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CHEMICAL CHANGES ASSOCIATED WITH REPETITIVE RE-USE OF VEGETABLE OIL DURING DEEP FRYING OF BEAN CAKE, PLANTAIN AND YAM

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ABSTRACT

Article History

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Keywords Oil re-use Chemical changes Palm oil Vegetable oil Frying Free fatty acid. Oil re-use is a common practice in households. Oxidative and hydrolytic reactions have been reported to cause significant changes in oil quality. This study was carried out to determine the chemical changes specific to beans cake (Vigna unguiculata), Plantain (Musa paradisiaca) and yellow yam (Discorea cayenensis) frying with repetitive re-use of oil. Refined vegetable and palm oil were used for five consecutive frying operations for bean cake, plantain and yam. Free fatty acids, iodine value, peroxide value and saponification value of the first, third and fifth frying operations were determined using standard methods. For refined vegetable oil, the FFA range for repeated frying operations obtained for bean cake, plantain and yam were 0.31-0.53, 0.37-0.52 and 0.40 to 0.53 % oleic respectively. While palm oil re-use had a range of 11.87 to 14.97 in the value of their FFA. Peroxide value (3.24- 4.92 meq/kg), Iodine value (91.09-107.00 mg/100g) and Saponification value (125.00-152.66 mgKOH/g) were obtained for reuse refined vegetable oil while Peroxide value (27.95-77.02 meq/kg), Iodine value (131.68-210.89 g/100g) and Saponification value (179.45-197.50 mgKOH/g) were obtained for re-use palm oil. Generally, frying operation led to increase in the FFA of refined vegetable oil. Frying operation for peroxide value significantly varied for all frying operation for plantain. Significant difference existed in iodine value at p < 0.05among frying operations for bean cake and yam. Changes in chemical properties of oil were affected by frying duration and food material fried.

Contribution/Originality: The present study reported variations in the chemical properties of vegetable oil as affected by the type of food material (bean cake, plantain and yam) during repeated frying operation. Extent of changes caused by hydrolytic and oxidative reactions is dependent on the food material used for deep frying operation. This work also was able to ascertain that acceptable oil re-use depended on the frying duration and food material.

1. INTRODUCTION

Vegetable oils are a major part of human diet considering its energy, fat soluble vitamins and essential fatty acid contribution. Aside the nutritional, physical and chemical properties, high quality vegetable oil are determined by its ability to withstand high temperature while still retaining its high quality. In the food industry, vegetable oil found one of its uses in its ability to serve as a processing medium. Deep frying of food involves the use of high temperature which alters oil properties (Debnath *et al.*, 2012).

Frying operation in food processing is known to be intense due to high temperature of processing which induces chemical reactions in the frying medium (Weisshaar, 2014; Park and Kim, 2016). These chemical reactions

may lead to the formation of different chemical compounds that could affect oil quality as well as determining the safety of consumption (Debnath *et al.*, 2009). The extent of changes and formation of these compounds depends on factors such as duration of exposure, temperature, condition of storage and the initial quality of the oil (Aladedunye and Przybylski, 2009; Kalogianni *et al.*, 2010). Food stability and frying efficiency is dependent on quality of the oil at the end of the frying operation (Ghidurus *et al.*, 2010). This in turn determines the general acceptability of the food product.

In industrial practices and for economic reasons, it is sometimes inevitable to encounter food products that are produced from re-used or recycled oil (Park and Kim, 2016). Traditionally, it is common to re-use oil for about 3-6 times before being discarded as waste.

In some cases, vegetable oil is re-used until there is no visible presence of oil or not enough for the frying operation. This makes the consumption of foods subjected to recycled oil a common feature. According to Choe and Min (2007) repeated heating of oil initiates a series of reactions which modifies its constituent. Aladedunye and Przybylski (2009) noted the complexity of these reactions and reported that repeated re-use of oil may result in loss of both quality and nutritional value of the vegetable oil. However, changes in re-use oil could be both chemical and physical in nature.

Chemical changes associated with commercially available vegetable oils in Nigeria during recycling for specific products require study. This is important so as to ascertain suitability of their consumption. Considering the fact that deep fried bean cake, plantain and yam constitutes major food materials consumed by Nigerians. Therefore, this research work is to study the chemical changes associated with vegetable oil re-use during deep frying of bean cake, plantain and yam.

2. MATERIALS AND METHODS

2.1. Materials

Commercially available refined vegetable oil with the brand name Moi Oil was purchases at Sango market, Saki, Oyo State, Nigeria. Plantain (*Musa paradisiaca*), yellow yam (*Discorea cayenensis*), cowpea (*Vigna unguiculata*), salt and dried pepper were also purchased at the same market.

2.2. Preparation of Fried samples

2.2.1. Preparation of Fried plantain

Ripe plantains were used for frying. Washing, sorting, peeling and dicing were done to prepare the plantain for deep frying. 200 g of diced plantain was weighed in triplicate and fried separately using palm oil and commercially refined vegetable oil.

Frying was done for 9 minutes for the plantain to be cooked and be of acceptable appearance expected for fried product. The frying operation was repeated 5 times and oil samples taken after each frying operation were refrigerated for subsequent analysis.

2.2.2. Preparation of Fried Yam

Yam was sorted, cleaned, peeled and diced. 200 g of Yam was used for each frying operation. The frying operation took approximately 17 minutes before the yam could be cooked and possess acceptable appearance. Two litres of oil (Palm oil and refined vegetable oil) was used for each frying operation. Frying operation was repeated 5 times with the same oil samples previously used.

2.2.3. Preparation of Beans Cake from Cowpea Flour

200g of cowpea flour was used alongside with ingredients such as salt and onion to taste. 250 ml of water was used for mixing. Two litres each of palm and refined vegetable oil were used for repeated frying operation for 5 times. The frying duration for each batch took about 5 min to be cooked and have acceptable appearance.

2.3. Determination of Chemical Properties of Oil

Acid value, Free fatty acid (FFA), Iodine value, saponification value and peroxide value were properties used to determine variation in chemical properties of oil due to re-use.

2.3.1. Determination of Acid Value and Free Fatty Acid

AOAC method 940.28 (AOAC, 2000) was used for the determination of free fatty acid. Briefly, 2ml of 1 % phenolphthalein solution was added to 20ml of a mixture of 1: 1 v/v ethanol and diethyl ether which was carefully neutralised with 0.1N NaOH. 1 g oil sample was added to the mixture and then titrated against 0.1 N NaOH solution. Titre value was taken when persistent pink colour end point was reached. The titre value was used to calculate the acid value and the free fatty acid.

2.3.2. Determination of Peroxide Value

20ml of 2:1 v/v of glacial acetic acid and chloroform together with 1 g of KI were added to 1 g of oil sample. The mixture was boiled for 60 seconds. The hot mixture was added to 20 ml of 5% KIO₃ solution after which starch solution was added in drop. The mixture was then titrated against 0.025 M $Na_2S_2O_3$ solution. The titre value was used to calculate the peroxide value.

2.3.3. Determination of Saponification Value

A mixture of 30 ml ethanolic KOH and 2g of oil samples were condensed for 30minutes to ensure that the oil sample was fully dissolve. When cool, 1ml phenolphthalein was added as an indicator before being titrated against 0.5N HCl to a pink end point. A blank test was also done. Equation 1 was used to calculate the saponification value.

$$Saponification \, value = \frac{56.1 \, N \, (V_o - V_1)}{M} \qquad equation \, 1$$

Where

$V_o = Volume of 0.5N HCl solution used for blank test V_1$

= Volume of 0.5N HCl solution used for oil samples

N = Normality of HCl used.

M= Mass of oil sample.

2.3.4. Determination of Iodine Value

20ml of Carbon tetrachloride was used to dissolve 0.4 g of oil sample. 25 ml of Dam's reagent was added to the solution in a fume chamber using a safety pipette. The mixture was shaking vigorously and placed in the dark for 2 hours 30minute. 20ml of 10% aqeous KI and 125ml of water was added. The eventual solution was then titrated against 0.1 N sodium thiosulphate solution until the yellow colour almost disappeared. 2 drops of 1 % starch indicator was added before continuing the titration drop-wise while shaking vigorously until blue coloration disappears. A blank test was also done following the same procedure. Iodine value was calculated as shown in Equation 2.

$$Iodine \ value = \frac{12.69 \ (V_1 - V_2)}{M} \qquad equation \ 2$$

Where $V_1 = Volume of sodium thiosulphate used for blank.$

 $V_2 =$ Volume of Sodium thiosulphate used for oil sample.

M= Mass of oil sample.

2.4. Statistical Analysis

Means of triplicates determination were separated using Duncan Multiple range test at 5 % level of significance. SPSS version 16.0 was used for the analysis.

3. RESULTS AND DISCUSSION

3.1. Effect of Repeated Frying Operation on Chemical Properties

Table-1. Chemical properties of refined vegetable oil re-use for frying operations.								
Sample	Free fatty acid	Acid value	Peroxide Value	Iodine Value	Saponification			
	(% Oleic)		(meq/kg)	(g/100g)	value (mgKOH/g)			
B1V	0.31 ± 0.01^{a}	0.62 ± 0.02^{a}	$3.235\pm0.02^{\rm b}$	91.17 ± 0.41^{a}	146.15 ± 0.80^{a}			
B3V	$0.47 \pm 0.01^{\circ}$	$0.94 \pm 0.02^{\circ}$	$3.42 \pm 0.02^{\mathrm{b}}$	98.40 ± 0.58^{d}	$135.01 \pm 0.36^{\rm e}$			
B5V	$0.53 \pm 0.03^{\rm d}$	$1.05 \pm 0.05^{\rm d}$	$3.81 \pm 0.05^{\mathrm{cd}}$	$97.52 \pm 0.49^{\rm cd}$	$127.60 \pm 0.50^{\circ}$			
P1V	$0.37 \pm 0.01^{\rm b}$	$0.73 \pm 0.01^{\rm b}$	$4.51 \pm 0.02^{\rm e}$	$102.93 \pm 0.28^{\rm e}$	$152.66 \pm 1.20^{\rm f}$			
P3V	$0.45 \pm 0.01^{\circ}$	$0.90 \pm 0.03^{\circ}$	$3.77 \pm 0.02^{\rm cd}$	$104.30 \pm 0.92^{\rm f}$	$129.80 \pm 1.04^{\rm d}$			
P5V	$0.52 \pm 0.01^{\rm d}$	1.03 ± 0.01^{d}	$4.92 \pm 0.02^{\rm f}$	107.00 ± 0.02 g	$125.00 \pm 0.22^{\rm b}$			
Y1V	$0.40 \pm 0.01^{\rm b}$	$0.79 \pm 0.01^{\rm b}$	$3.96 \pm 0.01^{\rm d}$	107.00 ± 0.30 g	$130.61 \pm 0.59^{\rm d}$			
Y3V	$0.45 \pm 0.02^{\circ}$	$0.88 \pm 0.02^{\circ}$	$3.52 \pm 0.02^{\rm bc}$	$93.46 \pm 0.06^{\rm b}$	$135.80 \pm 0.81^{\rm e}$			
Y5V	$0.53 \pm 0.02^{\rm d}$	1.06 ± 0.03^{d}	$3.90 \pm 0.18^{\rm d}$	$91.09\pm0.27^{\rm a}$	$147.56 \pm 0.58^{\rm f}$			
UVO	0.27 ± 0.01^{a}	0.55 ± 0.02^{a}	2.55 ± 0.02^{a}	$96.31 \pm 0.31^{\circ}$	$135.11 \pm 2.24^{\rm e}$			
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Note: Mean \pm Standard error on same row with same superscripts are not significantly different (p<0.05).

Where B1V = refined vegetable oil sample from first bean cake frying operation; B3V = refined vegetable oil sample from third bean cake frying operation; B5V = refined vegetable oil sample from fifth bean cake frying operation; P1V = refine vegetable oil sample from first plantain frying operation; P3V = refined vegetable oil sample from third Plantain frying operation; P5V = refined vegetable oil sample from fifth Plantain frying operation; Y1V = refined Vegetable Oil sample from first Yam frying operation; Y3V = refined vegetable oil sample from third yam frying operation; Y5V = refined vegetable oil sample from fifth Yam frying operation; UVO=unused refined vegetable oil.

3.1.1. Effect of Repeated Frying Operation on Free Fatty Acid

The Initial FFA value (0.27 % oleic) of refined vegetable oil used in this work is within the approved standard by Codex Alimentarius (1999). As presented in Table 1. Variation occurs in FFA value of refined vegetable oil based on the food material (Beans cake, Plantain and Yam) used in this work.

Significance differences existed in the FFA of oil samples from first, third and fifth frying operation for bean cake, plantain and yam. There was no significance difference (P < 0.05) between the FFA of oil after the first frying operation for beans cake production. However, there existed significant differences in FFA from the first frying operation of plantain and yam.

The FFA for repeated frying operation obtained for bean cake, plantain and yam ranged from 0.27 to 0.53 % oleic. The highest FFA was obtained at the fifth frying operation while the lowest was the initial quality of the refined vegetable oil. This is in agreement with the work of Lee *et al.* (2013). Increase in FFA was also reported by Belitz and Grosc (1992) when sunflower was used for repeated frying operation.

The FFA being a measure of the hydrolytic activities that has occurred in oil is dependent on the food material being fried. This is because the hydrolytic activities stems from a combination effect of heat, enzymes and moisture (Hamilton, 1994). The intensity of FFA has also been linked to its pro-oxidant effect (Frega *et al.*, 1999). The FFA measures to a great degree the stability of the oil.

Result for the chemical properties of palm oil sample is presented in Table 2. The FFA of the palm oil used in this study was 2.58 % oleic. Generally, frying operation led to decrease in FFA of oil samples (i.e. for bean cake, plantain and yam, FFA decreased from 2.58 to 1.39, 1.31 and 1.38 % oleic respectively). The FFA of oil samples for all food materials (Bean cake, plantain and yam) though originally decreased after the initial frying operation but later increased after the third frying operation before decreasing significantly (P>0.05) after the fifth frying operation.

Sample	Free fatty acid (% Oleic)	Acid value	Peroxide Value (meq/kg)	Iodine Value (g/100g)	Saponification value (mgKOH/g)
B1P	$13.90 \pm 0.05^{\circ}$	$27.81\pm0.11^{\rm c}$	$5.89 \pm 0.28^{\rm f}$	$182.50 \pm 0.30^{\rm f}$	$194.74 \pm 0.29^{\rm e}$
B3P	14.97 ± 0.09^{d}	$29.93 \pm 0.17^{\rm d}$	$7.70\pm0.68^{\rm g}$	$210.89\pm0.89^{\rm h}$	$197.50 \pm 1.20^{\rm f}$
B5P	12.31 ± 0.33^{a}	24.63 ± 0.67^{a}	$7.18\pm0.39^{\rm h}$	$201.20 \pm 0.25^{\rm g}$	$195.88 \pm 0.86^{\rm ef}$
P1P	13.06 ± 0.29^{b}	$26.13 \pm 0.33^{\mathrm{b}}$	$2.85\pm0.66^{\rm a}$	$145.00 \pm 0.33^{\rm d}$	$179.45 \pm 1.00^{\rm b}$
P3P	$14.18 \pm 0.10^{\circ}$	$28.36 \pm 0.21^{\circ}$	2.79 ± 0.30^{a}	$148.20 \pm 0.52^{\rm e}$	$180.09 \pm 0.16^{\rm b}$
P5P	12.16 ± 0.16^{a}	24.31 ± 0.19^{a}	$3.00\pm0.03^{\mathrm{b}}$	$148.13 \pm 0.56^{\rm e}$	$179.64 \pm 0.66^{\mathrm{b}}$
Y1P	$13.84 \pm 0.14^{\circ}$	$27.68 \pm 0.16^{\circ}$	$3.25 \pm 0.26^{\rm c}$	$131.68 \pm 1.13^{\rm b}$	$186.42 \pm 0.67^{\rm d}$
Y3P	14.86 ± 0.19^{d}	$29.72 \pm 0.22^{\rm d}$	$3.72\pm0.47^{\rm d}$	$134.37 \pm 0.19^{\circ}$	$181.13 \pm 0.88^{\rm bc}$
Y5P	11.87 ± 0.22^{a}	23.75 ± 0.25^{a}	$3.86 \pm 0.47^{\rm e}$	$148.02 \pm 0.67^{\rm e}$	$183.30 \pm 0.85^{\circ}$
UPO	$25.82 \pm 0.18^{\text{e}}$	$51.65 \pm 0.35^{\rm e}$	$8.14\pm0.34^{\rm i}$	119.90 ± 0.32^{a}	169.45 ± 0.55^{a}

Table-2. Chemical properties of palm oil re-use for frying operation.

Note: Mean \pm Standard error on same row with same superscripts are not significantly different (p<0.05).

Where B1P = Palm Oil sample from first bean cake frying operation; B3P = Palm Oil sample from third bean cake frying operation; B5P = Palm Oil sample from fifth bean cake frying operation; P1P = Palm Oil sample from first plantain frying operation; P3V = Palm Oil sample from third Plantain frying operation; P5P = Palm Oil sample from fifth Plantain frying operation; Y3P = Palm Oil sample from first Yam frying operation; Y3P = Palm Oil sample from third yam frying operation; Y5P = Palm Oil sample from fifth Yam frying operation; UPO = unused palm oil.

3.1.2. Effect of Repeated Frying Operation on Peroxide Value

At the initial stage of oxidative rancidity, formation of hydro-peroxides takes place in oil, and this is measured by the peroxide value. Oil stability to rancidity is dependent on the peroxide value (Debnath *et al.*, 2012). The lowest peroxide value of 2.53 meq/kg was obtained from the unused refined vegetable oil while the highest peroxide value of 4.92 meq/kg was obtained after the fifth frying operation of plantain. This showed that the stability of refined vegetable oil decreases as oil re-use increases.

Shen *et al.* (2001) reported correlation between peroxide value and result of sensory evaluation. High peroxide value has been linked to poor flavour scores. For beans cake, Peroxide value increases from the first frying operation to the fifth frying operation.

However, Peroxide value decreases after the third frying operation and later increase after the fifth frying operation for plantain and yam. At p< 0.05, significant differences existed in the Peroxide value of all frying operation for plantain. Whereas significant difference (p < 0.05) only existed between third and fifth frying operation for bean cake and yam. A decrease in peroxide value after an increase could be due to its oxidation to secondary oxidation products (Serjouie *et al.*, 2010; Falade and Oboh, 2015).

As presented in Table 2. There was significant (P>0.05) decrease of peroxide value from 8.139 meq/kg (Fresh palm oil) after the first frying operation of beans cake, plantain and yam to 5.893, 2.851 and 3.248 meq/kg. The lowest peroxide value obtained was from oil sample taken after the first frying operation of plantain.

The peroxide value increases significantly from the first frying operation to the fifth frying operation for deep frying of plantain and yam with palm oil. Increase in peroxide value due to continuous frying was also reported for heated arachis oil and thermoxidized palm oil (Oboh *et al.*, 2014; Falade and Oboh, 2015).

The peroxide value of palm oils samples obtained for all frying operations for plantain were the lowest when compared to bean cake and yam. While the highest average peroxide value was obtained from bean cake frying. However, values obtained in the present study is within recommended standard PV (10 mEq/Kg) for edible oil (Codex Alimentarius, 1999).

3.1.3. Effect of Repeated Frying Operation on Iodine Value

Iodine value was determined to measure unsaturation in oil samples. Results showed that significant differences at p<0.05 existed among all frying operations carried out with plantain and yam. Iodine value increases from 102.93g/100g to 107 g/100g for oil sample from plantain frying, while Iodine value decreases for oil samples from yam frying from 107 g/100g to 91.09 g/100g.

There was no significant difference at p>0.05 between oils samples taken from third and fifth frying operation of bean cake. Increase in iodine value for oil used for plantain frying could be due to the radical scavenging activities and short frying duration required for plantain frying compared to yam. Variation in iodine value has been attributed to the presence of radical scavenging compounds (Cao *et al.*, 2015).

The iodine value of Palm oil used in this work was 119.90 g/100g. There was a significant increase in the iodine value after the initial frying operation for all food materials (Bean cake, plantain and yam). Iodine value increases as the number of frying operation increases for yam. Significant differences existed in iodine value at p<0.05 among frying operations of bean cake and yam. However, there was no significant difference between third and fifth frying operations for plantain.

3.1.4. Effect of Repeated Frying Operation on Saponification Value

The saponification value which represents the molecular mass of fatty acids is also use to determine the extent of hydrolysis of oil samples (Nayak *et al.*, 2016). For refined vegetable oil, saponification values of frying oil decreases as the number of frying operation increases for bean cake and plantain.

The saponification value increases as the number of frying operation increases for yam. The saponification values of all the frying operations differs significantly (p<0.05) for the food materials used in this work. The lowest saponification value of 125 mgKOH/g was obtained from oil samples of fifth frying operation of plantain. The highest saponification value (152.66 mgKOH/g) was obtained from oil sample of refined vegetable oil from first frying operation of plantain.

Saponification value of oil sample increases after the first frying operation for all food material used in this study. For bean cake frying oil samples, there was only significant difference between first and third frying operation. There was no significant difference in the saponification value of oils sample from plantain frying. Result of saponification value from oil samples taken from third and fifth frying operation showed no significant difference at 5% level of significance.

4. CONCLUSION

Repeated frying operation of bean cake, plantain and yam led to significant changes in the quality of frying oil (refined vegetable and palm oil). Variation in chemical properties of oil sample was influenced by the type of food material (bean cake, plantain and yam) fried as well as the duration of frying operation. Significant continuous

decrease in the free fatty acid as time of use increase was a reflection of increase in oil deterioration, rancidity and decrease in suitability for consumption. However, Peroxide value of five times repeated use of vegetable is still within acceptable standard for edible oil.

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