Quality of Nigerian Palm Oil After Bleaching with Local Treated Clays

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Laboratory investigations into the possibility of using local Nigerian clays in refining the Nigerian crude palm oil revealed that the Okija clay may possess some potential as an adsorptive cleanser in the refining process. Activated bentonite was used as the standard clay of comparison, and the performance of two local natural clays, leached with various concentrations of sulfuric acid, was evaluated for their use as alternative adsorptive cleansers in refining Nigerian crude palm oil. Measurements of peroxide values, para-anisidine values, carotene content and stabilities of the oils using the active oxygen method were used in assessing the relative performance of the clays.

The clays exhibited similar trend of effects on identical batches of alkali-neutralized palm oil. In one set of experiments poor results were obtained when the degummed and alkali-neutralized palm oil was treated with clays leached with sulfuric acid at concentrations of 1M and 4M. Better results were obtained at acid concentrations of 2M and 3M. Bentonite proved better than Okija clay when the leaching was performed with 2M H_2SO_4, but both clays had comparable effectiveness when 3M H_2SO_4 was used for leaching. The Nsu clay gave the least encouraging results. In another series of experiments the results showed that for various dosages of clay, up to 3% by weight of the oil to be refined, the oxidative stability of the processed oil was reasonably good for an oil which was neither deodorized nor treated with antioxidants.

Palm oil is a fruit flesh fat derived from the species *Elaeis guineensis* and owes its distinctive orange-red color to its relatively high content of carotenoids. The crude palm oil is a major source of dietary vegetable fat in Nigeria, being used extensively in the preparation of stews, soups, in cooking, frying and in the preparation of African salad. Upon storage at ambient temperatures, this orange-red oil starts to separate into two phases, a lower solid phase and a top liquid phase. With time, a single solid phase finally emerges. Before use, therefore, the congealed oil must be melted. Reheating the oil limits the packaging materials for the crude palm oil to metal cans and glass bottles. One of the major inconveniences encountered during frying with the Nigerian crude palm oil is that the oil smokes very rapidly, and this smoke has an extremely choking effect within the vicinity of the frying perimeter. Refining the Nigerian crude palm oil would, however, eliminate its congealing tendencies, greatly facilitate the ease with which the oil is used when needed, expand the scope of packaging materials used for storage purposes and considerably raise the smoke point of the oil.

One aspect of this refining process to which our laboratory has devoted attention for the last three years is adsorptive cleansing. It is recognized that bleaching clay performs not only color removal, but also the removal of trace metals, adsorption of phospholipids and soaps, and decomposition of oxidation products such as peroxides (1,2). Thus, the important action of earth bleaching is one of adsorptive cleansing (3).

Clay deposits of the montmorillonite type, which are known to function efficiently as bleaching earth (3–6), are not mined in Nigeria. However, the problem of the final color of processed palm oil is not one of inefficient removal of the carotenoids. The final color appears to be associated with other pigments or, more likely, the precursors of pigments arising through oxidative deterioration (7). Fortunately, palm oil apparently is easily decolorized by heat.

The purpose of these laboratory studies was threefold: (a) to undertake preliminary laboratory investigations on the effectiveness of treated local clays from the Nsu and Okija areas of Eastern Nigeria as adsorptive cleansers in refining Nigerian crude palm oil; (b) to examine the behavior of local clays as adsorptive cleansers in refining the oil when the clays are activated under various concentrations of sulfuric acid, and (c) to determine the optimum dosage of clay necessary to bleach the palm oil commercially.

EXPERIMENTAL PROCEDURES

Natural local clays were obtained from the Nsu (NS) and Okija (OK) areas of Eastern Nigeria, while bentonite clay (BN) was purchased from Baroid of Nigeria Limited, Warri, Nigeria. For purposes of activation 50-g samples of each clay were placed in beakers, and 250 ml of the appropriate acid was added. The mixture was stirred occasionally at room temperature for three hr. In general, with clays NS and OK the acid layer turned yellow with time, while with the bentonite (BN) effervescence was observed upon treatment with acid and a smell of rotten egg was given off, while the acid layer turned yellow very gradually.

After any visible reactions ceased, the resulting slurry was filtered through a Buchner funnel and the clay was washed several times with distilled water, followed by filtration until the filtrate was almost neutral to pH indicator paper. The exchanged clay was dried in an oven at 140 C overnight, ground to a fine powder and sieved using a 0.1 mm sieve.

Freshly pressed palm oil was bought from a local supplier in Umuahia in Imo State of Nigeria. In the case when the palm oil was bought from the local Lafenwa market in Abeokuta, the oil was fractionated using a high speed centrifuge and the free flowing light layer was used for the studies.

The moisture content of the crude palm oil was determined using a Dean-Stark apparatus with xylene as solvent. Free fatty acid, peroxide and anisidine values of oils were determined by standard methods (8,9).

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Total oxidation value was calculated from the anisidine and peroxide values: OV = AV + 2PV (10). Measurement of residual β-carotene was made by ultraviolet-visible spectroscopy on a Zeiss spectrophotometer DMR 10.

The crude palm oil was treated with 0.05% by weight of 85% H_3PO_4 for 20 min at 45–50 C, and subsequently neutralized with 2M NaOH solution allowing for a 10% excess of base solution. After filtration of the resulting soapstock the oil was shaken successively, in a separatory funnel, with hot 8% brine and with hot distilled water until the aqueous extract was neutral to pH paper. The neutral oil was dried over silica gel and subjected to free fatty acid (FFA), peroxide (PV) and anisidine value (AV) determinations. For determinations of anisidine values optically pure hexane was used in our experiments, and the para-anisidine was recrystallized from water containing sodium sulfite and activated carbon, and then dried. Freshly prepared solutions were used for analysis. The active oxygen method (AOM) was used to measure the oxidative keepability and stability of the oils (11).

The neutralized oil, in 108 g batches, was stirred in a three-necked flask equipped with a magnetic stirrer, a thermometer and a vacuum outlet. A pressure equalizing funnel, with wide stopcock bore, was charged with 1.1 g activated clay and connected to one mouth of the flask. Vacuum was then applied to the entire system, and the oil was stirred and heated to 100 C and 30mm Hg pressure. The clay was then added to the hot oil by release through the stopcock, and the entire mixture was stirred by the magnetic stirrer at 100 C under a vacuum of 30mm Hg for 15 min. The mixture was allowed to cool to 35 C under vacuum before being filtered through a Buchner funnel. The filtered oil was subjected to the routine analysis previously described.

TABLE 1

Distribution Parameters on Samples of Experimental Crude Palm Oil and Neutralized Oil Used for Studies Involving Treatment of Clays with Various Concentrations of Sulfuric Acid, and Different Clay Dosage

Parameter	Crude palm oil	Refined palm oil
Moisture (%)	not detectable	not detectable
Free fatty acid[a] (as palmitic, %)	2.85	0.05
Peroxide value[a] (meq/kg oil)	4.0	4.5
para-Anisidine value[a]	2.0	2.4
Total oxidation[b]	10.0	11.4
β-Carotene content (%)	100.0	80.8
Active oxygen method (AOM) stability (hr)	45.0	35.0

[a] Determinations of free fatty acid (FFA), peroxide value (PV) and anisidine value (AV) were done in duplicate and average values reported.

[b] Total oxidation is twice peroxide value (PV) + anisidine value (AV).

RESULTS AND DISCUSSION

The effects of refining are shown in Table 1. The free fatty acid content of the crude palm oil was reduced considerably and 19% of the β-carotene (as calculated from UN-adsorption measurements) was removed by refining.

Tables 2 and 3 show the analyses data upon treatment of the refined oil respectively with 1% clay treated with various concentrations of sulfuric acid, and with varying dosages of clay treated with 3M H_2SO_4. From Table 2 it is observed that the range of acid concentrations used to treat the clays does not lead to significant changes in the free fatty acid content of the refined oil. Examination of the results in Tables 2 and 3 show a rise, albeit negligible, in the free fatty acid content of the oil when the clays were leached with 4M H_2SO_4, and when the clays treated with 3M H_2SO_4 were used at dosage levels of 3% and 4% by weight of the refined oil. If the role of the clays as adsorbent is dependent upon the acidity of the clays, then it is possible that at higher concentrations the acidity of the surface of the clays will increase. This increase in surface activity would contribute to free acid formation (12). An increase in clay dosage would also be expected to lead to an increase in free acid. As evidenced by the results in Tables 2 and 3 the use of 1% clay activated using 4M H_2SO_4 produces the same free fatty acid level, 0.07%, as obtained when the refined oil was treated with 3% and 4% clay activated with 3M H_2SO_4.

Peroxide value. This represents a quality assessment measuring the extent of primary oxidative deterioration in fats and oils. Fats consist of saturated and

TABLE 2

Characteristics of Oils After Treatment at 100 C for 15 Minutes With Clays[a] Activated with 1M, 2M 3M and 4M H_2SO_4

Characteristics	1M H_2SO_4			2M H_2SO_4			3M H_2SO_4			4M H_2HO_4		
	BN[b]	NS[c]	OK[d]	BN[b]	NS[c]	OK[d]	BN[b]	NS[c]	OK[d]	BN[b]	NS[c]	OK[d]
FFA as palmitic (%)	0.05	0.05	0.05	0.05	0.05	0.05	0.06	0.06	0.06	0.07	0.07	0.07
PV (meq/kg oil)	1.0	2.6	1.3	0.7	2.0	0.8	0.7	1.7	0.6	0.9	2.9	1.0
p-AV	4.6	8.6	6.6	3.2	6.7	3.0	3.2	6.1	3.0	6.0	8.9	7.5
Total oxidation	6.6	13.8	9.2	4.6	10.7	4.6	4.6	9.5	4.2	7.8	14.7	9.5
β-Carotene content (%)	71.6	79.5	74.7	57.0	70.0	60.0	55.0	65.0	57.0	61.0	70.0	63.0
AOM-stability (hr)	36	28	35	43	34	40	44	35	44	35	28	34

[a] Clay dosage in all cases was 1% by weight of refined oil used.

[b] BN, Bentonite clay.

[c] NS, natural clay from Nsu area of Eastern Nigeria.

[d] OK, natural clay from Okija area of Eastern Nigeria.

unsaturated acids. The unsaturated acids are susceptible to oxidation; thus, oxygen can add to the fatty acid chain to form peroxides or hydroperoxides. The peroxide value is a measure of the amount of these peroxides and hydroperoxides present in the fat or oil.

From Tables 2 and 3 it is seen that the peroxide value of the refined oil (Table 1) is reduced in all cases. The highest reductions of 0.6 and 0.7 meq/kg oil were obtained when bentonite and Okija clay, respectively, were treated with 3M H_2SO_4 (Table 2). Even for the Nsu clay, which gave the poorest performance overall, the highest reduction in peroxide value was achieved when the clay was leached with 3M H_2SO_4. The results in Table 3 show that when the clays were leached with 3M H_2SO_4 and used in varying dosages, the highest reduction in peroxide value occurs, with the bentonite and Okija clay, when the amount of clay used was 2% by weight of the oil. Further increases in clay dosage did not lead to any measurable reduction in peroxide value. However, for Nsu clay the highest reduction in peroxide value, 0.6 meq/kg oil, was achieved using 4% clay by weight of the oil. Clearly, in terms of the amount of oil to be lost on the clay surface during filtration of a large batch of oil, the reduction in filtration time and cost of clay to be used, both bentonite and the Okija clay proved better than the Nsu clay.

Anisidine values. The anisidine value (13,14) is defined by convention as 100 times the optical density of a solution consisting of 1.00 g of oil or fat in 100 ml of a mixture of solvent and reagent, measured in a 1-cm cell after reaction as described in the standard method. It is a quality assessment measuring the extent of secondary oxidative deterioration of the oil. Aldehydes, particularly α, β-unsaturated aldehydes, are estimated by spectrophotometric measurement at 350 nm after reaction with para-anisidine.

Comparison of the results shown in Tables 1-3 reveals that anisidine values generally were higher for the clay-treated oils than for the refined oil. From Table 2 it is observed that anisidine values were lowest when bentonite and Okija clay were treated with either 2M H_2SO_4 or 3M H_2SO_4, while for Nsu clay the value was lowest when leaching was performed with 3M H_2SO_4, although the value obtained in this case, 6.1, was about twice the values obtained for the oils treated with bentonite and Okija clay. The results in Table 3 show that when the clays were treated with 3M $H_2SO_4$the lowest anisidine value was obtained with Okija clay at a dosage level of 2%. The value obtained, 2.5, compares favorably with the value obtained for the refined oil, 2.4. The use of bentonite at 3% by weight of the refined oil afforded an oil whose anisidine value was 2.8, while Nsu clay used at 4% dose level yielded an oil which had anisidine value 6.0. Thus, the Okija clay treated with 3M H_2SO_4 and used at a dose level of 2% afforded an oil with the lowest anisidine value.

Under the conditions used when the refined oil was treated with clay, it is very likely that the peroxides and hydroperoxides responsible for primary oxidation are decomposed and transformed into carbonyl compounds and or polymeric products. This effect alone would reduce the peroxide value of the oil. However, the net effect will be an increase in the anisidine value of the oil, as is observed in Table 2. However, the further reduction of the anisidine values as seen from the results in Table 3 indicate that the bentonite and Okija clay are active in removing the oxidative breakdown products. According to Wiedermann (1), these oxidative breakdown products are not removed to any significant extent by deodorization; their only opportunity for removal is in the bleaching step.

Oxidation value. The total oxidation is calculated from the peroxide and anisidine values as follows: Totox = twice peroxide value + anisidine value. Johansson (11) has noted that a crude palm oil will, under proper conditions, give a bleached palm oil whose oxidation value decreases to half the original value. Comparison of the data shown in Tables 1 and 3 indicates that such proper conditions were satisfied by bentonite and Okija clay in all cases, but not satisfied by Nsu clay in any case. The best condition for Okija clay was when the clay was used at a dose level of 2% by weight of the oil, while for bentonite the best condition was at a dose level of 3%.

Carotenoids. The β-carotene content of the palm oil decreased progressively as the crude palm oil was subjected to refining and bleaching operations. As the clay dosage level increased the amount of residual β-carotene decreased, and all the tested clays exhibited maximum adsorptive ability in this regard at dosage levels of 4% (Table 3). However, treatment of the refined oil with clays leached using 4M H_2SO_4 did not lead to any further reduction in carotene content. The

TABLE 3

Analysis of Oils After Treatment at 100 C for 15 Minutes Using Varying Dosages of Clay Activated With 3M H_2SO_4

	1% Clay by wt of oil			2% Clay by wt of oil			3% Clay by wt of oil			4% Clay by wt of oil		
Parameters	BN[a]	NS[b]	OK[c]	BN[a]	NS[b]	OK[c]	BN[a]	NS[b]	OK[c]	BN[a]	NS[b]	OK[c]
FFA as palmitic (%)	0.06	0.06	0.06	0.06	0.06	0.06	0.07	0.07	0.07	0.07	0.07	0.07
PV (meq/kg oil)	0.7	1.7	0.6	0.2	1.5	0.2	0.2	1.0	0.2	0.2	0.6	0.2
p-AV	3.2	6.1	3.0	3.0	6.0	2.5	2.8	6.6	2.6	3.0	6.0	3.0
Total oxidation	4.6	9.5	4.2	3.4	9.0	2.9	3.2	8.6	3.0	3.4	7.2	3.4
β-Carotene content (%)	55	65	57	50	64	55	40	54	45	38	50	40
AOM stability (hr)	44	35	44	46	38	48	44	36	45	40	35	40

[a] BN, Bentonite clay.

[b] NS, Natural clay from Nsu area of Eastern Nigeria.

[c] OK, Natural clay from Okija area of Eastern Nigeria.

lower bleaching ability observed at this higher concentration of acid, as shown by less β-carotene removed, may be attributable to the collapse of the structure of the clays (6). Bentonite proved slightly superior to Okija clay in all the experiments whose results are tabulated. The inference from the results in Tables 2 and 3 indicates Okija clay can function as an adsorptive cleanser in refining Nigerian crude palm oil. Bleaching of palm oil to eliminate all carotenoids takes place, to a great degree, during deodorization of the oil; this aspect was not the focus of this investigation.

AOM—stability. In these experiments conducted under accelerated conditions the time elapsing before a peroxide value of 100 meq/kg oil is reached is recorded. However, the peroxide values do not represent the absolute state of oxidation of an oil because of the transitory nature of the peroxides (15). Nevertheless, the merit and accuracy of these determinations are most satisfactory (11).

The results from these experiments were used to measure the oxidative keepability of the oil and, hence, the overall performance of the clays under the various conditions of the experiments. We have, therefore, established that the optimum conditions for use of Okija clay as adsorptive cleansers to commercially bleach the Nigerian palm oil entail activation of the clay using 3M H_2SO_4 and use of 2% clay by weight of oil at 100 C for 15 min under a vacuum of 30mm Hg.

Stability of oils on storage. The edible crude palm oil bought from the local Lafenwa market had a free fatty acid content of 5.62 and a peroxide value of 6.5 meq/kg oil. This oil was regarded as being of high quality by market women who, organoleptically, assess the various crude palm oils available for sale. After refining, these values dropped to 0.1% and 6.0 meq/kg oil for the free fatty acid and peroxide value, respectively. The refined oil was then subjected to clay treatment.

The values which appear in Table 4 show the changes in peroxide values for refined oils treated with the clays and stored at 8 C for two yr. It was observed that treatment of the refined oil with bentonite initially reduced the peroxide value the greatest from 6.0 to 2.32 meq/kg oil. Oil treated with Okija clay reduced the peroxide value to 2.72 mel/kg oil, while for oil treated with Nsu clay the peroxide value (4.23 meq/kg oil) was not as low as the values in oils treated with the other two clays. After storage for 24 mo at 8 C the oil treated with bentonite had the lowest peroxide value, 5.23 meq/kg oil, compared to 5.82 and 7.83 meq/kg oil for the oils treated with Okija and Nsu clays, respectively. However, the differences in changes in peroxide values were not dramatic. An increase in peroxide value of 2.91 meq/kg oil was observed for the oil treated with bentonite, 3.60 meq/kg oil for the oil treated with Nsu clay and 3.10 meq/kg oil for the oil treated with Okija clay. It is rather surprising that such changes could occur at that seemingly low temperature. The literature is deficient on changes in peroxide values of palm oil at temperatures lower than ambient. While the changes in peroxide values for the first six months for the bentonite- and Okija clay-treated oils may be considered negligible, the changes in peroxide values after 12 months are significant. Thus, even in the semi-solid state autoxidation takes place in clay-treated nondeodorized palm oil.

TABLE 4

Changes in Peroxide Values for Refined Oils Treated With Bentonite (BN), Nsu (NS) and Okija (OK) Clays and Stored at 8 C in Amber Glass Bottles

Storage at 8 C (mo)	Peroxide values (meq/kg oil) for oils treated with clay types		
	BN	NS	OK
0	2.32	4.23	2.72
2	2.42	4.66	2.98
6	2.78	5.22	3.37
12	3.55	6.10	3.85
18	4.64	6.89	4.84
24	5.23	7.83	5.82

TABLE 5

Peroxide Values for Refined Oils Treated With Different Clays and Stored at 30 C and 60 C, in Amber Glass Bottles

Storage (days)	Peroxide values (meq/kg oil)					
	30 C			60 C		
	BN[a]	NS[b]	OK[c]	BN[a]	NS[b]	OK[c]
0	2.3	4.2	2.7	2.3	4.23	2.7
14	6.4	9.2	6.4	19.8	31.7	20.6
28	14.6	18.2	15.7	42.4	51.8	43.5
42	22.4	27.8	22.8	68.4	82.3	69.8
56	27.4	36.7	28.4	91.5	128.2	93.5
70	32.6	46.2	33.6	117.0	183.4	120.0
84	41.4	55.4	43.2	146.6	—	152.5
98	53.2	66.2	55.8	—	—	—

[a] BN, Bentonite clay.
[b] NS, Natural clay from Nsu area of Eastern Nigeria.
[c] OK, Natural clay from Okija area of Eastern Nigeria.

The effect of temperature on primary oxidation is evident from the results presented in Table 5. For samples stored at room temperature (30 C) over a period of 98 days an increase in peroxide value of nearly 51 meq/kg oil was observed for the oil treated with bentonite, while the corresponding changes were about 62 and 53 meq/kg oil, respectively, for oils treated with Nsu and Okija clays. The increases in peroxide values were relatively small up to 98 days, and a peroxide value of 100 meq/kg oil still had not been reached. As expected, the data in Table 5 also show that the formation of peroxides is more rapid at elevated temperature. After 49 days at 60 C the peroxide value of the oil treated with Nsu clay reached 100 meq/kg oil, whereas it took 63 days for oils treated with bentonite and Okija clay to reach the same peroxide value. The results presented in Table 5 gave us the preliminary indications that treated natural local clays from Okija and Nsu could be used as adsorptive cleansers in refining Nigerian crude palm, and this led to experiments the results of which (Tables 1-3) have been described extensively in this paper.

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