids and triacylglycerides. CPO sample from Nigeria Institute for oil Palm Research (NIFOR), Benin City and the CPO sample from the fifth wholesaler have greater fractions of palm olein while all other CPO samples have higher fractions of palm stearin. CPO from NIFOR and CPO from wholesaler 5 have peroxide values of 4.20 meq.O₂/kg and 5.35 meq.O₂/kg respectively which are significantly higher than the peroxide values of other samples $(0.83 \text{ meq.}O_2/\text{kg} - 2.41 \text{ meq.}O_2/\text{kg})$. This indicates that both NIFOR and wholesaler 5 CPO samples are less stable to oxidation and more prone to autoxidation than the other CPO samples because both samples contain relatively higher amounts of monounsaturated and poly unsaturated free fatty acids. Ohimain et al (2012) reported peroxide values ranging from 1.20 meq.O₂/kg to 1.93 meq.O₂/kg for CPO from smallholder processors in Rivers state; Nigeria while Udensi and Iroegbu (2007) reported relatively higher peroxide values (7.90 - 8.80 meq.O₂/kg) for CPO marketed in Abia state, Nigeria. However all peroxide values are below the 10 meq.O₂/kg limit recommended by SON (2000). The rancidity of oil can be assessed using the peroxide value. It is an important quality parameter because free radicals generated during oxidation are harmful to human health and odoriferous products formed during oxidation make the oil unappealing to direct consumers of CPO.

The free fatty acid (FFA) values of CPO samples from wholesalers and retailers were not statistically different (p>0.05). Likewise there is no significant difference between the free fatty acid values of CPO samples from retailers in four major markets of Benin City, Nigeria (p>0.05). FFA values of all CPO samples range from 6.33% - 21.33% thus, exceeding SON (2000) recommendations of 5% free fatty acid as palmitic acid limit. High FFA values might be as a result of poor harvesting techniques such as collection of over ripe fruits that may have been contaminated with lipase producing micro-organisms; poor handling techniques

that may result in bruising or wounding of fresh fruits; poor processing techniques such as undue fermentation of fruits before threshing; prolonged delay after harvesting of fresh fruit bunches before processing and high levels of FFA can as well be a result of long periods of storage of CPO under harsh conditions. The effect of lipases from micro-organism on triglycerides may be responsible for the observed buildup of fatty acids in some of the samples. Moisture and heat also contribute to hydrolytic degradation of triglycerides. FFA values of CPO samples from NIFOR (6.88%) and wholesaler 5 (6.33%) are relatively lower than the FFA contents of other CPO samples in the study (9.52% - 21.33%). CPO contains two major fractions; palm olein and palm stearin. Palm olein is the supernatant fraction while palm stearin is at the base. Moisture present in CPO settles at the base with the palm stearin fraction. Prolonged contact of palm stearin with moisture facilitates hydrolysis of triglycerides and buildup of free fatty acids. This explains the relatively higher FFA values of other CPO samples having greater fractions of palm stearin when compared to FFA values of CPO from NIFOR and wholesaler 5 that contain less fractions of palm stearin. Ohimain et al (2012) reported FFA values ranging from 8.44% to 10.30% for CPO samples from smallholder processors while Udensi and Iroegbu (2007) reported FFA values ranging from 2.73% to 2.89% for CPO sold in markets at Abia state. Hence the results from this study are in accordance with results reported by Ohimain et al (2012) but are contrary to results reported by Udensi and Iroegbu (2007). High levels of free fatty acid containing crude palm oil is not a quality concern to direct consumers of crude palm oil because there is no evidence that high FFA containing CPO is a health risk to consumers; at most they have mild laxative effects. In addition, free fatty acids enhance the flavor of crude palm oil. However, CPO containing high levels of free fatty acid is a quality issue in the edible oil refining industry because it affects the quality of the product as well as the efficiency of the refining process. The total carotene content of the oil samples from the wholesalers and retailers were not statistically different (p>0.05). Total carotene content of all samples studied range from 574.04 mg/kg to 1523.07 mg/kg, they fall within the range of total carotene content recommended by SON (2000) (500 mg/kg - 2000 mg/kg). B-carotene is a major source of vitamin A in most developing countries including Nigeria. If total carotenoid content is below permissible levels recommended by SON (2000) vitamin A deficiency might prevail. The findings of this current study are in accordance with results reported by Udensi and Iroegbu (2007) that carotenoid contents of palm oil marketed in Abia state range from 1274.4 mg/kg

There is no significant difference between the Thiobarbituric acid (TBA) value of oil samples from the wholesalers and CPO samples from the retailers (p>0.05). Likewise there is no statistical difference between the TBA values of the CPO samples from the retailers in the four major markets (p>0.05).TBA values of all CPO samples range from 0.0140 mg malonaldehyde (MD)/kg to 0.2400 mg malonaldehyde/kg. TBA assay measures the amount of malonaldehyde present in the CPO samples. Malonaldehyde is a reactive secondary product of oxidation of unsaturated free fatty acids. It is formed in the termination phase of lipid autoxidation from hydro peroxides formed in the propagation phase. It occurs naturally and is a marker for oxidative stress. Malonaldehyde is reactive and potentially mutagenic. (Hartman, 1983)

to 1882 mg/kg, hence they comply with SON (2000) recommendations for total carotenoid

There is no significant difference between the specific gravity of CPO samples from wholesalers and CPO samples from retailers (p>0.05). Likewise there is no statistical difference between the densities of oil samples from the four major markets of Benin City (p>0.05). Densities of all CPO samples range from 0.9142 g/cm³ to 0.9346 g/cm³ which is

content.

close to SON (2000) recommendations for density of crude palm oil (0.897 g/cm³ – 0.907 g/cm³). The results of this study are closely similar to results reported by Udensi and Iroegbu (2007) as density of palm oil marketed in Abia state (0.832-0.880 g/cm³). Density is a physical property and a quality assessment parameter of palm oil. A significantly high density can be an indication of the presence of 'foreign' materials.

CONCLUSION

This study result shows that the peroxide values, total carotene content, thiobarbituric acid value and density of oil palm from wholesalers and retailers in the major markets of Benin City are within the limits recommended by SON (2000). However, the free fatty acid values of the oil samples fall short of SON (2000) recommendations. There is no evidence that oil palm that contains high free fatty acid possess a health risk to humans. In fact, research is currently on going at NIFOR to show that oil palm with high fatty acid content are safe for human consumption. On the other hand, oil palm with high fatty acid content are difficult to process in the oil palm refining industry because they impair the efficiency the processes and product quality.

It is therefore logical to conclude oil palm sold in major markets of Benin City are suitable for domestic use as edible oil but may require some refinement before they can be used for industrial purposes.

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