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Full Length Research Paper

Effect of refining on the quality and composition of groundnut oil

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Crude groundnut oil was obtained by solvent extraction from groundnut seeds and refined. The crude and refined oils were then analyzed. The results obtained show that the acid value decreased from 2.890 to 0.420 mg/KOH. Free fatty acid decrease after refining from 2.82 to 2.02%; phospholipids decreased from 23.11 to 5.53%; copper content decreased from 0.37 to 0.0361% and iron decreased from 3.98 to 0.31%. These can be viewed as an improvement in the quality of the oil after refining. Refining did not have much effect on the fatty acids composition except for slight inconsistent decrease in saturated and unsaturated fatty acids.

Key words: Free fatty acids, phospholipids, crude, refined, gas chromatography.

INTRODUCTION

Arachis oil (peanut oil; groundnut oil) is derived from groundnuts (seed of *Arachis hypogaea* Linn). Groundnut oil is a vegetable oil which contains only a small propor-tion of non-glyceride constituents. Its fatty acid compo-sition is complex including saturated fatty acids covering a wide range of molecular weights. Groundnut oil is excellent food oil, with good flavor and high quality with its low free fatty acid value. Vegetable oils generally primarily consist of triglycerides but several other com-pounds are also present. Some of these additional compounds such as diglyceride, tocopherols, sterols and sterols ester need not necessarily be removed during processing. Compounds such as phosphatide, free fatty acids, odiferous volatiles, colorant, waxes and metal compounds negatively affect taste, smell, appearance and storage stability of the refined oil and hence must be removed. Carefully separated, however, some of these additional compounds, particularly the phosphatides are valuable raw materials (Belcher, 2008).

Although there are many methods that are described in the literature that may be used to analyze fatty acids of vegetable oils, high precision in gas chromatographic analysis of fatty acids is possible with careful attention to details during sample preparation, injection, and chroma-tograph and data collection. Small theoretical correction factors only should be necessary in most circumstance (Christie, 1993). Also the qualitative and quantitative determination of the constitution is done by gas chromatography of the compound or their derivatives (Cert et al., 2000).

A lot of works have been done in the past and many are still on by lipid analysts to explore the potentials of vegetable oils. The importance of analyzing vegetable oils cannot be overemphasized because in analyzing vegetable oil, the major feature influencing the physical and chemical properties, their application and uses are got. The analysis of phospholipids is important because they contribute to the stability and quality of edible oils, fats and fatty foods through their anti-oxidative activities. They are also responsible for oil discoloration during deodorization and steam distillation so that their determination is necessary to evaluate the efficiency of degumming (Mounts and Nash, 1990; Monte et al., 1992; Nzai and Proctor, 1998). Metals catalyze oxidation and they are responsible for both an increase rate of oxidation and colour fixation. With the analysis of phospholipids, Cu and Fe, the adverse effect of product stability and colour can be estimated. With the analysis of free fatty acids (FFA), suitability of vegetable oils for edible

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purposes can be determined (Esuoso and Odetokun, 1995). This research was to ascertain how the refining of groundnut oil affects its quality characteristics and its constituent

EXPERIMENTATION

Seed oil exraction

Groundnut oil seed was purchased from Lagos State, South–West, Nigeria. The groundnut seedS were separated from the shaft by hand picking method. The seedS that were freed of the dirt were collected into a separate pre- cleaned beaker. The samples were weighed and kept for pulverization. The grinding machine of make JANKE and KUNKEL (IKA-LABORTECHNIC) was used for grinding until the samples were finely grinded. The funnel and the hollow parts of the machine were cleaned before another sample was grinded to avoid cross contamination.

The pulverized samples were then extracted using the soxhlet extractor arrangement equipped with thimble. Hexane was used as the solvent. The duration of the extraction was 6 h. The process was repeated twice to ensure that most of the oil in the seed was removed using fresh solvent. The crude oil with solvent extracted was collected into the pre-cleaned beaker for distillation.

The extract was poured into the round bottom flask of the rotary evaporator arrangement. It separated by driving the hexane off the extract. Then the extracted oil was dried of water by using an anhydrous sodium sulphate.

Steps used in refining the groundnut oil

The crude groundnut oil has to be refined before it can be used for different applications either in the edible or industrial application. The crude oils contain small amount of naturally occurring materials such as proteinaceous free fatty acids and phospholipids.

The method used for the removal of the FFA was by reacting it with sodium hydroxide solution (alkali) in a read stoichiometric ratio to ensure complete reaction and to make sure that no alkali was left over in the oil. The intermediate then reacted with phospholipids. These reacted products and the proteinaceous materials were then removed by centrifuge. Following the alkali refining, the oil was washed with water to remove residual soap caused by saponification of small amount of the triglycerides oil. Colour producing substances within oil, for example carotenoids and chlorophyll, were removed by bleaching process. Acid activated alumina was employed for bleaching by allowing some contact time with the oil. The refined oil was then filtered and kept for usage.

Esterification procedure

The oil sample was air dried by blowing the air gently on it. 1.0 g of oil was weighed into the beaker. The oil sample was heated in a borosilicate beaker container at 140^{o} F with pump running to allow homogeneity of the sample. Some of drops of the acid were added to the oil in the container in a fairly fast manner of proper distribution. The samples are homogenized while the acid was being added with the aid of the mixer. About 3 ml of the methanol was put in a pre-cleaned beaker. The heater and the pump were off to allow the methanol to be added to the mixture. The methanol was added in a fast way. The mixture was mixed properly and fan was allowed to blow the fumes away. The mixture was covered properly and temperature was allowed to drop to ambient temperature (65^{o}F). The pump and fan were on occasionally for about 4 h. After cooling, the sweet fragrance ester was decanted in to a clean borosilicate container before injecting into the gas chromatography.

Fatty acids methyl ester gas chromatogaphy analysis condition

GC: HP 6890 Powered with HP ChemStation Rev. A 09.01 [1206] Software.
Initial temperature: 60^{o}C for 3.0 min.
First rate: 8^{o}C/min to 140^{o}C for 10.0 min, constant at 140^{o}C for 5.0 min.
Second rate: 10^{o}C/min to 250^{o}C for 11 min, constant at 250^{o}C for 10.0 min.
Detection Temp: 275^{o}C.
Injection Temp: 230^{o}C.
Detector: FID.
Carrier Gas: Nitrogen.
Column: HP-INNowax (Cross-Linked PEG).
Column Length: 30.0 m.
Column I.D: 0.32 mm.
Film Thickness: 0.50 µm.
Nitrogen Pressure: 30.0 psi.
Hydrogen Pressure: 22 psi.
Comp. Air Pressure: 28 psi.

Condition of analysis for phospholipids

Column used: ZB-5 column.
Column length:30 m.
Column ID: 0.25 mm.
Column Film: 0.25 µm.
Detector Temp: 300^{o}C.
Detector: PFPD (Pulse Flame Photometric Detector).
Initial Temp: 30^{o}C for 3 min.
First Rate: 4^{o}C/min for 20 min and maintained for 1 min
Second Rate: 15^{o}C/min for 10 min and maintained for 1 min Mobile phase or carrier:Hydrogen.
Hydrogen column pressure:25 psi.
Hydrogen Pressure: 22 psi.
Compressed oil pressure: 28 psi.

Atomic absorption analysis of the sample

Sample was sub sampled into the conical flask. The content of the flask was treated with 5% nitric acid. The samples were prepared for different metal analysis. The solution was allowed to cool at room temperature. Standard Iron (Fe) and copper (Cu solutions of 0.20, 0.40, 0.60, 0.80 and 1.00 mg/l) were made from each of the standard heavy metals. The sets of standard solutions and filtrate of the sample were analysed by AAS. The detection limits of the heavy metals in the sample were 0.0001 mg/l by means of UNICAM 929 London, atomic absorption spectrophotometer powered by SOLAAR software. Iron and Copper cathode lamps were used for the analysis of Fe and Cu ions, respectively. Air- acetylene gas mixture was used in the generating flame.

Determination of physico-chemical properties

Saponification value of oil sample was determined by dissolving 1 g of the oil in 12.5 ml of 0.5% ethanolic KOH and the mixture of refluxed for 30 min. 1 ml of the phenolphthalein indicator was added

Table 1. Physico-chemical properties of crude and refined groundnut oil.

Parameters	Groundnut oil	
	Crude	Refined
Specific gravity at 20°C	0.916	0.915
Refractive index at 40°C	1.462	1.460
Saponification value (mgKOH/g)	192.00	188.00
Acid value (mgKOH/g)	2.890	0.420
Iodine value (mg/100g)	91.00	86.00
Odour	Agreeable	Agreeable

and the hot soap solution titrated with 0.5 N HCL. A blank determination was also carried out under the same condition and saponification value determined using the equation:

To ascertain the iodine value, 0.1 g of the oil was weighed into the 200 ml bottle capacity. 5 ml of carbon tetrachloride was added and the 2 ml of Wij's solution stood for an hour in the dark before the analysis was carried out. The blank was prepared as the sample. 5 ml of the 10% potassium iodide solution and 50 ml of water to each bottle and titrated against the 0.1 N sodium thiosulphate using starch as the indicator until colour change to permanent pale yellow.

To find the acid value 0.1 g of the dissolved in 2.5 ml of 1:1 v/v ethanol: diethyl ether solvent and titrating with 0.1N sodium hydroxide while swirling using phenolphthalein as indicator.

The Specific Gravity was measured by means of a cleaned pycnometer which was weighed. The pycnometer was filled with cooled distilled water and was stoppered. It was kept in the water bath for 30 min. It was removed and the drops of water were wiped properly and the weight was measured.

The water was thrown away, oven dried and the pycnometer was filled with oil that has been previously dried over sodium sulphate. It was stoppered and kept in the water bath for 30 min. It was then removed, water wiped properly and the weighted was measured.

To find the refractive Index, the surface of the prisms was cleaned up with ether. 2 drops of the oil was applied at the lower prism and the prisms were closed up. Water was passed through the jacket at 45^0C. The jacket was adjusted for reading to be taken.

RESULTS AND DISCUSSION

The physico- chemical properties of crude and refined groundnut oil obtained are shown in Table 1. The specific gravity of groundnut oil decreases from 0.916 to 0.915 after refining. The decrease was not significant hence refining does not have significant effect on the specific gravity. However, the decrease may be due to the removal of gumming materials and some coloring matters which affected the weight of the oil after refining. According to Paul and Palmer (1972), the specific gravity of different refining oils varies with their molecular weights which are affected by refining process involved.

The refractive index of groundnut oil decreased from 1.462 to 1.460 after refining. The decrease was not significant hence refining does not affect the refractive index significantly. In addition, the oil did not differ significantly in refractive index both in crude and at the refined forms. The decrease could be as a result of continuous removal of impurities during the refining process. According to Pearson (1991), the amount of impurities that are contained in the oil affects the degree of reflection caused by a ray of light during refractive index determination of the oil.

The odour in the sample of oils is agreeable. This means that they all have no offensive smell. This shows that refining does not affect the odour of the oil. This could be as a result of the low free fatty acids present (groundnut oil: crude, 2.821644% and refined, 2.017714% in the oil (Kirk and Sawyer, 1991).

The saponification value of the groundnut oil decreased from 192 to 188 mg/KOH after refining. This decrease generally could be due to the neutralization of fatty acids which may have resulted from the hydrolysis of the oil sample. According to Kirk and Sawyer (1991), the number of milligram of potassium hydroxide (KOH) used to neutralize the fatty acid determine the degree of hydrolysis of the oil sample.

The iodine value for groundnut oil decreases from 910 mg/100 g to 860 mg/100 g after refining. The decrease was not quite significant. Hence, refining did not affect iodine value significantly. The decrease in iodine value denotes decrease in the degree of unsaturation of the oil caused by the extent of oxidation and degree of heat treatment given to the oil during refining process (Kirk and Sawyer, 1991).

The acid value for groundnut oil decreased after refining from 2.890 to 0.420 mgKOH/g. The decrease was significant for the groundnut oil. Acid value had the highest decrease after refining (85.47%). According to Demian (1990), the acid value is used to measure the extent to which glyceride in oil has been decomposed by lipase and other actions such as light and heat and that it determination is often used as general indication of the condition and edibility of oils. This decrease is an improvement in the quality of the oil. It is an expected result, since a reduction in acid value is targeted in the refining process.

The Fatty acid composition in crude and refined groundnut oil is as shown in Table 2. The oil shows a moderate decrease in fatty acid composition from its crude form to refined form. According to Achinewhu and Akpapunam (1985), refining does not have much effect on fatty acid composition except for some slight inconsistent decrease in saturated and unsaturated fatty acid. This inconsistency was observed in this work with palmitic and palmitoleic acid. However, Caprylic acid shows the highest decrease after refining (75.96%). Oleic acid was the major unsaturated fatty acid and it recorded 58.7% in crude and 57.7% in refined followed by palmitic acid, 8.23% in crude and 11.74% in refined and linoleic acid 21.8% in crude and 21.5% in refined. The percentage of saturated fatty acid was recorded to be16.82% in

Table 2. Fatty acid composition of crude and refined groundnut oil.

Fatty acid	Crude composition (%)	Refined composition (%)
Caprylic acid (C8:0)	0.013346	0.003208
Capric acid (C10:0)	0.008544	0.005542
Lauric acid (C12:0)	0.275816	0.116076
Myristic acid (C14:0)	0.115270	0.1061
Palmitic acid (C16:0)	8.2280	11.7378
Palmitoleic acid (C16:0)	0.1073	0.1296
Stearic acid (C18:0)	2.4581	2.0606
Oleic acid (C18:1)	58.6871	57.6784
Linoleic acid (C18:2)	21.7656	21.5413
Linolenic acid (C18:3)	0.3446	0.2810
Arachidic acid (C20:0)	1.8313	1.4804
Behenic acid (C22:0)	3.8852	2.36610

Table 3. Composition of crude and refined free fatty acids and phospholipids of groundnut oil after refining.

Composition	Crude	Refined
Free fatty acid composition in groundnut oil (%)	2.82	2.01
Phospholipids Composition in groundnut oil (%)	5.53	23.12

crude and 20.37% in refined with palmitic acid recording the highest both in crude (8.23%) and refined (11.74%) respectively followed by stearic acid. Capric acid recorded the least reduction in saturated fatty acid in its crude form with 0.0085%.

The free fatty acid for groundnut oil is given in Table 3. The free fatty acid for crude groundnut oil (2.82%) is slightly greater than that in the refined oil (2.01%) . From Table 3, it is vividly seen that groundnut oil shows higher percentage decrease after refining (28.49%). Crude oils with high free fatty acid content result in higher refined losses (International Conference on Palms and Palm Products, 1989) . According to Esuoso and Odetokun (1995) free fatty acid of oil suitable for edibility purpose should not exceed 5%. In view of this, groundnut oil both crude and refined is edible. The amount of free fatty acid present is a measure of the quality of the unrefined as well as the refined oil (International Conference on Palms and Palm Products, 1899). Therefore, in view of the low free fatty acid in groundnut oil, both crude and refined, it makes higher quality oil. The decrease in free fatty acid could be as a result of removal of some fatty materials and free fatty acids during refining process. According to Kirk and Sawyer (1991), the presence of free fatty acid and other fatty materials in oil brings about the offensive odour and taste in the oil on long storage.

The phospholipids composition of the groundnut oil is also shown in Table 3. The amount of phospholipids on crude groundnut oil (23.12%) is higher than that recorded for refined groundnut oil. Phospholipids contribute to the stability of edible oil fats and fatty food through their antioxidation activity (Singleton, 1993; Carelli et al., 1997).

This shows that the natural antioxidative activity of refined groundnut oil may be lower than crude groundnut oil. Phospholipids are responsible for oil discoloration during deodorization so that their determination is necessary to evaluate the efficiency of degumming (International Conference on Palms and Palm products, 1989; Mounts and Mash, 1990, Mounts et al., 1992; Nzai and Proctor, 1998). On heating crude groundnut oil to deodorization temperature, the brown coloration that will be observed will be more than observed for refined groundnut oil.

The copper concentration of groundnut oil decreased from 0.37 to 0.036 mg/Kg after refining and the iron concentration of same oil decreases from 3.98 to0.31 mg/Kg after refining as shown in Table 4.

The percentage decrease of iron in groundnut oil after refining is the most significant (92.19%). Metals such as iron and copper catalyze oxidation and therefore are responsible for both an increase rate of oxidation (International Conference on Palm and Palm materials products, 1989) . Therefore, in view of the higher concentration of metals in crude groundnut oil will be higher than that in refined groundnut oil.

Table 4. Copper and iron concentration in the groundnut oil samples.

Concentration of metals in the oils	Crude	Refined	% decrease in metals after refining
Concentration of copper in groundnut oil (mg/kg)	0.3738	0.0361	91.07
Concentration of iron in groundnut oil (mg/kg)	3.9832	0.3109	92.19

Conclusion

Refining slightly affects the physical and chemical characteristics of groundnut oil. There was decrease from the crude form to the refined form and there was a significant decrease in acid value. This significant decrease confirms the presence of oleic acid which is significant in groundnut oil. As for the major and minor constituents, refining did not have much effect on the fatty acid except for some slight inconsistent decrease in saturated and unsaturated fatty acids.

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