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Evaluation of the effects of processing on physicochemical properties of the freshly extracted crude groundnut oil

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ABSTRACT

The industrial processing of groundnut oil involves hydrothermal and chemical treatments that could affect its lipid constituents. The effect of this processing on physicochemical properties of freshly extracted crude groundnut oil was determined. Crude groundnut oil was extracted following the traditional method and half of it was processed as done industrially. Chemical properties [acid value, free fatty acid, peroxide value, saponification value, ester value, iodine value, total phenolic content (TPC), p-Anisidine value, total tocopherol (TT), total antioxidant capacity (TAC) and thiobarbituric acid reactive species (TBARS)] and physical properties (refractive index, surface tension, smoke point, flash point, viscosity and specific gravity) were determined following the AOAC and other standard methods. The results indicated that the processing of the crude groundnut oil, although improved the physical appearance and reduced free fatty acid by 56% consequently, could improve its stability but it also compromised the levels of antioxidant compounds such as tocopherols in the oil that reduced by 16.4%. TAC, an antioxidant parameter also reduced by 92% while TBARS increased by 15.1%. It can be concluded that processing of groundnut oil could either improve its stability or compromise it, therefore, there is a need for the stability study of processed groundnut oil.

KEYWORDS: Groundnut oil, p-anisidine value, Physicochemical, Total tocopherol, Thiobarbituric acid reactive substances

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1. INTRODUCTION

Groundnut, or peanut (*Arachis hypogaea* Linn), commonly called the poor man's nut is one of the most important cash crops in the world (Fletcher and Shi, 2016). It is an important food crop, the third most important source of vegetable protein and the sixth most important oilseed crop (FAOSTAT, 2010). It contributes significantly to the protein in the diets of people in many developing countries (Fletcher and Shi, 2016). It contains 48-50% of oil and 26-28% of protein and is a rich source of dietary fiber, minerals, and vitamins which is evident in its high caloric value (Fletcher and Shi, 2016). Worldwide, groundnut production is principally dedicated to the production of vegetable oil (49%) and the cake obtained as well as whole nuts (41%) are used as human food and also as feed for animals (Fletcher and Shi, 2016).

Groundnut oil is widely consumed domestically and all over the world. It contains more potassium than sodium and it is a good source for calcium, phosphorus and magnesium (Falade et al. 2008). It also contains thiamine, vitamin E, selenium, zinc and arginine (Falade et al. 2008; Hariod, 1990). Diets high in groundnut oil were proven to be as effective as olive oil in preventing of cardiovascular diseases (Hariod, 1990). The report of the US Department of Agriculture released in 2015 showed that the world vegetable oil consumption has increased from 151.68 to 177.16 million metric tons from 2011/2012 to 2015/2016, respectively (USDA/NASS, 2015). The prices released by the World Bank in 2020 for groundnut, coconut, palm kernel, palm oil and soybean oil were declared to be $1493, $993, $955, $835 and $874 per metric ton, respectively (World Bank, 2020).

Consequently, adequate protection must be given to vegetable oils reported to be barely enough for the world population that is growing astronomically (Aydar et al. 2016).

Vegetable oils are known to be susceptible to lipid auto-oxidation reaction. This reaction is a degradative free radical chain reaction that causes quality loss in food industries, oxidative stress and its attendant diseases such as diabetes, atherosclerosis and cancer (Sokmen et al. 2004). The free radicals generated in this reaction have also been reported to damage macromolecules such as DNA and the cellular membrane (Rahal et al. 2014).

The processing of crude vegetable oil is important due to the presence of some undesirable components of the oil such as lecithin, gum, protein, gossypol and so on. These components are known to cause sedimentation in vegetable oils, making the oil to be cloudy or outright formation of precipitate, thus, making them unattractive and unsuitable for some uses such as in salad dressing. Some of these unwanted constituents such as gossypol could also be toxic (Aluyor et al. 2009). Processing although makes vegetable oils attractive and improves their usage, it has been reported that it could compromise the shelf-life of the processed oil in some vegetable oils (Achinewhu and Akpapunam, 2005) and improved it in others (Aluyor et al. 2009).

The processing of vegetable oil involves conditions such as heat, steaming, neutralization, decolorization and so on. Some of these conditions are well known to enhance lipid auto-oxidation. As a result of the aforementioned, it has become imperative to examine the effects of processing on the physiochemical properties of groundnut oil with the aim of making recommendations on how to prevent or at least reduce this destructive reaction in groundnut oil.

2. MATERIALS AND METHODS

2.1. Materials

All the reagents used in this study were of analytical grade and were sourced from BDH Chemicals Ltd, Poole, UK and Sigma Aldrich chemicals Co., St Louis, Mo, USA.

Groundnut was purchased from New Market, Ile-Ife, Osun State, Nigeria.

2.2. Extraction of groundnut oil

The extraction of the groundnut oil was done following the traditional method. The groundnut seeds (17.69 kg) were roasted in a big pan with firewood as the source of fire for 30 minutes. The roasted groundnut seeds were immediately bagged in air tight sack bags for 24 hours. The roasted groundnut seeds were then de-hulled (removal of seed coat) manually and handpicked to separate nuts of good quality from the bad ones. The good nuts were pulverized using a locally fabricated mill (Lawood Metals, Osogbo, Osun State, Nigeria). Water (1000 mL) was added to the groundnut paste obtained and the mixture was kneaded manually. The oil content was oozed out during the process of kneading. The crude groundnut oil (5.2 L) obtained was scooped out and stored in the dark inside an amber bottle prior to further analysis. Half of the crude groundnut oil (2.6 L) was processed according to the methods described by AOAC, (2005). The processing involves four stages which are, degumming using acetic anhydride, neutralization to remove free fatty acid using KOH, bleaching which was done by heating the groundnut oil with Fuller's earth followed by vacuum filtration using Whatman No. 1 filter paper and finally the steaming of the oil to eliminate volatile organic compounds were carried out in this order (AOAC, 2005).

2.3. Determination of chemical parameters in the oil samples

The moisture content of the oil samples was determined using AOAC method (AOAC, 1990). Sample (2.0 g) was weighed in triplicate into a pre-weighed crucible and then dried in an oven at 105 ^{o}C until a constant weight was obtained after cooling. The difference in weight of the crucible with sample before and after drying was recorded as weight of moisture. The other chemical parameters (acid, iodine, peroxide, saponification and ester values) were also determined

according to the methods described by Association of Official Analytical Chemists (AOAC, 1990) methods (AOAC 936.16, AOAC, 920.158, AOAC, 965.33 and AOAC, 936.15, respectively). The determination of all these five parameters were based on titrimetric methods. Acid value (AV) was obtained by titrating the sample with standard solution of KOH using phenolphthalein as an indicator. The AV was then calculated from the titter value (AOAC, 1990). Iodine value (IV) was based on redox titration. Oil sample was reacted with KI solution and the unreacted liberated iodine was back titrated with a standard solution of Na2S4O6 and IV later calculated from the titer value (AOAC,1990). Saponification value (SV) was determined by reacting the oil sample with excess KOH solution and the unreacted KOH was back titrated with standard solution of HCl. The SV was calculated from the titer value (AOAC, 1990). The ester value was obtained as the difference between the saponification value and the acid value (AOAC, 1990).

2.4. Determination of chemical compounds associated with antioxidant property

2.4.1. Determination of total tocopherol content

Total tocopherol (TTC) content of the oil samples was determined spectrophotometrically using the method of Contreras – Guzman and Strong (1982). The tocopherol was extracted with heptane, reacted with batocuproine and absorbance measured at 545nm. The total tocopherol was calculated from the absorbance using the equation developed by Contreras – Guzman and Strong (1982).

2.4.2. Determination of total phenolic content

Total phenol content (TPC) was extracted from the crude and processed oils and determined as described earlier (Falade et al. 2008). The total phenol content was standardized against gallic acid and expressed as mg/kg gallic acid equivalent (GAE). The linearity range of the gallic acid standard was 0–40 mg/L GAE (R2 = 0.9795).

2.4.3. Determination of Thiobarbituric acid reactive substance (TBARS)

This parameter was determined by the spectrophotometric method (Lee and Ahn, 2003). The TBARS was standardized using 1, 1, 3, 3-tetraethoxy propane (TEP) and expressed as mg malonaldehyde (MDA) kg-1 oil. The linear range for this assay was between 0 – 2.0 μM TEP (R2 = 0.998).

2.4.4. Determination of p-anisidine value

The p-Anisidine value (p-AV) was determined spectrophotometrically using the IUPAC method (Paquot, 1979). Oil samples (0.2g) was weighed in triplicate into 10 mL standard flask, dissolved with isooctane and made up to mark with the same solvent to give test solution A. A portion (5.0 mL) of the test solution A was placed in a test tube and 1.0 mL of freshly prepared p-anisidine reagent (0.025 g of p-anisidine dissolved with acetic acid and then made up to the mark in the 10 mL standard flask with acetic acid) was added to give test solution B. The test solution B was shaken thoroughly and was incubated in the dark for 10 min. A reference solution was prepared by mixing 5.0 mL isooctane with 1.0 mL of p-anisidine reagent; the mixture was shaken thoroughly and incubated in the dark for 10 min. The absorbance of the test solution A was measured at 350 nm with UV spectrophotometer using isooctane as the blank while the absorbance of test solution B was measured using reference solution as the blank. The p-anisidine value was calculated from the expression given in equation 3.1 below:

$$p - AnV = \frac{25\,x\,(1.2\,A1 - A2)}{M} \quad \text{– Equation 3.1}$$

Where A_1 = absorbance of test solution B at 350 nm

A_2 = absorbance of test solution A at 350 nm

M = mass of the oil sample in grams.

2.4.5. Determination of total antioxidant capacity (TAC)

The TAC of the oil samples was carried out according to the spectrophotometric method described by Prieto et al. (1999). The method is based on the reduction of

Molybdenum (VI) to Molybdenum (V) by the sample and the subsequent formation of green phosphate/ molybdenum (V) complex in acidic medium which was then determined spectrophotometrically.

2.5. Determination of physical parameters

2.5.1. Determination refractive index

The refractive index of the oil samples was determined by AOAC method (AOAC, 1990). The refractive index of the oil samples was determined at room temperature using portable refractometer (PAL-3, Atago, Japan). The refractometer was charged by opening the double prism and then a few drops of the oil sample were poured on the prisms. The prisms were closed firmly by tightening the screw head. The instrument was allowed to stand for a few minutes before reading so that the temperature of the oil sample and the instrument would be the same.

2.5.2. Determination of surface tension

The surface tension was done by counting the number of drops (n) formed by equal volumes of oil sample and water using vertically held pipette (AOAC, 1990).

2.5.3. Determination of smoke point

Smoke point was determined according to the method reported earlier (Hoffmann, 1986). The temperature at which smoke started coming out from the oil sample was recorded as the smoke point.

2.5.4. Determination of flash point

The flash point was taken as the temperature when the vapor from the oil was ignited by the naked flame.

2.5.5. Determination of viscosity

The viscosity measurement was performed using a viscometer (AOAC, 1990) and it was determined at various temperatures (30, 50, 70, 90 and 100 °C). The time of flow of the oil sample under gravity through the capillary of the viscometer was also measured at a known temperature and the viscosity calculated as reported by AOAC (1990).

2.5.6.Determination of specific gravity (SG)

The specific gravity (SG) of the oil samples was also determined by AOAC method (AOAC, 1990). It was measured by using a clean and dry density bottle. The measurement was based on the ratio of the weight of the oil sample to the weight of the equivalent volume of water.

2.6. Statistical analysis

The results of this study were expressed as mean and standard deviation of triplicate analysis. Data were subjected to one-way analysis of variance using GraphPad InSat software (GraphPad software, Inc., San Diego, CA) to estimate the levels of significant difference by performing *unpaired t-test*, and were considered significant at $P \leq 0.05$. Pearson correlation coefficient was also used to determine the correlation between peroxide value (PV) and each of the antioxidant parameters (TP, p-AV, TT, TAC and TBARS) and considered significant at $P \leq 0.05$.

3. RESULTS AND DISCUSSION

3.1. Chemical properties of groundnut oil

The chemical properties of the oil samples were investigated to know the effects of processing conditions on the shelf life of the oil samples obtained.

3.1.1.Moisture content

Moisture content of plant-based food plays an important role in its shelf-life because moisture (as water activity, a_w) enhances some chemical reactions such as Millard reaction - a reaction between protein and reducing sugars as well as auto-oxidation in lipids.

The moisture content of the crude and processed oil samples is presented in Table 1. The values were 7.31 ± 0.2 and 1.63 ± 0.2%, respectively, which are significantly different ($p \leq 0.05$). It has been reported earlier that a very high or low moisture contents may compromise the quality of groundnut oils (Oyem, 2010). Zehra et al. (2018) reported a decrease in the oxidation of their flavored olive oil with decrease in water activity. The same observation was reported by Oyem (2010) who observed a progressive decrease in the formation of free fatty acids with decrease in water activity of crude palm oil stored for 21 days.

3.1.2.Acid value (AV) and free fatty acids (FFAs) content

The AV indicates the amounts of free fatty acid (FFA) that is present in a vegetable oil. It also provides information on extent to which triacylglycerol in oil has been hydrolyzed by endogenous lipase and other actions such as light and heat. The amount of free fatty acids present is a measure of the quality and stability of the oil (Farhan et al. 2013). It is well known that FFAs are more susceptible to lipid oxidation leading to rancidity and production of off-odor. The determination of AV is used as a general indication of the edibility of the oils and stability to rancidity. The mean acid value (mg KOH/g oil) and %FFA are presented in Table 1. The AV was observed to decrease significantly ($p \leq 0.05$) from 3.36 ± 0.23 mg KOH/g oil for crude groundnut oil to 1.49 ± 0.13 mg KOH/g oil after processing which represented 55.7% decrease. The %FFA value of 1.69 ± 0.12% obtained for crude groundnut oil in this study was significantly higher ($p \leq 0.05$) than the value 0.98 ± 0.03% reported for crude groundnut oil by Nkafamiya et al. (2010), 0.4 % reported earlier for groundnut oil (Falade et al. 2008) and 0.48 % obtained also for groundnut (Obioma and Banigo, 2021). The higher value obtained in this study compared with what was reported earlier in our laboratory could be attributed to the water used for the extraction of the oil (traditional method) as against n-hexane, a non-polar solvent used in Falade et al. (2008). Water is well known to aid the hydrolysis of lipids leading to the release of their constituent fatty acids. Thus, processing of the oil obtained could improve the shelf life as well as the quality of the groundnut oil.

3.1.3. Peroxide Value

Peroxide value (PV) is a primary oxidation product of lipid oxidation formed from the decomposition of hydro-peroxide. These compounds could react with heme proteins or low molecular weight metals to produce free radicals (Kilic and Richards, 2003) implicated in the etiology of some terminal diseases such as cancer and diabetes (Aderogba et al. 2006).

The results of PV are presented in Table 1. The values were 2.00±0.01 Meq/Kg oil and 10.00±0.01 Meq/Kg oil for crude and processed oils, respectively, which was observed to be significantly higher ($p \leq 0.05$) than the crude oil.

Table 1 Chemical Properties of Crude and Processed Groundnut Oil

TParameter	Crude Oil	Processed Oil
Moisture Content (%)	7.31 ± 0.2^{b}	1.63 ± 0.2^{a}
Acid Value	3.36 ± 0.23^{b}	1.49 ± 0.13^{a}
Free Fatty Acid (%)	1.69 ± 0.12^{b}	0.75 ± 0.07^{a}
Peroxide values of (meq / kg oil)	2.00 ± 0.01^{a}	10.0 ± 0.01^{b}
Saponification value (mg KOH/g)	266.94 ± 0.12^{b}	207.14 ± 0.25^{a}
Ester value (mg KOH/g)	263.58 ± 0.25^{b}	205.65 ± 0.12^{a}
Iodine value (I_2 g/100 g oil)	89.63 ± 2.89^{a}	103.21 ± 2.93^{b}
Total Phenol (mg GAE/g)	3.09 ± 0.04^{a}	3.83 ± 0.05^{b}
p-Anisidine	1.65 ± 0.03^{a}	11.29 ± 0.23^{b}
Total Tocopherol (mg of α-tocopherol/kg)	35.02 ± 1.13^{b}	29.26 ± 0.92^{a}
Total Antioxidant Capacity (mg AAE/g)	1.315 ± 0.015^{b}	0.101 ± 0.012^{a}
Thiobarbituric acid reactive species (mg / kg)	1.325 ± 0.021^{a}	1.525 ± 0.021^{b}

Results are means of triplicate determination ± standard deviation.

Data in the same row followed by the same superscript letters are not significantly different at the 5% probability level.

GAE, KOH and AAE are Gallic Acid Equivalent, Potassium Hydroxide and Ascorbic Acid Equivalent respectively.

The PV value from this study was marginally lower compare with 10.9±1.3 Meq/Kg oil obtained in our previous work (Falade et. al. 2008) and another report with (10.60±2.27Meq/Kg oil) for noni seed oil (Jahurul et al. 2022). On the other hand, desert date kernel oil was reported with lower PV value compared with this study (Aremu et al. 2022). The variation in the levels of this parameter across laboratories could be attributed to the extraction conditions, the climatic conditions under which the plants were cultivated as well as the age of the seeds before analysis. The processing of the groundnut oil was also observed to cause 400% increase in the PV value. The bench mark for PV is 5.0Meq/Kg oil (Rudan-Tasic and Klofutar, 1999). The processed oil was higher therefore, it may be necessary to use natural antioxidant compound to prevent the increase of this parameter because of oxidation reaction.

3.1.4.Saponification value (SV)

Saponification Value is an index of average molecular mass of fatty acid present in the oil sample (Oyekunle and Omode, 2008). High saponification values indicate that the fatty acids present in the oils have a high number of carbon atoms. The higher the SV, the higher the fatty acid chain length and the more suitable the oil is for soap making (Oyekunle and Omode, 2008). The results for the SV for both crude and processed groundnut oil are presented in Table 1. The Saponification Value of the oil decreased significantly ($p \leq 0.05$) from 266.94 ± 0.12 mg KOH/g for the crude groundnut oil to 207.14 ± 0.25 mg KOH/g after refining. This represents 22.3% reduction in SV due to processing. The reduction in SV is expected because during the neutralization step of the processing, free fatty acids in the oil were converted to soap using KOH and the soap stock removed, thus, the reduction in this parameter for the processed oil. The values obtained in this study were higher than the range of 188.00 – 193.25 mg of KOH/g earlier reported for groundnut oils obtained from two varieties of groundnuts (Farhan et al. 2013) and 162.40 ± 0.07 mg KOH/g reported for desert date kernel oil (Aremu et al. 2022) but compared well with 221.50 ± 0.21 – 220.20 ± 0.20 mg KOH/g reported by Nkafamiya et al. (2010) for different species of groundnut oils.

3.1.5. Ester value (EV)

The ester value is the difference between the saponification value and acid value. The EV is also presented in Table 1. The EV of the oil decreased significantly ($p \leq 0.05$) from 263.58 ± 0.25 to 205.65±0.12 mg KOH/g after refining, representing 22% reduction. The value was higher than 184.15±2.02 mg KOH/g and 206.86±0.79 mg KOH/g reported for sunflower and tithonian oils, respectively (Otemuyiwa et al. 2020). The reduction in ester value as a result of the processing could be due to the hydrolysis of some of the intact triacylglycerols by the KOH used during the neutralization step of the processing leading to the production of soap which was removed from the oil at the neutralization step.

3.1.6. Iodine value (IV)

This parameter is used for the estimation of the degree of unsaturation of vegetable oils. Oils with high IV are preferred from nutrition and health viewpoints because it indicates that the oils are rich in polyunsaturated fatty acids (PUFA). For example, oils that are rich in PUFA have been reported to reduce heart diseases that are associated with cholesterol (Yuan et al. 2004). IV is also used to measure the extent of lipid auto-oxidation. The IV is presented in Table 1. The values were 89.63±2.89 I2g/100g and 103.21±2.93 I2g/100g for crude and processed oils, respectively. The IV obtained in this study for groundnut was lower than 109.3±8.3I2g/100g reported earlier for groundnut (Falade et al. 2008) but higher than 5.52±0.05 I2g/100g reported for desert date oil (Aremu et al. 2022). The 15.1% increase in IV as a result of processing of groundnut oil in this study could be attributed to the removal of some of the constituents of the oil such as lecithin during the degumming stage which is expected to concentrate the remaining constituents of the oil left such as IV. This shows that the processing of groundnut oil will be beneficial from health and nutrition viewpoints.

3.1.7. Determination of antioxidant parameters the oil samples

3.1.7.1. Total tocopherol value

Tocopherol is the most important lipid-soluble antioxidant; it protects membranes from oxidation by reacting with lipid radicals produced in the lipid peroxidation chain reaction (Traber and Atkinson, 2007). This prevents the propagation reaction from continuing by removing the free radical intermediate. The total tocopherol values in the oil samples are presented in Table 1. The value for the processed oil (29.26±0.92 mg of α-tocopherol/kg) was significantly lower ($p \leq 0.05$) than 35.02 ± 1.13 mg of α-tocopherol/kg obtained for the crude oil. The value of total tocopherol was lower than 43.4 mg/ kg reported earlier for groundnut oil by Falade et al. (2008) and also below the range of 42 mg/kg and 2680 mg/kg reported for coconut oil and wheat germ

oil, respectively (Schwartz et al. 2008). The inconsistence in the level of this parameter is expected because tocopherols are not stable; they vary with time in the process of carrying out their function of stabilizing vegetable oils. Walker and Slinger (1975) had earlier reported a significant loss of total tocopherols of their processed rapeseed oil which is in agreement with our finding. The effect of processing on the total tocopherol content of groundnut oil was opposite of what was observed with TPC which was observed to increase after processing. It is well known that tocopherols are natural antioxidants; therefore, they are present in vegetable oils to provide vitamin E for human and animal nutrition as well as to defend vegetable oils from lipid oxidation. The role of these compounds in vegetable oil could account for the reduction of total tocopherol of the processed oil. The implication of this is that the processed oil will be more susceptible to lipid oxidation, thus, should be adequately protected with antioxidants.

3.1.7.2 Total phenolic content (TPC)

Phenolic compounds are known to play a significant role in stabilizing lipids against peroxidation (Falade et al. 2015) and inhibiting various types of oxidizing enzymes (Aderogba et al. 2006). The total phenolic content is a measure of phenolic compounds which may contribute to the antioxidant property. Phenolic compounds have been reported to be essential for human nutrition and also for the maintenance of health because they protect organism against several oxidative stress-related diseases such as cardio-vascular disease and some cancers (Sharma and Sultana, 2004). The total phenolic content of the oil samples is presented in Table 1. The values were 3.09 ± 0.04 and 3.83 ± 0.05 mg GAE /g for crude and processed oils, respectively. This represents 23.9% increase in the total phenolic after processing. The difference in these values between crude oil and the processed oil was significant ($p \leq 0.05$). The increase in TPC after processing could be due to the concentration of the phenolic compounds by the removal of some of the constituents of the vegetable oil such as lecithin, gum, proteins and so on during the processing. The value of this parameter was higher than 0.03 mg GAE /g reported earlier for groundnut (Falade et al. 2008) but lower than 48.85±0.28 mg GAE/g reported for noni seed oil (Jahurul et al.2022). This shows that the processed groundnut oil will be better protected against lipid oxidation, consequently a longer shelf life compared with the crude groundnut oil, but the value of PV for the processed oil was saying something else because it was significantly higher ($p \leq 0.05$) than the crude. A similar observation was reported earlier in our laboratory where the oil of a specie of watermelon seed (Sugar baby) with the highest TPC recorded the highest PV and the specie with the least TPC recorded the least value for PV (Falade and Obuseh, 2014). This shows that other antioxidant compounds such as tocopherol and carotenoid could be contributing significantly to the stabilization of vegetable oil. It was reported earlier that total phenolic content contributes 30% to the stabilization of vegetable oils (Ray et al. 1984).

3.1.7.3. Thiobarbituric acid reactive species (TBARS)

TBARS are secondary products of lipid oxidation. These products are very reactive and are believed to be responsible for the initiation of the oxidation of some macromolecules such as proteins, lipids and DNA leading to ageing and carcinogenesis in human (Shahidi and Wanasundara, 2008). The results of this parameter were 1.325± 0.021 and 1.525± 0.021 mg/kg for crude and processed oils, respectively. This represents 15% increase in TBARS as a result of the processing of the oil. The implication of these results is that some of the unsaturated fatty acids (PUFA) have be decomposed in to lower chains unsaturated hydrocarbons such as malonaldehyde thereby reducing the nutritional value and health benefits of the vegetable oil.

3.1.7.4 p-Anisidine value

This parameter measures the content of aldehydes (mainly 2-alkenals and 2, 4 -alkadienals) formed from the decomposition of hydroperoxides, products of

lipid auto-oxidation. It actually measures the extent of lipid oxidation.

The values of this parameter were 1.65±0.03 and 11.29 ± 0.23 for crude and processed oils, respectively. This shows that processing of this vegetable oil led to 584% increase in p-anisidine value. The implication of these results is that some of the polyunsaturated fatty acids would have been decomposed, hence compromising the nutritional value and quality of the oil. The value reported here for groundnut oil was higher than 0.86±0.11 reported earlier in our laboratory for crude groundnut oil (Falade et al. 2015). The difference in value could be due to different method used in the earlier study. Hexane (a non-polar solvent) was used for the extraction of the groundnut oil as against the traditional method which involves the use of water, a polar solvent used in this study. Water in term of water activity (aw) is known to enhance lipid oxidation.

3.1.7.5 Total antioxidant capacity (TAC)

Total antioxidant capacity is a versatile analytical tool for estimating the antioxidant potential of an oil sample. It is the measure of the amount of free radicals scavenged by a test solution (Manach et al. 2004). The total antioxidant capacity of groundnut oil is presented in Table 1. A high TAC value corresponds to high antioxidant capacity. The TAC of the crude groundnut oil 1.315 ± 0.015 mg AAE/g was significantly higher ($p \leq 0.05$) than 0.101 ± 0.012 mg AAE/g for the processed oil. The reduction in the TAC for the processed oil could be due to the effect of processing on the oil. Some of the endogenous antioxidant compounds like α-tocopherol present in rapeseed oil have been reported to be lost during the refining of the oil seed (Walker and Slinger, 1975). Reduction in total tocopherol was also observed in the study.

3.2. Physical properties of groundnut oil

3.2.1. Refractive index

The refractive index of oil has been reported to increase with increase in the number of double bonds (Farhan et al. 2013). Rudan-Tasic and Klofutan (1999) also observed that a high value of refractive index is an indication of high number of carbon atoms. The refractive index of both crude and processed oil samples are presented in Table 2. The results showed a significant decrease ($p \leq 0.01$) from 1.687 for the crude oil to 1.682 after processing. This shows that the processing of this oil has caused significant reduction in both carbon chain length and number of double bonds. Falade and Obuseh (2014) had earlier reported a linear relationship between refractive index and iodine value. The refractive indices of the samples were higher than 1.464 ± 0.002 earlier reported for groundnut oil (Falade et al. 2008).

3.2.2. Surface tension

Surface tension is the energy required to increase the surface area of a liquid due to its intermolecular forces. The surface tension values for both oil samples are presented in Table 2. The values were 37.84 ± 0.94 and 39.63 ± 0.02 mNm-1for crude and processed oils, respectively. These values were significantly different ($p \leq 0.05$) from each other. The difference in this parameter between crude and processed oils could be due to the stronger intermolecular forces that might have existed among the molecules of the purified oil over the crude oil which contains impurities that could affect these forces of attraction. It should be noted that low surface tension oil is suitable for use as a releasing agent in baking processes and in making shortenings (Oyekunle and Omode, 2008). This property given above suits crude groundnut oil over processed oil.

3.2.3. Smoke point and flash point

The smoke point is the temperature at which vegetable oil produces smoke. At this point, vegetable oil will give food that is been fried unpleasant taste and odor. The flash point on the other hand is the temperature at which the vapor of the oil ignites. Results of the

Table 2 **Physical Properties of Crude and Processed Groundnut Oil**

Parameters		Crude oil	Processed oil
Refractive Index		1.687±0.001[b]	1.682 ±0.001[a]
Surface Tension (mNm^{-1})		37.84±0.94[a]	39.63±0.02[b]
Smoke Point (°C)		230.00±2.00[b]	220.00±1.00[a]
Flash Point (°C)		300.00±1.00[b]	280.00± 2.00[a]
Viscosity (cSt)	30 °C	50.010±0.005[b]	45.779±0.001[a]
	40 °C	39.641±0.001[b]	37.312±0.001[a]
	50 °C	31.973±0.004[b]	25.058±0.004[a]
	60 °C	30.083±0.002[b]	23.707±0.002[a]
	70 °C	23.344±0.005[b]	20.375±0.002[a]
	80 °C	18.249±0.008[b]	13.664±0.005[a]
Specific Gravity	30 °C	0.912±0.012[a]	0.911±0.011[a]
	40 °C	0.910±0.010[a]	0.909±0.011[a]
	50 °C	0.909±0.010[a]	0.906±0.011[a]
	60 °C	0.904±0.001[a]	0.903±0.011[a]
	70 °C	0.903±0.011[a]	0.903±0.011[a]
	80 °C	0.902±0.011[a]	0.901±0.001[a]

Results are means of triplicate determination ± standard deviation.
Data in the same row followed by the same superscript letters are not significantly different at the 5% probability level.

smoke and flash points of the crude and processed oils are presented in Table 2. The smoke points for the crude and processed oils were 230±2.00 and 220±1.00oC, respectively. The results showed a significant decrease ($p \leq 0.05$) as a result of processing of the groundnut oil. The 4.3% reduction in smoke point as a result of processing is expected based on the colligative properties of liquid. Impurity is known to raise the boiling point of a liquid, therefore, the removal of the impurities in the oil will account for the reduction in its smoke point. The flash points for crude and processed oils are 300±1.00 and 280±2.00oC, respectively, representing 6.7% reduction. This significant ($p \leq 0.05$) reduction can also be explained using colligative properties of liquid given above because; whatever reduces the boiling point of oil will eventually reduce its flash point. Crude vegetable oils generally have a high FFA content with a corresponding high smoke point and consequently, a high flash point (Falade et al. 2008). The implication of these results is that processed oil may not be suitable for deep frying; thus, crude groundnut oil will be better for deep frying.

3.2.4. Viscosity

Viscosity of oil is a measure of the oil's resistance to shear. The viscosity values of the oil samples measured at temperatures between 30 and 80 oC are presented in Table 2. The values ranged from 50.010 ± 0.005 to 18.249 ± 0.008 cSt and 45.779 ± 0.001 to 13.664 ± 0.005 cSt for crude and processed oils, respectively. The viscosity of the processed oil was consistently and significantly ($p \leq 0.05$) lower than that of the crude oil at all the temperatures used for this study. This could be attributed to the removal of the impurities in the processed oil. Low viscosity has been reported to be crucial for any vegetable oil to be suitable for use in biodiesel because it will allow a high degree of atomization with short ignition delay as well as easy flow through pipes (Traber and Atkinson, 2007). In order to use this oil for biodiesel, it is important to first process the oil since processing was observed to reduce the viscosity by 8.5% making it to be at par with Olive pomace oil (45.27 cSt) used for making biodiesel (Selaimia et al. 2015).

3.2.5. Specific gravity

The specific gravity of the oil samples at temperatures between 30 and 80 oC is presented in Table 2. The values ranged from 0.912 ± 0.012 to 0.902± 0.011and 0.911± 0.011 to 0.901 ± 0.001for crude and processed oils, respectively. Although the values of this parameter reduced consistently with the temperatures used, the reductions were not significant ($p \geq 0.05$). The reduction in specific gravity although not significant could be attributed to the removal of some of the impurities (lecithin, gum, proteins, free fatty acids et cetera) thereby reducing its weight.

4. CONCLUSION

The study reveals that processing of the crude oil could increase peroxide value (to 400%) and significantly decreased acid value (55.7%). Saponification value of

the oil was also observed to decrease significantly ($p \leq 0.05$) after processing, consequently, processing of the oil is not recommended for oil to be used in soap making. However, processing led to 15.1% increase in the iodine value, and 23.9% increase in total phenolic, therefore processed oil is desirable for nutritional and health viewpoints but this cannot be said of total tocopherol which decreased by 16%. In addition, processing of the vegetable oil led to increase in both p-anisidine value and TBARS and decrease in TAC. The processing of this vegetable oil also affected some of the physical parameters such as refractive index, viscosity, smoke and flash points which decreased significantly ($p \leq 0.05$). Likewise, specific gravity decreased marginally but surface tension increased significantly ($p \leq 0.05$).

The processing of the vegetable oil seemed to have both advantages and disadvantages; hence, processing of this oil should be based on what the oil is to be used for. In order to protect the antioxidant compounds in this oil such as tocopherol, it is imperative to defend this oil with antioxidant compounds extracted from medicinal plants. The removal of pro-oxidants (Fe, Cu, Zn and other multiple valence transition metals) using sequestrants such as EDTA could also be helpful. These could form the basis for future study.

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CONFLICT OF INTEREST

All authors have declared that no competing interests exist.

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