

Characterization of the Physicochemical Properties of Virgin and Used Vegetable Oil

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ABSTRACT

Vegetable oils form a vital part of the diet in many homes. The repeated use of same oil for deep frying is widespread in commercial as well as domestic cooking processes. This study aimed at investigating the physicochemical properties of popular brands of virgin and used edible oils sold in Nigeria to ascertain the effects of using the same oil for repeated frying. Standard methods prescribed by the Association of Analytical Chemists (AOAC) and American oil Chemists Society recommended practice (AOCS) were used to determine relative density (RD), peroxide value (PV), iodine value (IV), acid value (AV), free fatty acid (FFA), volatile matter (VM), viscosity (VY) and insoluble impurities (IP). Results revealed that the temperature change in the oil samples induced a difference in their RDs, AVs and PVs. This was also observed in the proportions of the FFA content of the oil samples before they were used and after two frying cycles. PVs in the study ranged from 1.40 - 13.60 meqO₂/kg; IVs ranged from 48.22-118.02 gI₂/100g; RDs ranged from 0.91 -0.95 kg/l; AV ranged from 1.37 - 49.56 mgKOH/g; FFA ranged from 0.59 - 11.56%; VM range was 0.0003 to 0.0484 %. VY range was 136.04 - 220.53 mgKOH/g and IPs ranged from 5.03 - 9.02 %.

Keywords: Virgin oil, Used oil, Vegetable oils, Physicochemical properties, Nutritional value.

Introduction

Vegetable oils (VOs) are very important in the dietary patterns of many countries (Szabo *et al.*, 2022). They serve as good energy source, and contain lipids, fatty acids and proteins, required to repair worn-out tissues and form new cells. (Aremu *et al.*, 2013). Several physicochemical properties (PCPs) such as (RD), (PV), (IV), (AV), (FFA), (VM), (VY), (IP), to mention but a few, are pivotal in establishing the shelf life and economic worth of comestible oils (Mousavi *et al.*, 2012). VOs are essential and frequently used as lipid source for our daily nutrition. Their application as food and manufacturing of several toiletry products is

increasing daily. However, some VOs are not up to standards in meeting consumer satisfaction in terms of their PCPs or texture and stability in food products (Kumar *et al.*, 2018). Some heart related disorders and cholesterol accumulation are traceable to wrong oil-aided cooking techniques. The PCPs exhibited by oils is depends on the extent of heating they are subjected to (Valantina *et al.*, 2016).

Cooking meals in VOs at elevated heating is a routinely common food preparation technique (Baig *et al.*, 2022). Repeated frying, causes thermal

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and oxidative reactions, which alters the nutritive properties of oil (Che Man and Jasvir, 2000). The components, taste and strength of comestible oils change during frying (Chang *et al.*, 2020). This is occasioned by processes like polymerization, hydrolysis and oxidation occurring within the oil's compounds (Gloria and Aguilera, 1998). During deep frying different reactions driven by factors like fresh oil regeneration, frying state, oil's initial quality and reduction in its oxidation strength occur (Choe and Min, 2007; Jinfeng *et al.*, 2011). Degradation in the structure of oils is accentuated primarily by lipids oxidation, resulting in food quality loss (Bhattacharya *et al.*, 2008). Monitoring edible oil quality is pivotal to preventing consumption of unwholesome VOs (Vijayan *et al.*, 1996). This study examines the PCPs of common VOs in Nigeria and the impact of elevated temperatures on these properties. It provides baseline data in predicting how many frying cycles particular VOs can be subjected to before losing nutritional value or causing any harmful effect.

Materials and Methods

Sampling

Five samples (A, B, C, D and E) of VOs were purchased from local markets in Abraka, a sprawling university town in Delta State, Nigeria. Samples A, B and C are branded VOs. Samples D and E are unbranded VOs. The unbranded VOs were to serve as control. Unbranded VOs are largely processed by local farmers for sale without additives and modern preservatives unlike the branded VOs. They were utilized for deep frying below 180 °C in the laboratory by the authors. The frying was done in the laboratory to ensure the oils were subjected to two frying cycles at high temperatures. After the first frying cycle, the samples were labelled A₁, B₁, C₁, D₁ and E₁ respectively. The oil samples were subsequently labelled A₂, B₂, C₂, D₂ and E₂ respectively, after the second frying cycle. In the first cycle, the five virgin oil samples were used to fry parboiled meat, after

which they were stored for 24 hours. In the second cycle, the VOs previously used to fry meat were reused to fry plantain.

Methods

The RD of the VOs was determined by density bottle method described by the AOAC (AOAC, 2000). Suspended particles were removed by vacuum filtration. 50 mL density bottle was weighed empty as W₀ when filled with water, the weight was W₁. The weight of latter containing equivalent volume of oil was W₂. The RD was calculated by the expression:

$$RD = \frac{W_1 - W_0}{W_2 - W_0} \quad (1)$$

VY measurements were done with thermostatic bath fitted with Petrotest thermometer, viscometer (Cannon Fenske) of 200 capillary (K=0.08992 mm².s²), an ASTM 12°C mercury thermometer, and KINGTECH chronometer with resolution of one hundredth of a second. 40 °C was the test temperature. Ambient conditions were controlled at 25 °C and relative humidity 65%. Determination of PV was by AOCS indorsed procedure (AOCS, 1998). Standard 0.01 N Na₂S₂O₃.5H₂O was used for the titration. A blank titration was also carried out. PV was calculated as:

$$PV (g) = \frac{1000 \times (V_1 - V_2) \times N}{W} \quad (2)$$

Where: W = weight of oil; V₁= volume of Na₂S₂O₃.5H₂O used for test; V₂= volume of Na₂S₂O₃.5H₂O used for blank and N = normality of the Na₂S₂O₃.5H₂O.

IV was determined in accordance with AOCS recommendation (AOCS, 1998), as shown in equation (3):

$$IV = \frac{(a - b) \times M \times 0.127 \times 100}{W} \quad (3)$$

Where: 0.127 = Molar mass of iodine/1000; M = Molar concentration of Sodium thiosulphate; a = Volume (mL) of Sodium thiosulphate used for blank; b = Volume (mL) of thiosulphate required for

the test and w = Weight of oil sample. AV was obtained by the British Standards Institution's protocol (BS EN ISO 660: 2009). The mathematical expression is shown in equation (4):

$$\text{Page | 4343 } AV = \frac{(a-b)M \times 56.1}{W} \quad (4)$$

Where: a = amount of KOH in mL for blank; b = volume of KOH in mL for test; M = molarity of KOH; W = oil sample's weight (g) and 56.1 = molecular mass of KOH. The FFA was determined as described by Harid (1990). It is expressed in percentage as shown in equation (5):

$$\% \text{ FFA} = \frac{\text{Titre value} \times M \times 28.2}{W} \quad (5)$$

Where: 28.2 = conversion factor in relation to oleic acid; W = Weight of sample; M = Molar concentration of HCl. VM was determined by adapting the AOCS method (AOCS, 1990). For amount of insoluble impurities, 2g of the sample was weighed into a conical flask and 20 mL of 1:1 solvent mixture (petroleum ether + diethyl ether) was added. The flask was vigorously shaken and made to stand for 30 minutes at 30 °C. The resulting solution was then filtered through a dried and weighed Whatman number 1 filter paper. The latter was carefully washed with 10 mL of the solvent mixture. It was then dried to a constant weight in an oven at 103 °C. Increase in weight represents amount of impurity and was expressed as a percentage of the initial sample.

Statistical Analysis

Analysis of Variance (ANOVA) using Statistical Package for Social Sciences (SPSS) version 20 Software was used to analyze generated data. At a significant level (p – value) of 0.05; variations in the means of the sets of data for each parameter were considered not significant at $p > 0.05$.

Results and Discussion

The results of the PCPs of the virgin and used VOs are presented on tables 1 – 3. Table 4 is a summary of the properties before and after the two frying

cycles. Density significantly affects heat transfer by natural convection and buoyant movement of gas bubbles in a liquid. The density of different types of oil varies based on differences in their composition. The agency that regulates food and drug administration in Nigeria sets a limit of 0.891 – 0.927 for RDs of VOs at 20 °C (NAFDAC, 2019). ANOVA with a degree of freedom (df) equal to 9 and p -value of 0.384, showed that there was no significant variation between the RDs of the virgin and used oil samples. However, after the first frying cycle, the RD for sample E_1 increased sharply as can be seen on figure 1, indicating the production of compounds with higher molecular weight via polymerization and oxidation.

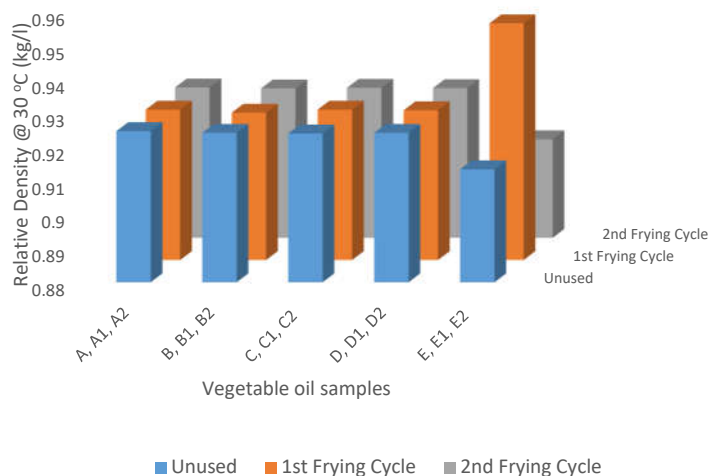


Figure 1: RD of the VOs.

VY for the VOs ranged from 32.15 to 50.90 centistokes. VY is frequently employed to monitor physical alterations in edible oil. It depends on density, molecular weight and temperature. Higher amount of saturation in FFAs increases VY, the reverse occurs when unsaturation in FFAs is pronounced (Kim *et al.*, 2010). The variation in the VY values of the virgin oil and VOs after the first and second frying cycles as can be seen from figure 2, was not significant.

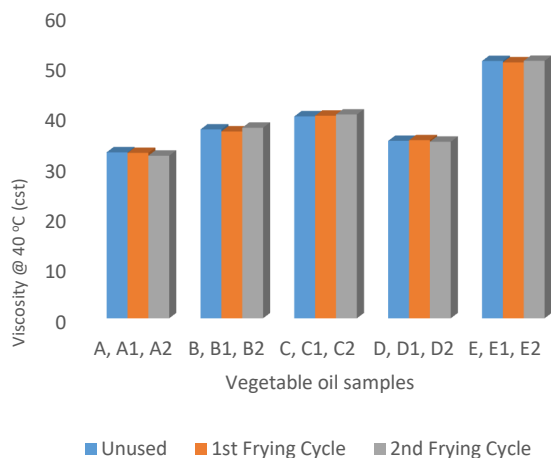


Figure 2: VY of the VOs.

PV of the VOs are within the limit for any particular edible oil as specified by NAFDAC, that is, not more than 10 milliequivalents peroxide oxygen /kg oil (NAFDAC, 2019). PV measures extent of rancidity during storage. It is a suitable indication of stability of fats and oils (Ekwu and Nwagu, 2004). The PV is the commonest oxidation indicator in lipids. As shown on figure 3; PV ranged from 1.40 to 13.60 meqO₂/kg. Except samples B₂, E₁ and E₂ that had relatively high PV of 11.80, 11.80 and 13.60 respectively, others had values lower than the standard value of 10 meqO₂/kg specified by NAFDAC (2019). If PV is high it implies antioxidants may not be readily available in the oil; if present at all, the levels may be very low. Such oils are prone to oxidative rancidity (Gotoh and Wada, 2006). These low PVs indicate a relatively good quality of the oils.

The IV of the VOs were more than 10gI₂/100g of oil recommended by NIS (1992) for edible oils. IV indicates level of unsaturation (AOCS, 1993; Asuquo *et al.*, 2012). Moreover, it assists in quantifying amount of double bond the VOs contain, which reflects its susceptibility to oxidation. IV ranged between 48.22-118.02 gI₂/100g for the VOs. As shown on figure 4, IV of

the VOs decreased after the first and second frying cycles. It shows that repeated frying with the same oil leads to greater saturation of fatty acids in VOs.

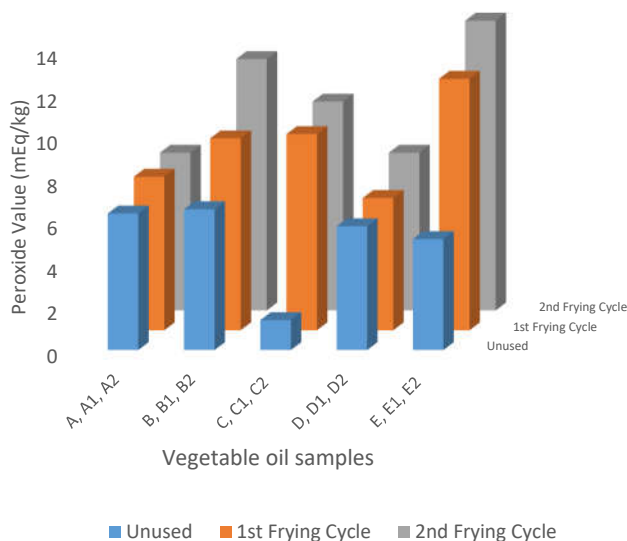


Figure 3: PV of the VOs.

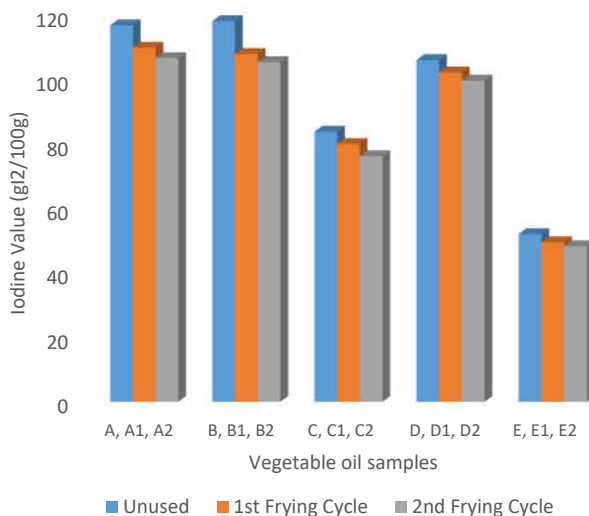


Figure 4: IV of the VOs.

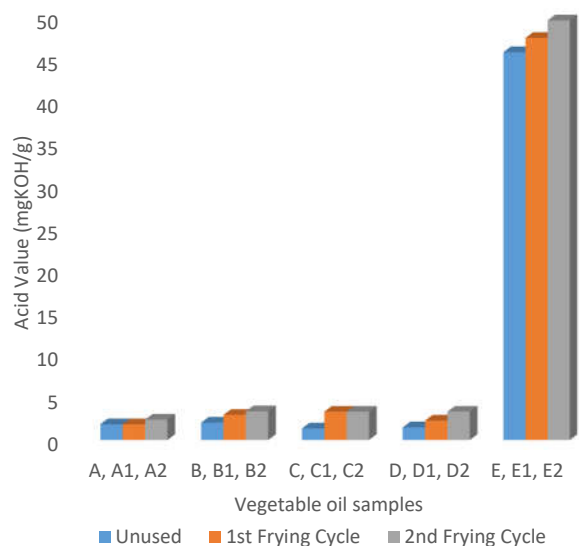


Figure 5: AV of the VOs.

The AV of the VOs ranged from 1.37 to 49.56mgKOH/g) which were higher than the maximum value of 0.6mg KOH/gmax recommended by NIS (NIS, 1992) for edible oils. The disparity in the AVs of the virgin and used VOs was not significant. However, samples E, E₁ and E₂ recorded high AV. These values accounted for presence of FFAs in the oils; which also indicates level of hydrolysis by lipolytic enzymes and oxidation (Aremuet *et al.*, 2015). When AV is low, the VOs will be stable over a long period, in which case peroxidation and rancidity are minimised. This is good for edible oils. High AV makes oils suitable for the production of paints, liquid soap and shampoos (Aremu *et al.*, 2006).

On table 4, FFA in the VOs ranged from 0.59 to 11.56%. The maximum amount of FFAs acceptable in a base-catalyzed system is about 2% by weight of oil (SON, 2000). Amount of FFA in the VOs were lower than the standard of 2% as recommended by SON except samples E, E₁ and E₂ that had relatively high value of 10.15%, 10.99% and 11.56% respectively. These unbranded samples were obviously poorly refined and processed. The difference in the FFAs of the virgin and used VOs was insignificant. High amount of FFA makes oils

more susceptible to oxidative aging, they become rancid more quickly, which implies that VOs analysed except samples E, E₁ and E₂, have low rancidity potentials.

From table 4, SV of the VOs ranged from 134.64 - 220.53mgKOH/g. These values fell below the stipulated range of 245-255 mg KOH/g by NIS (1992). A df of 13 and p-value of 0.550 from ANOVA, indicates that the difference in the SVs of the virgin and used VOs was not significant. Low SV shows that average molar mass of fatty acids in the VOs are less (Denniston *et al.*, 2004). Oil with high SV contains high percentage of lower fatty acids. Therefore, the low SV of oils indicates that they might contain higher ratio of fatty acid.

The values of VM on table 4 ranged from 0.0002 - 0.0484 %, which are below 0.5% recommended by SON, (2000). The general rule is that as VM decreases, the oil burns more slowly. VM content is an indication of the ease of combustion of a substance (Zumdahl, 2007; Felder, 2015).

The values of IP ranged from 5.03 - 9.02%. IP are indicative of dirt, minerals, and resins, fatty acids that have been oxidized, alkaline soaps of stearic acids, palmitic acids and proteins suspended in the VOs. The relatively high percentage of insoluble matter in the branded oil samples may be attributable to additives and preservatives.

Table 1: Physicochemical properties of the virgin oil samples.

Properties	Samples					Mean ± SD
	A	B	C	D	E	
RD @ 30°C (kg/l)	0.9248	0.9243	0.9241	0.9243	0.9135	0.922 ± 0.005
AV (mgKOH/g)	1.87	2.06	1.37	1.50	45.82	10.524 ± 19.733
FFA (%)	0.66	0.81	1.16	0.59	10.15	2.674 ± 4.185
SV (mgKOH/g)	180.76	213.27	171.45	180.55	134.64	176.134 ± 28.123
ID (gI ₂ /100g)	116.73	118.02	83.75	105.96	52.03	95.298 ± 27.815
PV (mEq/kg)	6.40	6.60	1.40	5.80	5.20	5.080 ± 2.129
VM (%)	0.0259	0.0125	0.0002	0.0003	0.0129	0.010 ± 0.011
IP (%)	6.11	7.01	7.74	7.22	6.61	6.938 ± 0.617
VY @ 40°C (cst)	32.82	37.34	39.92	35.08	50.87	39.206 ± 7.033

Table 2: Physicochemical properties of the oils after first frying cycle.

Properties	Samples					Mean ± SD
	A ₁	B ₁	C ₁	D ₁	E ₁	
RD @ 30°C (kg/l)	0.9246	0.9237	0.9246	0.9244	0.9502	0.930 ± 0.012
AV (mgKOH/g)	1.87	2.99	3.37	2.31	47.50	11.608 ± 20.073
FFA (%)	0.68	1.05	1.21	0.61	10.99	2.908 ± 4.525
SV (mgKOH/g)	204.23	215.94	174.68	185.30	136.04	183.238 ± 30.854
ID (gI ₂ /100g)	109.77	107.86	79.95	102.15	49.49	89.844 ± 25.492
PV (mEq/kg)	7.20	9.00	9.20	6.20	11.80	8.680 ± 2.148
VM (%)	0.0389	0.0080	0.0484	0.0013	0.0088	0.021 ± 0.021
IP (%)	6.28	7.09	7.10	5.34	9.02	6.966 ± 1.357
VY @ 40°C (cst)	32.70	36.94	40.06	35.21	50.61	39.104 ± 6.967

Table 3: Physicochemical properties of the oils after second frying cycle.

Properties	Samples					Mean ± SD
	A ₂	B ₂	C ₂	D ₂	E ₂	
RD @ 30°C (kg/l)	0.9246	0.9243	0.9245	0.9244	0.9092	0.921 ± 0.007
AV (mgKOH/g)	2.43	3.42	3.37	3.37	49.56	12.430 ± 20.760
FFA (%)	0.90	1.12	1.22	0.66	11.56	3.092 ± 4.739
SV (mgKOH/g)	206.70	220.53	181.16	192.17	136.04	187.320 ± 32.286
ID (gI ₂ /100g)	106.59	105.33	76.14	99.62	48.22	87.180 ± 25.003
PV (mEq/kg)	7.40	11.80	9.80	7.40	13.60	10.000 ± 2.728
VM (%)	0.0056	0.0007	0.0186	0.0019	0.0045	0.006 ± 0.007
IP (%)	5.03	7.05	6.80	6.41	5.78	6.214 ± 0.817
VY @ 40°C (cst)	32.15	37.68	40.30	34.90	50.90	39.186 ± 7.221

Table 4: Properties of the VOs before and after the first and second frying cycles.

Properties	Samples															
	A	A ₁	A ₂	B	B ₁	B ₂	C	C ₁	C ₂	D	D ₁	D ₂	E	E ₁	E ₂	
RD @ 30°C (kg/l)	0.9248	0.924	0.924	0.924	0.923	0.924	0.924	0.924	0.924	0.924	0.924	0.924	0.913	0.950	0.909	
Page 4347		6	6	3	7	3	1	6	5	3	4	4	5	2	2	
AV (mgKOH/g)	1.87	1.87	2.43	2.06	2.99	3.42	1.37	3.37	3.37	1.50	2.31	3.37	45.82	47.50	49.56	
FFA (%)	0.66	0.68	0.90	0.81	1.05	1.12	1.16	1.21	1.22	0.59	0.61	0.66	10.15	10.99	11.56	
SV (mgKOH/g)	180.76	204.2	206.7	213.2	215.9	220.5	171.4	174.6	181.1	180.5	185.3	192.1	134.6	136.0	136.0	
		3	0	7	4	3	5	8	6	5	0	7	4	4	4	
ID (gI ₂ /100g)	116.73	109.7	106.5	118.0	107.8	105.3	83.75	79.95	76.14	105.9	102.1	99.62	52.03	49.49	48.22	
		7	9	2	6	3				6	5					
PV (mEq/kg)	6.40	7.20	7.40	6.60	9.00	11.80	1.40	9.20	9.80	5.80	6.20	7.40	5.20	11.80	13.60	
VM (%)	0.0259	0.038	0.005	0.012	0.008	0.000	0.000	0.048	0.018	0.000	0.001	0.001	0.012	0.008	0.004	
		9	6	5	0	7	2	4	6	3	3	9	9	8	5	
IP (%)	6.11	6.28	5.03	7.01	7.09	7.05	7.74	7.10	6.80	7.22	5.34	6.41	6.61	9.02	5.78	
VY @ 40°C (cst)	32.82	32.70	32.15	37.34	36.94	37.68	39.92	40.06	40.30	35.08	35.21	34.90	50.87	50.61	50.90	

Conclusion

The study considered three samples of popular brands and two unbranded samples commonly used for deep frying domestically and commercially. To confirm changes in composition of the VOs, proximate analyses was carried out on the virgin samples and after the first and second cycles of deep frying. Results showed that temperature change in the VOs, occasioned by repeated frying, led to continuous increase in the FFAs, AV and PV of the VOs. High temperatures make it easy for atmospheric oxygen to cause structural changes in the FFAs of VOs, converting some to carbonyls and peroxides. This degrades the quality of VOs for cooking purposes.

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Conflict of Interest

Funding for this research is entirely by the authors, there are no conflicting interests in this publication.

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