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HEAT TREATMENT OXIDATIVE REACTIONS IN SOME EDIBLE VEGETABLE OILS

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ABSTRACT

The influences of microwave heating (Microwave oven Electrolux, model EMM2005, 2450 MHz, 400 W) and thermal heating (Hot plate Thermostat, Temperature range: 25 to 125^{o}C) for 30 min on the oxidation of groundnut oil (*Arachis hypogaea*) and palm oil (*Elias guineensis*) were studied. The heating treatments increased dry matter and oils contents at given conditions and therefore, with reduced moisture content. Analyses of the two oils determined were the acid values, peroxide values, saponification and iodine values using the method of analysis of Association of Official Analytical Chemists (AOAC). Except saponification values, all the chemical properties of the two oils from different heating treatments showed no significant ($p<0.5$) variations over the temperature ranges. However, the changes in percentages of free fatty acids composition of palm oil at both heating conditions were very significantly (<0.5) higher than those determined for groundnut oil. The oxidative changes of chemical parameters were significantly dependent on the mode of heating and temperature, but largely agreed to codex minimum standard requirements for oil consumption. The saponification value was the highest changing parameter in palm oil (369.21 mgKOH/g) and in groundnut oil (248.20 mgKOH/g), and both were exposed to microwave treatment.

Keywords: *heating, microwave, oxidation, thermal, vegetable;*

INTRODUCTION

Vegetable oils are extracted from nuts, seeds and some fruits of plants. The type and proportion of the fatty acids are significantly influenced by their physical and chemical properties of the triacylglycerol were reported by Hesham *et al.,* (2016). Oils are triglyceride that consists of three units of fatty acids and one unit of glycerol. Oils such as sunflower, soybean, cottonseed, canola, olive, palm, coconut, palm kernel groundnut and corn are ingredients commonly used for food preparations and non-edible varieties are used in soaps, paints and biodiesels formulations.

The tropical plant (*Elias guineensis*) has two species namely, *E. oleifera* and *E. guineensis*. From which the palm oil is extracted from the fleshy orange-red mesocarp of the fruits (Siew, 2002). The plant belongs to palmae family with unbranched stem that can grow from 20 - 30 meters high and life spans of 25 - 30 years are grown for economic importance. Kalyana *et al.,* (2003), reported the female bunch with about 2000 fruits can weigh from 30-40 kilogram and fruits colour changes from young and unripen black in colour to yellow to orange-red when fully ripen.Groundnuts or peanut (*Arachis hypogaea*) is a popular leguminous food crops that is widely grown by millions of people for edible and commercial interests. Anyasor, *et al.,* (2009),reported many different varieties of herbaceous plant such as Boro Red, Boro Light, Campala, Mokwa, Ela. In Nigeria, peanuts after roasting are snacks that are mostly consumed by people Jambunathan, *et al.,* (1993). Diets in many countries are made up of groundnut oil, serving as a good source of fatty acids for human nutrition, cells formation and energy sources (Bansal *et al.,* 1993; Grosso and Carlos, 1995; Gaydou, *et al.,* 1993). Several uses of processed seed include peanut butter, stews, soups and other infant food. This provides dietary requirements of minerals to supplement farm animals and humans (Grosso, *et al.,* 1997; Asibuo*, et al.,* 2008; Ayoola and Adeyeye, 2010; Yusuf, *et al.,* 2014).

Healthy population with good nutrition promotes development and equally important nutritional requirement for oil is the method of preparations that are unknown and consequently not enforced. Popular local dishes and soup ingredients uses the groundnut and palm oils and considerable research on their heating conditions and mode are necessary to maximize consumption benefits. Therefore, the aim of the present work was to study the oxidative changes in chemical parameters of the two commonly consumed vegetable oils caused by the excessive microwave and thermal heating after prolonged exposure. It is hoped that this would improve and expand the scope of oils utilizations and knowledge in our diets.

MATERIALS AND METHODS

Samples of palm oil and groundnut oil were obtained from a local retail in Ilorin, Kwara State, Nigeria. Triplicate measurement of each sample (100.0 g ±1.0 g) was weighed in conical flasks and covered with a thick PVC. The microwave model (Electrolux, model EMM2005, 2450 MHz, 400 W) was used to heat the samples in the centre of microwave oven with a rotating disc diameter of 27 cm for 25, 50, 75, 100 and 125^{o}C. The second independent experiments were conducted with the thermal heating (Hot plate Thermostat, Temperature range: 25 to 125^{o}C) were carried out under similar temperature conditions for 30 minutes. After each heating treatment, the microwave and hot plate were stopped and allowed to cool before the next heating in the series. The treated samples were stored in sealed tubes till the chemical analyses.

Chemicals and Reagents: Sigma Aldrich (Gillingham Dorset, UK) and LGC (Teddington Middlesex, UK) supplied the chemicals under license.

Chemical Analysis: The analyses of the two vegetable oils for the acid, peroxide, saponification and iodine values were conducted using the method of analysis of Association of Official Analytical Chemists (AOAC, 2012) and Pearsons(1981 and 1991).The acid and saponification values (mg KOH/g lipid) were by titration; iodometric method was employed for peroxide value (meq/kg) and iodine value (Wiji's method) expressed in (mg/iodine/100g). The acid value multiplied with the factor 0.503 was used to determine the percentage free fatty acid (% FFA = 0.503 x acid value) (Pearson, 1991).

Statistical Methods. The one-way Analysis of Variance (ANOVA), SPSS 17used to evaluate data with the Software StatSoft, Inc. (USA). Differences at $p<0.05$ were considered significant.

RESULTS AND DISCUSSION

In the equation below, the percentages of free fatty acid value in oils leads to hydrolytic rancidity. The quality of oils and fats depends on the acid values which measures the breakdown of triacylglycrols to free fatty acids as follows:

RCOOH + KOH → RCOO- K + H2O.

In Table 1, the results of the analyses of palm oil (Elias guineensis) and groundnut oil (Arachis hypogaea) during the thermal and microwave heating using the method of analysis of Association of Official

Analytical Chemists (AOAC, 2012) is presented. The analyses of acid values (AV), peroxide values (PV), iodine values (IV), saponification values (SV) and free fatty acids (FFA) revealed marked variations in the chemical parameters. The two heating treatments in various food preparations have significant effects on the quality of the two studied vegetable oils. The presence of acid phosphates and amino acids components may result in overestimation of acid value.It gives the indication of quality arising from inadequate processing and storage. Within the same oil, the significant differences ($p<0.05$) showed variations for both treatments. Between the oils, the mean acid values compared with the thermal (30.48 mgKOH/g) and microwave (32.76 mgKOH/g) treatments for palm oil were significantly ($p<0.05$) higher than for groundnut oil thermal (0.94 mgKOH/g)) and microwave (1.32 mgKOH/g) treatments.

The heating treatments over the temperature range of 50 to 250^{o}C for 10 minutes of heating each is shown in Figure 2. The mean acid values determined were however higher than those earlier reported for palm by Akubugwo and Ugbogu(2017), which may be due to refining, deodorization and moisture processes.

Table 1: Effect of microwave and thermal heating on the chemical properties of palm and groundnut oils

Palm Oil (*Elias guineesis*)

Sample Temp (oC)	Acid value (mgKOH/g)		Peroxide value (meq/kg)		Iodine value (mg/iodine		Saponification value (mgKOH/g)/100g)		Percentage Free Fatty Acid (% FFA)	
	Thermal	Microwave	Thermal	Microwave	Thermal	Microwave	Thermal	Microwave	Thermal	Microwave
25	33.4	34.8	5.0	4.0	44.4	48.2	176.8	422.2	16.8	17.5
50	32.4	33.4	5.0	5.0	22.2	10.2	162.7	420.8	16.3	16.8
75	29.6	32.2	7.0	6.0	11.8	10.0	135.4	405.2	14.9	17.2
100	28.8	31.8	9.0	8.0	6.9	10.0	106.6	362.6	14.5	17.2
125	28.2	31.6	12.0	11.0	4.3	8.9	90.9	235.2	14.2	17.5
∑	152.4	163.8	38.0	34.0	89.6	87.3	672.4	1846.0	76.7	86.2
Mean	30.48	32.76	7.60	6.80	17.92	17.46	134.50	369.21	15.34	17.24
STD	2.2917	1.3372	2.9665	2.7749	16.3088	17.1918	36.2792	78.6879	1.1459	0.2881
SL	$p < 0.05$*		$p < 0.05$*		$p < 0.05$*		$p < 0.05$		$p < 0.05$	

Groundnut Oil (*Arachishypogaea*)

Sample Temp (oC)	Acid value (mgKOH/g)		Peroxide value (meq/kg)		Iodine value (mg/iodine		Saponification value (mgKOH/g)/100g)		Percentage Free Fatty Acid (% FFA)	
	Thermal	Microwave	Thermal	Microwave	Thermal	Microwave	Thermal	Microwave	Thermal	Microwave
25	1.4	2.2	19.0	7.0	48.9	54.9	228.7	290.4	0.7	1.1
50	1.1	1.6	23.0	18.0	24.4	22.1	176.8	282.3	0.6	0.8
75	0.8	1.4	28.0	21.0	14.6	13.6	162.7	239.9	0.4	0.7
100	0.8	0.8	31.0	45.0	8.3	13.3	135.4	230.4	0.4	0.4
125	0.6	0.6	32.0	47.0	6.5	12.7	106.6	198.0	0.3	0.3
∑	4.7	6.6	133.0	138.0	102.7	116.6	810.2	1241.0	2.4	3.3
Mean	0.94	1.32	26.6	26.6	20.54	23.32	162.04	248.2	0.48	0.66
STD	0.3130	0.6419	5.5045	17.6011	17.3307	18.0724	45.9487	38.2408	0.1643	0.3209
SL	$p < 0.05$*		$p < 0.05$*		$p < 0.05$*		$p < 0.05$		$p < 0.05$*	

Note: ∑ = sum; STD = standard deviation; SL = significance level; $p < 0.05$= significance difference; $p < 0.05$* = no significance

Okechalu, *et al.,* (2011) reported the peroxide value is an indication of oxidation and levels of deterioration as well as the levels of oxygen in 1gram of oils and fats. The susceptibility to rancidity (Fig. 1) due to the levels of unsaturation of fatty acids in the glycerides is measured the iodine values. In current work, no significant differences ($p<0.05$) were observed in iodine values but it occurred in peroxide values for both palm and groundnut oils with respect to the thermal and microwave heatings as shown in Figure 1. However, the mean iodine values was (89.6 mg/iodine/100g) for thermal and microwave (87.3 mg/iodine/100g) for palm oil and similarly for groundnut oil, thermal and microwave values were (102.7 mg/iodine/100g) and (116.6 mg/iodine/100g), respectively. However, the iodine values > 100 as observed in groundnut oil heating suggested the presence of unsaturated fatty acids and disposed the groundnut oil to drying oil due to the excessive heating.

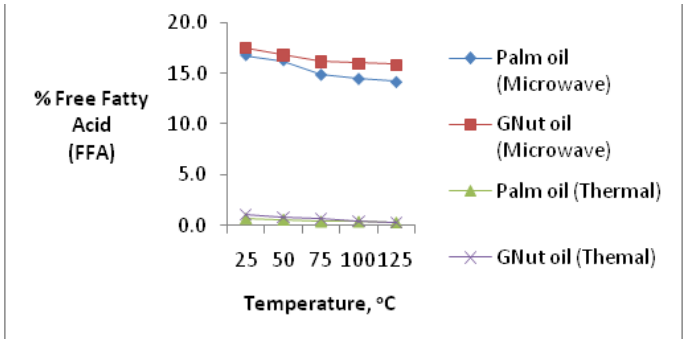

Figure 1: Changes in acid values of oils during thermal and microwave heating

Step 1: $ROOH + 2KI + 2H+ \rightarrow ROH + I_2 + H_2O + 2K+$

Step 2: $I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_2O_6 + 2NaI$

Figure 2: Primary oxidation to determine the degree of unsaturation

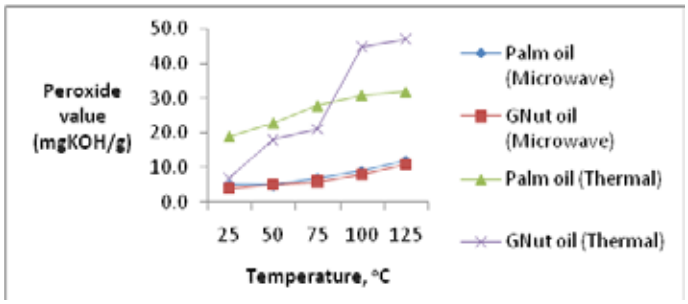

Figure 3: Changes in peroxide values of oils during thermal and microwave heating

The determined iodine value were higher than typical peanut oil iodine values (85-100) and palm oil (37-54) as obtained by the literatures (Okechalu, *et. al.,* 2011; Knothe, 2000). Figure 5 illustrates the 3 – steps reactions for iodine determination:

Step1:R-CH=CH-R+IBR(excess)→R-CHI-CHBr+IBR (remaining)

Step 2: IBR(remaining)+2KI →KBr + KI + I_2

Step 3: I_2 + starch + $2Na_2S_2O_3$ (blue) → 2NaI + starch + $Na_2S_4O_6$ (colourless)

Figure 4: Reaction of unsaturated lipids to determine iodine values.

Similarly, the trend in iodine values of oils during thermal and microwave heating are given in Figure 5. The fatty acids average molecular weight in oil fractions is inversely related to the saponification value, implying the higher the saponification values, the higher the shorter carbon chain of fatty acids were reported by Abayeh, *et al.,* (1998) and also Kirk and Sawyer (1991).

Figure 5 shows that the trend for thermal and microwave heating treatments were significantly different ($p<0.05$) with the mean saponification values of 134.50 mgKOH/g and 369.21 mgKOH/g for palm oil and 162.04 mgKOH/g and 248.2 mgKOH/g for groundnut oil.

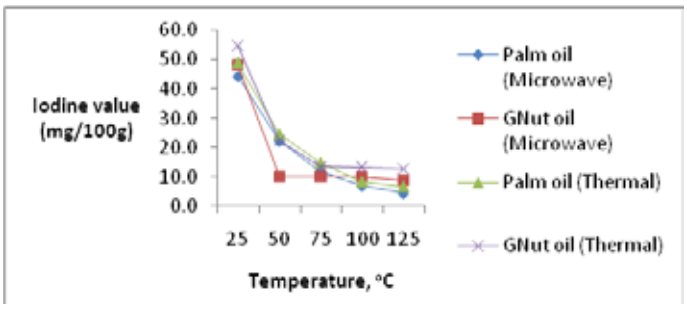

Figure 5: Changes in iodine values of oils during thermal and microwave heating

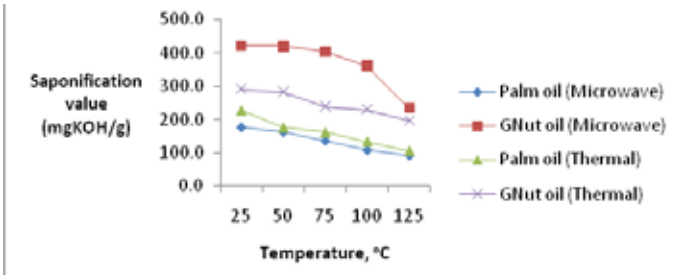

Figure 6 shows saponification reaction of lipids with potassium hydroxide

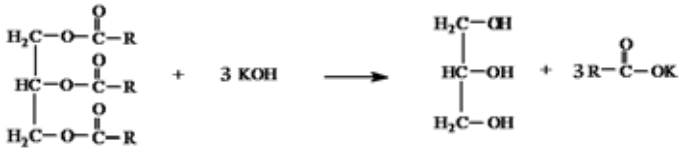

Figure 7: Saponification reaction of lipids with potassium hydroxide

The saponification value of 193 (mgKOH/g sample) for groundnut oil and 200 (mgKOH/g sample) for palm oil were cited in the literature (Kirk and Sawyer, 1991;Kyari, 2008)

CONCLUSION

The results obtained shows that the most chemical changes were within the stipulated limits recommended by Codex (1992). However, the high iodine values from microwave heating suggested groundnut oil was highly unsaturated and may be prone to rancidity. The physicochemical properties of the two vegetable oil, prior to the

investigation, largely agreed to codex standards. The physicochemical properties were also dependent on the mode of heating which changed significantly with temperature . The stipulated limits (Codex Alimentarius, 1992) recommended by international standards for the edible oils were not exceeded by excessive heating except iodine (> 100) in groundnut oil which may be unacceptable for consumption. The saponification values were the highest changing property in palm oil (369.21 mgKOH/g) followed by groundnut (248.20 mgKOH/g) and both were exposed to microwave treatment. The observed changes in chemical parameters of the oils caused by excessive microwave and thermal heating may affect nutritional potentials during food preparations.

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