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Evaluation of the effects of degumming on the quality and stability of physically refined palm oil

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Abstract

This work investigated the effects of degumming stage on the stability of physically refined palm oil. The raw palm oil used in the investigation was obtained from Adah palm Oil mill, in Imo 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 refining depends on the conditions of degumming, and on the nature of the degumming chemicals used. The degumming was done at a temperature range of 35 to 75^{o}C, and the optimum temperature was found to be 65^{o}C, at the contact time of 30 minutes. It was established that colour fixation during deodorization is mainly due to 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,2.5 Red units, Free Fatty Acid(FFA) 0.01%, Peroxide Value(PV) 2.8m.eq/kg, Anisidine Value(AV) 6.8m.eq/kg, Iodine Value(IV) 4.9, Iron (Fe) 4.3 x 10^{3}(ppb), and Phosphorous content 0.01(ppm), all of which were compared with those of the American Oil Chemist Society (AOCS).

1. Introduction

In the past few years demand for refined vegetable oils has increased worldwide. This might be due to increase in world population, rising standard of living and consumer preference. Vegetable oils find 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.

Palm Oil fruit, is a monocotyledonous fruit obtained from oil palm (Elacis Guineasis) 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%.

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 order than filtration or decantation. In Nigeria, palm oil is still consumed crude.

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 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. 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 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.

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 oils, 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 and deodorized in order to remove its objectionable properties. The degumming process is a well-established operation in the processing of edible oils, and is one of the major stages for the stabilization of the refined oils. All the colloidal and suspended particles, and soluble phosphotides would have been removed at this stage.

This paper, has therefore demonstrated how an effective degumming stage 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 degumming is carried out.

2. Experimental

2.1. Materials/equipment

The materials and equipment used in the investigation include; raw (crude) palm oil received from Adah palm Industry, Imo 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, 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	0.9182
Slip/Melting point	35^{o}C
Moisture	1.3%
Refractive index	1.4512
Free fatty acid (FFA)	3.8%
Colour in 1 inch cell	23Red units
Anisidine value m.eq/kg	8.2
Peroxide value m.eq/kg	5.8
Acid value	9.8
Phosphorous (Ppm)	9.0
Iodine value	48.0
Iron (Ppb)	3.0

Table 2
Laboratory physical refining conditions with 1% bleaching earth

Parameters	Degumming	Bleaching	Deodorization
Temp.(^{o}C)	65	120	200
Time (mins)	30	30	60

2.1.1. Properties

The properties of the oil that were determined include, the PO_4 (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.

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 is done to reduce the phosphotide so as to minimize the foaming tendency of the finished product observed during frying. The experiment was done using Citric acid, phosphoric acid and water, and the result presented in Fig. 1.

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	2.8	0.12	3.2	3.5	0.1

PV m.eq/kg	5.8	4.2	3.00	4.8	3.2	1.0
AV m.eq/kg	7.5	6.4	4.05	6.6	6.0	3.7
IV (Ppb)	50.6	45.2	45.0	50.6	46.0	45.0
Phosphorous	0.54	0.5	0.015	0.52	0.35	0.012
Iron	350	20.0	4.30	280	200	0.05

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% by weight of water. Temperature was subsequently varied.

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.

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.

2.2.3. Deodorization

Deodorization, which essentially is steam distillation, was 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 b - Carotene pigment bond are broken and the pigments, as well as Iron metal which is pro-oxidant are removed with the odoriferous materials, thereby improving the colour and taste of the refined product.

1 liter of degummed oil was taken into the distillation equipment and pre - heated to a temperature of 373K. Steam is 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. Vapourized moisture, odoriferous matter, FFA, and colour pigments were 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 refined oil was then analyzed for FFA, colour, PV, AV, PO_4 and Fe.

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, PO_4 and Fe contents

2.3.1. Phosphorous

The phosphorous in the oil sample is determined by ashing. The phosphate obtained is transferred into phosphomolybdate which is reduced to a blue- coloured compound . The concentration of the blue compound is 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 is dissolved in 10 - 15 cc of 2N hot dilute hydrochloric acid, and filtered into a 100cc volumetric flask. The dish is washed into the volumetric flask and filtered, and, made up to 100cc. A blank experiment was similarly prepared, but with no oil sample present. 5cc of the filtrate was taken in a tube and 2cc and 1cc of molybdate and hydroquinone solution added in that order. The mixture is allowed to stand for 5 minute for the green phosphate colour to develop. 2cc of carbonate/sulphate solution is quickly added and stirred, (CO_2 evolved). Both the main experiment and its blank are placed in the comparator against a uniform light for comparison. The result is reported as ;

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

Where A - comparator scale reading of PO_4 (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. 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.

2.3.3. 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. 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.

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

Where, N - Normality of NaOH; V - Volume of NaOH; W - Weight of oil sample, M- Molecular weight of oil.

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.

2.3.5. 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 vapory 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;

$$PV = \frac{V \times N \times 1000}{G} \quad \ldots(3)$$

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

2.3.6. 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. 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.

2.3.7. 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. 0.2mg Fe stock solution was pipetted into 100ml conical flask. 10ml of 10% hydroxylamine hydrochloride was added. The solution was diluted with water and mixed. 10ml 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

3. Results

We, have investigated how the degumming stage of palm oil refining affects the quality stability of the final product. The ideal conditions under which the degumming chemicals should be used 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, chemical concentration, and contact time. Their variation necessitated the modification of the degumming stage, so as to achieve the quality standard mentioned earlier. The results of this work are presented in Tables and graphs.

4. Discussion

4.1. Effect of degumming temperature

Table 4 presents the degummed oil colour, (Red unit), as a function of temperature. The subsequent deodorization colour is shown when deodorized at constant temperature.

From the table, the degummed oil colour reduces as temperatures increases, with optimum at 65 ^{o}C. The corresponding bleached temperatures is optimized at the degumming temperature in the range of between 65 and 70^{o}C, while the deodorized temperature is optimized at a degumming temperature of 60 - 65^{o}C. The peroxide value of the degummed/bleached oil, is reduced as degumming temperature increases, but the rise in Anisidine Value is an indication 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 degummed oil rises more rapidly for oil degummed at 75^{o}C than 65 ^{o}C. The FFA, and PO_4 are gradually reduced up to the degumming temperature of 65 ^{o}C, beyond which they start to rise again. However, Fe continued to reduce even at the degumming temperature of 75^{o}C. Table 5 shows that there is colour reversion during storage for deodorized oil degummed at any given temperature, but reversion is much more when degummed at higher temperatures than 65^{o}C. This gives a darker oil as shown by a sudden change observed from the 14th day.

4.2. Chemical concentration

Figure 1 shows that for any given degumming chemical, bleached oil colour continues to reduce as the concentration is increased. There appeared to be an optimum at a concentration of between 0.03 and 0.05, beyond which colour starts to rise again, and this colour is fixed at the high temperature of the deodorizer. However, it was noticed that bleached oil colour reduces sharply when degummed with citric acid than phosphoric acid, but the corresponding deodorized oil colour gives minimum with phosphoric acid than citric acid. It then means that best colour reduction can be achieved at a concentration range of between 0.02 and

0.05 with optimum at 0.03. However, H_2PO_4 offers better colour reduction than citric acid. The removal of Iron and phosphorous from the oil, is also a function of bleaching chemical concentration as shown in Figs. 2 and 3 respectively.

Table 4
The effect of degumming- temperature on the colour, the properties of physically refined palm oil

Temp ^oC	Colour in 1 inch cell			PV m.eq/kg	AV m.eq/kg	FFA %	PO_4 (Ppm)	Fe (Ppb)
	Degummed Oil	Bleached oil	Deodor oil					
35	21.2	14.2	3.8	6.8	3.5	0.62	0.83	8.1
40	20.8	13.8	3.6	6.5	3.55	0.61	0.65	8.0
45	20.6	13.5	3.5	5.3	3.72	0.58	0.48	7.8
50	20.3	13.3	3.2	5.0	3.85	0.55	0.22	7.3
55	20.1	12.6	3.0	4.2	3.92	0.38	0.15	6.8
60	19.8	11.6	2.9	2.0	4.00	0.20	0.02	5.0
65	19.5	9.8	2.8	1.12	4.20	0.12	0.02	4.3
70	19.8	9.8	3.0	1.50	9.8	0.15	0.03	4.2
75	20.3	10.5	3.8	1.28	12.4	0.18	0.08	4.0

Table 5
The effects of colour and PV on the keeping quality of physically refined palm oil, (deguming temperature constant)

Time(days)	Colour (red), 1" Cell		PV Deodorized oil	
	Degummed at 65^oC	Degummed at 75^oC	Degummed at 65^oC	Degummed at 75^oC
1	3.20	5.8	0.00	0.00
4	3.26	5.9	0.46	1.80
7	3.30	6.2	0.82	2.00
14	3.40	6.8	1.17	2.32
21	3.45	7.4	1.50	2.80
28	3.81	8.6	1.75	3.48

From the figures, it is shown that the higher the concentration, the increase in the reduction of Iron and phosphorous until the optimum of 0.02N is reached, at which phosphorous starts to rise.

As shown in Fig. 2, the reduction of iron with chemical is higher with phosphoric acid than with citric acid. The reduction is sharp up to a 0.02N phosphoric acid concentration, beyond which, it is marginally reduced. Peroxide value and AV are reduced by increasing acid concentration, until a concentration of 0.1, at which it is marginal, Fig. 4. As shown in Table 4 however, as PV is reduced at the degumming temperature of 65^oC, AV is sharply increased from a temperature of 65 - 75^oC. There should therefore be a compromise between increasing acid concentration, which reduces AV, and Temperature, which also increases AV. The optimum is found in the range of 0.1- 0.12.

4.3. Effect of contact time

A contact time of 30 - 60 minutes at the degumming temperature is enough to reduce the PV to minimum. Beyond this time, the PV begins to rise, Fig.5. AV and FFA, decrease marginally, but AV reduces at a rate greater than the FFA. The colour however, is not so much affected by prolonged contact time, provided the degummed oil temperature is not beyond 75^oC beyond 120^0C .

5. Conclusion

The results obtained in section 3, have demonstrated that the quality stability of finished palm oil product, can be greatly influenced by the degumming stage. Variation of the degumming conditions has shown how temperature, degumming chemicals and time conditions can affect the stability of the final product. The result showed that the degumming temperature should not be more than 65^oC, since the lower marginal colour obtained by increasing temperature does not improve the colour quality of the final product.

A very high increase in concentration of degumming chemical will not improve the quality stability of the final product. However, the exact level required for optimum result, depends on the type of oil and chemical, and on the concentration of the chemical. Since an effective degumming can improve the quality of the final product, effective removals 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.

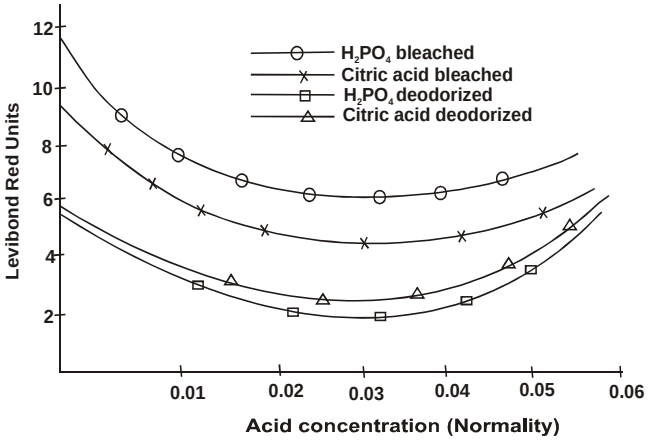


Fig. 1. The effects of chemical concentration on the colour of physically refined palm oil.

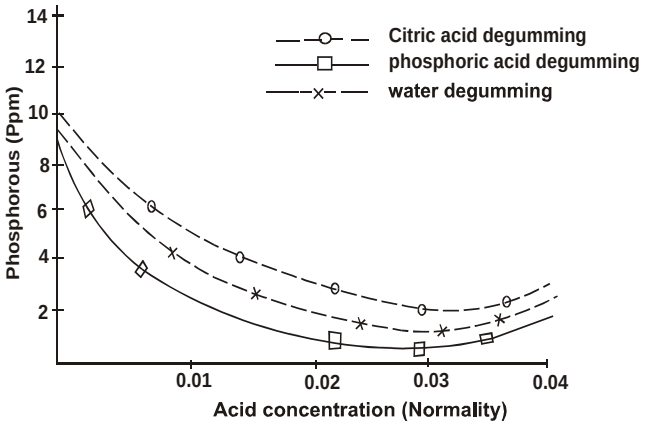


Fig. 2. The effects of chemical concentration on the phosphorous content of physically refined palm oil.

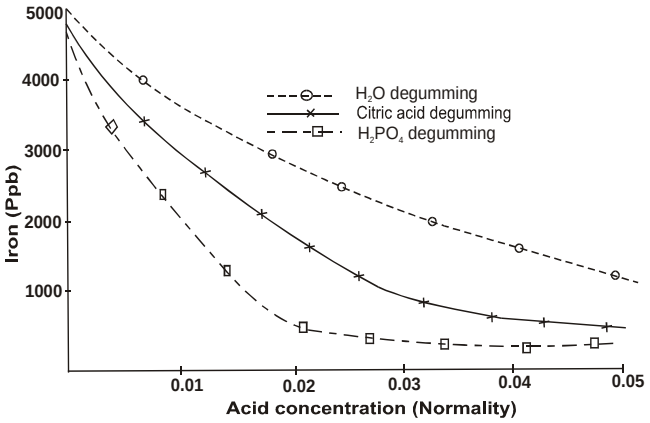


Fig. 3. The effects of chemical concentration on the iron content of physically refined palm oil.

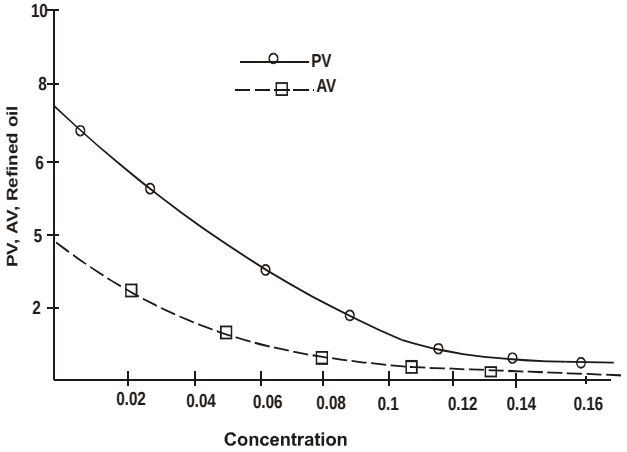


Fig. 4. The effects of chemical concentration on the PV and AV of physically refined palm oil.

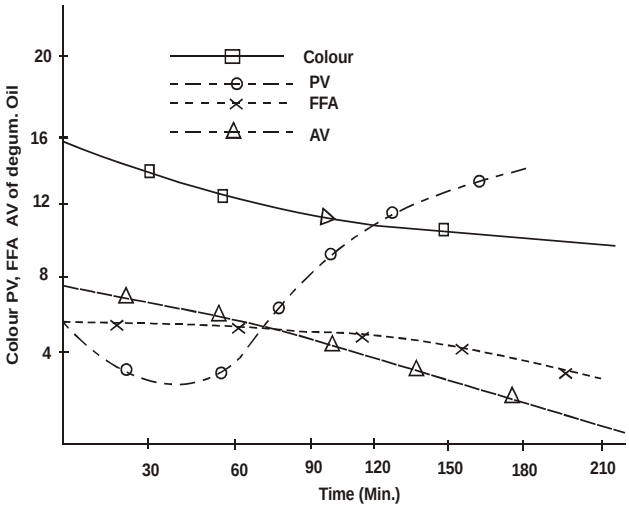


Fig. 5. The effects of contact time on the colour, PV, AV and FFA of physically refined palm oil.

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