Refining of Groundnut Oil Using Activated Clay and Melon Husk

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Abstract
Refining of groundnut oil was carried out by degumming the oil, neutralization, bleaching using activated clay and melon husk, and deodorization. The physicochemical properties of the refined groundnut oils analysed show that activated melon husk done at 700 °C for 60 minutes gave the best results for free fatty acid and acid value in terms of reduction in values between crude and the refined oil as they reduce from 1.55 to 0.71 and 3.09 to 1.40 mg KOH/g respectively. The peroxide value obtained for activated clay has the least value and it conforms with Codex standards. Activated melon husk at 300 °C in40 minutes gave the best saponification value which decreased from 193.55 to 154.28 mg KOH/g while activated clay gave the least Iodine value from 84.01 to 77.41 mg I_2 /g.Both activated melon husk and clay were efficient in improving the quality of the groundnut oil for consumption.

Keywords: Groundnut oil, Refining, Activated Clay, Melon Husk, Physicochemical Properties.

Introduction

Vegetable oil from various agricultural products have found their applications in major food industries. They are essential diet components and also responsible for specific textures and flavours in foods (Anyasor*et al.*, 2009). Quality and stability place a demand on vegetable oil refiners to run at peak efficiency because of application in industries and consumers' health (Berbesi, 2006). Groundnut oil a typical example of edible vegetable oils, in its crude form is deeply coloured. Impurities in the oil include pigments such as xanthophyll, chlorophyll, carotenoid, and tocopherol (Wu and Li, 2009), peroxides, traces of soap, trace metals, free fatty acids and phosphatides. It is therefore necessary to remove these colour impurities from oil not only before use but also after use, thus enabling recycling and reusing of the oil (Akinwande*et al.*, 2015). Processes involved in groundnut oil refining include degumming, neutralization, bleaching, and deodorization (Akinwande*et al.*, 2015).

The aim of this work is to refine groundnut oil using activated clay and activated melon husk in order to improve the quality of the oil. This research was carried out to remove the coloured impurities and undesirable odour from crude groundnut oil to make the end product acceptable and attractive to consumers.

Materials and Methods

The groundnut oil was purchased from Bosso market, Minna, Nigeria. All chemicals used were sourced from Chemical Engineering and Water Aquaculture and Fisheries Technology (WAFT) Laboratory, Federal University of Technology Minna, Nigeria.

Activation of the Adsorents

Preparation of Activated Clay

Natural clay was obtained from Gidan-Kwano village, Minna, Nigeria. The clay was filtered in order to separate unwanted materials from it. A 2 L solution of hydrochloric acid was measured into a 10 L bucket filled with an unmeasured quantity of filtered clay and stirred for 10 minutes. The essence of acid treatment is to increase the specific surface area, porosity and adsorptive capacity of the activated clay(Akinwande*et al.*, 2015). The clay-acidmixture was allowed to settle for 30 min after which the slurry solution was decanted. Distilled water was boiled to about 100°C, poured into the clay, then decanted and sun dried afterwards for 12 h before use.

Preparation of Activated Melon Husk (MH)

Melon husk was collected from Gidan-Kwano village, Minna, washed, dried and crushed using a mortar and pestle. This was sieved to 0.75-0.85 mm and 40 g of the sample was mixed with 400 cm^3 NaOH solution at impregnation ratio of 1:1 (NaOH pellet: sample). Impregnation was carried out at 50 °C with continuous stirring for 2 h. The mixture was filtered using a filter paper and washed with distilled water in order to make the sample free from trace amounts of NaOH. The sample was air dried overnight at room temperature. The dried sample was then calcined at 300 °C and 700 °C with the aid of a furnace within 40 and 60 minutes respectively. The activated melon husks were cooled to room temperature (Abechi*et al.*, 2013).

Refining of Groundnut Oil

The groundnut oil refining comprises of a four (4) basic unit operation namely degumming, neutralization, bleaching, and deodorization (Berbesi, 2006).

Degumming

2 L of distilled water was boiled to a temperature of 100 °C using a heating mantle. The hot water was then poured into a 4 L groundnut oil in a 10 L capacity plastic bucket. The solution was stirred vigorously with a stirrer and then allowed to settle for about 30 minutes. The water was then separated through a tap at the base of the bucket and the oil remaining (Agidi*et al.*, 2014).

Neutralization

6 g of sodium hydroxide (NaOH) was dissolved in 500 ml of distilled water and mixed with the degummed groundnut oil. This mixture was then stirred and allowed to settle for 1 h. The sodium hydroxide (NaOH) reacted with free fatty acids present in the oil and neutralized them forming a soap stock. Distilled water was poured into the oil mixture to wash the soap stock which was then separated through the tap at the base of the bucket (Agidi*et al.*, 2014).

Bleaching

Activated clay (0.85-0.95 mm) and melon husk (0.75-0.85 mm) were used as the bleaching agents. 80 g of activated clay was packed into an adsorption column and the oil was allowed to run through it for 2 h after which the filtrate was collected as shown in Plate I. This process was repeated using the activated melon husk at

different conditions (at 300°C and at 700°C in 40 and 60 minutes respectively).

Plate I: Experimental Set-up for Bleaching Groundnut Oil

Deodorization

The filtrates collected using activated clay and melon husk at different process conditions were heated for 30 minutes in order to vaporize water and other volatile compounds present in the oil to the desired level for safe storage (Agidi*et al.*, 2014).

Characterization

Determination of Saponification Value (SV)

Saponification value is the amount of mg KOH needed to saponify 1 g of the oil. 1 g of the oil was weighed into a conical flask and 25 ml of alcoholic KOH was added. The flask was kept in the oven at 100 °C for 30 min. 1 ml of phenolphthalein solution was added and the hot excess KOH was titrated with 0.5 M HCl until a colourless change was observed. A blank titration was carried out at the same time (Sulaiman*et al.*, 2012).

The Saponification value (SV)was calculated following Nkafamiya*et al.*,(2010)

$$\text{Peroxide Value} = \frac{b-a \times 1000 \times N}{W}$$

Where b is the blank titre value,

a is the oil titre value,

N is the Normality of $Na_2S_2O_3$,

W is the weight of oil (0.6 g).

Determination of Iodine Value

This method is based on the treatment of a known weight of oil with a known volume of standard solution of iodine trichloride. 0.5 g of oil was weighed into a glass-stoppered bottle of 250 ml capacity. 10 ml carbon tetrachloride was added to the oil and dissolved. 20 ml of Wiji's solution was added, a stopper was inserted, and the contents were allowed to stand in the dark for 30 min. 15 ml of potassium iodide (KI) solution (10%) and 100 ml of water were added, mixed, and titrated with 0.1 M thiosulphate solution ($Na_2S_2O_3$) using 3 drops of starch as indicator until the blue colourdisappeared. A blank titration was also carried out (Sulaiman*et al.*, 2012). The Wiji's solution was prepared by dissolving 8 g of iodine trichloride in 200 ml glacial acetic acid, 9 g of iodine in 300 ml carbon tetrachloride, mixing the two solutions, and diluting to 1000 ml with glacial acetic acid.

The Iodine value was calculated as given byNkafamiya*et al.*,(2010)

$$\text{Iodine Value} = \frac{b-a \times 12.69 \times N}{W}$$

Where b is the blank titre, value,
a is the oil titre value,
N is the Normality of $Na_2S_2O_3$.
W is the weight of oil (1 g).

Determination of Acid Value/Free Fatty Acid

Acid value is the amount of KOH required to neutralize the free fatty acid in grams of the oil. 1 g of the oil was weighed into a conical flask. 25 ml of petroleum ether and 25 ml of ethanol were added into the flask. 3 drops of phenolphthalein solution was added and titrated with 0.1 M KOH until a pink colour was observed (Sulaiman*et al.*, 2012).

The Acid value was calculated following Sulaiman*et al.*, (2012).

$$Acid\ Value = \frac{Titre\ volume \times 56.1 \times N}{W}$$

Where N is the Normality of KOH
W is the weight of oil.

The free fatty acid amount is usually calculated as oleic acid (1 ml 0.1 M NaOH = 0.0282 goleic acid). The percentage free fatty acid was calculated as given byOkene and Evbuomwan, (2014)

$$\%\ FFA = \frac{Titre\ volume \times 28.2 \times N}{W}$$

Where N is the Normality of KOH,
28.2 mg is the conversion factor for oleic acid
W is the weight of oil.

Determination of Specific Gravity

A 50 ml pycnometer bottle was thoroughly washed with water, dried, and weighed. The bottle was filled with water and reweighed. After drying the bottle, it was filled with the oil sample and weighed (Sulaiman*et al.*, 2012).

The value was calculated according to Pandurangan*et al.*, (2014)

$$Specific\ gravity = \frac{Weight\ of\ Oil}{Weight\ of\ Water}$$

Results and Discussion

The results of oil appearance obtained before and after refining the crude groundnut oil are presented in Plate II. The result obtained from characterizing the crude and refined oil . werecompared with standard value of edible groundnut oil as amended in Codex Alimentarius Commission, (2011) and are as presented in Table 1.0.

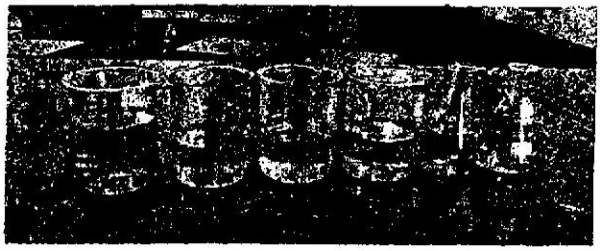

Plate II: Unrefined Groundnut oil, Refined Groundnut Oil: A – MH 700°C, 60 minutes;B – MH 700°C, 40 minutes;C – MH 300°C, 60 minutes;D – MH 300°C, 40 minutes; E – Activated Clay.

Table 1.0 Chemical and Physical Properties of Groundnut Oil after Bleaching withActivated Clay and Melon Husk (M H)

Properties	Crude Groundnut Oil	A	B	C	D	E	F
Saponification Value (mg KOH/g)	193.55	165.50	157.08	176.72	154.28	162.69	187 – 196
Acid Value (mg KOH/g)	3.09	1.40	1.96	1.68	1.68	1.96	0.6
Free Fatty Acid (%)	1.55	0.71	0.99	0.85	0.85	0.99	35 – 69
Iodine Value (mg I2/g)	84.01	81.22	90.71	78.93	79.69	77.41	86 – 107
Peroxide Value (mEq/kg)	3.00	5.67	10.00	8.00	9.83	4.67	10
Specific Gravity	0.91	0.91	0.91	0.91	0.91	0.91	0.912 – 0.920

Samples A, B, C, D, E and F are activated melon husks at 700°C, 60 minutes; 700°C, 40 minutes;

300°C, 60 minutes; 300°C, 40 minutes; activated clay and Codex Standard respectively.

Saponification Value

The saponification value of the refined samples A, B, C, D and E were lower than values of the crude sample and the Codex standard range. The free fatty acids obtained for melon husk samples B and A at the same temperature increased with increase in time from 157.08 – 165.50 mgKOH/g while those of samples D and C at the same also increased with increase in time from 154.28 – 176.72 mgKOH/g. The least saponification value of 154.28 mgKOH/g was obtained for sample D after refining. Lower saponification value suggests that the groundnut oil is edible and the number of ester bond or the mean molecular weight of fatty acid is low, but higher saponification value indicate that the oil can be used for industrial purposes (Pandurangan*et al.*, 2014).

Acid Value

The acid values of samples A, B, C, D and E were all lower than the value obtained for the crude groundnut oil, but were all higher than the values stated by Codex, (2011). The acid values of activated melon husk samples B and A decreased from 1.96 – 1.40 mgKO/g with increase in time at 700°C while the acid values for samples D and C remained constant with increase in time at a temperature of 300°C. Low acid value retards theoxidation of oil which eventually retards sludge or gum formation and corrosion hazards (Pandurangan*et al.*, 2014).

Free Fatty Acid

The quantity of free fatty acid is an indicator of its overall quality. The percentage of free fatty acid were lower for samples A, B, C, D and E compared to the values obtained for the crude groundnut oil and the Codex standard after refining. The free fatty acids obtained for melon husk samples B and A at the same temperature decreased with increase in time from 0.99 – 0.71% while the free fatty acid for samples D and C remained constant with increase in time with a value of 0.85%. Sample A gave the least free fatty acid value of 0.71% after refining indicating that lesser impurities and low level of lipolytic and hydrolytic activities in the oil (Pandurangan*et al.*, 2014).

Peroxide Value

The peroxide value increased for samples A, B, C, D and E were higher than the crude groundnut oil value but were within the Codex standard value. The peroxide value of melon husk samples B and A decreased from 10.0 – 5.67 mEq/kg with increase in time at 700°C likewise samples D and C decreased from 9.83 – 8.0 mEq/kg at 300°C with increase in time. The high peroxide value is an indication that the oil can easily spoil due to the concentration of the peroxide causing oxidative rancidity thereby resulting in unpleasant odour and flavour (Ronald, 1991). The sample E obtained using activated clay gave the least peroxide value of 4.67 mEq/kg, hence, low peroxide value suggests low level of oxidative rancidity, high level of antioxidants, and not easily vulnerable to deterioration. The peroxide values obtained are less than the maximum standard value (10

mEq/kg) as accordingto Codex (2011).

Iodine Value

The iodine value for samples A, B, C, D and E were lower than the crude groundnut oil value and the range given in the Codex standard. The Iodine values of melon husks samples B and A at 700°C increased from 80.71 – 81.22 mg I_2/g with increase in time, whereas samples D and C decreased with increase in time from 79.69 – 78.93 mg I_2/g at 300°C. Sample E gave the lowest Iodine value of 77.41 mg I_2/g. High iodine value suggests dehydrogenation, hence a measure of unsaturation in lipids which determines the degree of the flow (Nkafamiya*et al.,* 2010). The iodine values of the samples A, B, C, D and E are semi-siccative mono-unsaturated oil (50 – 100 mg I_2 /g) (Pandurangan*et al.*,2014) and they were lower than the standard range of 86 – 107 mg I_2 /g as specified by the amended Codex standard of (2011).

Specific Gravity

The specific gravity suggests the compatibility of groundnut oil with water or the ability of groundnut oil to separate from water (Briggs and Victor, 2014). The specific gravity of the crude groundnut oil, the refined oil using activated melon husks and clay gave a constant value of 0.91. This shows that the refining process did not have effect on the specific gravity. The constant value indicates that there was no difference in the degree of flow or thickness of all the oil samples at room temperature (Cocks and von Rede, 1992). The values were all within the standard range of (0.914 – 0.920) as stated by Codex (2011).

Conclusions

The refining of crude groundnut oil using activated melon husk at 300°C and 700°C between 40 and 60 minutes and activated clay was successfully achieved. The quality of the crude groundnut oil was improved as the activated melon husk at 700°C in 60 minutes gave better free fatty acid value and acid value thereby decreasing the oxidation of the oil while activated melon husk at 300°C in 40 minutes gave the least saponification value improving the edibility of the oil. Activated clay on the other hand gave better results for the Iodine and Peroxide value thereby making flow easily and less susceptible rancidity. The results obtained were within the literature value as amended by Codex in 2011. Hence, both activated melon husk and clay were efficient in improving the quality of the groundnut oil for consumption.

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