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A comparative Study on the Antioxidant Activity of TBHQ and Extracts from Rosemary and Oregano on Oxidative Stability of Palm Olein during Deep Fat Frying of Beef Meatballs

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ABSTRACT

Nowadays, there is a tendency toward using of natural antioxidants to avoid toxic effects of synthetic antioxidants. This study was aimed to investigate the effect of antioxidants addition in protection of palm olein as frying media during the deep fat frying of beef meatballs, since antioxidants were added to palm olein (frying media) separately as follows 200 ppm tertiary butyl hydroquinone (TBHQ), 2500 ppm rosemary extract (ROS) and 2500 ppm oregano extract (OREG) beside control treatment (antioxidants free palm olein). The results showed that the addition of antioxidants to palm olein reduce the increment in refractive index during frying process as compared to control, while ROS was have the lowest refractive index among the natural antioxidant containing treatments. In regard to relative viscosity the addition of antioxidants to palm olein results in lower relative viscosity values as compared to control treatment. Since, ROS was exhibited superior ability in reducing the formation of free fatty acids which increased during the frying process in all treatments with low rates for antioxidant containing treatments. In regard to peroxide value, TBHQ and ROS has been kept peroxide value under the ESS limit for long period of deep fat frying (150 min.) followed by OREG containing treatment (90 min.), while control sample still only 60 min under the Codex Stand (No. 210/1999) and ESS (1706/2005) peroxide limit. Changes in TBA values were increased as frying process progressed, but TBA value increasing rate was low in antioxidant containing treatments as compared to control, also TBHQ and ROS showed lower TBA values than that of OREG treatment along the frying period. Polymerization of oil increased with increasing frying time, the results showed that the addition of antioxidants to palm olein reduce the polymer compounds formation during the frying process as compared to control, but the low polymerization percent was observed for TBHQ and ROS treatments. The iodine values of frying oil were decreased as the frying time increased, but TBHQ and ROS treatments exhibited high iodine value than other treatments. Finally ROS was exhibit superior ability in protection the oil from oxidation during frying process which suggests that ROS may be a good natural antioxidant alternative to TBHQ.

Key words: Natural antioxidant, Rosemary extract, Oregano extract, TBHQ, Deep fat frying, Palm olein, Beef meatballs.

Introduction

Deep-fat frying involves immersion of food in hot oil for a period of time. It is a popular food preparation technique in both industry and restaurants for being fast and convenient. Frying temperature is usually above the boiling point of water, between165 to 185°C, since heat is transferred to the food through the oil as the heat transfer medium (Gunstone, 2004). This leads to the moisture outflow from the food and oil absorption from the frying medium in replacement of the evacuated water and prevents migration of flavor and nutritive components from the product (Dan and Saguy, 2001). Frying process involves physical, chemical and sensory changes in the food being fried. The rapid dehydration of the surface develops the crispy texture of the crust, fat absorption, development of flavors and surface color, which are the unique attributes of fried foods that are highly favored by consumers (Stier, 2000).

Vegetable oils with higher contents of unsaturated fatty acids are more susceptible to the oxidation (Mohdaly *et al.,* 2010), especially when the oil is exposed to oxygen, light, high temperatures or trace metals (Sikwese and Duodu, 2007). Lipids oxidation during food processing or storage led to changes in

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organoleptic properties, decrease shelf life and nutritional value of the food (Iqbal and Bhanger, 2007; Choe and Min 2007 and Katragadda *et al.* 2010).

Both natural and synthetic antioxidants are widely used in protection oils from oxidation (Frutos and Hernandez-Herrero, 2005). The most common synthetic antioxidants used in food lipid preservation, namely butylated hydroxyl toluene (BHT), butylated hydroxyl anisole (BHA), propyl gallate (PG) and tertiary butyl hydroquinone (TBHQ), have been suspected to cause or promote harmful effects to the health (Ozcan and Arslan, 2011and Chen *et al.* 2014). So that, there are increasing demand for using natural antioxidants from plant sources, which characterized with high Phenolic compounds content can act as either radical scavengers or metal chelators resulting in retardation lipid oxidation (Sikwese and Duodu, 2007).

Palm olein is widely used in industrial frying because it does not emit undesirable odors, free of trans fatty acids, resistant to oxidation since it free from linolenic acid (Basiron, 2005 and Gee, 2007).

Spices and herbs containing antioxidant compounds are used as antioxidants in the form of extracts or essential oils. Among them, rosemary (*Rosmarinus officinalis* L.) and oregano (*Origanum vulgare* L.) which have gained considerable attention as spice with high antioxidant potential (Zhang *et al.* 2010 and Chen *et al.* 2014).

The antioxidant properties of rosemary and oregano extracts has contributed to the presence of phenolic compounds, which break free radical chain reactions by hydrogen atom donation or chelating metal ions (Erkan *et al.* 2008).

Oregano is a widely used spice in the food industry because of its aromatic properties with a primary role to enhance the taste and aroma of foods. Due to high content of flavonoids, tannins, and phenolic glycosides, oregano has been shown to exhibit antioxidant properties and antimicrobial activity (Nakatani, 2003 and Hernandez-Hernandez *et al.,* 2009).

The aim of this study was to evaluate the antioxidant effectiveness of ethanol extracts of both rosemary and oregano during accelerated oxidation of palm olein oil (deep fat frying) by measuring both primary and secondary oxidation products and compare their antioxidant activity with tertiary butyl hydroquinone (TBHQ) as commercially used antioxidant.

Materials and Methods

Materials:

Oil samples used:

Refined, bleached, deodorized and antioxidant free palm olein was obtained from the Savola Group, Afia International Company, Suez, Egypt. The freshly refined oil samples packed in dark brown glass bottles were stored under frozen storage conditions (at -18°C) till further analysis and using. All chemicals and reagents used in the analytical methods (Analytical grade) were obtained from either Sigma Chemical Co. (St. Louis, MO, U.S.A.) or El- Gamhouria Trading Chemicals and Drugs Co., Egypt.

Rosemary and oregano:

Rosemary and oregano leaves were purchased from Harraz market (dealer in plant seeds), Cairo, Egypt.

Other Ingredients:

Frozen beef meat was purchased from the Egyptian armed force sources, branch of Faculty of Agriculture, Al- Azhar University. Fresh eggs, onion, garlic, sugar and salt (sodium chloride) were obtained from the local market.

Sodium tripolyphosphate and sodium nitrite were obtained from Adwic Laboratory Chemicals Co., Cairo, Egypt.

Methods:

Preparation of rosemary and oregano extract:

Rosemary and oregano extracts were prepared by using ethanol according to the method described by (Kamkar *et al.,* 2014).

Preparation of Meatballs:

Meatballs (10 kg) were prepared in Laboratory of Food Science and Technology Department, Faculty of Agriculture, Al-Azhar University, Cairo, Egypt. Meatballs were formulated to contain 75% minced beef meat, 10% (w/w) water (ice water), 1.6% (w/w) sodium chloride, 1.8 % spices, 0.3% sugar, 2.4 onion, 0.6% garlic, 3% wheat flour, 5% whole liquid egg, 0.3% Sodium tripolyphosphate, and 150 ppm Sodium nitrite according to Das *et al.,* (2008), meatball mixture was manually shaped into meatballs weighing 55± 5g, which kept in frozen storage till using in frying process.

Addition of antioxidants to oil:

Antioxidants were added separately to palm olein oil batches weighing 2 kg, with the following ratios: 2500 ppm rosemary extract (ROS), 2500 ppm oregano extract (OREG), 200 ppm tertiary butyl hydroquinone (TBHQ) and an antioxidant free batch as control.

Frying process:

Deep frying was carried out in palm olein using deep-fat fryer (SASHO Deep Fryer- SH 308) at 180 °C in the fryer, since meatballs were consecutively introduced into hot oil and fried for 8 min. along the frying period, which reach to180 min. (Alizadeh *et al.* 2016).

Sample of fresh oil (zero time) was stored at −18 °C. While samples of frying oils (100 g) were taken each thirty minutes, cooled to room temperature and frozen at −18 °C for further analysis.

Physical and chemical properties oil samples used:

Refractive index of oil samples was measured using Carl Zeiss Refractometer at 40 °C, Viscosity (CPs)was determined at 40°C using Brookfield Viscometer, Free fatty acid (FFA) (as % Oleic acid); Peroxide value (meq. active O_2/kg) and Iodine Value (gI_2/100g) were determined according to AOAC, (2011), while TBA was determined as described by Sidwell *et al.* (1954).

Fatty acids profile:

Fatty acid composition of studied oil samples were determined using gas liquid chromatography technique.Methylation process was carried out using BF3 in methanol (20%) (AOAC, 2011).

Determination of oxidative stability by Rancimat (Stability test):

The oxidative stability (induction period, IP) of oil samples was evaluated by the Rancimat method (Mod 679 MetrohmUd. CH-9100, Herisau, Switzerland) (AOCS, 2011). The assays were carried out using 5 g of oil sample at 120 ± 0.5°C with an air flow of 20 L/h. Oil parameters were expressed as induction period (IP), expired and shelf life in months according to the method described by Tsaknis *et al.* (1999), while protection factor was calculated by the method of De Leonardis *et al*. (2007).

Determination of polymer Compounds (%):

The insoluble polymers were determined according to the method described by Wu and Nawer (1986).

Statistical analysis:

Obtained results were statistically analyzed by one-way analysis of variance using SPSS 16.0 for windows performed on all experimental data sets. Post-hoc multiple comparisons were carried out by Duncan analysis to determine significant differences between sample means at 5% level as described by SPSS (2007).

Results and Discussion

Fatty acids profile and oxidative stability:

Table (1) indicates that fresh palm olein had the following fatty acid composition: 38.50% of palmitic acid ($C_{16:0}$), 3.80% of stearic acid ($C_{18:0}$), 41.13% of oleic acid ($C_{18:1}$) and 11.33%of linoleic acid ($C_{18:2}$) which in agreement with the foundation of Chnadhapuram and Sunkireddy (2012) and Nagachinta and Akoh, (2012).

Table 1: Fatty acids profile of palm olein.

Palm olein	Fatty acids profile %					
	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	Saturated fatty acids	Unsaturated fatty acids
	38.50	3.80	41.13	11.33	43.84	53.34

Oxidative stability of oil samples investigated:

The induction period (IP) is taken as an indicator for the oxidative stability of oils and fats, consequently as an indicator for the shelf-life of pure oils and fat (Anwar *et al*., 2003).

Table (2) shows that the oxidative stability (induction period at 120°C) was increased by addition of antioxidant as compared to control sample. which result in increasing of the calculated parameters of oxidative stability (protection factor, induction, Expired and shelf life at ambient temperature), while palm olein containing rosemary extract showed markedly the highest oxidative stability among oil samples (IP 13.9 hrs.), followed by palm olein containing TBHQ and oregano extract (IP 13.1 and 13.0 hrs. respectively), while control treatment had the lowest corresponding stability (IP 11.7 hrs.).

Results in table (2) indicate that adding of rosemary extract to palm olein led to a significant increment of oxidative stability when compared with oregano extract and TBHQ during frying meatballs at 180 °C, which agree with foundation of Fasseas *et al.,* (2008) and Camo *et al*., 2008.

Table 2: Oxidative stability of oil samples containing different antioxidants during frying periods for meatballs at 180 °C.

Rancimat at 120°C	Treatments*				LSD
	Control	TBHQ	ROS	OREG	
Induction period (hrs.)	11.7^{c}	13.1^{b}	13.9^{a}	13.0^{b}	0.188
Protection factor	-	1.12^{a}	1.19^{a}	1.11^{a}	0.188
Induction period (Months)	26.12^{d}	28.64^{b}	30.1^{a}	28.46^{c}	0.219
Expired (Months)	17.35^{c}	19.42^{b}	20.61^{a}	19.28^{b}	0.183
Shelf life (months)	21.35^{c}	24.03^{b}	25.32^{a}	23.87^{b}	0.165

**Control , antioxidant free ; TBHQ, 200 ppm tertiary butyl hydroquinone; ROS, 2500 ppm rosemary extract; OREG, 2500 ppm oregano extract.*
*** In the same row values with different superscript are significantly different (P<0.05).*

Changes in Refractive index:

The refractive index of the edible oils and fats is an important quality assurance characteristic because it is useful for identification purity, processing purposes and following the reactions which occurred in lipids and fatty acids such as isomerization, hydrolysis, polymerization and oxidation throughout thermal processing. Refractive index is affected with oil saturation degree, free fatty acids content and its oxidative state Kiritsakis *et al.,* (1983) and Lalas, (1998).

Table (3) shows that there is gradual increase in refractive index of all tested frying oil samples used in frying meatballs. Also, table (3) shows that addition of antioxidants to palm olein caused reduction in the refractive index of frying oil during frying of meatballs when compared to control treatment, which reached a maximum value 1.4678, while corresponding values were 1.4638, 1.4640 and 1.4656, for TBHQ, ROS and OREG treatments respectively. The highest inhibitory effect on oxidation was observed for the rosemary extract treatment which exhibit highest ability to retard oil degradation during the frying process, which agree with Alizadeh *et al.* (2016) since they reported that rosemary extract protect oil from degradation, since it has higher content of antioxidants, which reduce oxidation and polymerization.

These results indicate that the refractive index increased as oil degradation increased, but the rate of degradation clearly depend on content of antioxidants and the nature of food fried in the oil (Bansal, *et al.* 2010).

Table 3: Changes in Refractive index (at 40 °C) of oil samples containing different antioxidant during frying periods for meatballs at 180 °C

Time of frying (min.)	Treatments				LSD
	Control	TBHQ	ROS	OREG	
Zero time	1.4596^{a}	1.4596^{a}	1.4596^{a}	1.4596^{a}	0.0018
After 30	1.4599^{a}	1.4599^{a}	1.4599^{a}	1.4605^{a}	0.0008
After 60	1.4605^{b}	1.4603^{b}	1.4604^{b}	1.4613^{a}	0.0008
After 90	1.4621a^{b}	1.4610^{b}	1.4610^{b}	1.4626^{a}	0.001
After 120	1.4653^{a}	1.4622^{c}	1.4619b^{c}	1.4635^{b}	0.003
After 150	1.4657^{a}	1.4630^{c}	1.4627^{c}	1.4643^{b}	0.009
After 180	1.4678^{a}	1.4640^{c}	1.4638^{c}	1.4656^{b}	0.001

**Control, antioxidant free; TBHQ, 200 ppm tertiary butyl hydroquinone; ROS, 2500 ppm rosemary extract; OREG, 2500 ppm oregano extract.*
*** In the same row values with different superscript are significantly different (P<0.05).*

Changes in viscosity:

The flow time reflects the magnitude of oil viscosity and is generally considered as an adequate indicator of the alteration in frying oils viscosity as a result of changes occur in their chemical constituents during frying process such as polymerization of the unsaturated fatty acids and formation of viscous high molecular weight compounds (Lalas and Tsaknis, 2002).

Table (4) shows that there a successive increase in the relative viscosity values of the all investigated oil samples during frying of meatballs. Results in table 3 show that addition of antioxidants resulted in low viscosity of frying oil samples containing antioxidants as compared to the control sample. At the end of frying periods, the viscosity of control treatment reached a maximum value 68.5 CPs as compared to 65.5, 66.0 and 66.5 CPs for TBHQ, ROS and OREG treatments, respectively. The lowest change was observed for TBHQ and rosemary treatments, which is in agreement with foundation of Jaswir *et al.* (2000) and similar to which reported by Tsaknis and Lalas, (2002).

Table 4: Changes in viscosity of oil samples containing different antioxidants during frying of meatballs at 180 °C**.**

Time of frying (min.)	Treatments				LSD
	Control	TBHQ	ROS	OREG	
Zero time	60.5^{a}	60.5^{a}	60.5^{a}	60.5^{a}	0.85
After 30	62.5^{a}	61.0^{a}	61.0^{a}	61.0^{a}	1.48
After 60	64.0^{a}	61.5^{b}	62.0^{b}	62.5^{b}	1.24
After 90	65.0^{a}	62.0^{b}	62.5^{b}	63.0a^{b}	2.20
After 120	65.5^{a}	63.0^{b}	63.0^{b}	63.5^{b}	1.69
After 150	67.0^{a}	64.0^{b}	64.5^{b}	64.5^{b}	1.48
After 180	68.5^{a}	65.5^{b}	66.0^{b}	66.5^{b}	1.24

**Control, antioxidant free; TBHQ, 200 ppm tertiary butyl hydroquinone; ROS, 2500 ppm rosemary extract; OREG, 2500 ppm oregano extract.*
*** In the same row values with different superscript are significantly different (P<0.05).*

Changes in Free fatty acids:

During frying, oil is exposed to air and moisture at high temperature resulting in hydrolysis of triglycerides releasing free fatty acids, which are more susceptible to thermal oxidation and cause off flavors and odors in the frying medium and fried foods Horuz and Maskan (2015).The free fatty acids (FFA) content of oil is an important standard measurement of oil suitability for human consumption.

Table (5) shows that addition of antioxidant to oil caused significant decrement in FFA content as compared to the control sample. At the end of frying operation, the FFA content of oils treated with TBHQ, rosemary extract and oregano extract reached maximum values of 0.393, 0.389 and 0.401 %, respectively, which were significantly lower than that of control sample (0.604%),since rosemary extract and TBHQ containing treatments showed significantly the slightest increase rate of free fatty acids ($p< 0.05$). These results are in agreement with those of Zhang *et al*. (2010) and Alizadeh *et al.* (2016).

Table 5: Changes in Free fatty acids content (as oleic acid %) of oil samples containing different antioxidant during frying periods for meatballs at 180 °C

Time of frying (min.)	Treatments				LSD
	Control	TBHQ	ROS	OREG	
Zero time	0.015^{a}	0.015^{a}	0.015^{a}	0.015^{a}	0.001
After 30	0.187^{a}	0.126^{c}	0.119^{d}	0.135^{b}	0.0024
After 60	0.240^{a}	0.160^{c}	0.149^{c}	0.198^{b}	0.0136
After 90	0.362^{a}	0.218^{c}	0.212^{d}	0.227^{b}	0.0029
After 120	0.443^{a}	0.272^{c}	0.267^{d}	0.285^{b}	0.0043
After 150	0.489^{a}	0.332^{b}	0.329^{b}	0.334^{b}	0.0087
After 180	0.604^{a}	0.393^{c}	0.389^{c}	0.401^{b}	0.005

**Control, antioxidant free; TBHQ, 200 ppm tertiary butyl hydroquinone; ROS, 2500 ppm rosemary extract; OREG, 2500 ppm oregano extract.*
*** In the same row values with different superscript are significantly different (P<0.05).*

Changes in peroxide value:

Peroxide value (PV) is one of the most widely used methods in monitoring the initial stage of lipid oxidation and reflects the concentration of peroxides and hydroperoxides.

Table (6) illustrates that all treatments showed gradually increment in peroxide value as frying time increased, then began to decrease, which in agreement with the findings of Guillén *et al.* (2005). Peroxide value reduction can be explained by the decomposition of unstable hydroperoxides to secondary oxidation products such as: hydrocarbons, alcohols, ketones and aldehydes.

Table 6: Changes in peroxide value (meq O_2/kg oil) of oil samples containing different antioxidant during frying periods for meatballs at 180 °C

Time of frying (min.)	Treatments				LSD
	Control	TBHQ	ROS	OREG	
Zero time	0.844^{a}	0.844^{a}	0.844^{a}	0.844^{a}	0.00188
After 30	5.144^{a}	1.625^{c}	1.609^{d}	2.143^{b}	0.00188
After 60	9.855^{a}	4.113^{c}	3.987^{d}	6.157^{b}	0.00188
After 90	6.216^{b}	5.480^{c}	5.523^{d}	10.585^{a}	0.00955
After 120	5.110^{d}	7.014^{a}	6.457^{b}	5.357^{c}	0.00955
After 150	4.365^{c}	10.721^{a}	9.283^{b}	4.069^{c}	0.54271
After 180	3.210^{b}	6.534^{a}	5.485^{b}	2.132^{d}	0.00955

**Control , antioxidant free ; TBHQ, 200 ppm tertiary butyl hydroquinone; ROS, 2500 ppm rosemary extract; OREG, 2500 ppm oregano extract.*
*** In the same row values with different superscript are significantly different (P<0.05).*

Also, results in table (6) show that during frying process, PV of oil sample contain TBHQ used in frying meatballs reached to 10.721 meq O_2/kg oil after 150 min of the initial of frying process, while sample contain ROS reached to 9.283 meq O_2/kg oil after the same frying time which is lower than the peroxide value limit of the Egyptian Standard Specifications (ESS, 2005), and reflect the high oxidative activity of rosemary extract. In this concern PV of OREG treatment reached to 10.585 after 90 min. of frying process, while control treatment reached to 9.855 meq O_2/kg oil after 60 min. only.

These results showed that addition of ROS to palm olein used as frying media of meat balls significantly retarded the formation of hydroperoxides and kept peroxide value under the Egyptian standard specifications limit after 150 min. of frying process as reported in Codex Stand (No. 210/1999) and ESS (1706/2005) and (2142/2005)). These results are in agreement with those obtained by Jaswir *et al.* (2000), Chen *et al*. (2014) and Alizadeh *et al.* (2016).

Changes in TBA:

Thiobarbituric acid (TBA) test is a condensation reaction between TBA and malonaldehyde, the most predominate product of the secondary oxidation of oil and measure aldehyde contents in oil, principally 2, 4-dienals and 2-alkenals, produced from decomposition of hydroperoxides, which are formed during food lipids oxidation. Therefore, the TBA value considered a good chemical quality criterion to identify the oxidative state of edible oils and fats, since it reflects the extent of occurred oxidation (Lalas, 1998).

Table (7) shows that TBA values of all treatments increased significantly with increasing frying time. The addition of antioxidants to oil results insignificant reduction of TBA values as compared to control sample. At the end of frying periods, the TBA of control sample reached maximum value 2.353 mg malonaldehyde/kg oil, which was higher than that of oil samples containing TBHQ, ROS and OREG 1.2641.236 and 1.727mg malonaldehyde/kg oil respectively.

From Tables (6) and (7) it could be noticed that rosemary extract has a clear inhibitory effect on the propagation stage of oxidation in oil used in frying meatballs. SO, rosemary extract exhibited high inhibitory effects towards both primary and secondary oxidation changes, which is higher than that of TBHQ. This results are in agreement with that of Zhang *et al* (2010) and Alizadeh *et al.* (2016). This fact might be contributed to the presence of donate hydrogen donating compounds in rosemary extract, which change peroxides to stable hydroperoxides resulting in slower decomposition rate of hydroperoxides and formation of fewer secondary products (Decker *et al.,* 2005).

Table 7: Changes TBA (mg malonaldehyde/kg oil) of oil samples containing different antioxidant during frying periods for meatballs at 180 °C

Time of frying (min.)	Treatments				LSD
	Control	TBHQ	ROS	OREG	
Zero time	0.167^{a}	0.167^{a}	0.167^{a}	0.167^{a}	0.00188
After 30	0.415^{a}	0.281^{c}	0.267^{d}	0.376^{b}	0.00188
After 60	0.915^{a}	0.463^{c}	0.415^{d}	0.513^{b}	0.00188
After 90	1.410^{a}	0.704^{c}	0.689^{d}	0.726^{b}	0.00955
After 120	1.716^{a}	0.880^{c}	0.876^{c}	1.041^{b}	0.00955
After 150	1.924^{a}	1.075^{c}	1.050^{d}	1.532^{b}	0.00955
After 180	2.353^{a}	1.264^{c}	1.236^{d}	1.727^{b}	0.00188

**Control , antioxidant free ; TBHQ, 200 ppm tertiary butyl hydroquinone; ROS, 2500 ppm rosemary extract; OREG, 2500 ppm oregano extract.*
*** In the same row values with different superscript are significantly different (P<0.05).*

Changes in Polymer compound (%):

Polymerization of frying oil cause formation of compounds with high molecular weight and polarity, which can formed from free radicals or triglycerides by the Diels-Alder reaction. Oxidized polymer compounds accelerate oxidation, further degradation, increase oil viscosity (Tseng *et al.,* 1996), reduce heat transfer, produce foam during deep fat frying, develop undesirable color in fried food and cause high oil absorption by foods (Yoon *et al., 1*988). Oil quality control regulations (IUPAC, 1987) indicate that polymer levels must not exceed 1.5%.

Table (7) shows that polymer compounds (%) in all analyzed oil samples increased as frying process progressed and increased with high rate at the end of frying process. Addition of antioxidants to oil caused a significant reduction in formation of polymer compounds. Since at the end of frying process, the polymer compound percent of control sample reached maximum value (5.73%), while polymer compound percent of antioxidants containing oil samples were 1.61, 1.68 and 1.94% for TBHQ, ROS and OREG respectively. This is in agreement with the results of Tabee *et al.* (2009), Farhoosh and Tavassoli-Kafrani (2010) and Alizadeh *et al.* (2016).Polymer compound levels of TBHQ and ROS treatments were lower than that of OREG and control samples, which in agreement with the foundation of Jaswir *et al.* (2000).

Changes in Iodine Value:

The alteration in the iodine value of frying media is considered one of the most chemical constants of oils quality assurance and a good measure for changes occurring in the unsaturated fatty acids during the frying process.

Table (8) indicates that the iodine value of oils was decreased as the frying progressed since it was 56.4 g I_2/100g oil at the initial zero time of frying for all treatments, but it decreased to 45.6, 52.5, 51.6 and 49.8 g I_2/100g oil for control, BHTQ, ROS and OREG treatments respectively after 180 min. of frying process of meatballs at 180 ºC. The reduction in the iodine value could be attributed to the thermal oxidative degradation of the unsaturated fatty acids throughout frying process. Also, the results indicate that addition of TBHQ and ROS to frying oil result in high protection of frying oil from oxidation, which observed in higher iodine values at the end of the frying process, these results were in close agreement with those reported by Tsaknis *et al.,* (1998), Jaswir *et al.* (2000), Tsaknis and Lalas, (2002) and Anwar *et al.,* (2003).

Table 8: Changes in Polymer compound (%) of oil samples containing different antioxidants during frying of meatballs at 180 °C.

Time of frying (min.)	Treatments				LSD
	Control	TBHQ	ROS	OREG	
Zero time	0.00	0.00	0.00	0.00	-
After 30	0.92^{a}	0.11^{d}	0.14^{c}	0.19^{b}	0.0188
After 60	1.53^{a}	0.28^{d}	0.31^{c}	0.38^{b}	0.0188
After 90	2.56^{a}	0.41^{d}	0.45^{c}	0.56^{b}	0.0188
After 120	3.17^{a}	0.83^{d}	0.88^{c}	0.97^{b}	0.0339
After 150	4.68^{a}	1.02^{c}	1.10^{c}	1.32^{b}	0.0955
After 180	5.73^{a}	1.61^{d}	1.68^{c}	1.94^{b}	0.0297

**Control , antioxidant free ; TBHQ, 200 ppm tertiary butyl hydroquinone; ROS, 2500 ppm rosemary extract; OREG, 2500 ppm oregano extract.*
*** In the same row values with different superscript are significantly different (P<0.05).*

Table 9: Changes in Iodine value (gI_2/100g oil) of oil samples containing different antioxidants during frying of meatballs at 180 °C.

Time of frying (min.)	Treatments				LSD
	Control	TBHQ	ROS	OREG	
Zero time	56.4^{a}	56.4^{a}	56.4^{a}	56.4^{a}	0.188
After 30	55.6^{b}	56.0^{a}	55.9^{a}	54.7^{c}	0.188
After 60	54.8^{c}	55.7^{a}	55.2^{b}	53.4^{d}	0.188
After 90	52.4^{c}	55.1^{a}	54.6^{b}	52.5^{c}	0.188
After 120	50.7^{d}	54.4^{a}	53.8^{b}	51.1^{c}	0.188
After 150	48.9^{d}	53.6^{a}	52.5^{b}	50.3^{c}	0.188
After 180	45.6^{d}	52.2^{a}	51.6^{b}	49.8^{c}	0.188

**Control, antioxidant free ; TBHQ, 200 ppm tertiary butyl hydroquinone; ROS, 2500 ppm rosemary extract; OREG, 2500 ppm oregano extract.*
*** In the same row values with different superscript are significantly different (P<0.05).*

Finally, it could be concluded that the rosemary extract exhibited inhibitory effects towards both primary and secondary oxidation changes, as effectively as TBHQ during deep frying of meatballs. Based on the overall results of this study, rosemary extract could be recommended as a good alternative to TBHQ.

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