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Investigation of the effects of bleaching clay particles on the quality and stability of physically refined palm oil

S.O. Egbuna, N.A.G. Aneke and T.O. Chime

Department of Chemical Engineering, Enugu State University Of Science And Technology, Enugu.

Abstract

This work investigated the effects of bleaching clay particles on the quality and stability of physically refined palm oil. The raw palm oil used in the investigation was obtained from a local palm Oil mill, in Enugu State. The oil was characterized before and after refining and used in the investigation. The result showed that quality of final product of palm oil during and after refining, depends on the conditions of filtration at the bleaching and deodorization stages. The deodorization was done at a temperature of 200^{o}C and at a contact time of eight hours. It was established that colour fixation during deodorization is mainly due to the presence of fine particles in the oil during deodorization and on the decomposition of the oxidation products of aldehydes and ketones at the deodorization temperature of 200^{o}C and above. The stability standard of the refined oil was however, measured in terms of colour, 3.2 Red units, Free Fatty Acid (FFA) 0.12%, Peroxide Value (PV) 3.0 m.eq/kg, Anisidine Value(AV) 4.85 m.eq/kg, Iodine Value (IV) 49, Iron (Fe) 4.3 x 10^{3}(Ppm), and Phosphorous content 0.015 (Ppm), all of which were compared with those of the American Oil Chemist Society (AOCS) standard values.

Key words: Quality, Stability, Filtration, Deodorization, and characterization

1.0 Introduction

Palm Oil fruit, is a monocotyledonous fruit obtained from oil palm (Elaeis Guinensis) found in abundance in the Eastern part of Nigeria. It is 0.5 to 5mm long, and oval in shape and weighs about 6 - 8g on the average. The oil content of the fruit is about 50%. This oil is a water insoluble substance which consists predominantly of glycerol esters of fatty acids or triglycerides, according to Jamieson (1943). The triglycerides contain approximately 95% of fatty acid and 5% glycerol, combined as part of the glyceride molecules and the reactive portion. It is this triglycerides that we wish to purify.

Human beings have known how to extract oils from their natural sources since ancient time, and make them fit for their use. The oils were consumed crude since very little treatment was done other than filtration or decantation. In Nigeria, palm oil is still consumed crude.

In the past few years, demand for refined palm oils has increased worldwide. This might be due to increase in world population, rising standard of living and consumer preference. The oil finds applications as cooking and frying oils, as well as in the manufacture of margarine, shortening, baker's fat, soap, grease, lubricants, creams, etcetera, and hence the need to stabilize its quality for these purposes.

Two methods are used in the extraction of the oil in the recent times, namely mechanical expression and solvent extraction. The former is pressure dependent, while the latter works with diffusion principles, making use of n - hexane as solvent. The oil contains considerable amount of impurities like Free Fatty acid, carotene and chlorophyll pigments, phosphotides, odour, and oxidation products, which are usually removed by refining, because they impart unpleasant odour and flavour to the finished product.

Two refining methods are available; the chemical process, which makes use of caustic lye to neutralize the FFA content, and the physical process, which came into use by the 20th century, and is essentially a distillation process. The latter was so much improved upon at the deodorization

stage, with the effect of reduction in overall processing cost.

Practical experience has distinguished the two process routes. There is a substantial colour reduction at the neutralization stage, and fuel savings on steam distillation of the chemical process, due to the moderate temperature applied to preserve the anti oxidants, sterol and tocopherol present in the oil. Capacity is also improved, and quality is assured. The physical process offers advantages of improved deodorizer efficiency, low water consumption, reduced oil loss, savings on chemical, manpower reduction, less corrosion and pollution tendencies, and equally high quality stability, and hence its choice of the process method.

Bailey (1950), asserts that the chemical and physical properties of fats and oils are determined by the properties of their component fatty acids. Markley (1964), also noted that, as the average molecular weight of the fatty acid increases, fats progressively have higher melting points and can more easily solidify. Egbuna and Aneke, (2005), have shown that bleaching stage of the refining of palm oil and the nature of the bleaching clay used play a vital role in the stability of the finished product. Hymore and Ajayi, (1989), have also demonstrated that Local activated Clay can effectively remove caroteniod from palm oil.

Many factors influence the stability of refined palm oil, and have been the subject of much study. Among them are; type of raw oil, its colour, Phosphotides, Free fatty acid content, taste, and other physical and chemical characteristics. To be refined, the raw oil has to be degummed, bleached, deodorized, and filtered at the bleaching and deodorizing stages, in order to remove its objectionable properties. The deodorization and filtration processes are well-established operations in the processing of edible oils, and are major stages for the stabilization of the refined oils. All the suspended particles would have been removed at this stage. This paper, has therefore demonstrated how an effective filtration after bleaching can lead to good oil quality, and why it remains a vital part of palm oil refining. It has also shown how the stability of the refined palm oil is affected by the conditions under which the refining is carried out.

2.0 EXPERIMENTAL

2.1 Materials/Equipment:

The materials and equipment used in the investigation include; raw (crude) palm oil received from Inyi in Enugu state, bleaching earth (Activated clay), test chemicals, titration apparati, a set of sieves, Lovibond Tintometer, Steam/vacuum apparatus, Distillation apparatus, conical flasks, beakers, and test tubes, magnetic stirrer, funnel, and steam bath. Table 1 shows the physio-chemical properties of the palm oil used in the investigation, while Table 2, shows the conditions of temperature and time used in the experiments.

Table 1. Physio - Chemical properties of the palm oil used in the investigation.

Characteristics	*Crude palm oil*
Physical Colour	Deep orange red
Odour	Slight palm oil odour
Taste	Palm fruit taste
Sp. Gravity	0.9201
Slip/Melting point	36^{o}C
Moisture	1.2%
Refractive index	1.4520
Free fatty acid (FFA)	4.0%
Colour in 1 inch cell	22 Red units
Anisidine value m.eq/kg	7.8
Peroxide value m.eq/kg	5.6
Acid value	8.6
Phosphorous (Ppm)	9.0
Iodine value	50
Iron (Ppb)	2.8

2.1.1 Properties:

The properties of the oil that were determined include, the P (Ppm), and FFA(%), PV(m.eq/kg), AV(m.eq/kg), Colour, Fe(Ppb), etcetera, of the degummed, bleached and deodorized palm oil. This was done by using the American Oil Chemists Society (AOCS) test standard methods. Their values are presented in Table 3.

Table 2. Laboratory physical refining conditions with 1% bleaching earth.

Parameters	Degumming	Bleaching	Deodorization
Temperature (^{o}C)	65	120	200
Time (minutes)	30	30	60

2.1.2 Sample:

The crude and refined oil samples used for the stability tests were stored in full, glass bottles at 313K for 28 days. Colour, phosphorous, FFA , PV, and AV, were measured at intervals. The activated bleaching clay used was sieved to 70 - 5 microns and the same sample was used throughout the experiment.

2.2 Experimental procedure:

2.2.1 Degumming Process :

Degumming of crude Palm oil was done to reduce the phosphatide so as to minimize the foaming tendency of the finished product observed during frying. The experiment was done using phosphoric acid, citric acid, and water, and the result presented in Fig. 1.

One per cent (1%) by weight each of citric acid and phosphoric acid were added to 100g of the crude oil sample in a conical flask. The mixture was heated to a constant temperature of 338K, and stirring done with the magnetic stirrer for 30 minutes. The whole mass was poured into a separating funnel and allowed to settle for 30 minutes. The lower layer (the lecithin), was run off through a valve. Similar experiment was done with 1%wt, of water.

2.2.2 Bleaching:

The aim of bleaching was to reduce the carotene pigments so as to minimize the formation of hydroperoxides during deodorization and storage. The experiment was done with the activated clay.

One per cent (1%) by weight of the clay was added to 100g of the oil sample. The mixture was heated to a constant temperature of 373K, with stirring for 30 minutes. The oil was then filtered at the same temperature, and the filtrate characterized. The results are shown in Table 3. The filtration was done with funnel and vacuum pump.

2.2.3 Deodorization:

Deodorization, which essentially is steam distillation, is aimed at removing odour, colour, FFA and undesirable flavour in the oil. This was done at a temperature of 473^{o}C and for 60 minutes. At these conditions, the β - carotene pigment bonds are broken and the pigments, as well as Iron metal, which is a pro-oxidant, are removed with the odoriferous materials, thereby improving the colour and taste of the final product.

1 liter of Filtered oil was taken into the distillation equipment and pre - heated to a temperature of 373K. Steam was generated by heating water in a around bottom flask and passed into the oil through a delivery tube. Temperature was then increased to 473 K, and vacuum was applied by means of the vacuum pump and maintained at 20mmHg absolute. Vaporized moisture, odoriferous matter, FFA, and colour pigments were

$$\text{Phosphorous (Ppm)} = \frac{A \times V \times 5 \times 0.326}{G \times v \times 10000} \quad \ldots\ldots\ldots 1$$

condensed in the reflux condenser in which water is used as a cooling medium. The condensate which was essentially Fatty acid , was collected in a beaker. This is a batch process. The experiment was repeated by putting 0.02g of the bleaching clay into another portion of the bleached and filtered oil before deodorization The refined oil was then analyzed for FFA, Colour, PV, AV, P and Fe after 1, 4, 7, 14, 21, and 28 days as shown in table 5

2.3 Characterization of degummed, bleached, and deodorized oils

The degummed, bleached, and deodorized oil samples were subjected to analyses to determine their physical and chemical properties. Among the properties determined, which will be reported here include; Colour, FFA, PV,AV, P and Fe contents

2.3.1 Phosphorous:
The phosphorous in the oil sample was determined by ashing. The phosphate obtained was transferred into phosphomolybdate which was reduced to a blue-coloured compound. The concentration of the blue compound was determined by comparison with blue colored glass disks.

Procedure:
5g oil sample was weighed into a platinum dish, and 0.5g calcium oxide added and both ashed. The ash was dissolved in 10 - 15 cm^3 of 2N hot dilute hydrochloric acid, and filtered into a 100 cm^3 volumetric flask. The dish was washed into the volumetric flask and filtered, and, made up to 100 cm^3. A blank experiment was similarly prepared, but with no oil sample present. 5 cm^3 of the filtrate was taken in a tube and 2 cm^3 and 1 cm^3 of molybdate and hydroquinone solution added in that order. The mixture was allowed to stand for 5 minute for the green phosphate colour to develop. 2 cm^3 of carbonate/sulphate solution was quickly added and stirred, (CO_2 evolved). Both the test experiment and its blank were placed in the comparator against a uniform light for comparison. The result was reported as ;

Where A - comparator scale reading of P (Ppm), V - Volume of ash solution, v - volume of ash solution taken for the colour development, G - weight of oil sample.

2.3.2 Colour pigments: Colour pigments present in Palm oil include; carotenoids, chlorophyll, and gossypol. The carotene has been found to be an excellent indicator of crude oil quality.

Table 3 Laboratory experimental results compared with the international standard. (Test temperature is 65^{o}C, and bleaching earth dosage is 1%)

Parameters	Laboratory experiment			International standard		
	Degummed Oil	Bleached Oil	Deodorized Oil	Degummed Oil	Bleached Oil	Deodorized Oil
Colourin1inch cell	19.5 Red unit	11.5Red units	3.2Red units	20.0 Red unit	10.5Red units	2.5 Red units
FFA%	3.5	3.6	0.12	3.2	3.5	0.100
PV m.eq/kg	4.6	3.0	1.15	**4.8**	3.2	1.000
AV m.eq/kg	7.0	5.8	3.85	6.6	6.0	3.700
IV (Ppb)	50.6	45.2	45.0	50.6	46.0	45.00
P (Ppm)	0.54	0.38	0.015	0.52	0.35	0.012
Iron x 10^3	28.9	20.0	0.08	28.0	20.0	0.050

$$FFA\ (\%) = \frac{V \times M \times N}{10W} \text{ .... .2}$$

Procedure: Lovibond Tintometer with 1-inch cell was used for the analysis of colour, and the latter read in terms of red colour band that matched the colour of the refined oils.

2.3.2 Free Fatty acid:
Free fatty acid results from chemical or enzymatic hydrolysis of the fatty acid glycerides. Its presence in oil sample is a measure of the quality of the crude and refined oils.

Procedure: 2.8ml of oil of known FFA, was measured into a conical flask and diluted with 25ml of ethanol. A drop of phenolphthalein was added. This was titrated against 0.1N sodium hydroxide until a permanent pink colour was registered, and the results recorded.

Where, N - Normality of NaOH; V - Volume of NaOH; W - Weight of oil sample, M- Molecular weight of palm oil sample used. 2.3.4 Oxidation products:
When an unsaturated fatty acid chain reacts with air at room temperature, (a process known as autoxidation), hydroperoxides are formed. At high temperature, these peroxides break down to hydrocarbons, aldehydes and ketones. These cleavage products impart odour and flavour to oil and must be removed.

i) Peroxide Value;
This is a measure of primary oxidation whose product is hydrocarbons. These hydrocarbons are further oxidized to water, which causes rancidity of the oil on storage.

Procedure:
30ml of chloroform - glacial ethanoic acid mixture in the volume ratio of 1:2 was transferred to a conical flask connected to a reflux condenser. The mixture was then heated to boiling and the vapour condensed in the lower part of a jacketed tube. When the reflux became steady, about 1.6 ml of potassium iodide was added from the top of the condenser. The precipitate of KI was dissolved by adding 5 drops of water. The mixture was heated for 5 minutes and 2ml of the oil was pipetted into the mixture through the top of the condenser also. The pipette was rinsed with 2ml of chloroform into the boiling mixture, and boiling continued for 5 minutes. 50ml of distilled water was added, and 2ml of the sample was then titrated with 0.02N thiosulphate solution, using starch solution as indicator. The result is reported as;

$$PV = \frac{V \times N \times 1000}{G} \text{ ....3}$$

Where V - vol. of thiosulphate used (ml), N - normality of thiosulphate solution, and G - vol. of oil sample (ml)

(ii) Anisidine value;
This measures the amount of secondary oxidation in a sample of oil. Its products are aldehydes and ketones, whose oxidation induces higher rancidity effect to the oil.

Procedure;
The procedure for analysis for AV is the same as in the PV, except that the temperature at which these cleavage products are formed is higher.

2.3.4 Iron (Fe): This is a metal element which, with copper, induces oxidation of the unsaturated fats and oils at the double bond. Removal of iron will reduce the rate of oxidation reaction at the high temperature of deodorization.

Procedure:
0.2mg Fe stock solution was pipetted into 100ml conical flask. 10ml of 10% hydroxylamine hydrochloride was added The solution was dilutedwith water and mixed. 10 ml of 0.25% phenolphthalein was added and allowed to stand for 15 minutes and diluted to the mark. Using about 5ml test tube, the transmittance was read in spectrophotometer 20 at 510 UV light.
Note that all the characterization experiments were repeated with the deodorized oil containing 0.02g bleaching clay particles.

Table 4 The effect of deodorized palm oil temperature on the Colour and FFA of physically refined oil (for filtered oil and oil with 0.02% fines)

Temp ^oC	Colour in 1 inch cell		Deodor oil (Filtered)		Deodor oil (with 0.02g bleaching clay)	
	Degummed Oil at 65^oC	Bleached oil at 120^oC	Colourin 1 inch cell	FFA%	Colourin 1 inch cell	FFA%
150	21.2	14.2	3.8	0.62	3.8	1.20
160	20.8	13.8	3.7	0.61	3.7	1.00
170	20.6	13.5	3.6	0.58	3.5	0.80
180	20.3	13.3	3.4	0.55	3.2	0.60
190	20.1	12.6	3.3	0.38	2.9	0.20
200	19.5	11.5	3.2	0.12	2.8	0.15
210	19.5	9.8	2.8	0.14	2.8	0.20
220	19.8	9.8	2.9	0.15	3.3	0.42
230	20.3	10.5	3.0	0.18	3.8	0.65

3.0 RESULT

We, have investigated how the presence of bleaching earth particles during filtration stage of palm oil refining affects the quality and stability of the final product. The ideal conditions under which the filtration should be done to optimize oil quality, were also established by monitoring their influence on oil colour, FFA, AV and PV contents of the oil. These conditions include, temperature, particle size distribution, and contact time. Their variation necessitated the effective operation of the filtration stage, so as to achieve the quality standard mentioned earlier. The results of this work are presented in Tables and graphs.

4.0 DISCUSSION

4.1 Temperature

Table 4 presents the deodorized oil colour, (Red unit), as a function of temperature. The subsequent deodorization colour is shown when 0.02g bleaching clay was added.

From the table, the degummed oil colour reduces as temperatures increases, with optimum at 200 - 210^oC. The corresponding bleached and deodorized colours are optimized at the deodorization temperature in the same range, beyond which the colour begins to rise marginally for the oil without "fines". With 0.02g fines in the bleached oil before deodorization, there is a little variation in colour as shown in the table. However, FFA is increased as temperature increases from the optimum level but at a greater margin than the former. This explains why it is necessary to filter the oil properly before deodorization The Peroxide value of the degummed/bleached/deodorized oil, increases rapidly on storage showing that oxidation products of aldehydes and ketones are not effectively removed at high temperature. This is confirmed on storage as shown in Table 5, when the PV of deodorized oil rises more rapidly for oil deodorized with clay fines than without fines.

Table 5. The effect of colour and PV on the keeping quality physically refined palm oil

Time(days)	Colour (red), 1" Cell				PV Deodorized oil	
	Degummed at 65^oC	Bleached at 120^oC	Deodorized (without tfines)	Deodorized (with fines)	Deodorized (without fines)	Deodorized (with fines)
1	19.2	14.2	3.8	3.8	0.00	0.00
4	19.8	14.8	4.7	5.7	0.46	1.80
7	20.2	15.4	5.6	6.6	0.82	2.00
14	20.6	15.9	6.4	8.4	1.17	2.32
21	21.2	16.5	7.3	9.8	1.50	2.80
28	21.8	17.0	8.2	12.2	1.75	3.48

Table 5 shows that there is colour reversion during storage for deodorized oil degummed at any given temperature, but reversion is much more when deodorized with clay fines present than when absent. This gives a darker oil as shown by a sudden change observed from the 14th day.

4.2 Particle size distribution:

Fig.1 shows that for any given particle size, deodorized oil colour continues to reduce as the particle size is increased. There appeared to be an optimum at a particle size of between 10 and 15 microns, beyond which colour starts to rise more rapidly, and this colour is fixed at higher temperature. It was however, noticed that colour reduces sharply when deodorizing with no fines in the bleached oil than when it contains some fines. It then means that best colour reduction can be achieved at a particle size in the range between 10 and 15 micron with optimum at 8 micron.

The removal of FFA and PV from the oil is also a function of particle size as shown in Figs. 2 and 3 respectively. From the figures, it is shown that the lower the particle size, the increase in the reduction of FFA and PV until the optimum of 8 micron is reached, at which FFA starts to rise marginally.

As shown in table 4, the reduction of FFA with clay is higher when deodorized at 200°C than at other temperatures. The reduction is sharp up to a 10 micron particle size, beyond which, it is marginally reduced as shown in Fig 2.

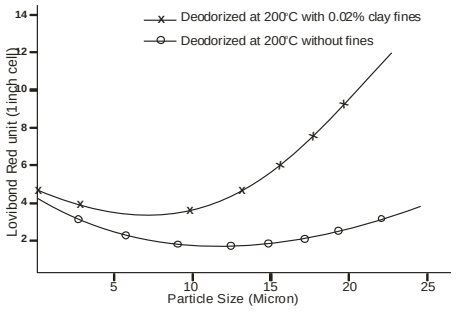


Figure. 1 The effects of particle size on the colour of physically refined

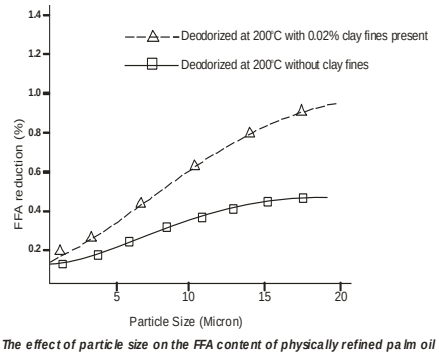


Figure. 2 The effect of particle size on the FFA content of physically refined palm oil

Peroxide value and AV are reduced by reducing particle size, until a size of 15 micron is reached at which it is marginal, Fig.3. As shown in Table 4 however, as PV is reduced at the deodorization temperature of 200°C, AV is sharply increased from a temperature of 210 - 230°C. There should therefore be a compromise between reducing particle size, which reduces AV, and Temperature, which also increases AV. The optimum is found in the range of 10 - 15 microns

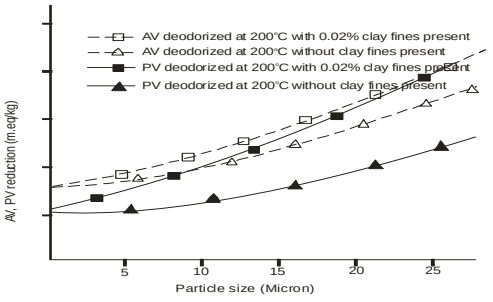
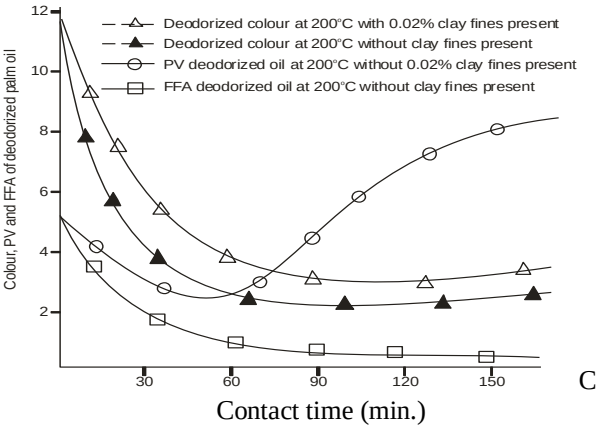


Figure 3 Effects of particle size on PV of physically refined palm oil.

4.3 Contact time:

A contact time of 60 minutes at the deodorization temperature, is enough to sharply reduce the PV, FFA, and colour to minimum. Beyond this time, the PV begins to rise, Fig.4. FFA, and colour however, decrease marginally, but FFA reduces at a rate greater than the colour which, is not so much affected by prolonged contact time beyond a contact time of 60 minutes, provided the deodorized oil temperature is not beyond 200°C, and that the deodorization is under vacuum.



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Fig 4 The effects of chemical concentration on the PV and AV of physically refined palm oil.

5. CONCLUSION

The results obtained, have demonstrated that the quality and stability of finished palm oil product, can be greatly influenced by the presence of particles and particle size distribution. Variation of the deodorization conditions has shown how temperature, particle size and time conditions can affect the stability of the final product. The result showed that the deodorization temperature should not be more than 200°C, since the lower marginal colour obtained by increasing temperature does not improve the colour quality of the final product. A very high reduction in particle size will not improve the quality stability of the final product,

since particle fines will pass through the filtration apparatus to foul the oil. However, the exact level required for optimum result, depends on the type of oil, distribution of size of particles and on the time of contact between the oil and the bleaching earth. Since an effective degumming can improve the quality of the final product, effective removal of the colour and FFA, and the reduction of PV and AV, are very necessary in order to stabilize the quality of the physically refined palm oil.

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