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EFFECT OF SHORT TIME REPEATED HEATING ON THE PHYSICOCHEMICAL CHARACTERISTICS AND FATTY ACID PROFILE OF PALM OIL

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Abstract

Palm oil is a commonly consumed vegetable oil either in fresh or thermo-oxidised form. This study investigated the effect of repeated short time heating on the physicochemical parameters of thermo-oxidized palm oil compared to a fresh palm oil. Fresh and thermoxidised palm oil were prepared and subjected to some physicochemical and Gas chromatography profiles using standard methods. Results showed the presence of 5-Hydroxymethylfurfural, 9,12-Octadecadienoic acid and uracil in the thermo-oxidized palm oil. The fresh palm oil indicated increased linoleic and oleic acid relative to myristic and palmitic acid. The acid value, peroxide values, and saponification value were significantly ($p < 0.05$) increased while the alpha-tocopherol, beta carotene and total carotenoid indicated significant decreases in the thermo-oxidized palm oil compared to the fresh palm oil. We therefore conclude that repeated heating of palm oil for a short duration is inappropriate due to reduction in the β-carotene content.

Keywords: Palm oil, β-carotene. thermo-oxidation.

1.0 Introduction

Palm oil is gotten from palm fruit's mesocarp [1]. It is the most commonly used cooking oil in Nigeria its colour ranges from yellowish-red to brownish or orange-red. The palm fruit, a crop from tropical tree, takes approximately five to six months to mature after pollination and is primarily cultivated for vegetable oil production [2]. Red palm oil contains about 500 ppm carotene, with 90% of it being α- and β-carotene. The oil has approximately 800 ppm of vitamin E, and 70% are in the form of tocotrienols (mainly as α-, β-, and δ-tocotrienols). The oil also contains other valuable minor components such as ubiquinones and phytosterols [3]. The refining process partially reduces the vitamin A and E composition in palm oil. Studies show that refined palm oil retains only about 70% of the vitamin E present in crude palm oil, while almost all of the vitamin A is lost during refining [4].

Palm oil is either eaten fresh or at different thermal oxidation stages. The overall benefit of palm oil is linked to fresh palm oil over thermally oxidised palm oil. Thermal oxidation takes place once the fresh palm oil is exposed to heat at increased temperatures and at various time interludes. Thermal oxidation is practiced in most homes to increase its deliciousness [5]. However, intake of thermally oxidised oil has been said to bring about the creation of peroxides, and other reactive and cytotoxic products. The free radicals and dihydroxy esters derived from reaction with oxygen contained in thermally oxidised palm oil have been proven to bring about cell injury [6,7]. Moreover, the generated free radical species which are more reactive are described to cause arthritis, atherosclerosis, diabetes, cancer and synthesis of cataract. The intake of oxidised fats and oils in a long-term basis has been stated to lead to thrombosis, growth retardation, lack of essential fatty acid, anaemia, fatty liver and deactivation of nucleic acid of vital metabolic enzymes [8, 7]. Repeated heating of oil decreases the percentage of unsaturated fatty acids, enhances foaming, and changes properties like colour, density, viscosity, and specific heat. It also raises the levels of polymeric compounds, free fatty acids, and polar materials. The characteristics of cooking oil after frying depend on various factors, including frying temperature and duration, type and number of times of reheating, initial oil quality, type of fryer, food composition, and the presence of antioxidants [9].

This study compared the effect of short time repeatedly heated palm oil to fresh palm oil sample on its physical and chemical properties.

2.0 Materials and methods

2.1 Sample collection and preparation

Palm oil fruits were gotten from Marian market, a local market in Cross River State, Nigeria. The palm fruits were processed to produce palm oil using the methods of [10]. A portion of the processed fresh palm oil was not subjected to thermoxidation while the remaining 1.5 litres of the freshly prepared palm oil was heated using an electric hot pate at 160^{o}C in a stainless-steel frying pan at five minutes for five times. The oil was left to cool for two hours at each interval to obtain a thermoxidised palm oil. The two palm oil samples were stored in airtight amber bottles at room temperature before carrying out the physicochemical and the GC-MS analyses.

2.2 Determination of the fatty acid profile of the palm oils using GC-MS

Fatty acid methyl ester was obtained and the methylated oil was mixed with pure hexane and injected into a GC-MS gas chromatographic system (Mass Hunter 5977, Agilent technologies) according to the method used by [11].

2.3 Determination of the physicochemical properties

Determination of peroxide value

Pearson's method was utilized from [12]. The peroxide value was determined using:

$$\mathrm{P.V} = \frac{T \times M}{g} \times 10$$

Where P.V=Peroxide Value,

g = Weight of oil sample used,

M=Molarity of sodium thiosulphate solution,

T=Titre value of sodium thiosulphate solution,

2.4 Determination of acid value

The method reported by [13] was adopted.

The acid value was derived from the equation.

$$\text{Acid Value} = \frac{56.1 \times C \times V}{W}$$

Where, C=Concentration of KOH,
56.1=Molar mass of KOH,
V=Volume of KOH,
W= Weight of oil (cm3).

2.5 Determination of saponification value

Pearson's method was used as reported by [13]. Saponification value was determined using:

$$S.V = \frac{(b-a)\times 28.05}{g}$$

Where S.V=Saponification value,
a=Titre value of the sample,
b=Titre value of blank,
28.05=Constant,
g=Weight of oil sample

2.6 Vitamin A determination

The vitamin A levels were measured using the methods described by [14]

2.7 Determination of concentration of β-carotene

The samples carotenes constituent was evaluated by Ultraviolet-Visible (UV-vis) spectrophotometer after sample treatment with n- hexane and bringing the volume up to the 25ml mark in the volumetric flask. The absorbance was then read at 446nm using a UV-VIS Spectrophotometer.

2.8 Determination of lycopene content

Lycopene standard was used and the different solutions of lycopene in n-hexane were subjected to absorbance readings in a spectrophotometer at 503 nm.

2.9 Determination of Alpha-Tocopherols

This was carried out following the method described by [2].

3.0 Statistical Analysis

The obtained data was analysed using a one-way ANOVA and differences between pairs of groups using post hoc multiple comparisons. Results were presented as the mean ± standard error of the mean (SEM). Data were taken to be substantial at $p < 0.05$. Statistical package SPSS version 17.0 and MS excel (2010 version) were utilised for analyses.

4.0 Results and discussion

The effect of short term heating at 160^{O}C at 5 minutes for five times on the fatty acid content of the thermoxidised palm oil was investigated and the results are presented in Table 1. The Gas chromatography (GC) profile of fatty acids identified in the thermoxidised palm oil indicated high content of 5-Hydroxymethylfurfural (43.37%), followed by 9,12-Octadecadienoic acid, methyl ester (21.80%) and uracil (13.16%). Other compounds (1, 2-Cyclopentanedione, Hexadecanoic acid, methyl ester, 3,4-Difluoroanisole, 2H-pyran-2,6(3H)-,3-dione, 4H-Pyran-4-one and 2-Thiazolamine) were found in trace amounts.

Table 1: Gas Chromatography profile of Thermoxidised Palm Oil (TPO) sample

S/N	Name/Library Identity	Type of fatty acid	Composition (%)	Retention time
1.	1,2-Cyclopentanedione	saturated	1.857	6.282
2.	Hexadecanoic acid, methyl ester	saturated	5. 665	7.032
3.	3,4-Difluoroanisole		5. 231	8.302
4.	2H-pyran-2, 6(3H)-,3-dione		4.959	9.172
5.	2-Thiazolamine, 4,5-dihydro- Butanoic acid		1.612	11.298
6.	Uracil,1-methyl-4,5-Diamino-2-hydroxypyrimidine		13.160	13.413
7.	9,12-Octadecadienoic acid, methyl ester	PUFA	21.798	15.070
8.	4H-Pyran-4-one		2.349	16.659
9.	5-Hydroxymethylfurfural	Saturated	43.369	18.523

Results of the Gas chromatography (GC) profile of fatty acids identified in the fresh palm oil (FPO) sample are presented in Table 2. The profiles indicated 9,12-Octadecadienoic acid (Linoleic acid) (40.88%) as the major compound identified, this was followed by 9-Octadecenoic acid (Oleic acid) (17.277%), Tetradecanoic acid (16.227%) then, Cyclopropaneoctanal (8.573%) and Hexadecanoic acid (Palmitic acid) (8.26%), other fatty acids such as (Hexadecanedioic acid, Octadecanedioic acid, Tetradecanedioic acid and Squalene) were present in trace amount.

Table 2: Gas chromatography profile of fresh Palm Oil sample

S/N	Name/Library Identity	Type of fatty acid	Common name	Composition (%)	Retention time
1.	Tetradecanoic acid	Saturated	Myristic acid	16.227	37.464
2.	Hexadecanoic acid	Saturated	Palmitic acid	8. 573	37.571
3.	9,12-Octadecadienoic acid	PUFA	Linoleic acid	40.876	38.647
4.	9-Octadecenoic acid	MUFA	Oleic acid	17.277	38.828
5.	Tetradecanedioic acid	Saturated		1.387	39.128
6.	Hexadecanedioic acid	Saturated		2.960	39.347
7.	Cyclopropaneoctanal	Saturated		8. 256	40.260
8.	Octadecanedioic acid	Saturated		3.204	40.492
9.	Squalene	Unsaturated	squalene	1.342	43.22
Saturated fatty acid (SFA) (%)				41.949	
Monounsaturated fatty acid (MUFA) (%)				17.277	
Polyunsaturated fatty acid (PUFA) (%)				40.876	

The fresh palm oil sample quality before and after thermoxidation were evaluated by analysing the physicochemical characteristics such as peroxide value, acid value, saponification value, and nutrients such as vitamin A, Beta carotene and lycopene. The findings are shown in Table 3.

Table 3: The oil quality and vitamin a parameter

Parameters /Samples	TPO	FPO	$P < 0.05$
Acid value (mg KOH/g)	2.141 ± 0.62	1.756 ± 0.68	Significant
Saponification value MgKOH/g	40.115 ± 0.11	30.439 ± 0.58	Significant
Peroxide value (m.eq of peroxide/100g)	13.955 ± 0.12	9.624 ± 0.00	Significant
Beta carotene (mg/100g)	1.68 ± 0.01	1.79± 0.01	Significant
Lycopene(iu/100g)	0.920 ± 0.00	0.993 ± 0.00	Not Significant
Vitamin A (iu/100g)	84.441 ± 2.99	89.287 ± 3.40	Significant

TPO = thermoxidised palm oil, FPO = Fresh palm oil

The effect of the heating process on the composition of vitamin E (α-Tocopherol) in the palm oil samples (thermoxidised palm oil) and fresh palm oil are presented in Table 4.

Table 4 showed the concentration of vitamin E (α-tocopherol) in all palm oil samples analyzed which varied from 52.98 to 129.94 iu/100g. It was observed that the concentration of vitamin E (α-Tocopherol) were greater in FPO matched to TPO.

Table 4: Vitamin E Content of Fresh and Thermoxidised Palm Oil Sample

Palm oil sample	Peak ID	Retention time	Concentration (iu/100g)
TPO	α- Tocopherol	13.132	52.9784
FPO	α- Tocopherol	6.282	129.94 1

The extent and duration of thermal treatment differ from one home to another, both before and during food preparation [15]. The fresh oil had higher unsaturated fatty acid content while the repeatedly heated palm oil had the higher saturated fatty acids. Though numerous researches have described the fatty acid constituent of palm oil, to possess equal or nearly equal percentage (%) of saturated to unsaturated fatty acids [16, 17, 18} Repeated heating of the fresh palm oil decreased the value of unsaturated fatty acids compared to the saturated fatty acids with 9,12-Octadecadienoic acid, methyl ester (21.8%) being the only unsaturated fat present and the saturated fatty acids content increased in the repeatedly heated palm oil.

A significant ($p \leq 0.05$) increase in the acid value was observed in the thermoxidized palm oil sample relative to the fresh palm oil. Acid value (AV) is an indication of the degree of the triacylglycerols conversion into free fatty acids within the oil by the action of lipase and other environmental factors such as heat and light [11]. The acid values data obtained were lower than the recommended value set by *Codex Alimentarius* Commission (4mgKOHg-1) for refined oils meant for consumption by human [19, 20], and lower than the SON [20] suggested maximum acid value of 3.5 mg KOH/g.

However, this finding is not in agreement with a previous report of [15] where, no significant change was found in the acid values of thermoxidised palm oil at 0, 5, 10 minute and 20-minute time of thermal treatment. This discrepancy detected could be because of the variation in the saturation level of the various oils examined [6].

The saponification value can be used to evaluate the degree of hydrolysis in oil [24]. The saponification value of the oil assesses its oxidation throughout storage and serves as an indicator of oil degradation. A higher saponification value suggests the existence of fatty acids with more carbon atoms. The saponification values gotten in this study are lower than the suggested range for palm oil [21, 26]. The reduced saponification value is an indication that, the oil might be unsuitable for soap production [22]. These values indicate that the oils are not suitable for soap making [22] except for human consumption.

Peroxide levels are a valuable indicator of the extent of oxidation that the oil has experienced [29]. The fresh palm oil is below the SON [20] and NIS standard [21]. Low peroxide values show that the oil sample is stable [11]; but the thermoxidised palm oil values in this research exceeded the recommended value/specified standard.

Vitamin E is a good antioxidant which prevents the oxidation of unsaturated fatty acids in vegetable oil [30]. In this study, the fresh palm oil had higher α-tocopherol value relative to report of [20]. In this study, the application of heat on the palm oil brought about a substantial reduction in the constituent of α-tocopherol in the thermoxidised palm oil. Sathianathan *et al.* [32] reported that the vitamin E antioxidant is totally depleted at an increased temperature.

The carotenoids in crude palm oil are responsible for the orange-red colour characteristic. They also prevent oxidation by being oxidised first, before the triacylglycerols [31]. The carotenoids level in palm oil is affected by numerous factors, like, processing method, hybrid palms or variety and species [17]. The results obtained for carotene level for the fresh sample was within the SON/NIS recommended range, indicating the freshness of the palm oil samples. Palm oil contains high levels of vitamin A, derived from carotene [2]. The outcomes revealed that the β-carotene and vitamin A profile of the palm oil sample was affected by heating .Thermoxidation could be attributed to thermal deterioration as a result of heating and oxidation of the carotenoid constituents [6]. This observation is consistent with the trend of how the total carotenoid and total β-carotene content of palm oil as affected by varying heating durations and temperatures [15]. This study supports the evidence of Falade *et al.,* [33] that cooking of palm oil for extended periods during food preparation may not be advisable, as it could lead to significant loss of its β-carotene content. This study proposes that thermal oxidation leads to loss of carotenoid in palm oil. The heating process led to substantial alterations in the physical and chemical characteristics, carotenoid contents of palm oil, thus decreasing its health benefit and nutritive values. The lycopene in this present study was 0.993 ± 0.00 iu/100g which was insignificant to the themoxidised palm oil value.

5.0 Conclusion

We therefore conclude that short term duration in heating palm oil affects the fatty acid constituent, the carotenoid content as well as the physico-chemical characteristics of palm oil, thus modifying its nutritive qualities. Therefore, repeated heating of palm oil for even a short duration is inappropriate due to significant reduction in β-carotene content.

Conflict of interest

We have no conflict of interest to declare.

Authors contributions

JEE, MAA, SOB conceived and designed the study, JEE carried out the study and wrote the initial manuscript, OO carried out literature search while CIOU analyzed the data. All authors have read and approve the final draft of the manuscript for submission

Authors declaration:
The authors hereby declare that the research work is original and future request for data can be made to corresponding author.

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