Effect of Additives on the Physicochemical Properties of Fried Groundnut Oil

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***Abstract* — Fried groundnut oil was obtained from a commercial chin-chin seller. The same product (king's oil) was bought from a commercial market in Uyo, Akwa Ibom State. Air dried additives (orange peels) were cut into chips, different quantity were added to the fried oil and heated to 60^{o}C for 10min. The additive was filtered from the fried oil. The fresh oil, fried oil and fried oil + additive were characterized using standard methods. The results revealed the heating/frying of oil affects the physicochemical properties of oil. The results also revealed that most of the chemical properties of the oil that were altered by frying were restored by the addition of additive. However the groundnut oil that is presently discarded as waste after frying for several time can be utilized in the production of some industrial products like soap, shaving cream and margarine and can also be re-use for cooking, if suitable additive such as orange peels which is eco- friendly, cheep and readily available is added to it.**

***Keywords*: Groundnut oil, frying, additive, orange peels, physicochemical properties.**

1. INTRODUCTION

Groundnut oil is a mild tasting vegetable oil extracted from groundnut kernels. It contains only a small proportion of non-glyceride constituents. Its fatty acid composition is complex including saturated fatty acids covering a wide range of molecular weights (Aluyor, 2009).

Groundnut oil is widely used in cooking, including frying, basting, and in the manufacture of margarines. It is important food oil, with a good flavor, high quality and low free fatty acid value (Angaye, 2015). Groundnut oil processing is based on mechanical pressing technology which is generally grouped into three stages: groundnut seeds preparation, groundnut pressing and crude groundnut oil refining.

Heating oil changes its characteristics. Oils that are healthy at room temperature can become unhealthy when heated above certain temperatures (Ngassapaa *et al*., 2012; Angaye *et al*., 2015). When choosing cooking oil, it is important to match the oil's heat tolerance with the cooking method because all oils degrade in response to heat, light, and oxygen *(Kochhar et al., 2009).*

During frying, oils undergo chemical modification which may alter their properties. Exposure to heat and light creates an environment favorable to chemical and enzymatic reactions resulting in hydrolysis and oxidation (Angaye, 2015). Oxidative rancidity in oil occurs due to the oxidation of the double bonds in unsaturated fatty acids present in the constituent triacylglycerols forming peroxides or hydroperoxides that later decompose producing aldehydes, ketones and low molecular weight acids. The process of oxidative rancidity or peroxidation and the consequent rancidification is the major cause of loss of quality of edible oils. Oxidative rancidity affects flavor, aroma, colour, texture, and also decreases the nutritive value of edible oils via the destruction of fat-soluble vitamins (especially vitamins A and E) and proteins (Angaye, 2015).

The dynamics of oxidation or oil deterioration depends mostly upon the fatty acid composition of the constituent oil (Vidrih, *et al*., 2010). Effects of heat on the properties of oil have been reported by Adejumo *et al*., (2013), Choudhary and Grover (2013).

When additives are added to the oil it affects both physical and chemical properties of the oil. Some of the properties of groundnut oil that are lost during heat/frying can be restored when additives are added. However the properties of the oil restored depends on the type of additives added. Effect of some local additives on the chemical constituent of palm oil was investigated by Eddy *et al.*, (2007) and Etuk *et al*., (2012). Additives such as lime increase the saponification value and iodine number and also cause a decrease in the peroxide value of palm oil (Etuk *et al*., 2012).

Groundnut oil used for frying are discarded as waste after series of frying. During frying the properties of this oil are lost, this research work aim at investigating the effect of frying on the physicochemical properties of groundnut oil and also attempt to restore these properties using orange peels as eco-friendly additive.

2.0 MATERIALS AND METHODS.

Waste groundnut oil was obtained from chin-chin seller after series of frying with the oil. The oil was filtered. 1g and 2g of air dried orange peels were added separately to 10ml of oil and heated for 10min at 60^{o}C. The oil was allowed to cool and the additives were filtered.

2.1 Characterization of the oils

Fresh groundnut oil, fried groundnut oil and fried oil after additive has been added were characterized in order to compare their properties.

2.1.1 Determination of moisture content (AOAC, 1997)

A known weight of the empty beaker and that of the oil samples were measured. The oil in beaker were kept in an oven for 6 hours and maintained at a temperature of 105°C, it was removed and cool in the desiccators and reweighed and cooled to constant weight.
The percentage of moisture content was calculated as:

$$\text{Moisture content}(\%) = \frac{b-c}{b-a} \times 100$$

Where; a = weight of empty beaker
b = weight of beaker + oil before drying in the oven
c = weight of beaker + oil after drying in the oven

2.1.2 Determination of viscosity

The viscosity of the oil was measured using Ostwald viscometer; in which oils were drawn up into the upper bulb of a 2 bulbs separated with capillary tubing. The time required for its meniscus to fall between calibration marks above and below the upper bulb was accurately measured. A similar measurement was made with water which serves as a standard. Both samples and the standard were performed in duplicate to obtain the average.

$$Viscosity = \frac{n1}{n2} = \frac{p1\ t1}{p2\ t2}$$

Where n_1= viscosity of the sample, n_2= viscosity of water, ρ_1= density of the sample, ρ_1= density of water, t_1= flow time of the sample and t_2 = flow time of water

2.1.3 Determination of refractive index (RI)

A concave mirror was placed at the base of the stand with a search pin clamped appropriately to enable the adjustment of its position until coincided with its image at point C. The distance (CA) was measured as its initial measurement. Small quantity of each oil sample was poured separately into the mirror and the position of the pin adjusted again until a new position C' was found and where it coincided with its image was measured again to be C'A. The Refractive index was calculated as:

$$\text{Refractive index}(RI) = \frac{CA}{C'A}$$

2.1.4 Determination of Density

Density was determined using British Standard Methods, (1984),a nd it was calculated using this formula:

$$\text{Density} = \frac{Mass\ of\ sample}{Volume\ of\ sample}$$

2.1.5 Determination of pH value

The pH values of the oil samples were determined using a pH meter.
Chemical parameters of the oil samples were determined as follows:

2.1.6 Determination of free fatty acid value (British Standard Methods, 1958)

The percentage of free fatty acid (FFA) was obtained after 25 mL of ethanol was added to 1.5 g of the sample in a conical flask. The mixture was heated to 60°C then cooled. 1 cm^3 of phenolphthalein indicator was added to the solution. Titration was done using 0.1M NaOH solutions while shaking the mixture constantly for proper mixing. FFA was calculated using this formula:

$$\text{FFA}(\%) = \frac{Titre\ value \times 0.0282 \times 100}{Weight\ of\ the\ sample}$$

2.1.7 Determination of acid value (British Standard Methods, 1988)

Exactly 25 cm^3 of chloroform was measured into 100 ml conical flask, 1 g of each oil was added, 2 drops of phenolphthalein indicator were also added to the mixtures. Titration was done with 0.1M alcoholic potassium hydroxide until a colour change was obtained. Blank determination was also carried out. Similar method was repeated for other oil samples.
The acid value was calculated using this formula:

$$\text{Acid value} = \frac{Sample\ titre - Blank}{Weight\ of\ the\ sample}\ 0.1 \times 56.1$$

2.1.8 Determination of saponification value: (AOAC methods,1984)

2 g of the oil samples were weighed into 25 ml, of 0.5 ethanolic potash in a conical flask. To another flask, 25 cm^3 of the 0.5 ethanolic potash was placed without the oil, this was used as blank. Both flasks were boiled in a water bath for 30 minutes with frequent shaking and 2 drops of phenolphthalein indicator were added. Titration was done with 0.5M HCl without delay with vigorous shaking to get the end point. The S.V. was calculated using this formula:

$$S.V. = \frac{Average\ blank\ titre - Average\ sample\ titre}{Weight\ of\ sample} \times 28.01$$

2.1.9 Determination of iodine value (British standard method, 1988)

Using the method above, 0.5 g of the sample was dissolved in 10ml of chloroform in a conical flask, 25 ml of the Hanus solution was added to the chloroform and corked. This was kept in desiccator for 30 minutes in the dark. A blank was also carried out under the same conditions. When reaction was completed, 15cm^3 of 10% potassium iodide solution and 10 ml of distilled water was added to each flask and mixed by gentle shaking. The content of both flaks were titrated with 0.1N $Na_2S_2O_3$ to pale yellow and 2 ml of starch solution indicator was added. Titration was continued until the blue-black colour was completely discharged
Iodine value was calculated using this formula:

$$Iodine\ value = Blank\ titre\ value - Titre\ value \times 6.35$$

2.1.10 Determination of peroxide value (AOCS Method, 1997)

5.00g of oil was weighed into a 250ml glass stoppered Erlenmeyer flask, 30ml of acetic acid-chloroform solution (3:2) was added and the flask was swirled until the sample was completely dissolved (careful warming on a hot plate was necessary). Using 1ml Mohr pipette, 0.5ml of saturated potassium iodide solution was added and the flask was

stoppered and swirled the contents for exactly 1 minute. Immediately, 30ml of distilled water was added using a graduated cylinder, stoppered and shake vigorously to liberate the iodine from the chloroform layer, and 1ml of starch solution indicator was added using a dispensing device. Titration was done with 0.1N sodium thiosulfate until blue-gray colour disappeared in the upper layer. Similar method was repeated for other oils samples. A blank solution was prepared with the sample. The peroxide value was calculated using the formula:

$$\text{Peroxide value} = \frac{(\text{Sample titre} - \text{Blank titre}) \times N\ \text{thiosulfate} \times 1000}{\text{Weight of sample}}$$

3. RESULT AND DISCUSSION

Table 1: Physical parameters of oils

Parameters	Fresh oil	Used oil	Used oil + 1g additive	Used oil + 2g additive
Colour	Light yellow	Light yellow	Light yellow	Light yellow
Moisture content	0.1	1.2	0.25	0.5
Refractive index	1.4	1.4	1.0	1.2
pH	6.97	7.09	7.23	7.79
Density kg/m^3	0.904	0.9540	0.928	0.921
ViscosityM^2S^{-1} (40^oC)	12.32	26.57	40.83	44.67

The result of the physical parameters of the fresh fried and fried groundnut oil plus additives are presented in Table 1. These results revealed that fried oil and fried oil plus additives contain greater moisture content than the fresh oil. This may be due to the moisture added during frying and the moisture from the additives. It was also found that the higher the mass of the additive, the greater the moisture content of the oil. This results agreed with the earlier work reported by Ekop *et al*., (2007). Heating/frying of the oil increased the density, viscosity and pH of the oil. The increase in these parameters is attributed to the formation of higher molecular weight product (peroxides) in the oil during the peroxidation process. Fekarurhobo, *et al*., (2009), Angaye, *et al*., (2013), Etuk *et al*., (2012), Eddy and Ekop, (2007) made similar observations when they were working with different oils and additives.

Table 2: Chemical Parameters of Oils

Parameters	Fresh oil	Used oil	Used oil + 1g additive	Used oil + 2g additives
Saponification value	255.25	164.09	237.00	247.26
Free faty acid %	0.376	0.940	0.676	0.564
Acid value	1.683	2.244	1.683	1.336
Peroxide value	21.8	58.0	38.6	16.04
Iodine value	36.9	31.03	42.13	53.06

The results of effect of frying and additive addition are presented in Table 2. The results showed that frying and additive addition significantly affect the properties of the groundnut oil.

Frying reduced the saponification and iodine value. These properties were restored by addition of additive. These results showed that fried oil is not suitable for many industrial purposes. Saponification value is less than 180. Wollat , (1985) reported that the higher the saponification value, the better the quality of oil for soap making and manufacture of lather shaving creams. However the fried oil that could not be used for soap making could be useful when additive such as orange peels has been added because addition of additive increased the saponification value as shown in Table 2. On the other hand, iodine value is directly proportional to the level of unsaturation of fat and oil. The decrease in iodine value with increase in temperature is a proof that lipid oxidation had occurred (Joseph, 1997). The increase in iodine value due to the addition of additive to fried oil may be as a result of limonene presence in the orange peels which was extracted to the oil. The degree of unsaturation of oil determines the potentials of the oil for margarine production.

Peroxide value of the oil after frying was found to increase significantly. This parameter was reduced when additive was added to the fried oil. Peroxide value is a measure of the degree of oxidation of the oil, hence low peroxide value indicate a decreasing rate of oxidation. The increase in peroxide values with increase in temperature indicates that hydroperoxides were formed in the oils as a result of oxidation. Hydroperoxides have been identified to be the primary products of oil oxidation (Shahidi and Zhong, 2005). The decrease in the peroxide value observed when additive was added might be due to the presence of antioxidant such as citrus acids, flavonoids and vitamin C in the oil which was extracted from orange peels. The antioxidant reduced the peroxide value of the fried oil by acting as scavengers of damaging oxygen free radicals that developed during frying.

Acid value is defined as the number of milligram KOH requires to neutralize 1g of fatty acid in oil. As presented in

Table 2, acid value increased when the oil was heated and decreased when additive was added to the fried oil. This is because acid value is directly proportional to the level of rancidity of the oil. Wollat (1985) reported that increase in acid vale of oil is an indication of the onset of rancidity, and rancidity of oil is accelerated by moisture, air and presence of some metals ions.

Heating/frying of the oil increased free fatty acid content of the oil, while addition of the additive to the fried oil decreased the free fatty acid content as shown in Table 2. Free fatty acids represent the fatty acid molecule that has been free by lipase oxidation (Ekop *et al.,* 2007). The decrease in the free fatty acid value might be due to the presence of antioxidant in the orange peels which was extracted into the oil (Eddy, 2004).

Conclusion

Heating and frying of the groundnut oil altered its physicochemical properties. Groundnut oil after frying could not be utilized for cooking and for any industrial purposes. The properties such as saponification and iodine value which determined the potentials of the oil in industrial applications that were altered during frying were restored significantly after additive has been added. Other properties such as peroxide value, free fatty acid and acid value which determined its nutritive value were also restored. Therefore orange peels which are environmentally friendly, cheep and readily available should be exploited and use as additive to improve the properties of oil for both domestic and industrial applications.

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