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INFLUENCE OF PHENOLIC ANTIOXIDANTS ON CHANGES IN QUALITY CHARACTERISTICS OF *PALM OLEIN* DURING INTERMITTENT FRYING OF POTATO CHIPS

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A B S T R A C T

Consumption of deep fried foods is continuously increasing because they are easily and quickly prepared, relatively cheap, with typical appealing flavor, golden brown color and have a crispy texture. In common practice, mostly the frying process is conducted again and again in the same oil. So this repeatedly heating of the same oil at high temperatures causes several deteriorative reactions such as oxidation, polymerization and thermal degradation. Among them oxidation is one of the major problems that affect the edible oils. The use of antioxidants is one of the easiest and cheapest method which my address this issue, especially in developing countries. In this study effectiveness of four different types of phenolic antioxidants such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), tertiary butylhydroquinone (TBHQ) and vitamin E (tocopherol) against the changes in quality characteristics of palm olein during deep-fat frying (at 180 °C) of potato chips (for seven consecutive days) was compared at their five different concentrations i.e. 40 ppm, 80 ppm, 120 ppm, 160 ppm and 200 ppm and also with control. Potato chips were fried in palm olein containing different levels of these phenolic antioxidants. Fried oil samples were analyzed for three parameters such as peroxide value (POV), free fatty acid (FFA) contents and iodine value (IV). In general, BHA showed lowest rate of increase in POV and FFA at each concentration and day compared to control and three other antioxidants. The mean value of POV for BHA, TBHQ, BHT, Vit E and Control was 8.7144, 8.9924, 9.3094, 9.5964 and 9.8671 meq/kg respectively. Similarly, mean values of FFA for BHA, BHT, TBHQ, Vit E and Control were 0.1454, 0.1861, 0.1992, 0.2700 and 0.2998 % respectively. While in case of IV, BHA showed lowest rate of decrease in IV at each concentration and day compared to control and other three antioxidants. The mean value of IV for BHA, TBHQ, BHT, Vit E and Control was 50.154, 49.664, 49.615, 49.615 and 48.321 g/100g respectively. The sequence of effectiveness of antioxidants against oxidative deteriorations in palm olein during intermittent frying of potato chips at each concentration (40 ppm, 80 ppm, 120 ppm,160 ppm and 200 ppm) and day (day 1st to 7th) was BHA >TBHQ >BHT >Vit E >Control. Overall, BHA showed highest protection against oxidation at each concentration and day as compared to rest of the antioxidants, after BHA, TBHQ was most effective against the rate of oxidation at each level of concentration and day then rest two antioxidants, after TBHQ, BHT was on third position when compared to other antioxidants while Vit E was least effective antioxidant against the oxidation of oil. From the results of this research it can be concluded that BHA with the concentration level ranging from 160 ppm to 200 ppm could be used to improve the oxidative stability of palm olein during deep fat frying, due to its low cost, easy availability and high performance.

Keywords: Deep fat frying; BHA; BHT; Phenolic antioxidants; TBHQ; palm olein

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INTRODUCTION

Deep frying is one of the very popular cooking methods used almost in every kitchen, restaurant and food industry and is gaining more and more popularity among the people of all age groups due to the distinct taste, crispy texture, pleasant aroma, attractive flavour and appealing colour of fried products (Ganesan, 2020). In developing countries, to make the frying process cost effective mostly the process of

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frying is conducted again and again in the same oil at very high temperature under uncontrolled conditions of atmospheric air and moisture, regardless of its physical and chemical changes. This repeated frying cause's different chemical deteriorative reactions such as oxidation, polymerization, hydrolysis, isomerization and thermal degradation (Liu, 2023). These deteriorative reactions result in the generation of FFA, aldehyde, acids, lactone & hydrocarbon, small molecular alcohol, diglyceride, and monoglyceride (Pandohee, 2023), cyclic and epoxy compounds, trans isomers, TGA monomers, dimmers, oligomers etc. which also react, interact and impact upon each other. Consequently the phenomena of off-flavor, foaming, color deepening and increase in viscosity would appear in frying oil (Kmiecik, 2011).

Oxidation is the principal reaction which is responsible for the major deterioration of fats and oils (Uluata, 2015). It causes significant deteriorative changes in chemical, sensory and nutritional properties of repeated fried oils (Yılmaz, 2023). Highly oxidized oils & fats may result in several diseases such as cardiovascular disease, inflammation, diabetes, cancer, mutagenesis, neurological disorders and stroke etc. To avoid oxidative degradation and possible health risks the use of permitted antioxidants is one of the easiest and cheapest method which my address this issue in developing countries (Xu, 2021).

Oxidative deterioration is a large economic concern in the food industry because it affects many quality parameters such as flavour (rancidity), colour, texture, and the nutritive value of foods (Amit, 2017). In addition, it produces potentially toxic compounds. Lipid oxidation is important to food manufacturers especially when they increase unsaturated lipids in their products to improve nutritional profiles (Roby, 2017). Thus lipid oxidation is one of the major processes that limit the shelf life of foods (Kaleem et al., 2015). By retarding oxidation of lipids not only raw material waste and nutritional loss could be reduced but the range of lipids which can be used in different items can be increased and the shelf life of products can also be extended (Budilarto and Kamal-Eldin, 2015). Hence by controlling the oxidation of lipids, more available, cheap in cost and more nutritional and favorable oils could be used by food processors for different products formulation (Kaleem et al., 2015).

Since food habits worldwide are generally based on deep fried foods, oxidative-resistant (resistance to oxidation of lipids) oils are desired and demanded (Mohamed, 2017). One of the available options to fulfill this need by enhancing frying stability and inhibiting the development of such changes occur due to thermal degradation of oils and fats, include the use of antioxidants (Machado, 2023). Antioxidants have largely been viewed as tools in the fight against oxidation they act as "free radical scavengers" and thereby prevent damage done by these free radicals. The addition of antioxidants to oils help to preserve constituents of oil by preventing oxidation (Mittu, 2023) and hence effectively increase the shelf liande of oils & foods fried in these oils (Aluyor and Jesu, 2008). Antioxidants prevent such changes by retarding or slowing down the process of oxidation or rancidity (Machado, 2023). Numerous experimental works have established the positive effect of anti-oxidants on the oxidative stability of vegetable oils for both edible uses and industrial uses (Patil, 2013).

In the food industry, both natural and synthetic antioxidants are used (Wong, 2019). Generally due to their low cost, easy availability and high performance synthetic antioxidants are widely used in food industry as compared to natural antioxidants. Butylated hydroxytoluene (BHT), Tertiary butyl hydroquinone (TBHQ) and Butylated hydroxyanisole (BHA) are the commonly used synthetic antioxidants, to prevent rancidification in edible vegetable oils. (Kim et al., 2010). Phenolic antioxidants may prevent the oxidation of frying oils and improve the performance of deep-fat frying practice. Specifically, they reduce the formation of total polar compounds, 4-hydroxynonenal, trans fatty acids, sterol oxidation products (Machado, 2023) and acrylamide.

Just like palm oil, palm olein is also widely used for deep fat frying of food products both at domestic and industrial level as well. Palm olein is a good alternative to palm oil in frying operations (Ling, 2022), however more research is required to evaluate its suitability in frying operation with respect to oxidative stability for producing safe and wholesome fried products during deep frying process (Xu, 2021). In the present study effectiveness of different types of phenolic antioxidants such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), tertiary butylhydroquinone (TBHQ) and vitamin E (tocopherol) against the changes in quality characteristics of palm olein are compared at their five different levels i.e. 40 ppm, 80 ppm, 120 ppm, 160 ppm and 200 ppm.

The objective of the study was to assess the frying performance and qualitative stability of palm olein treated with different permitted levels of phenolic antioxidants by evaluating the changes in different parameters of palm olein, occurred during intermittent deep-fat frying of potato chips and also to compare the effectiveness of those antioxidants.

MATERIALS AND METHODS

This research was conducted at Punjab Oil Mills Islamabad in industrial conditions, while some of the tests were performed in the Department of Food Technology, PMAS-UAAR Pakistan. Palm olein, BHT, BHA, TBHQ and Vit E (Tocopherols) from synthetic source were obtained from Punjab Oil Mills Islamabad. Potatoes were purchased from a local supermarket.

Fresh potatoes were peeled and sliced to a thickness of 2 mm using an electric slicer (Presto 02970) just before every frying operation. Sliced samples were kept submerged in distilled water at room temperature for a few minutes until the oil reached to its optimum temperature for frying (180 ^{0}C). They were then slightly dried with tissue paper before weighing into 120 g batch for frying.

Frying experiments

Frying experiments were performed in five different systems that consist of the following treatments in each system: Palm olein without antioxidant or control (System I); Palm olein with 40 ppm, 80 ppm, 120 ppm, 160 ppm and 200 ppm of BHA respectively (System II); Palm olein with 40 ppm, 80 ppm, 120 ppm, 160 ppm and 200 ppm of BHT respectively (System III); Palm olein with 40 ppm, 80 ppm, 120 ppm, 160 ppm and 200 ppm of TBHQ respectively (System IV) and Palm olein with 40 ppm, 80 ppm, 120 ppm, 160 ppm and 200 ppm of Vit E respectively (System V). All these five systems i.e. 21 treatments were heated for the frying of potato chips for seven consecutive days (3.5 hours per day).

Palm olein (3 Litter) was used in separate batch fryers for each treatment. The temperature was brought up to 60°C, followed by addition and mixing of 40 ppm, 80 ppm, 120 ppm, 160 ppm and 200 ppm of BHA, BHT, TBHQ and Vit E and coded the samples as were added in systems II, III, IV, and V respectively. After the addition of five different concentrations of all these four types of antioxidants the oil was stirred for next 10 minutes to properly dissolve the antioxidants in oil. In case of system I (control), the oil was also held for 10 min at 60 °C, although no antioxidant was added. The temperature was then raised to 180 °C during next 20 minutes. Frying process was started when the temperature of all treatments reached to the specified temperature of 180 °C. Five batches of 120 g raw potato chips were fried for 2.5 minutes at approximately 30 minutes intervals for a frying period of 3.5 hours per day for seven consecutive days for each treated system. During the process of frying, the fryer was kept uncovered to mimic the commercial conditions. At the end of the fifth frying, the heat source was turned off and the oil was allowed to cool down up to the temperature of 60 °C. Oil samples (250 ml at 60 °C) were collected in bottles for further analyses (FFA, POV, IV) and were stored under uniform conditions. The fryers were covered with lid and the oil was allowed to cool overnight. All frying processes were repeated for the whole week (Seven days) with same oil for each system. Fresh oil was not added to the frying vessel. Analysis of oil for the specified parameters was carried out on the same day after the completion of frying experiments.

Analyses of oils

Oil samples collected on daily basis were analyzed for peroxide value, iodine value and free fatty acid contents. The peroxide value (POV) of oil, expressed in meq of the active oxygen per kg of oil (meq/kg) was determined using AOAC official method 965.33. Iodine value (IV) was determined using AOAC official method 920.158 while free fatty acid (FFA) content, expressed in percentage was determined using AOAC official method 940.28 (AOAC, 1990).

Statistical analysis

Data obtained through results was subjected to statistical analysis by calculating means and using three way analysis of variance techniques. Comparison of mean values was carried out by applying LSD method using Statistix 8.1 software.

RESULTS AND DISCUSSION

Characteristics of fresh palm olein used in frying experiments

In Table 1 the initial characteristics of Palm olein used in this study are presented. Initial values of all parameters showed that before frying the quality of palm olein was very good and within the standards.

Changes in quality characteristics of palm olein during repeated deep fat frying

Effectiveness of all antioxidants (BHA, TBHQ, BHT and Vitamin E) during deep-fat frying of potato chips (for seven consecutive days) is compared at their five different levels (40 ppm, 80 ppm, 120 ppm, 160 ppm and 200 ppm) and also with control. Results obtained for each parameter are presented in Tables 2-4. Three major parameters were used to determine the extent of deterioration i.e. POV, IV and FFA. Based on the results of these three parameters, it was found that overall, BHA showed highest protection against oxidative deteriorations at each day and each concentration as compared to rest of the antioxidants, after BHA, TBHQ was most effective against deterioration at each level of concentration and day then rest two antioxidants, after TBHQ, BHT was on third position when compared to other antioxidants while Vit E was least effective antioxidant against the deteriorative changes caused by oxidation.

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Table 1. Characteristics of fresh palm olein before frying experiments[a].

Characteristics of the oil	Value[b]
Peroxide value (meq hydroperoxide/kg oil)	3.0± 0.06
Iodine value (g of I_2/100 g oil)	56± 0.20
FFA content (%)	0.04± 0.02
Refractive Index	1.465± 0.00
Color L* (Lightness)	46± 0.04
a* (Redness)	2.5± 0.02
b* (Yellowness)	2.5± 0.05
Saponification value (mg KOH/g oil)	192± 0.23
Cloud point (⁰C)	10± 0.04
Melting Point (⁰C)	24± 0.05
Specific Gravity	0.8968 ±0.03

[a]FFA, free fatty acid; Color, CIE L*a*b* System

[b]Each value is the mean of three analyses of one sample.

While in control system maximum deterioration was observed as compared to the rest four systems in which antioxidants were used.

Changes in peroxide value (POV)

Results showed highly significant ($P<0.01$) effect of all three factors (antioxidants, concentrations and frying days) over peroxide value (POV) of palm olein (Table 2). The POV of fresh palm olein (before frying) was 3.0 meq/kg which increased significantly during frying process. It was noted that as the concentration of antioxidants increased from 40 ppm to 200 ppm the rate of oxidation/increase in POV was decreased with the increase in concentration of antioxidants for each treatment. In systems II, III, IV and V (in which antioxidants were used), means of POV were maximum at 40 ppm while minimum at 200 ppm concentration, showing higher rate of oxidation at 40 ppm and relatively less oxidation at 200 ppm. Similarly, in case of frying days it is noted that the POV of palm olein significantly increased with each increasing day (due to increase in oxidation) for all antioxidants and as well for control. Mean value of POV for 1st day of frying was 3.708 meq/kg, which was increased day by day, and reached to its maximum value at 7th day of frying i.e. 14.484 meq/kg. This increase in POV was maximum in control followed by Vit E, BHT, TBHQ and BHA i.e. their mean values were 9.8671, 9.5964, 9.3094, 8.9924 and 8.7144 meq/kg respectively. These findings are in resemblance with the work of Bangash & Khattak., (2006); they used *Silybum marianum* oil and sunflower oil for repeated deep fat frying of potato chips for five consecutive days at 180 ^{o}C, and showed a significant increase in POV with the increase in number of frying days. Similarly work done by Kaleem, 2015 and Ahmed et al., (Kaleem, 2015; Ahmed, 2012) also showed that the process of frying resulted in a significant increase in peroxide value. Results (Table 2) depicted that increased concentration of antioxidant is highly effective against the POV increase, while increase in frying days have significant effect in increasing the POV. Hence it can be concluded that as per concentration of antioxidants is concerned; higher the concentration of antioxidant is used lower will be the POV (Higher will be the oxidative stability) and as the number of days/fryings increases the rate of oxidation and hence value of POV increases gradually.

Overall, lowest POV was observed at 1st day of frying with 200 ppm of BHA i.e. 3.213 meq/kg, while highest POV was noted at 7th day of frying with control system (i.e. 15.959) followed by at 40 ppm of TBHQ i.e. 15.600 meq/kg. This increase in POV with increase in days was maximum for control as compare to other systems in which antioxidants were used. The mean value of POV for BHA, TBHQ, BHT, Vit E and Control was 8.7144, 8.9924, 9.3094, 9.5964 and 9.8671 meq/kg respectively. On the whole, BHA showed highest protection against oxidative deteriorations at each day and each concentration as compared to rest of the antioxidants, after BHA, TBHQ was most effective against deterioration at each level of concentration and day then rest two antioxidants, after TBHQ, BHT was on third position when compared to other antioxidants while Vit E was least effective antioxidant against the deteriorative changes caused by oxidation. While in control system maximum deterioration was observed (due to absence of antioxidants) as compared to the rest four systems in which antioxidants were used.

Table 2. Mean values of POV (meq/kg) for Treatments*Concentration* Days[a].

Treatments	Conc.	Days							Mean (Conc.)	Mean (Treatments)
		D1	D2	D3	D4	D5	D6	D7		
Control	0 ppm	3.810 wx	5.912 lm	7.961 cd	9.896 T	11.843 N-P	13.689 HI	15.959 A	9.8671 A	9.8671 A
	40 ppm	3.510 x-z	5.410 o-q	7.810 de	9.350 VW	11.496 O-Q	13.502 IJ	14.567 E-G	9.3778 D	
	80 ppm	3.513 x-z	5.362 pq	7.283 g-i	9.508 UV	10.522 RS	12.467 LM	14.663 DE	9.0454 F	
BHA	120 ppm	3.407 yz	5.881 m	6.961 i-k	8.516 Z-b	10.737 R	11.897 N	13.521 IJ	8.7027 H	8.7144 E
	160 ppm	3.310 yz	4.952 rs	6.810 k	8.350 ab	9.593 T-V	11.817 NO	13.220 J	8.2930 J	
	200 ppm	3.213 z	4.823 st	6.927 jk	8.233 bc	9.648 T-V	11.577 N-Q	12.648 K-M	8.1528 K	
	40 ppm	3.510 x-z	5.451 n-p	7.332 f-h	9.567 T-V	11.491 PQ	13.679 HI	15.600 A	9.5186 BC	
	80 ppm	3.507 x-z	5.851 m	7.317 gh	9.836 T	10.733 R	12.817 K	14.348 E-G	9.2012 E	
TBHQ	120 ppm	3.413 yz	5.210 p-r	7.510 e-g	8.8 YZ	10.607 RS	12.715 K-M	14.251 G	8.9296 FG	8.9924 D
	160 ppm	3.410 yz	5.142 p-s	6.891 jk	8.800 YZ	10.839 R	12.767 KL	13.870 H	8.8170 GH	
	200 ppm	3.310 yz	5.110 q-s	6.910 jk	8.577 Za	10.374 S	11.497 O-Q	13.689 HI	8.4953 I	
	40 ppm	3.613 xy	5.291 pq	7.181 h-j	9.135 WX	11.743 N-P	13.646 HI	15.550 A	9.4512 CD	
	80 ppm	4.520 tu	6.231 l	7.961 cd	9.663 T-V	11.593 N-P	13.600 HI	14.917 CD	9.7836 A	
BHT	120 ppm	4.167 v	5.771 mn	7.591 e-g	9.390 VW	11.739 N-P	12.432 M	14.622 D-F	9.3873 D	9.3094 C
	160 ppm	3.830 wx	5.252 p-r	7.310 gh	8.950 XY	10.677 RS	12.501 K-M	14.311 FG	8.9759 F	
	200 ppm	3.510 x-z	5.252 p-r	7.643 d-f	8.829 X-Z	10.563 RS	12.413 M	14.433 E-G	8.9491 F	
	40 ppm	4.133 vw	5.912 lm	7.821 de	9.786 TU	11.581 N-P	13.617 HI	15.433 A	9.7548 A	
	80 ppm	4.133 vw	5.881 m	7.783 de	9.786 TU	11.667 N-P	13.589 HI	15.347 AB	9.7408 A	
Vit E	120 ppm	3.810 wx	5.691 m-o	7.582 e-g	9.470 UV	11.517 O-Q	13.510 IJ	15.091 BC	9.5244 BC	9.5964 B
	160 ppm	4.133 vw	5.811 m	7.682 de	9.480 UV	11.493 O-Q	13.510 IJ	14.923 CD	9.5760 B	
	200 ppm	4.200 uv	5.782 m	7.693 de	9.541 T-V	11.255 Q	12.560 K-M	14.672 DE	9.3861 D	
Mean (Days)		3.708 G	5.503 F	7.400 E	9.178 D	10.933C	12.806 B	14.484 A		

$LSD_{0.05}$ (Antioxidant*Concentration*Days) = 0.32

[a]Means within each row with different superscripts are significantly (*P* < 0.05) different. Means within each column with different subscripts are significantly (*P* < 0.05) different. BHA, butylated hydroxyanisole; BHT, butylated hydroxytoluene; TBHQ, tertiary butylhydroquinone; Vitamin E, tocopherol

Changes in Iodine Value (IV)

Results showed non-significant (P>0.05) effect of all three factors (antioxidants, concentrations and frying days) over Iodine Value (IV) of palm olein (Table 3). The IV of fresh palm olein (before frying) was 56 g/100g, which decreased non-significantly during frying process according to the extent of oxidation. It was noted that as the concentration of antioxidants increased from 40 ppm to 200 ppm the rate of oxidation of unsaturated fatty acids was reduced (in the presence of antioxidants) and hence decrease in iodine value was also reduced. Similarly, in case of frying days it is noted that the IV of palm olein significantly decreased with each increasing day, due to increase in oxidation of unsaturated fatty acids with each increasing day. Mean value of IV for 1st day of frying was 56.0 g/100g, which was decreased day by day, and reached to its minimum value at 7th day of frying i.e. 42.325 g/100g. This decrease in IV was highest in control followed by Vit E, BHT, TBHQ and BHA i.e. 48.321, 49.615, 49.615, 49.664 and 50.154g/100g respectively.

Table 3. Mean values of IV (g/100g) for Treatments*Concentration* Days [a].

Treatments	Conc.	Days							Mean (Conc.)	Mean (Treatments)
		D1	D2	D3	D4	D5	D6	D7		
Control	0 ppm	56.0 a	52.133 de	50.12 ef	49.0 gh	47.0 ij	43.0 mn	41.0 pq	48.321 C	48.321 E
BHA	40 ppm	56.0 a	54.0 bc	51.0 ef	49.0 gh	47.0 ij	44.0 lm	41.0 pq	48.857 G	50.154 A
	80 ppm	56.0 a	54.0 bc	52.133 de	50.0 fg	48.0 hi	45.0 kl	42.0 n-p	49.590 EF	
	120 ppm	56.0 a	54.0 bc	52.133 de	51.0 ef	48.0 hi	46.0 jk	43.0 mn	50.019 C-E	
	160 ppm	56.0 a	54.0 bc	53.0 cd	51.0 ef	49.0 gh	47.0 ij	45.0 kl	50.714 B	
	200 ppm	56.0 a	55.0 ab	54.0 bc	52.133 de	50.0 fg	48.0 hi	46.0 jk	51.590 A	
TBHQ	40 ppm	56.0 a	54.0 bc	51.0 ef	49.0 gh	48.0 hi	44.0 lm	41.0 pq	49.0 G	49.664 B
	80 ppm	56.0 a	54.0 bc	52.133 de	54.0 bc	48.0 hi	45.0 kl	41.500 op	49.519 F	
	120 ppm	56.0 a	54.0 bc	52.133 de	50.0 fg	48.0 hi	45.0 kl	42.333 no	49.638 D-F	
	160 ppm	56.0 a	52.133 de	52.133 de	50.0 fg	48.0 hi	45.0 kl	43.0 mn	49.733 D-F	
	200 ppm	56.0 a	54.0 bc	53.0 cd	51.0 ef	49.0 gh	46.0 jk	44.0 lm	50.429 BC	
BHT	40 ppm	56.0 a	54.0 bc	51.0 ef	49.0 gh	47.0 ij	43.0 mn	41.0 pq	48.714 G	49.615 B
	80 ppm	56.0 a	54.0 bc	52.133 de	49.0 gh	47.0 ij	43.0 mn	41.0 pq	48.876 G	
	120 ppm	56.0 a	54.0 bc	52.133 de	50.0 fg	48.0 hi	45.0 kl	42.333 no	49.638 D-F	
	160 ppm	56.0 a	54.0 bc	52.133 de	50.0 fg	48.0 hi	45.0 kl	42.333 no	49.638 D-F	
	200 ppm	56.0 a	54.0 bc	52.133 de	51.0 ef	48.0 hi	46.0 jk	43.0 mn	50.019 C-E	
Vit E	40 ppm	56.0 a	54.0 bc	51.0 ef	50.0 fg	48.0 hi	44.0 lm	41.0 q	49.0 G	49.615 B
	80 ppm	56.0 a	54.0 bc	52.133 de	51.0 ef	49.0 gh	45.0 kl	41.0 pq	49.733 D-F	
	120 ppm	56.0 a	54.0 bc	52.133 de	50.0 fg	48.0 hi	45.0 kl	42.333 no	49.638 D-F	
	160 ppm	56.0 a	54.0 bc	52.133 de	50.0 fg	48.0 hi	45.0 kl	42.333 no	49.638 D-F	
	200 ppm	56.0 a	54.0 bc	52.133 de	51.0 ef	48.0 hi	47.0 ij	42.333 no	50.067 CD	
Mean (Days)		56.0 A	54.050 B	52.087 C	50.207 D	48.100 E	45.150 F	42.325 G		

$LSD_{0.05}$ (Antioxidant*Concentration*Days) = 1.2071

[a]Means within each row with different superscripts are significantly (*P* < 0.05) different. Means within each column with different subscripts are significantly (*P* < 0.05) different. BHA, butylated hydroxyanisole; BHT, butylated hydroxytoluene; TBHQ, tertiary butylhydroquinone; Vitamin E, tocopherol

The results of this study are similar to the findings of Bangash & Khattak., (2006) showing a significant decrease in IV with the increase in number of frying days in *Silybum marianum* oil and sunflower oil during repeated deep fat frying of potato chips for five consecutive days at 180 ^{0}C. Actually increased number of fryings and time reduces the degree of un-saturation of repeated frying oil and hence IV of repeated frying oil also reduced (Bangash, 2006). Kaleem et al., (2015) used 20 different oils purchased from the local market of Lahore (Pakistan) and find a decrease in degree of unsaturation in all oil samples. Similarly work done by Ahmed et al., (2012) also showed that the process of frying resulted in a significant decrease in number of double bonds due to the process of oxidation of fried oils.

The statistical analysis (Table 3) indicated that increased concentration of antioxidants is highly significant against the IV decrease, while increase in frying days have significant effect in decreasing the IV. Hence it can be concluded that as per concentration of antioxidants is concerned; higher the concentration of antioxidant is used higher will be the IV and lower will be the rate of oxidative deterioration and as the number of days/fryings increases the rate of oxidation also increases and hence value of IV decreases gradually. The results of this study are similar to the findings of Bangash & Khattak., (2006) showing a significant decrease in IV with the increase in number of frying days in *Silybum marianum* oil and sunflower oil during repeated deep fat frying of potato chips for five consecutive days at 180 ^{0}C. Actually increased number of fryings and time reduces the degree of un-saturation of repeated frying oil and hence IV of repeated frying oil also reduced (Bangash, 2006). Kaleem et al., (2015) used 20 different oils purchased from the local market of Lahore (Pakistan) and find a decrease in degree of unsaturation in all oil samples. Similarly work done by Ahmed et al. (2012) also showed that the process of frying resulted in a significant decrease in number of double bonds due to the process of oxidation of fried oils. The statistical analysis (Table 3) indicated that increased concentration of antioxidants is highly significant against the IV decrease, while increase in frying days have significant effect in decreasing the IV. Hence it can be concluded that as per concentration of antioxidants is concerned; higher the concentration of antioxidant is used higher will be the IV and lower will be the rate of oxidative deterioration and as the number of days/fryings increases the rate of oxidation also increases and hence value of IV decreases gradually.

Overall, highest IV was observed at 1st day of frying with 200 ppm of BHA i.e. 56.0 g/100g, while lowest IV was noted at 7th day of frying with 40 ppm of all treatments i.e. 41.0 g/100g. This decrease in IV with increase in days was maximum for control as compare to other systems in which antioxidants were used. The mean value of IV for BHA, TBHQ, BHT, Vit E and Control was 50.154, 49.664, 49.615, 49.615 and 48.321 g/100g respectively. On the whole, BHA showed highest protection against oxidative deterioration at each concentration and day as compared to rest of the antioxidants, after BHA, TBHQ was most effective against the rate of oxidative deterioration at each level of concentration and day then rest two antioxidants, after TBHQ, BHT was on third position when compared to other antioxidants while Vit E was least effective antioxidant against the deteriorative changes caused by oxidation. While in control system maximum deterioration was observed (due to absence of antioxidants) as compared to the rest four systems in which antioxidants were used.

Changes in Free Fatty Acids (FFA) content

Results showed that all these factors (antioxidants, concentrations and frying days) have highly significant ($P<0.01$) effect over FFA of palm olein (Table 4). The FFA of fresh palm olein (before frying) was 0.04 %. Oxidation of oils causes an increase in FFA of oils, in this research FFA was also increased according to the extent of oxidation. It was noted that as the concentration of antioxidants increased from 40 ppm to 200 ppm the rate of FFA (i.e. rate of oxidation) was decreased with increase in concentration of antioxidants, for each system. In these systems, values of FFA were maximum at 40 ppm while minimum at 200 ppm concentration, showing higher rate of oxidation at 40 ppm and relatively less oxidation at 200 ppm. Similarly, in case of frying days, it is noted that the FFA of palm olein significantly increased with each increasing day (due to increase in oxidation) for all antioxidants and as well for control. Mean value of FFA for 1st day of frying was 0.0652 %, which was increased day by day, and reached to its maximum value at 7th day of frying i.e. 0.3477 %. This increase in FFA was maximum in control followed by Vit E, TBHQ, BHT and BHA i.e. 0.2998, 0.2700, 0.1992, 0.1861 and 0.1454 respectively. Findings of this study are similar to the findings of various other researchers (Ahmed, 2012). Bangash & Khattak used *Silybum marianum* oil and sunflower oil for repeated deep fat frying of potato chips for five consecutive days and showed a significant increase in FFA with the increase in number of frying days (Bangash, 2006). Kaleem et al., used 20 different oils and find an increasing trend in the value of FFA for all oil samples during the process of frying (Kaleem, 2015). The statistical analysis indicated that increased concentration of antioxidants is highly significant in decreasing the FFA, while increase in frying days has significant effect in increasing the FFA. Hence it can be concluded from Table 4 that as per concentration of antioxidants is concerned; higher the concentration of antioxidant is used lower will be the FFA/ rate of oxidation and as the number of days/fryings increases the rate of oxidation and hence value of FFA increases gradually.

Overall, lowest FFA was observed at 1st day of frying with 200 ppm of BHT i.e. 0.0433 %, while highest FFA was noted at 7th day of frying with control system and 80 ppm of Vit E i.e. 0.48 %.

Table 4. Mean values of FFA (%) for Treatments*Concentration* Days[a].

Treatments	Conc.	Days							Mean	Mean
		D1	D2	D3	D4	D5	D6	D7	(Conc.)	(Treatments)
Control	0 ppm	0.0767 r-u	0.14 f-h	0.23 uv	0.3533 j-l	0.3933 f	0.4253 d	0.48 a	0.2998 A	0.2998 A
BHA	40 ppm	0.0767 r-u	0.11 j-m	0.1433 fg	0.1633 cd	0.18 ab	0.2233 vw	0.2467 st	0.1633 M	0.1454 E
	80 ppm	0.0533 y-b	0.0767 r-u	0.1067 k-m	0.1333 gh	0.18 ab	0.2167 wx	0.2667 r	0.1476 NO	
	120 ppm	0.06 w-z	0.0933 n-p	0.1133 j-l	0.1467 ef	0.1833 ab	0.2133 wx	0.24 tu	0.15 NO	
	160 ppm	0.0533 y-b	0.0833 p-s	0.1067 k-m	0.1467 ef	0.18 ab	0.21 xy	0.23 uv	0.1443 O	
	200 ppm	0.0467 ab	0.07 t-w	0.0867 p-r	0.1167 jk	0.1433 fg	0.1733 bc	0.2167 wx	0.1219 P	
TBHQ	40 ppm	0.0767 r-u	0.1067 k-m	0.1467 ef	0.1667 cd	0.2467 st	0.3033 op	0.3733 g	0.2029 G	0.1992 C
	80 ppm	0.0733 s-v	0.1333 gh	0.1733 bc	0.1867 a	0.24 tu	0.3033 op	0.37 gh	0.2114 F	
	120 ppm	0.0667 u-x	0.1133 j-l	0.1633 cd	0.21 xy	0.2567 rs	0.3367 l	0.36 hi	0.2152 F	
	160 ppm	0.0667 u-x	0.1 m-o	0.1467 ef	0.1567 de	0.24 tu	0.2933 pq	0.34 kl	0.1919 I	
	200 ppm	0.05 z-b	0.07 t-w	0.1033 l-n	0.1367 f-h	0.2667 r	0.2933 pq	0.3033 op	0.1748 L	
BHT	40 ppm	0.0733 s-v	0.1067 k-m	0.1433 fg	0.1667 cd	0.19 za	0.3067 o	0.3933 f	0.1971 H	0.1861 D
	80 ppm	0.08 q-t	0.09 o-q	0.1 m-o	0.1433 fg	0.1833 ab	0.3033 op	0.36 hi	0.18 K	
	120 ppm	0.07 t-w	0.0867 p-r	0.1333 gh	0.1833 ab	0.2433 t	0.29 q	0.35 i-k	0.1938 HI	
	160 ppm	0.0567 x-a	0.8 q-t	0.13 hi	0.1833 ab	0.24 tu	0.2833 q	0.32 n	0.1848 J	
	200 ppm	0.0433 b	0.08 q-t	0.14 f-h	0.1733 bc	0.2167 wx	0.2633 r	0.3067 o	0.1748 L	
Vit E	40 ppm	0.0767 r-u	0.14 f-h	0.23 uv	0.29 q	0.3333 lm	0.4067 e	0.4767 a	0.279 C	0.2700 B
	80 ppm	0.0767 r-u	0.14 f-h	0.2067 xy	0.3433 j-l	0.3933 f	0.4233 d	0.48 a	0.2948 A	
	120 ppm	0.0733 s-v	0.1367 f-h	0.2 yz	0.3233 mn	0.3933 f	0.4167 de	0.46 b	0.2862 B	
	160 ppm	0.0633 v-y	0.12 ij	0.18 ab	0.2467 st	0.3233 mn	0.3767 g	0.4367 c	0.2495 D	
	200 ppm	0.0667 u-x	0.1167 jk	0.1833 ab	0.2367 tu	0.3033 op	0.3533 ij	0.4233 d	0.2405 E	
Mean (Days)		0.0652 G	0.1027 F	0.1468 E	0.1927 D	0.2468 C	0.2995 B	0.3477 A		

LSD $_{0.05}$ (Antioxidant*Concentration*Days) = 0.0123

[a]Means within each row with different superscripts are significantly (P < 0.05) different. Means within each column with different subscripts are significantly (P < 0.05) different. BHA, butylated hydroxyanisole; BHT, butylated hydroxytoluene; TBHQ, tertiary butylhydroquinone; Vitamin E, tocopherol

This increase in FFA with increase in days was maximum in control as compare to other systems in which antioxidants were used. The mean values of FFA for Control, Vit E, TBHQ, BHT and BHA were 0.2998, 0.2700 %, 0.1992, 0.1861 and 0.1454 respectively.

On the whole, BHA showed highest protection against oxidation/increase in FFA at each concentration and day as compared to rest of the antioxidants, after BHA, BHT was most effective against the rate of oxidation at each level of concentration and day then rest two antioxidants, after BHT, TBHQ was on third position when compared to other antioxidants while Vit E was least effective antioxidant against the oxidation of oil. While in control system maximum deterioration was observed (due to absence of antioxidants) as compared to the rest four systems in which antioxidants were used.

The results of this study have shown that the addition of antioxidants to palm olein improves its oxidative stability when used as a deep-fat frying oil. Overall, the sequence of effectiveness of antioxidants against oxidative deteriorations in palm olein during intermittent frying of potato chips at each concentration (40 ppm, 80 ppm, 120 ppm,160 ppm and 200 ppm) and day (day 1^{st} to 7^{th}) was BHA >TBHQ >BHT >Vit E >Control. From the results of this research it can be concluded that BHA with the concentration level ranging from 160 ppm to 200 ppm could be used to improve the oxidative stability of palm olein during deep fat frying, due to its low cost, easy availability and high performance.

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CONFLICT OF INTEREST

The authors declared no conflict of interest.

AUTHOR'S CONTRIBUTION

All authors contributed and supported towards writing of this manuscript.

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