

# **Research Article**

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# Physicochemical Studies on Sunflower Oil Blended with Cold Pressed Tiger Nut Oil, during Deep Frying Process

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# Abstract

Blends consisting of sunflower oil and cold pressed tiger nut oil in different proportions were evaluated for various physicochemical parameters over 30 hours of frying process. The phenolic content of native oils was determined. Some physical and chemical parameters (Free Fatty Acid, FFA), Peroxide Value (PV), thiobarbituric acid value, iodine value, Total Polar Compounds (TPC), color and viscosity of fresh and fried blended oils measured at different frying periods. Native and blended oils were heated at 180°C+5°C, then frozen French fries potato were fried every 30 min. Oil samples were taken every 5 hours and the entire continuous frying period was 30 hours. The results showed that phenolic content of cold pressed tiger nut oil was about 3.3 times higher than that of sunflower oil. The analytical data showed that the lowest deterioration during frying process occurred in tiger nut oil and the highest in sunflower. The changes of physicochemical parameters were controlled and significantly (P<0.05) decreased when tiger nut /sunflower oil (W/W) proportions were varied between 20/80 to 50/50. The obtained results indicate that mixing sunflower oil with cold pressed tiger nut oil increased the stability and hence improved the quality of sunflower oil during frying process.

**Keywords:** Tiger nut oil; Sunflower oil; Stability; Antioxidants; Oxidation; Blending

# Introduction

Deep-fat frying is one of the oldest and most popular food preparation methods [1]. Deep-fat frying is a process of immersing food in hot oil with a contact among oil, air and food at a high temperature of 150 to 190°C [2]. In the presence of oxygen, moisture, trace elements and free radicals, physiochemical reactions such as thermoxidation, hydrolysis, polymerization, isomerization or cyclization take place at high temperatures of the frying process, thus leading to the decomposition of frying oil and formation of monomeric, polymeric, primary and secondary oxidative compounds, thereby affecting the quality of oil and fried product [3].

These reactions in deep-fat frying process depend on factors such as replacement with fresh oil, frying conditions, original quality of frying oil, food materials, type of fryer, type and concentration of antioxidants and oxygen concentration [4]. Other factors such as frying temperature, quantity of frying, initial content of free fatty acids, polyvalent metals, type of food material, design and maintenance of fryer, light, use of filters and unsaturated fatty acid content of the oil also affect the oxidative stability and overall quality of oil during the frying process [5-8]. Various method to improve oxidative stability of soybean oil has been developed and studied, for example, partial hydrogenation, fatty acid modification and blending with more saturated or monosaturated oils to reduce the amount of polyunsaturated fatty acids [9-11]. Partial hydrogenation decreases polyunsaturated fatty acid but increases saturated fatty acid and trans-fatty acid to produce more stable frying oil. However, trans fatty acid may have adverse effects on cardiac health [12]. Blending has long been used to modify oils and fats to improve the fat functionalities and thus optimize their application in food products. It modifies the physicochemical properties of oils without changing their chemical composition [13]. The oils can be blended even to derive the protective advantage due to the presence of specific ingredients that offer protection against oxidation to improve frying recyclability [14].

Sunflower oil (SFO) and soybean oil (SBO) have a good nutritional

profile, with poor oxidative stability and is, accordingly, prone to flavor deterioration because of their high proportion of unsaturated fatty acids, especially, linolenic acid in SBO [15]. Oxidation of unsaturated fatty acids is one of the major causes in the development of off-flavor compounds and in the reduction of nutritional value of food products [16].

Tiger nut (Cyperus esculentus L.) is an underutilized crop which belongs to the division-Magnoliophyta, class-Liliopsida, order-Cyperales and family-Cyperaceae and was found to be a cosmopolitan perennial crop of the same genus as the papyrus plant. Tiger nut is not really a nut but a small tuber, first discovered some 4000 years ago in ancient Egypt and is cultivated today in China, Spain and West Africa for its small tuberous rhizomes which are eaten raw or roasted, used as hog feed or pressed for its juice to make a beverage. Non-drying oil (usually called chufa) is equally obtained from the rhizome [17]. The tubers contain 20-36% oil. C. esculentus has been suggested as potential oil crop for the production of biodiesel [18]. The nut was found to be rich in myristic acid, oleic acid, linoleic acid [18,19]. From our previous study [20], which was about the effects of feeding blended oils consisting of coconut oil (CNO) with different proportions of Tiger nut oil (TNO) on serum lipid levels in Albino rats? Our results showed that coconut oil had 86 % saturated fatty acids. TNO on the other hand contain 66% oleic acid. Therefore, blending coconut oil with tiger nut oil can reduce proportions of saturated to unsaturated fatty acids in CNO. The rats fed on blended oils showed significantly

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reduced levels of serum cholesterol as compared to those on CNO. The HDL levels were marginally enhanced in rats on blended oils. The total cholesterol and LDL cholesterol levels were controlled when TNO/ CNO proportions were varied between 25/75 to 70/30. Similar changes were observed with serum triglyceride levels also.

Although quality of pure vegetable oils before and after frying has been evaluated by many researchers but the physicochemical properties for binary oil blends have not been studied extensively. Actually, stability of unsaturated vegetable oils can be increased by blending with stable oil that has high saturation [21,22]. Therefore, the main objective of the present study was to evaluate the effects of fatty acid compositions of tiger nut oil, sunflower oil and binary mixtures of them on the changes in physicochemical parameters of during deep frying process by assessing Free Fatty Acid (FFA), Peroxide Value (PV), thiobarbituric acid value (TBA value), iodine value, Total Polar Compounds (TPC), color and viscosity of the oils.

# **Materials and Methods**

# Materials

Tiger nut tubers (*Cyperus esulentus*) were obtained from Harraz Spices and Herbs Co. Cairo, Egypt. Refined sunflower oil was purchased from the local market (Giza, Egypt). The oil peroxide and acid values were 0.70 (meq/kg oil) and 0.018 (mg KOH/g oil) respectively.

All reagents and chemicals that were used in this work were of analytical grade.

# Methods

**Tiger nut oil (TNO) extraction:** Dried tiger nut tubers (*Cyperus esulentus*) were crushed and pressed by hydraulics laboratory press model C S/N 37000-156 Freds from Carver (WI, USA). Anhydrous sodium sulphate was added to the extracted oil and allowed to stand for 30 min to remove excessive residual moisture. The resultant dry oil was centrifuged at 1080 g and filtered through Whitman filter paper No.1 and kept in a brown glass bottle at  $4 \pm 0.5^{\circ}$ C.

**Blends preparation:** Cold pressed tiger nut oil (TNO) was blended with sunflower oil (SO) in varying proportions. The following TO: SO (% v/v) blends were prepared; 0:100, 10: 90, 20: 80, 30: 70, 40: 60, 50:50 and 100: 0. The oil blends were mixed at 60°C in an oven prior to initial analysis.

**Frying process:** A known amount (ca.1250g) of each of the refined sunflower oil , tiger nut oil and binary mixtures of them were placed separately in a stainless steel pan fryer (40 -cm diameter x 10-cm height). The aforementioned oils were separately heated at 180°C  $\pm$  5°C, then 50 g of frozen French fries potato were fried every 30 min. The fryer temperature decreased by approximately 10°C within 1.5 min of the addition of the frozen potatoes and then increased until the end of frying time 4 min. Oil samples were taken every 5 hour and the entire continuous frying period was 30 hours. The oil samples were left to cool down and then stored at -18°C for physicochemical analysis.

# **Chemical analysis**

The phenolic content of oil was extracted according to the method described by [23,24]. Approximately, 15 g of oil was weighed into a 50 ml Falcon tube. Ten milliliters of n-hexane was mixed with the oil. The mixture was extracted with 10 ml of methanol:water (60:40). The mixtures were shaken for 5 min and then centrifuged at 5500 rpm for 5 min. The hydroalcoholic phase was collected and the hexane phase

was re-extracted twice with 10 ml of methanol:water (60:40) each time. The combined hydroalcoholic fractions from three extractions were subjected to final washing with 10 ml of n-hexane to remove residual oil in a separatory funnel. The excess solvent was evaporated under vacuum at 40°C until dryness in a rotary evaporator. The residue was reconstituted in 20 ml methanol: water (60:40). The total phenolic content was determined by the Folin-Ciocalteu reagent assay (Lim et al. 2007). First, 0.5 ml of the extract obtained was mixed with 1.5 ml of Folin-Ciocalteu reagent previously diluted with distilled water (1:10). After standing at room temperature for 3 min, 1.2 ml of 15% sodium carbonate solution was added. The mixture was placed in dark room for 60 min. After that, absorbance was measured at 765 nm against the blank using a spectrophotometer (Secomam UVi ligh XTD). The calibration curve was obtained by repeating the above procedures with known concentrations of gallic acid solutions. The results were expressed as milligrams of gallic acid equivalents (GAE) per 100 gram of oil (mg GAE per 100 g of oil). Since the assay quantifies all phenolic compounds, the selection of gallic acid as a standard is based on the availability of a stable and pure compound. In addition, gallic acid is cheaper than other options. Analyses were performed in triplicate for each of the extract.

Acid value was determined according to the A.O.A.C. method (969.17, 2000) as follows: A known weight (2 g) of the oil was dissolved in a neutral ethyl alcohol (30 ml). The mixture was boiled on a water bath for 2 min and then titrated with potassium hydroxide solution (0.1 N) in the presence of phenolphthalein as an indicator. Acid value is expressed as mg KOH required to neutralize the acidity in one gram oil. The peroxide value was determined according to A.O.A.C method (965.33, 2000). A known weight of the oil sample (2.5 g) was dissolved in a mixture consisting of glacial acetic acid: chloroform (30 ml, 3:2, v/v) then freshly prepared saturated potassium iodide solution (1 ml) was added followed by distilled water (30 ml) and then titrated slowly with sodium thiosulphate solution (0.1 N) in the presence of starch solution (1%) as an indicator. Peroxide value is expressed as milliequivalent peroxides/1kg oil. The method of [25] was conducted to determine the TBA value as follows. A known weight of oil (3g) was dissolved in a carbon tetrachloride (10ml) followed by the addition of TBA reagent (10ml, 0.67% TBA in 50% acetic acid). The mixture was transferred to a separatory funnel and the aqueous layer was drawn into a test tube and immersed in a boiling water bath for 30 min. The absorbance of the developed pink colour was then recorded at 532 nm against a blank reagent. The iodine value was determined using the Hanus method as described in A.O.A.C. (920.158, 2000). A known weight of oil (0.2 g) was dissolved in chloroform (20 ml), then Hanus iodine (I2+Br / ACOH) solution (25 ml) was added and left in the dark for 30 min. Potassium iodide solution (10 ml, 15%) was added followed by freshly distilled water (100 ml) and the excess iodine was titrated by sodium thiosulphate (0.1 N) until the yellow color of solution had almost disappeared. Titration was continued after adding few drops of starch as an indicator until the blue color had entirely disappeared. A blank was conducted where the total halogen content of Hanus solution (25 ml) was determined by sodium thiosulphate solution without the addition of oil. Iodine value is expressed as grams of I<sub>2</sub> absorbed by 100 g oil. Total polar compounds (TPC) content of oil samples were measured by column chromatography according to the method described by [26].

# Physical analysis

Lovibond Tintometer (Tintometer Limited Solstice Park, Amesbury, UK) was used to measure the colour of the oil samples

# Page 3 of 8

under investigation, the yellow glass filter was fixed at 30 and the intensity of red glass colour was measured according to the A.O.A.C. method (2000). Brookfield LV viscometer Model TC-500 (Brookfield Engineering Laboratories Stoughton, MA, USA) was used to measure the viscosity of the oil samples at 30°C according to the method described by [27].

# Statistical analysis

Data are expressed as mean  $\pm$  SD. Data were statistically analyzed in completely randomized design in factorial arrangement according to the procedures outlined by [28] and the treatment means were compared by least significant differences (L.S.D) and Duncan multiple range using SPSS program package. Data are presented in text and tables as means of five determinations.

# **Results and Discussion**

#### Total polyphenols content

Indeed, the level of phenol in seed oils is an important factor while assessing the quality of oil because these compounds have been correlated with colour and the shelf-life of oil, and particularly its resistance to oxidation [29]. These compounds are the main factor rendering nutritional importance to cold-pressed oil [24]. Tiger nut oil showed higher level of total polyphenols was 16.5 mg GAE per 100 g of oil compared to sunflower oil 5.0 mg GAE per 100 g of oil. This means that phenolic content of Tiger nut oil was about 3.3 times as higher than that of sunflower oil. Tiger nut oil (TNO) had been shown to be rich in the content of polyphenols [20,30-32].

#### Changes in acid value (AV)

Acid value was used to assess frying oil degradation and is related to fried food quality [5,33]. The changes in the acid values of sunflower blended with different portions of Tiger nut oil during deep fat frying at (180°C  $\pm$  5°C) are given in Table 1. The initial acid values of the fresh oils under investigation were seen to range from 0.13 for sunflower oil to 0.31 for tiger nut oil, these low values reflect the quality of these oils .The maximum level of acid value of refined and cold pressed oils were 0.6 and 4.0 mg KOH/g oil respectively [34]. Generally , frying the oils under study at 180°C  $\pm$  5°C for 30 hour led to a gradual and significant(P<0.05) increase in the acid values. The formation of free

fatty acids was found to increase with increase in time of frying. The increase in FFA could be attributed to oxidation and hydrolysis, which produces FFAs [35,36]. Moreover, FFA content is a dynamic value because at the same time when the acids are being produced, they have sufficient vapor pressure at frying temperatures to evaporate from the surface [35]. The highest change in acid value at the end of frying period was shown for sunflower oil (AV increased from  $0.13 \pm 0.04$ at the beginning of the frying experiment to  $0.69 \pm 0.06$  at the end of frying period 30 h), whereas the lowest change was observed for tiger nut oil. The AV of tiger nut oil increased from of  $0.31 \pm 0.03$  to 0.73± 0.02 during 30 hour of frying. Blending sunflower oil with different portions of tiger nut oil led to significant (P<0.05) decrease in acid values during frying periods. This decrement increased by increasing of the blending ratio of tiger nut oil. The higher oxidative stability of tiger nut oil, compared to sunflower oil is due to the high oleic acid (monounsaturated) and low polyunsaturated fatty acid content of the triacylglycerols. Hydrolysis is more preferable in oil with short and unsaturated fatty acids than oil with long and saturated fatty acids because short and unsaturated fatty acids are more soluble in water than long and saturated fatty acids. Water from foods is easily accessible to short-chain fats and oils for hydrolysis [37]. On the other hand, tiger nut oil contains high levels of phenolic compounds; these compounds have antioxidative effects and possessed anti-hydrolytic effects during frying process.

#### Changes in peroxide value (PV)

Determination of peroxide value can give an idea about the early stages of oil oxidation. (Table 2) presents the peroxide values of sunflower blended with different portions of Tiger nut oil during deep fat frying at  $(180^{\circ}C\pm5^{\circ}C)$ . The peroxide values for the fresh oils were very low which indicate the high quality of the oils used in this work. The range of peroxide values for the unfried oils was 0.96-1.32 meq.O<sub>2</sub>/kg oil. which is less than 10 meqO<sub>2</sub>/Kg, and therefore within the acceptable value range for fresh oil [34]. The peroxide values for the fried oil were progressively and significantly increased during the frying process, but not as sharply as the free acidity. Peroxides are unstable compounds particularly under high temperature conditions; therefore, the peroxides decompose to form carbonyl and aldehydic compounds causing the decrease in peroxide value [38,39]. Sunflower oil had significantly (P<0.05) the highest value of peroxide which was

Frying period (hr)	Tiger nut oil (TNO)	Sunflower oil			TNO + SO	(v/v)	
	<b>C (</b> <i>)</i>	(SO)	10: 90	20:80	30: 70	40: 60	50: 50
0	0.31° <sup>p</sup>	0.13 <sup>w</sup>	0.15 <sup>vw</sup>	0.16 <sup>uvw</sup>	0.16 <sup>uvw</sup>	0.18 <sup>uvw</sup>	0.20 <sup>uvw</sup>
	±0.03	±0.04	±0.03	±0.03	±0.01	±0.02	±0.03
5	0.40 <sup>hij</sup>	0.25 <sup>rst</sup>	0.21 uvw	0.19 <sup>uvw</sup>	0.19 <sup>uvw</sup>	0.20 uvw	0.22 <sup>t uv</sup>
	±0.04	±0.03	±0.07	±0.03	±0.04	±0.06	±0.02
10	0.54 <sup>de</sup>	0.30 <sup>opq</sup>	0.26 <sup>rst</sup>	0.24 <sup>stu</sup>	0.23 tuv	0.24 <sup>stu</sup>	0.23 tuv
	±0.03	±0.03	±0.04	±0.01	±0.06	±0.03	±0.05
15	0.62 bc	0.35 Imn	0.34 mno	0.29 pqr	0.27 <sup>qrs</sup>	0.29 pqr	0.27 <sup>qrs</sup>
	±0.06	±0.05	±0.01	±0.03	±0.04	±0.01	±0.02
20	0.69 <sup>ab</sup>	0.42 hij	0.38 <sup>jkl</sup>	0.37 klm	0.36 klm	0.34 mno	0.31 opq
	±0.02	±0.07	±0.06	±0.04	±0.03	±0.08	±0.04
25	0.70 ª	0.53 def	0.45 <sup>ghi</sup>	0.42 hij	0.40 hij	0.39 <sup>ijk</sup>	0.37 <sup>jkl</sup>
	±0.03	±0.03	±0.03	±0.03	±0.03	±0.03	±0.03
30	0.73 ª	0.69 <sup>ab</sup>	0.58 <sup>cd</sup>	0.56 <sup>cde</sup>	0.52 def	0.49 efg	0.48 <sup>fgh</sup>
	±0.03	±0.03	±0.03	±0.03	±0.03	±0.03	±0.03
ISD at 0.05 = 0.07246							

LSD at 0.05 = 0.07246

Data are expressed as mean  $\pm$  SD. Values given represent means of three determinations Values followed by the same letter are not significantly different (p<0.05)

Table1: Changes in acid values (mg KOH/g Oil) of sunflower blended with different portions of Tiger nut oil during deep fat frying at (180°C ± 5°C).

9.64 meq.O<sub>2</sub>/kg oil at the end of frying period (30 h). Unsaturated fatty acids easily react with oxygen to form peroxides [40]. Whereas, the lowest values (6.51 and 6.76 meq.O2/kg oil) were recorded for tiger nut oil and its mixture with sunflower at level 50%, respectively. These findings are in line with the degree of oil unsaturation. At the same time, these findings were expected due to the faster oxidation [41] of the polyunsaturated fatty acids of sunflower oil and the presence of high levels of natural antioxidants, vitamins E and C (Belewu and Belewu, 2007) in tiger nut oil, which act as potent antioxidants during frying process.

# Changes in thiobarbituric acid value (TBA)

The changes in the TBA values (absorbance at 532 nm) of sunflower blended with different portions of Tiger nut oil during deep fat frying at  $(180^{\circ}C \pm 5^{\circ}C)$  are shown in Table 3. An increase in the TBA values of all oil samples under study was observed with prolonging the frying time. This finding could be explained by the fact that the less stable primary oxidative compounds (i.e. hydroperoxides) decompose further to form aldehydic compounds. These carbonyl compounds react with TBA reagent to produce coloured compounds which absorb usually at 532 nm [7,42]. The highest (P<0.05) TBA value was recorded for sunflower oil (0.97 as absorbance at 532 nm) at the end of frying period. On the other hand, Tiger nut oil and its mixture with sunflower oil at level 50% (v/v) had significantly (P<0.05) the lowest values at the end of frying period were 0.55 and 0.61 as absorbance at 532 nm, respectively. This means that TBA value of tiger nut oil at the end of frying period was about 1.76 times as low as that for sunflower oil at the end of frying period. It is well known that linoleate hydroperoxides decompose faster than oleate ones. The oleate:linoleate: linolenate oxidation ratio has been reported to be in the order of 1:12:25, based on peroxide formation [43]. These facts support the results of the present study. At the same time, the presence of natural antioxidants, in tiger nut oil had inhibitory effects on the formation of these secondary oxidation products during frying process.

# Changes in iodine value (IV)

The iodine value is a measure of the unsaturation of the oils. It is one of the parameters used to measure the oil quality [44]. (Table 4) demonstrates the IV of sunflower blended with different portions of Tiger nut oil during deep fat frying at (180°C  $\pm$  5°C). The initial iodine values of tiger nut and sunflower oil were 105.80 and 123.00 g I2/100 g oil respectively. Bending sunflower oil with various levels

		Sunflower oil			TNO + SO(v/v	')	
Frying period (nr)	liger nut oli (INO)	(SO)	10: 90	20:80	30: 70	40: 60	50: 50
0	0.96 <sup>t</sup>	1.32 <sup>t</sup>	1.29 <sup>t</sup>	1.23 <sup>t</sup>	1.18 <sup>t</sup>	1.16 <sup>t</sup>	1.15 <sup>t</sup>
	±0.20	±0.15	±0.16	±0.05	±0.10	±0.18	±0.10
5	2.35 <sup>pqr</sup> ±0.17	2.33 <sup>pqr</sup> ±0.21	2.15 <sup>pqr</sup> ±0.16	2.14 <sup>pqr</sup> ±0.13	0.94 <sup>pqr</sup> ±0.22	1.88 <sup>pqr</sup> ±0.17	1.86 <sup>pqr</sup> ±0.14
10	2.00 <sup>pqr</sup>	2.00 <sup>pqr</sup>	3.86 <sup>lmn</sup>	3.75 <sup>lmn</sup>	3.52 <sup>mn</sup>	1.44 <sup>st</sup>	2.67°
	±0.09	±0.33	±0.76	±0.11	±0.09	±0.32	±0.30
15	3.45 <sup>n</sup>	4.82 <sup>fgh</sup>	4.73 <sup>ghi</sup>	2.64°	4.43 <sup>hij</sup>	4.35 <sup>ijk</sup>	2.42 <sup>opq</sup>
	±0.44	±0.22	±0.33	±0.20	±0.22	±0.30	±0.04
20	2.47° <sup>p</sup>	5.21 <sup>f</sup>	4.00 <sup>klm</sup>	4.86 <sup>fg</sup>	4.20 <sup>jkl</sup>	4.65 <sup>ghi</sup>	4.31 <sup>ijk</sup>
	±0.22	±0.41	±0.50	±0.12	±0.60	±0.05	±0.06
25	4.89 <sup>fg</sup>	8.46°	7.82 <sup>d</sup>	7.65 <sup>d</sup>	6.81°	4.50 <sup>hij</sup>	4.64 <sup>ghi</sup>
	±0.66	±0.18	±0.10	±0.40	±0.15	±0.02	±0.22
30	6.51°	9.64ª	8.98⁵	8.41°	7.63 <sup>d</sup>	7.44 <sup>d</sup>	6.76°
	±0.08	±0.13	±0.012	±0.06	±0.11	±0.14	±0.71
I SD at 0 05 = 0 4668							

Data are expressed as mean ± SD

Values given represent means of three determinations

Values followed by the same letter are not significantly different (p<0.05)

Table 2: Changes in Peroxide values (meq.O<sub>2</sub>/kg) of sunflower blended with different portions of Tiger nut oil during deep fat frying at (180°C ± 5°C).

Frying period (hr)	Tiger nut	oil Sunflower oil			TNO + SO	v/v)	
, , ,	(TNO)	(SO)	10: 90	20:80	30: 70	40: 60	50: 50
0	0.04×	0.07 <sup>vwx</sup>	0.04 <sup>wx</sup>	0.05 <sup>wx</sup>	0.05 <sup>wx</sup>	0.06 <sup>wx</sup>	0.06
	±0.01	±0.01	±0.02	±0.01	±0.01	±0.01	±0.00
5	0.11 <sup>uv</sup>	0.16 <sup>tu</sup>	0.15 <sup>tu</sup>	0.15 <sup>tu</sup>	0.14 <sup>tu</sup>	0.14 <sup>tu</sup>	0.10 <sup>vw</sup>
	±0.05	±0.04	±0.04	±0.03	±0.02	±0.01	±0.00
10	0.15 <sup>tu</sup>	0.32°	0.25 <sup>pqr</sup>	0.20 <sup>rst</sup>	0.20 <sup>rst</sup>	0.19 <sup>st</sup>	0.15 <sup>tu</sup>
	±0.06	±0.04	±0.03	±0.05	±0.02	±0.03	±0.02
15	0.21 <sup>qrs</sup>	0.53 <sup>ij</sup>	0.52 <sup>ij</sup>	0.49 <sup>jkl</sup>	0.46 <sup>klm</sup>	0.42 <sup>mn</sup>	0.26 <sup>pq</sup>
	±0.06	±0.03	±0.02	±0.04	±0.00	±0.02	±0.03
20	0.27 <sup>op</sup>	0.79 <sup>b</sup>	0.59 <sup>gh</sup>	0.55 <sup>hi</sup>	0.50 <sup>ijk</sup>	0.49 <sup>jkl</sup>	0.40 <sup>n</sup>
	±0.01	±0.02	±0.03	±0.04	±0.05	±0.05	±0.06
25	0.30 <sup>op</sup>	0.92ª	0.72°	0.71 <sup>cd</sup>	0.66 <sup>def</sup>	0.60 <sup>fg</sup>	0.44 <sup>lmn</sup>
	±0.00	±0.01	±0.03	±0.02	±0.04	±0.02	±0.00
30	0.55 <sup>hi</sup>	0.97ª	0.81⁵	0.73°	0.70 <sup>cde</sup>	0.65 <sup>ef</sup>	0.61 <sup>fg</sup>
	±0.04	±0.02	±0.01	±0.03	±0.01	±0.09	±0.01
LSD at 0.05 = 0.05124							

Data are expressed as mean ± SD. Values given represent means of three determinations

Values followed by the same letter are not significantly different (p<0.05)

Table3: Changes in thiobarbituric acid value (Absorbance at 532 nm) of sunflower blended with different portions of Tiger nut oil during deep fat frying at (180°C ± 5°C).

of tiger nut oil caused significant (P<0.05) decrease in iodine values (degree of oil unsaturation), this decrease was due to the increase in the predominance of monounsaturated fatty acids of tiger nut oil in the blended oils. Frying process induced significant (P<0.05) decrease in the IV of all oil under study. It is well known that during frying some of the non-conjugated double bonds are converted to conjugated ones. The conjugated system, in general, precludes the complete addition of iodine. This fact indicates the decrease of IV for the oils under study during frying at 180 °C  $\pm$  5 °C for 30 hour frying time. The decrease in iodine value denotes decrease in the degree of unsaturation of the oil caused by the extent of oxidation [45]. The highest decrease in IV was recorded for sunflower oil, the reduction percentage in iodine value was 8.95% at the end of frying period. On the other hand, tiger nut oil and its mixtures with sunflower oil at levels 30, 40 and 50% (v/v) had significantly the lowest reduction in iodine values which were 5.6, 7.2, 6.4 and 6.1%, at the end of frying period respectively. Autoxidation of sunflower oils affected their fatty acids composition, as polyunsaturated fatty acids were oxidized faster than saturated and mono unsaturated fatty acids [46]. The addition of tiger nut oil which contains high levels of oleic acid and natural antioxidants to sunflower oil during frying process effectively reduced the oxidation rate in sunflower oil, as detected by relatively low reduction in iodine values (Table 4).

# Changes in total polar compounds (TPC)

The level of polar compounds is a good indicator of the overall quality of frying oils, providing critical information about the total amount of newly formed compounds having higher polarity than triacylglycerols. Many European countries have established regulatory limits for TPC in frying oils (Blumenthal, 1996). Most of these countries have considered a limit of 25% TPC. (Table 5) shows the TPC of sunflower blended with different portions of Tiger nut oil during deep fat frying at (180°C ± 5°C). Fresh oils under study had a TPC content ranged from 2.4 to 2.8%, reflecting the good quality of these oils, as TPC content of unused oils normally ranges between 0.4% and 6.4% [47]. Frying process caused significant (P<0.05) and gradual increase in total polar content, this increase was linearly with frying time. Frying time increases the content of free fatty acids [48], polar compounds such as triacylglycerol dimers and oxidized triacylglycerols [49,50], dimers [51], and polymers [52]. Sunflower oil had significantly(P<0.05) the highest value of TPC was 19.40% at the end of frying period 30 hour, this value was about 8.08 times as high as that of fresh sunflower oil. The lowest value of TPC was observed for tiger nut oil and its blends with sunflower oil at levels 40 and 50% (v/v). The levels of TPC of tiger nut oil and its mixtures at levels 40 and 50 were about 1.42, 1.34 and 1.35 times as

	Tiger nut o	il Sunflower oil	TNO + SO(v/v)						
Frying period (iir)	(TNO)	(SO)	10: 90	20:80	30: 70	40: 60	50: 50		
0	105.80 <sup>wx</sup>	123.00ª	120.70 <sup>b</sup>	119.10 <sup>cd</sup>	116.50 <sup>fg</sup>	113.5 <sup>⊮</sup>	112.00 <sup>mn</sup>		
	±0.26	±0.29	±0.34	±0.09	±1.12	±0.31	±0.63		
5	105.00 <sup>xy</sup>	121.50 <sup>b</sup>	119.45 <sup>°</sup>	118.00 <sup>e</sup>	115.10 <sup>hi</sup>	112.10 <sup>mn</sup>	111.50 <sup></sup>		
	±0.10	±1.05	±0.18	±0.51	±0.38	±0.38	±0.52		
10	104.73 <sup>yz</sup>	119.55℃	117.30 <sup>ef</sup>	116.85 <sup>f</sup>	113.65 <sup>⊧≀</sup>	111.00 <sup>no</sup>	109.44 <sup>pqr</sup>		
	±0.08	±0.21	±0.05	±1.10	±0.43	±0.25	±0.12		
15	103.44 <sup>z</sup>	118.10 <sup>de</sup>	115.60 <sup>gh</sup>	115.40 <sup>jkl</sup>	112.00 <sup>mn</sup>	110.21 <sup>op</sup>	108.00 <sup>stu</sup>		
	±1.21	±0.31	±0.23	±0.08	±1.36	±0.03	±0.92		
20	102.65 <sup>z</sup>	117.22 <sup>ef</sup>	114.22 <sup>ijk</sup>	113.95 <sup>iki</sup>	110.12 <sup>opq</sup>	109.00 <sup>qs</sup>	107.15 <sup></sup>		
	±0.05	±0.35	±1.19	±0.97	±0.90	±0.05	±1.14		
25	101.23/	114.85 <sup>hij</sup>	113.10 <sup>klm</sup>	113.00 <sup>lm</sup>	109.25 <sup>pqr</sup>	107.90 <sup>tu</sup>	106.00 <sup>vwx</sup>		
	±0.38	±0.90	±0.07	±0.75	±0.75	±1.11	±1.12		
30	99.90//	111.10 <sup>no</sup>	112.75 <sup>im</sup>	112.10 <sup>mn</sup>	108.33 <sup>rst</sup>	106.30 <sup>vw</sup>	105.26 <sup>wxy</sup>		
	±0.13	±0.38	±0.43	±1.10	±0.21	±0.20	±0.30		
LSD at 0.05 =1.039									

Data are expressed as mean ± SD. Values given represent means of three determinations

Values followed by the same letter are not significantly different (p<0.05)

Table 4: Changes in iodine value (g 12/100 g oil) of sunflower blended with different portions of Tiger nut oil during deep fat frying at (180°C ± 5°C).

	Tiger nut	oil Sunflower oil			TNO +	SO(v/v)		
Frying period (hr)	(TNO)	(SO)	10: 90	20:80	30: 70	40: 60	50: 50	
0	2.80× ±0.13	2.40× ±0.15	2.40× ±0.55	2.40× ±0.35	2.50× ±0.15	2.50× ±0.35	2.50× ±0.48	
5	4.12 <sup>w</sup> ±0.21	5.55 <sup>v</sup> ±0.09	5.11 <sup>vw</sup> ±1.01	5.10 <sup>vw</sup> ±0.35	5.00 <sup>vw</sup> ±0.52	4.60 <sup>vw</sup> ±0.34	4.44 <sup>vw</sup> ±0.33	
10	6.32u ±0.34	9.34 <sup>opq</sup> ±0.20	9.20 <sup>pq</sup> ±1.05	8.63 <sup>pqr</sup> ±0.73	8.00 <sup>rst</sup> ±0.18	7.50 <sup>st</sup> ±0.36	7.31 <sup>t</sup> ±0.08	
15	8.45 <sup>qrs</sup> ±0.32	12.13 <sup>⊾</sup> ±0.22	11.00 <sup>mn</sup> ±0.28	10.22 <sup>no</sup> ±0.76	9.53 <sup>op</sup> ±0.81	9.20 <sup>pq</sup> ±0.63	9.00 <sup>pqr</sup> ±0.55	
20	12.60 <sup>ijk</sup> ±0.59	14.65 <sup>ef</sup> ±0.39	13.96 <sup>fgh</sup> ±0.69	13.55 <sup>ghi</sup> ±0.45	12.81 <sup>ijk</sup> ±0.11	12.23 <sup>jkl</sup> ±0.33	11.53 <sup>lm</sup> ±0.47	
25	13.25 <sup>hij</sup> ±0.62	16.54° ±0.59	15.45 <sup>de</sup> ±1.04	1435 <sup>fg</sup> ±0.18	14.00 <sup>fgh</sup> ±0.47	13.41 <sup>ghi</sup> ±0.64	13.21 <sup>hij</sup> ±0.34	
30	13.61 <sup>ghi</sup> ±0.72	19.40ª ±0.15	18.00⁵ ±0.76	16.92 <sup>°</sup> ±1.16	15.95 <sup>cd</sup> ±1.02	14.46 <sup>fg</sup> ±0.20	14.32 <sup>fg</sup> ±0.22	
LSD at 0.05 =0.9350	)							

Data are expressed as mean ± SD. Values given represent means of three determinations

Values followed by the same letter are not significantly different (p<0.05)

Table 5: Changes in total polar compounds (TPC) content (%w/w) of sunflower blended with different portions of Tiger nut oil during deep fat frying at (180°C ± 5°C).

#### Page 6 of 8

low as that for sunflower oil at the end of frying period, respectively. Decreasing the linolenic acid and increasing the oleic acid of canola oil produced good frying stability as measured by total polar compounds [53]. The low values of TPC in tiger nut oil and its blends may be due to the presence of high level of polyphenlic compounds in tiger nut oil as acted as an antipolymerization agent at high temperatures of frying process.

# Changes in viscosity value

In deep-fat frying process, the viscosity of the oil changes considerably with frying time and oil temperature [54]. The viscosity values of sunflower blended with different portions of Tiger nut oil during deep fat frying at ( $180^{\circ}C \pm 5^{\circ}C$ ) are shown in Table 6. Unfried oils under study had native viscosity values ranged from 45.40 to 46.10 mPa-s. Viscosity values of all oils under investigation increased (P<0.05) gradually and significantly over 30 hours of frying process. This increase has been attributed to polymerisation and the concomitant formation of high-molecular-weight compounds via carbon-to-carbon and/or carbon-to-oxygen-to-carbon bridges between fatty acids [55]. The tendency of viscosity to increase during frying of the oil has been found to correlate well with formation of polymers [56]. The fried oils

can be arranged according to their viscosity values at the end of the frying period in the following decreasing order: sunflower oil > 10% TNO+90% SFO> >20% TNO+80% SFO > 30% TNO+70% SFO > 40% TNO+60% SFO>>50%TNO+50% SFO> tiger nut oil. As already mentioned that there is a relationship between the viscosity and the degree of oil unsaturation, one would report that mixing sunflower oil with different portions of Tiger nut oil led to decrease the changes of viscosity values during frying process. It means that the highest level of tiger nut blended with oil induced the lowest change on oil viscosity. These results could be explained by the fact that polyunsaturated fatty acids tend to be rapidly oxidized and form polymer compounds [57]. At the same time, the addition of tiger nut oil with polyphenolic compounds significantly lowered the viscosity of SFO by retarding polymerization reactions during frying process.

#### Changes in colour

Colour of oil is one of the most eminent physical properties which attract the consumer appellant. In general, this property affects the colour of fried food. The instrument used for the measurement of colour in oils is the Lovibond tintometer. The colour was measured at the fixed yellow glass slide (35) and variable red glass slides. Table 7

Frying	period Tiger nut	oil Sunflower oil					
(hr)	(TNO)	(SO)	10: 90	20:80	30: 70	40: 60	50: 50
0	46.10 <sup>t</sup>	45.40 <sup>t</sup>	45.45 <sup>t</sup>	45.70 <sup>t</sup>	45.90 <sup>t</sup>	46.00 <sup>t</sup>	46.00 <sup>t</sup>
0	±0.13	±0.43	±1.13	±0.20	±0.35	±0.19	±0.10
-	48.00 <sup>t</sup>	48.70 <sup>s</sup>	48.50 <sup>s</sup>	48.50 <sup>s</sup>	48.50 <sup>s</sup>	48.00 <sup>s</sup>	48.00 <sup>s</sup>
5	±0.12	±1.27	±1.10	±0.67	±1.28	±0.76	±0.13
10	50.00 <sup>r</sup>	52.30 <sup>nop</sup>	52.00 <sup>opq</sup>	52.00 <sup>opq</sup>	51.00 <sup>qr</sup>	51.00 <sup>qr</sup>	51.10 <sup>pqr</sup>
10	±0.22	±0.46	±0.28	±0.36	±1.25	±0.72	±0.12
45	52.00 <sup>opq</sup>	53.50°	53.50°	53.00 <sup>no</sup>	53.00 <sup>no</sup>	52.70 <sup>no</sup>	52.50 <sup>no</sup>
15	±0.32	±0.28	±0.25	±0.38	±0.13	±0.80	±0.22
20	56.60 <sup>Im</sup>	57.70 <sup>jkl</sup>	56.20 <sup>m</sup>	57.00 <sup>klm</sup>	57.00 <sup>klm</sup>	58.00 <sup>ijk</sup>	57.00 <sup>klm</sup>
20	±1.10	±0.30	±0.25	±0.26	±0.66	±0.57	±0.33
25	58.75 <sup>hij</sup>	65.35 <sup>b</sup>	62.60 <sup>d</sup>	62.00 <sup>de</sup>	61.00 <sup>ef</sup>	59.50 <sup>gh</sup>	59.00 <sup>ghi</sup>
20	±0.94	±0.18	±0.36	±0.24	±0.21	±0.34	±1.10
20	59.00 <sup>ghi</sup>	70.50ª	65.00 <sup>bc</sup>	64.00°	62.50 <sup>d</sup>	61.00 <sup>ef</sup>	60.10 <sup>fg</sup>
30	±1.13	±1.16	±0.36	±0.23	±1.10	±1.41	±0.90
LSD at 0	05 =1 091						

Data are expressed as mean ± SD. Values given represent means of three determinations

Table 6: Changes in Viscosity (mPa-s at 30°C) of sunflower blended with different portions of Tiger nut oil during deep fat frying at (180°C ± 5°C).

Frying	period Tiger nut oil (TNO)	Sunflower oil					
(hr)		(SO)	10: 90	20:80	30: 70	40: 60	50: 50
0	4.00 <sup>q</sup>	2.50 <sup>r</sup>	2.50 <sup>r</sup>	2.60 <sup>r</sup>	2.80 <sup>r</sup>	2.90 <sup>r</sup>	3.00 <sup>r</sup>
	±0.38	±0.25	±0.50	±0.30	±0.40	±0.35	±0.25
5	7.01°	6.50 <sup>op</sup>	6.50 <sup>op</sup>	6.00 <sup>p</sup>	6.50 <sup>op</sup>	6.50°°	6.00 <sup>p</sup>
	±0.42	±0.50	±0.25	±0.35	±0.20	±0.50	±0.00
10	8.50 <sup>n</sup>	10.00 <sup>i</sup>	10.00 <sup>1</sup>	10.52 <sup>⊮</sup>	10.00 <sup>i</sup>	9.33 <sup>m</sup>	9.00 <sup>mn</sup>
	±0.50	±0.80	±0.35	±0.25	±0.25	±0.40	±0.25
15	10.50 <sup>ki</sup>	13.00 <sup>hi</sup>	13.00 <sup>hi</sup>	12.50 <sup>i</sup>	11.50 <sup>j</sup>	11.00 <sup>jk</sup>	10.50 <sup>kl</sup>
	±0.50	±0.45	±0.30	±0.50	±0.50	±0.00	±0.50
20	12.50 <sup>i</sup>	16.00 <sup>bc</sup>	14.00 <sup>fg</sup>	13.50 <sup>gh</sup>	14.00 <sup>fg</sup>	13.00 <sup>hi</sup>	12.50 <sup>i</sup>
	±0.36	±0.40	±0.30	±0.50	±0.50	±0.25	±0.40
25	13.00 <sup>hi</sup>	16.50 <sup>ab</sup>	15.50 <sup>cd</sup>	15.50 <sup>cd</sup>	15.00 <sup>de</sup>	14.50 <sup>ef</sup>	14.00 <sup>ef</sup>
	±0.59	±0.60	±0.40	±0.40	±0.25	±0.50	±0.30
30	14.50 <sup>ef</sup>	17.00ª	16.50 <sup>ab</sup>	16.00 <sup>bc</sup>	15.50 <sup>cd</sup>	15.00 <sup>de</sup>	14.50 <sup>ef</sup>
	±0.40	±0.35	±0.00	±0.50	±0.10	±0.50	±0.45
I SD at (	0.05 = 0.6149						

Data are expressed as mean  $\pm$  SD. Values given represent means of three determinations Values followed by the same letter are not significantly different (p<0.05)

Table 7: Changes in colour (Red slide) value of sunflower blended with different portions of Tiger nut oil during deep fat frying at (180°C ± 5°C).

Values followed by the same letter are not significantly different (p<0.05)

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shows the changes of colour values of sunflower blended with different portions of Tiger nut oil during deep fat frying at ( $180^{\circ}C \pm 5^{\circ}C$ ). Fresh sunflower oil had a lighter colour of 2.50. However, tiger nut oil had significantly the darker value which was 4.00. The dark color of tiger nut oil was attributed to high levels of pigments, polyphenolic compounds and carotenoids that were extracted into the oil. Blending sunflower oil with tiger nut oil caused significant decrease in the darkening value of the blended oils due to the dilution effect. Frying caused gradual and significant (P  $\leq$  0.05) increase of colour value in all oils under investigation. The intensity of red glasses increased by prolonging the frying period. Darkening of the oil during deep-fat frying is due to the polymer formation of unsaturated carbonyl compounds and non-polar compounds of foodstuff solubilized in the oil and [58,59,7]. Although tiger nut oil started with the highest colour value, the lowest values of colour were observed for tiger nut oil and its blends with sunflower oil at levels 40 and 50% were about 1.21, 1.17 and 1.13 time as low as that for sunflower oil at the end of frying period, respectively. These findings may be attributed to the presence of high level of polyphenlic compounds in tiger nut oil. Cold pressed marionberry, boysenberry, raspberry, blueberry, black caraway, black currant, carrot, cranberry and hemp seed oils have been reported to contain antioxidants and possess a remarkable radical scavenging activity and oxygen radical absorption capacity, when tested with the DPPH (1,1-diphenyl-2picrylhydrazyl) and ABTS cation {2,20-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt} radical-scavenging assays or the oxygen radical absorption capacity (ORAC) assay (60, Parry et al., 2005). The nature of the antioxidants is not yet known, but due to the mode of preparation these oils retain phenols present in the seed and they may have the potential for applications in the promotion of health and prevention against oxidation damages mediated by radicals.

# Conclusion

In conclusion, our study shows that tiger nut oil had higher level of total polyphenols which was 16.5 mg GAE per 100 g of oil compared to sunflower oil 5.0 mg GAE per 100 g of oil. At the same time, blending sunflower oil with various portions of tiger nut oil as a source of phenolic compounds and MUFA was suggested for improving the quality and the stability of sunflower oil during frying process. Our findings indicate that the changes of physicochemical parameters were controlled and significantly (P<0.05) decreased when tiger nut / sunflower oil (W/W) proportions were varied between 20/80 to 50/50. These blended oils had better stability against oxidation during deep fat frying process.

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Page 8 of 8