

## Effect of Hydrothermal Processing on Carotenoids, Tocopherol, Fatty Acids and Oxidative Parameters of Palm (*Elaeis guinensis* Jacq) Oil

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### ABSTRACT

The study investigated the impact of hydrothermal processing on carotenoids, total tocopherol, fatty acids and oxidative changes in palm (*Elaeis guinensis*) oil. The palm oil sample was subjected to 100 min hydrothermal treatments: boiling (oil with water), stir-frying (frying oil alone) and batch food frying (frying plantain in oil) as done in home cooking and in each of the operation, sample of oil were withdrawn at interval of 20 min and kept for analysis. The oil sample obtained from each operation was analysed for chemical parameters using standard methods, fatty acid profile by gas chromatography, carotenoids and tocopherol by spectrophotometric and colorimetric method, respectively. The results showed that  $\beta$ -carotene and tocopherol decreased by 55 % and 20 %, respectively within 2 min and then decrease became gradual as frying and boiling time is increased. The peroxide values recorded in stir-frying and boiling increased from 6.8 to 95.2 and 8.5 to 118 meq/kg, and thiobarbituric acid values from 9.5 to 18.9 and 2.2 to 5.4 TBA value/kg, respectively. In batch frying, free fatty acid, acid value and peroxide value decreased from 0.93 to 1.42, 1.85 to 2.82 and 9.48 to 33.2 meq/kg, correspondingly. Tocopherol and carotenoid decrease from 2.7 to 1.15 mg/g and 6.6 to 1.8  $\mu$ g/g respectively. The saturated and monosaturated fatty acid contents increased with reduction of polyunsaturated fatty acids while trans fatty acid was found to be formed as frying time increased. The study revealed that hydrothermal treatment of palm oil could lead to loss of lipophilic vitamins and essential fatty acids with formation of trans fatty acid and oxidative products that could lead to deterioration of the oil. Hence, repeatedly used vegetable oil should be constantly analysed as it may be detrimental to nutrition and health of consumers.

**KEYWORDS:** Hydrothermal, carotenoids, tocopherols, fatty acids, peroxide value

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### 1. INTRODUCTION

Palm (*Elaeis guinensis* Jack) oil is one of the major edible plant oils used for culinary purposes in the tropical countries especially West and Central Africa (Wattanapeupaiboon and Wahlqvist, 2003). In Nigeria, it is traditionally produced in high quantity and at affordable price; it is used for seasoning foods and also in deep frying. Palm oil has been reported to be free from trans-fatty acids because its production does not involve industrial processes such as hydrogenation (Wiege, et al., 2020)). Red palm oil has been identified as the richest source of  $\beta$ -carotene – a precursor of vitamin A, in addition to its high content of phytonutrients which exhibit unique antioxidant

properties. Therefore, there is the possibility that palm oil could offer some health advantages by reducing oxidative stress and free radical induce diseases, cognitive impairment and Alzheimer's disease (van-Rooyen et al., 2008).

During food preparation, palm oil is subjected to either boiling or stir-frying processes otherwise known as hydrothermal processes. During the process of frying, the oil is repeatedly used and as a consequence of reheating of the oil, hence, a variety of chemical reactions occur which led to a spectrum of chemical changes. The oil undergoes various physical reactions such as formation of foam, increased viscosity, darkening of colour and deterioration of flavour. These changes may affect the organoleptic qualities such as

the odour and taste, and also the nutritional value of the fried foods (Xin-Fang et al., 2012). Also, processed oil undergoes three deleterious chemical reactions: such as hydrolysis caused by water, oxidation and thermal alteration caused by oxygen and heat (Aladedunye et al., 2017). Decomposition products are also formed as a result of reactions between food ingredients and oil affecting products' taste, flavour and shelf life (Dobarganes et al., 2000).

The presence of natural antioxidants such as  $\alpha$  - tocopherol, tocotrienol and  $\beta$ -carotene in palm oil could prevent lipid peroxidation by acting as peroxy radical scavengers that terminate the chain reactions. These antioxidants could have their concentrations affected by hydrothermal processing during food preparation; in fact, many scientific evidences have shown that these natural antioxidants are preferentially destroyed during frying (Dauqan et al, 2011)

Apart from home cooked fries, it is a common scene on the highway and street roads to see people hawking assorted fried foods like bean cake (akara), plantain chips, yam and potato chips, fried fish and meat, buns, doughnut etc. The oil employed in the preparation of these food items is often used repeatedly, and on many occasions, more oil is added to the cooking vessel when the level is going down in order to increase the volume and probably to maintain the colour of the oil so as not to affect the sensory properties of the food.

Few research reports exist on the chemical and nutritive value of fried foods, however not much was reported on lipophilic vitamins and quality of the oil especially during repeated usage. Therefore, the objectives of this study were to simulate hydrothermal processes in food preparation using palm oil and evaluate the effects of the process on the fatty acid, total tocopherol and carotenoids, as well as chemical composition of repeatedly used palm oil.

## 2. MATERIALS AND METHODS

### 2.1 Sample and sample preparation

Freshly processed palm oil sample was collected in a sterilized five litres plastic container from local Palm

oil processing plant and of ripe plantain was obtained from local market in Osu, Osun State, Nigeria.

### 2.2 Hydrothermal Treatment of Palm Oil

**No treatment:** The fresh palm oil sample was taken for analysis without thermal processing

**Stir – frying treatment:** The sample of oil (500 g) was poured into the stainless-steel frying pan and placed on hot plate and heated to 100 oC to mimic the frying process. When the temperature of both systems reached 100 oC, 5.0 g portions of the oil were withdrawn at intervals (0 to 100 min) while stir-frying continues

**Boiling Treatment:** The sample of oil (500 g) was poured into 1.0 L stainless steel saucepan and distilled water (10 ml) was added and then boiled to 100 oC. This mimics the traditional cooking process. 5.0 g portions of the oil were withdrawn at intervals (0 to 100 min) while the boiling continues.

#### Batch frying treatment:

**Frying oil without plantain:** The portion of oil sample (500 g) was placed in frying pan placed on an electric stove; the oil was heated for 10 min at 170 oC without plantain and 20 g of the oil was withdrawn for analysis.

**Batch Frying of plantain in palm oil:** Sliced plantain (400 g batch) was introduced into the hot oil maintained at 170 oC and fried within 5 min, fried plantain was removed and 5.0g oil was withdrawn from frying pan. The oil was allowed to cool to 100 oC and then heated to 170 oC, the frying of plantain was repeated until 12th batch frying, sample of oil were withdrawn at 4th, 8th and 12th batch frying.

The samples of oil withdrawn during the processes was added 1% butylated hydroxyanisole (BHA) and kept for further analysis.

### 2.3 Analytical procedures

#### Determination of Pro Vitamin A Carotenoids

Carotenoid content of the oil was determined by open column chromatography / visible absorption Spectrophotometric method of AOAC, method 970.64 (AOAC 2000). To the sample, 20 mL of cold acetone was added with constant shaking in a separating funnel

then 20 mL of petroleum ether (boiling point 60–68 °C) was added to extract the carotenoids in the acetone layer. The ether extract was collected, and the process was repeated until the acetone layer was devoid of colour. The ether extract was pooled together and washed with distilled water to remove excess acetone and dried over anhydrous sodium sulphate. The dried ether extract was concentrated in a rotary evaporator under vacuum at 30 °C, transferred in to 25 ml standard flask and made to the mark with petroleum ether (Pet ether). Ether extract (5.0 ml) was chromatographed on a magnesium oxide: Hyflo Supercel (1:2) column (15mm i.d x 15cm long). The following fractions were eluted from the column using 10 ml each of the eluting solvents:  $\alpha$  – carotene was eluted with 1.0 % acetone in Pet ether,  $\beta$  – carotene with 5.0 % acetone in pet ether and cryptoxanthin with 10 % acetone in pet ether. Each of the fractions collected above was placed in to 25 ml standard flask and diluted to volume with Pet ether. Absorbance of each fraction was scanned between 350 and 530 nm using Pye Unicam Spectrophotometer (Pye Unicam Ltd, UK).

The concentrations of the carotenoids were calculated using following extinction coefficient:  $\alpha$ –carotene (2640),  $\beta$ –carotene (2480) and cryptoxanthin (2460) as described by Klein and Perry (1982). The pro-vitamin carotenoids were converted to international unit (retinol equivalent) by taken 1.0 I.U. as equivalent to 0.6  $\mu\text{g}$   $\beta$ –carotene or 1.2  $\mu\text{g}$  of both  $\alpha$ –carotene and cryptoxanthin (NAS–NRC, 1980).

$$\text{Total carotenoid } (\mu\text{g} / \text{g}) = \frac{A_{\text{total}} \times \text{volume (ml)} \times 10}{E_{1\text{cm}}^{1\%} \times \text{sample weight}} \quad (1)$$

#### Determination of Tocopherol

The total tocopherol was determined using Colorimetric Method (AOAC, 2000) method 971.30. To 5.0 g of oil sample was added 20 mL ethanol and the mixture was placed in water bath at 85 °C for 30 min. Tocopherol was extracted from the mixture with 10 mL petroleum ether. The ether extract was kept for analysis. The standard curve was prepared by taking 5 – 50  $\mu\text{g}$  tocopherol through the procedure outlined for the sample. To the sample extract, the standard and the blank was added 1.00 mL of bathophenanthroline

solution, 0.5 mL FeCl<sub>3</sub> and 0.5 mL H<sub>3</sub>PO<sub>4</sub> and the absorbance measured at 534 nm. Total tocopherol content was extrapolated from the standard curve and I.U potency was calculated using conversion method that 10 I.U = 4.5 mg  $\alpha$ –tocopherol.

#### Chemical characteristic of the oil

The acid value, free fatty acid, peroxide value and thiobarbituric acid value were determined by AOAC (2000) while fatty acid profile was analyzed using Gas Chromatography (GC–FID).

#### Determination of Acid Value and Free Fatty Acid

The acid value and free fatty acid content were determined by AOAC, (2000) method 940.28. The oil sample (0.2 g) was dissolved in 10 mL ethanol and titrated with 0.1M NaOH solution using phenolphthalein indicator until pink colour disappeared. The acid value and the percentage fatty acid were calculated from the expression below:

$$\text{Acid Value} = \frac{56 \times \text{molarity of NaOH} \times \text{titre value}}{\text{weight of oil}} \quad (2)$$

$$\% \text{ Free Fatty Acid as Oleic acid} = 0.503 \times \text{Acid Value}$$

#### Determination of Peroxide Value (PV)

The oil sample (5.0 g) was weighed into a 250 mL conical flask, dissolved with 30 mL solvent mixture containing 12 mL chloroform and 18 mL glacial acetic acid. Saturated aqueous potassium iodide solution (0.5 mL) was added; the flask was stoppered and allowed to stand for one min. Thereafter, 30 mL of distilled water was added and the solution was titrated against 0.1 M sodium thiosulphate solution until the yellow colour had almost disappeared. At this point, starch solution (0.5 mL) was added and the titration continued until the blue–black colour disappeared. The same procedure was carried out for a ‘blank’ determination, where the oil sample was excluded. The peroxide value was calculated from the expression below:

$$\text{Peroxide value (meq/kg)} = \frac{M \times (S - B) \times 1000}{\text{Weight of oil (g)}} \quad (3)$$

where; meq/kg = milliequivalent peroxide/kg sample; S = Titre value (mL) of sodium thiosulphate for sample; B = Titre value (mL) of sodium thiosulphate for blank; and M = Molarity of sodium thiosulphate solution

#### Determination of thiobarbituric acid value

The heat-treated oil samples (200 mg) were weighed separately in triplicate into 25 mL standard

flask. Little butanol was added to dissolve the oil sample; the solution was then made up to the mark with butanol. The solution (2.5 mL) was then pipetted into a test tube with stopper. To the pipetted solution was added 2.5 mL of thiobarbituric acid reagent and the solution was mixed thoroughly. The test tube with its content was then placed in a boiling water bath for 2 h. After boiling, the solution was allowed to cool down and its absorbance taken along with blank (2.5 mL each of butanol and thiobarbituric acid mixed together and boiled for 2 h) at 530 nm using distilled water to zero the UV spectrophotometer.

The TBA value was calculated using the equation given below:

$$\text{TBA value} = \frac{50 \times (\Delta - B)}{m} \quad (4)$$

A= absorbance of the test solution; B= absorbance of the blank; and m = mass in mg of the sample.

#### Statistical Analysis

Statistical analysis was carried out by the use of Microsoft Excel Statistical Packages (Microsoft Corporations, USA) and Graph-Pad InStat -3 Packages (Graph Pad software Inc, USA). Analysis of variance was used to compared the values. The results were presented as mean and standard deviation. P-value < 0.05 was considered not significant.

### 3. RESULTS

#### 3.1 Stir-frying /boiling processes

The effects of hydrothermal processing on the carotenoid content of palm oil were presented in Figures 1 and 2. The stir - frying process (without addition of water) was found to cause a drastic reduction in the level of carotenoids within 2 min of frying. The percentage reduction (Figure 1) of  $\alpha$ -carotene,  $\beta$ -carotene and cryptoxanthin were 40, 80 and 89 %, respectively. The boiling process (with water) showed a lesser extent of carotenoids degradation compared to stir frying process.

The effect of the heat treatments (boiling and stir-frying) was monitored on the levels of  $\beta$ -carotene alone over a period of 100 min and the results were presented in Table 1. The observed drastic reduction of

$\beta$ -carotene within 2 min of heating at 100 oC was confirmed. The percent reduction of  $\beta$  -carotene was 25 % nder stir-frying process and 18 % in boiling process. This showed that  $\beta$  - carotene was more stable

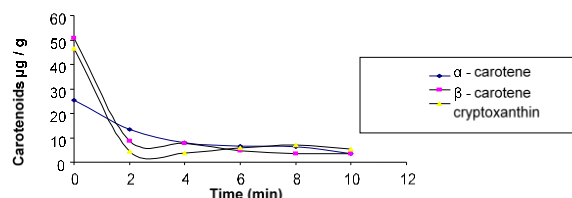


Figure 1 Effect of stir-frying the Carotenoids content of palm oil.

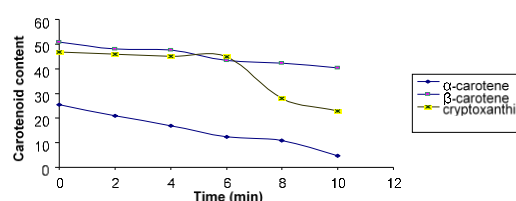


Figure 2 Effect of boiling on the Carotenoids content of palm oil

when palm oil was cooked with water as against its rapid degradation when palm oil fried. The vitamin activity measured as retinol equivalent is also more affected by heating of the oil in absence of water.

The effect of hydrothermal treatment on tocopherol (Table 1) showed the same trend of rapid deterioration as observed for carotenoids, the percentage reduction in the tocopherol content due to stir frying and boiling processes were 51 % and 36 %, respectively within 2 min of treatment. Heating caused reduction in the tocopherol content of the oil, this is seen from the fresh oil which has a value of 11.87 mg/g but decreased to 2.06 mg/g at 100 min for the stir-frying process, and from 12.36 mg/g to 2.66 mg/g at 100 min for the boiling process.

The thiobarbituric acid value and peroxide value which are measure of chemical deterioration of the oil were presented in Table 2. The TBA value increased from 9.49 to 18.94/kg for time zero and 100 min in the stir-frying process, whereas for the boiling process, the value increased from 2.23 to 7.54 TBA value/kg within 20 min of boiling and then decreased thereafter up to 60 mins, at the end of the heat processing, the TBA value was 5.04 TBA value /kg. The peroxide.

**Table 1** Variation of  $\beta$ -carotene of Palm oil due to hydrothermal processing

Time(min)	$\beta$ - Carotene ( $\mu\text{g/g}$ )		Retinol ( $\mu\text{g/g}$ )		Total tocopherol (mg/g)	
	Stir-fry <sup>1</sup>	Boiling <sup>1</sup>	Stir-fry <sup>2</sup>	Boiling <sup>2</sup>	Stir-fry <sup>3</sup>	Boiling <sup>3</sup>
0	60.4 $\pm$ 0.06 <sup>a</sup>	60.8 $\pm$ 0.12 <sup>a</sup>	100 $\pm$ 0.11 <sup>a</sup>	100 $\pm$ 0.05 <sup>a</sup>	11.87 $\pm$ 0.13 <sup>b</sup>	12.36 $\pm$ 0.15 <sup>a</sup>
0.5	55.3 $\pm$ 0.03 <sup>b</sup>	60.1 $\pm$ 0.13 <sup>a</sup>	92.1 $\pm$ 0.04 <sup>b</sup>	100 $\pm$ 0.2 <sup>a</sup>	6.97 $\pm$ 0.14 <sup>b</sup>	7.96 $\pm$ 0.08 <sup>a</sup>
1.0	52.8 $\pm$ 0.18 <sup>b</sup>	55.3 $\pm$ 0.05 <sup>a</sup>	88.2 $\pm$ 0.30 <sup>b</sup>	92.2 $\pm$ 0.08 <sup>a</sup>	6.40 $\pm$ 0.10 <sup>b</sup>	7.24 $\pm$ 0.02 <sup>a</sup>
1.5	50.6 $\pm$ 0.04 <sup>b</sup>	53.5 $\pm$ 0.13 <sup>a</sup>	84.4 $\pm$ 0.05 <sup>b</sup>	89.2 $\pm$ 0.2 <sup>a</sup>	5.84 $\pm$ 0.05 <sup>b</sup>	6.75 $\pm$ 0.04 <sup>a</sup>
2.0	45.4 $\pm$ 0.4 <sup>b</sup>	49.7 $\pm$ 0.07 <sup>a</sup>	75.7 $\pm$ 0.6 <sup>b</sup>	82.8 $\pm$ 0.1 <sup>a</sup>	5.38 $\pm$ 0.10 <sup>b</sup>	6.32 $\pm$ 0.15 <sup>a</sup>
20	44.2 $\pm$ 0.03 <sup>b</sup>	46.6 $\pm$ 0.20 <sup>a</sup>	73.6 $\pm$ 0.06 <sup>b</sup>	77.6 $\pm$ 0.3 <sup>a</sup>	4.98 $\pm$ 0.11 <sup>b</sup>	5.51 $\pm$ 0.16 <sup>a</sup>
40	40.8 $\pm$ 0.2 <sup>b</sup>	44.1 $\pm$ 0.07 <sup>a</sup>	68.1 $\pm$ 0.3 <sup>b</sup>	73.5 $\pm$ 0.1 <sup>a</sup>	4.36 $\pm$ 0.01 <sup>b</sup>	4.86 $\pm$ 0.06 <sup>a</sup>
60	37.4 $\pm$ 0.03 <sup>b</sup>	39.9 $\pm$ 0.05 <sup>b</sup>	62.4 $\pm$ 0.06 <sup>b</sup>	66.6 $\pm$ 0.08 <sup>a</sup>	3.51 $\pm$ 0.07 <sup>b</sup>	3.93 $\pm$ 0.07 <sup>a</sup>
80	35.1 $\pm$ 0.04 <sup>b</sup>	36.7 $\pm$ 0.2 <sup>a</sup>	58.5 $\pm$ 0.05 <sup>b</sup>	61.1 $\pm$ 0.3 <sup>a</sup>	3.04 $\pm$ 0.09 <sup>b</sup>	3.41 $\pm$ 0.19 <sup>a</sup>
100	32.4 $\pm$ 0.1 <sup>b</sup>	34.0 $\pm$ 0.05 <sup>a</sup>	53.9 $\pm$ 0.3 <sup>b</sup>	56.7 $\pm$ 0.08 <sup>a</sup>	2.06 $\pm$ 0.08 <sup>b</sup>	2.66 $\pm$ 0.16 <sup>a</sup>

Values are mean  $\pm$  SD of triplicate analysis.

1, 2, 3 values across the table with the same superscripts were not significantly different at  $P \leq 0.05$ .

**Table 2** Variation of Peroxide value and thiobabutaric acid value in hydrothermal processed palm oil

Time (mins)	Peroxide (meq /kg)		TBA g / kg	
	Stir-frying <sup>1</sup>	Boiling <sup>1</sup>	Stir frying <sup>2</sup>	Boiling <sup>2</sup>
0	6.8 $\pm$ 0.9 <sup>b</sup>	8.5 $\pm$ 0.00 <sup>a</sup>	9.5 $\pm$ 0.31 <sup>a</sup>	2.20 $\pm$ 0.7 <sup>b</sup>
0.5	13.5 $\pm$ 0.0 <sup>b</sup>	23.2 $\pm$ 2.8 <sup>a</sup>	10.9 $\pm$ 0.2 <sup>a</sup>	4.52 $\pm$ 0.3 <sup>b</sup>
1.0	16.8 $\pm$ 2.8 <sup>b</sup>	30.2 $\pm$ 2.8 <sup>a</sup>	11.7 $\pm$ 0.3 <sup>a</sup>	5.60 $\pm$ 0.4 <sup>b</sup>
1.5	23.5 $\pm$ 0.0 <sup>b</sup>	33.5 $\pm$ 0.0 <sup>a</sup>	12.3 $\pm$ 0.3 <sup>a</sup>	6.94 $\pm$ 0.4 <sup>b</sup>
2.0	28.5 $\pm$ 0.0 <sup>b</sup>	45.2 $\pm$ 2.8 <sup>a</sup>	12.8 $\pm$ 0.2 <sup>a</sup>	7.23 $\pm$ 0.4 <sup>b</sup>
20	40.2 $\pm$ 2.8 <sup>b</sup>	60.2 $\pm$ 2.8 <sup>a</sup>	13.6 $\pm$ 0.16 <sup>a</sup>	7.54 $\pm$ 0.9 <sup>b</sup>
40	51.8 $\pm$ 0.7 <sup>b</sup>	76.8 $\pm$ 2.8 <sup>a</sup>	14.3 $\pm$ 0.2 <sup>a</sup>	6.05 $\pm$ 0.7 <sup>b</sup>
60	65.2 $\pm$ 5.7 <sup>b</sup>	88.5 $\pm$ 0.0 <sup>a</sup>	16.9 $\pm$ 0.4 <sup>a</sup>	5.64 $\pm$ 0.7 <sup>b</sup>
80	78.5 $\pm$ 0.00 <sup>b</sup>	105.2 $\pm$ 2.8 <sup>a</sup>	18.2 $\pm$ 0.4 <sup>a</sup>	7.59 $\pm$ 0.8 <sup>b</sup>
100	95.2 $\pm$ 5.7 <sup>b</sup>	118.5 $\pm$ 0.0 <sup>a</sup>	18.9 $\pm$ 0.3 <sup>a</sup>	5.04 $\pm$ 0.2 <sup>b</sup>

Values are mean  $\pm$  SD of triplicate analysis.

1, 2 values across the table with the same superscripts were not significantly different at  $P \leq 0.05$ .

**Table 3** Variation of carotenoids, tocopherol, retinol activity and chemical parameters in batch fried oil

Processing Time	0 min	10 min	40 min	70 min	100 min	Heating without food
		Heating	(4 <sup>th</sup> batch)	(8 <sup>th</sup> batch)	(12 <sup>th</sup> batch)	
Acid value	1.85 $\pm$ 0.01 <sup>c</sup>	1.90 $\pm$ 0.01 <sup>c</sup>	2.16 $\pm$ 0.02 <sup>d</sup>	2.40 $\pm$ 0.01 <sup>c</sup>	2.82 $\pm$ 0.02 <sup>b</sup>	2.96 $\pm$ 0.02 <sup>a</sup>
Free fatty acid	0.93 $\pm$ 0.01 <sup>c</sup>	0.96 $\pm$ 0.01 <sup>c</sup>	1.1 $\pm$ 0.02 <sup>d</sup>	1.21 $\pm$ 0.02 <sup>c</sup>	1.42 $\pm$ 0.02 <sup>b</sup>	1.49 $\pm$ 0.02 <sup>a</sup>
PV (meq/kg)	9.48 $\pm$ 0.06 <sup>c</sup>	9.5 $\pm$ 0.02 <sup>c</sup>	11.8 $\pm$ 0.02 <sup>d</sup>	14.2 $\pm$ 0.07 <sup>c</sup>	33.2 $\pm$ 0.08 <sup>b</sup>	42.7 $\pm$ 0.06 <sup>a</sup>
Tocopherol (mg/g)	2.7 $\pm$ 0.0 <sup>a</sup>	2.5 $\pm$ 0.03 <sup>b</sup>	1.7 $\pm$ 0.01 <sup>c</sup>	1.6 $\pm$ 0.02 <sup>d</sup>	1.15 $\pm$ 0.08 <sup>c</sup>	0.9 $\pm$ 0.01 <sup>f</sup>
Carotenoid ( $\mu\text{g/g}$ )	6.6 $\pm$ 0.1 <sup>a</sup>	6.0 $\pm$ 0.1 <sup>b</sup>	5.5 $\pm$ 0.1 <sup>c</sup>	2.3 $\pm$ 0.09 <sup>d</sup>	1.8 $\pm$ 0.03 <sup>c</sup>	1.3 $\pm$ 0.07 <sup>f</sup>
RAE ( $\mu\text{g/g}$ )	11.0 $\pm$ 0.1 <sup>a</sup>	10.1 $\pm$ 0.2 <sup>b</sup>	9.3 $\pm$ 0.08 <sup>c</sup>	3.7 $\pm$ 0.02 <sup>d</sup>	3.05 $\pm$ 0.01 <sup>c</sup>	2.2 $\pm$ 0.04 <sup>f</sup>

value also increased from 6.83 to 95.17 meq /kg and 8.5 to 118 meq / kg in stir-frying and boiling processes, respectively, boiling process recorded significantly higher value.

### 3.2 Effect of batch frying

As observed for stir-fried and boiled oil, batch frying impact negatively on the content of both tocopherol and carotenoids. From Table 3, the tocopherol content of palm oil was 2.72 mg/g, batch frying (12th cycle) decreased the content to 1.15 mg/g (42 % loss). Also,

carotenoid decreased from 6.62 to 1.83  $\mu\text{g/g}$  (72.4 % loss) after 12th cycle. Acid value, free fatty acid and peroxide value increased from 1.85 to 2.82 mg KOH/g (152 %), 0.93 to 1.42 (132 %) and 9.48 to 33.21 meq / kg (350 %), respectively, after 12th cycle of batch frying, Fatty acid profile (Table 4), the percentage saturated fatty acid (SFA), mono unsaturated fatty acid (MUFA) and poly unsaturated fatty acid (PUFA) were 16.36 %, 27.35 %, and 52.82 % , respectively in fresh oil, trans fatty acids

(TFA), respectively in fresh oil, trans fatty acids (TFA) were absent. Of the total saturated fatty acids, linoleic acid accounted for 10.64 % whereas linolenic acid (48.48 %) was the most abundant PUFA. Heating of oil within 10 min caused formation of linoeladic acid (C18:2 trans) (0.14 %), though the level decreased when plantain is fried in the oil.

#### 4. DISCUSSION

Hydrothermal treatments of vegetable oils have been reported to adversely affect the chemical compositions as well as the nutritive values of the food. The content of carotenoid (a precursor of vitamin A) was found to be markedly reduced by heat treatments; similar trend of destruction was reported for lycopene when tomato is subjected to heat treatment (Norizzah, et al., 2014). Carotenoids due to its high conjugated double bonds, are prone to oxidation and geometric isomerization when exposed to heat and oxygen (Cervantes-Paz, et al., 2014; Flores et al., 2021). The polyene chain is the cause of instability of carotenoids including their susceptibility to oxidation and geometric isomerization. Heat, light and acids promote isomerization of trans-carotenoids to the cis-form (Amorim-Carrilho et al., 2014).

Apart from the effect of conjugation of bonds in carotenoids, lipids are well known to be susceptible to oxidation reaction and as a result, natural antioxidant such as  $\beta$ -carotene will deteriorate in the process of defending palm oil. Sun et al., (2002) reported decrease in the lipid oxidation with increase in water activity and (Tannenbaum et al., 1985) observed that the stability of carotenoids was parallel to that of unsaturated fatty acids in a given food. The degradation of  $\beta$ -carotene is of high health concern due to their dual purpose of protecting human systems against oxidative stress related diseases (Cilla et al., 2012), and useful pro-vitamin A activity (Harrison, 2012). When the  $\beta$ -carotene was converted in to retinol equivalent, stir-fried / boiled palm oil showed a progressive reduction in retinol content with time, an indication that methods

employed in food processing could significantly affect the content of vitamin A content of plant foods

Vitamin A is necessary for normal vision, chronic shortage of dietary vitamin A results in vitamin A deficiency disease (VAD), the most specific clinical effect of which is xerophthalmia and its various stages, including night blindness. Though recent health policies have mandated the compulsory fortification of vegetable oils with vitamin A.

Vitamin E is a strong antioxidant. All its isomers (tocopherol and tocotrienols) possess good antioxidant properties in vitro with tocotrienols being more potent (Falade et al., 2017). The observed loss of total tocopherol due to hydrothermal treatment of oil is in agreement with the study of Holownia et al., (2001). It has been observed that the decrease in total tocopherol may not necessarily be as a result of degradation but could result from it being used up while acting as antioxidant in protecting the oil (Puah et al, 2007). However, preferential oxidation of tocopherol has a protective (antioxidant) effect which is particularly important, since the majority of the frying oils are of vegetable origin, showing great amount of unsaturated, rapidly oxidized fats. This essential lipophilic nutrient is well known for its role as a chain-breaking antioxidant during lipid peroxidation, it protects polyunsaturated fatty acids from oxidation (Vollhardt and Schore, 2004) and are capable of inhibiting cholesterol synthesis (Odia et al 2015).

The level of oxidative deterioration of the oil monitored by the use of peroxide value (PV) and thiobarbituric acid (TBA) value (Table 2) indicated that both values increased but was more pronounced in stir frying than in boiling. The only explanation for this is that water could have prevented contact between oxygen and the oil sample there by reducing the extent of lipid oxidation, hence lower level of oxidative products like malondialdehyde. Vitrac et al., (2000) had earlier observed that steam acted as blanket over oil and prevented oxygen – oil contact. The added water could also play a role as a physical agent for “steaming out” the volatile oxidative products such as malondialdehyde from the oil and enhancing their

**Table 4** Effect of frying on Fatty acid profile of vegetable oil (as % of the total fatty acids)

FATTY ACID	Fresh oil	Frying Point	4 <sup>TH</sup> batch	8 <sup>TH</sup> batch	12 <sup>TH</sup> batch
		10mins	40min	70min	100min
Saturated fatty acid					
C8:0	ND	ND	0.03	0.03	0.05
C12:0	0.18	0.16	0.20	0.20	0.19
C14:0	0.16	0.18	0.20	0.20	0.16
C15:0	ND	0.01	ND	ND	ND
C16:0	10.64	10.50	10.83	10.83	11.03
C17:0	0.06	0.08	0.12	0.12	0.09
C18:0	4.07	4.02	4.10	4.10	4.18
C20:0	0.47	0.46	0.45	0.45	0.49
C22:0	0.53	0.55	0.55	0.55	0.54
C24:0	0.25	0.29	0.23	0.23	0.28
Total SFA	16.36	16.24	16.8	16.8	17.01
Mono-unsaturated fatty acids					
C16:1, cis	0.11	0.10	0.12	0.12	0.11
C17:1, cis	0.02	0.09	0.11	0.11	0.10
C18:1, cis	27.50	27.31	27.27	27.27	27.87
C20:1, cis	0.32	0.33	0.31	0.31	0.32
Total MUFA	27.95	27.83	16.81	16.81	17.01
Poly-unsaturated fatty acids					
C18:2, cis	48.48	48.55	48.11	48.11	45.47
C18:3, cis	4.15	4.85	5.03	5.03	4.87
C20:2, cis	0.19	0.19	0.19	0.19	0.20
Total cis PUFA	52.82	53.59	53.33	53.33	50.54
C18:2, trans	ND	0.14	0.05	0.05	0.10
P/S ratio	0.31	0.30	0.31	0.31	0.32

SFA: saturated fattyacids, MUFA: monosaturated fatty acids; PUFA: Polyunsaturated fatty acids, P/S: ratio of polyunsaturated to saturated fatty acid

evaporation thereby making it unavailable for reaction with TBA. Also, the intermittent heating and cooling of oils have been reported to cause higher deterioration of oils than continuous heating due to increase in oxygen solubility in the oil when the oil cools down after frying (Chaves et al., 2012). Peroxide value (PV) increases with frying time, the PV values markedly increased beyond 8th frying batch (33.21 meq / Kg), which indicated that substantial lipid oxidation had occurred at this point. Suleiman et al., (2006) reported increase in the peroxide value of cottonseed oil, sunflower oil and palm olein heated at 180°C for 8 h. It is well known that peroxide value is useful as an indicator of oxidation at the initial stages. However, during frying the changes in PV were not related to duration of frying but were dependent on rate of formation and breakdown of oxidation products. Another problem is that the peroxides may increase after the sample is taken from the fryer before analysis. Butylated hydroxyl anisole (BHA) an antioxidant was added to the oil immediately

after sampling. Siddique et al., (2010) mentioned that a good quality vegetable oil should have a peroxide value of lower than 2.0 meq / kg, though oil with peroxide value less than 10 meq/kg is still regarded as fresh oil whereas values between 20 and 40 meq/kg result to rancid taste and offensive odour. The result of acid value and free fatty acids indicated that the fresh palm oil has an acid value (1.85 mg KOH/g) which is within the value proposed for fresh vegetable oils (Dorbaganes and Marquiz-Ruiz, 2015). There was a significant increase (2.82 mg KOH / g) at 12th batch frying, this indicated that as the frying time is increased so also the acid value. This increase can be expected due to increased rate of hydrolysis since water is introduced into the frying system by the raw plantain. However, the increase though noticeable still falls within the range of healthy edible oil, thus indicating a substantial resistance to hydrolysis and other chemical mechanisms which breakdown glycerides during frying. The acid value and % free fatty acids provide

information on the status of the vegetable oils, as they show the extent of hydrolysis of triglyceride chains (FAO/WHO, 1998). Acid value and % free fatty acids are useful as chemical indicators for edibility of oil.

Fatty acid profiles (Table 4) indicated a progressive decrease in the content of unsaturated fatty acids and formation of trans fatty acids. For instance, the content of linolenic acid (C18:2) progressively decreased from 48.48 % to 45.47 % (6.28 %) at 12th batch frying, at this point percentage reduction of PUFA was 4.32 % whereas SFA was increased by 4.0 % with increase of 4.95 and 2.70 % in both stearic and palmitic, respectively. However, there could be migration and exchange of fatty acid between the oil and foods during frying.

Formation of volatile compounds such as aldehydes, ketones, dienes and acids during degradation of oils induced by heating has been a major concern. Thermally oxidized oil does not only create unpleasant flavor it may also cause health challenges. Several articles have established that thermoxidized oil produce adverse effect such as mild enlargement of liver, spleen and adrenals, induce oxidative stress and impaired digestibility (Dorbarganes and Marquiz-Ruiz, 2015). Since frying oil is absorbed by food, the findings of this study would help us to recognize the point at which the repeatedly frying oil should be discarded to maintain optimum product quality and health of the consumers because the quality of food products is directly correlated to the quality of the frying medium (Wiege, et al., 2020).

## 5. CONCLUSION

The findings of this study revealed among other things that palm oil though rich in polyunsaturated fatty acids (PUFAs), carotenoids and total tocopherol, however, hydrothermal processing could lead to destruction of these fat-soluble vitamins and formation of deleterious compounds that could expose consumers to risk of cardiovascular, chronic respiratory, neural and degenerative diseases and certain cancer. Therefore, to enhance adequate intake of the lipophilic vitamins and

essential fatty acids from palm oil, thermal treatment of oil should be monitored.

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## CONFLICT OF INTEREST

There is no conflict of interest

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