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EFFECT OF DEEP-FAT FRYING ON CHARACTERISTICS OF SOME VEGETABLE OILS

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ABSTRACT: *Deep-fat frying is one of the very oldest and popular food preparations Frying is a process of immersing food in hot oil with a contact among oil, air, and food at a high temperature of 150 °C to 190 °C. In the presence of oxygen, food moisture and high temperature, the oil undergoes three main reactions: hydrolysis, oxidation and thermal alteration. The aim of this work was to study the affects of deep frying on thermal behavior of some vegetable oils with different omega fatty acid composition. The effect of using different oils on the quality of potato chips and the shelf life of oil during deep-frying up to 8 hrs (32 cycles) of frying and the thermal behavior of some vegetable oils during deep-heat process, were studied. The physicochemical characteristics (quality parameters, Peroxide value (PV), Anisidine value (An-V), Free fatty acids (FFA %), Thiobarbituric Acid (TBA), Iodine Value (IV), fatty acid composition and sensory evaluation of fried potato chips of some vegetable oils during frying up to 8 hrs were evaluation.*

To achieve this aim three different oils were selected olive, flaxseed and sunflower oils. The results revealed that the percentage of the PV, An-V, FFA%, TBA, generally increased with increasing the frying time up to 8 hours, while the IV decreased with increasing the frying time up to 8 hours. Generally, all values were affected by the degree of fatty acid unsaturation and frying time up to 16 hours.

The frying process increased the saturated fatty acids in the vegetable oils and decreased the unsaturated fatty acids by increasing of the number of frying process due to the thermal oxidative and double bound's breakage in the unsaturated fatty acids which lead to change in the chemical composition of the oil. They conclusion that potato chips fried in sunflower oil had a higher flavour quality and stability. Moreover, these results are confirmed with sensory evaluation by panel taste.

The selection of frying oil used in frying process is based on price, quality, flavor, oxidation susceptibility, functionality and availability.

***Key words**: Vegetable oils, Deep-fat frying, Chemical and quality.*

INTRODUCTION

Frying is a traditional heat processing method for the food preparation throughout the world. Deep fat frying involves simultaneous heat and mass transfer process in food processing operations (Debnath *et al.,* 2003, 2009, 2012). In deep frying, oil immersion frying is a popular means of food preparation due to its high cooking rate and unique sensory properties (i.e. color, flavor, and texture) it produces (Barutcu *et al.*, 2009, Nelson *et al.,* 2013). The food is totally immersed in the hot fat/oil, which acts as a medium for heat transfer. Basically, frying is a dehydration process at high temperature (160-190 °C) (between 160 and 180 °C, Debnath *et al.,* 2012).

The purpose of frying is the formation of a unique crust, colour, flavour and texture. Frying is useful in the cooking of all types of foods, such as meat, fish and vegetables. However, potato is probably the food most subjected to frying, since potatoes are used to produce French fries and potato crisps (Rossell, 2001). French fries contain between 8 and 15% fat. In contrast, potato crisps contain rather high amounts of fats, up to 35% (Saguy and Dana, 2003). The high temperatures used during frying, in the presence of oxygen and water, induce important chemical changes of the oils, namely by oxidation, polymerization, cyclization, and hydrolysis (Casal *et al.,* 2010).

During frying, oils are subjected to various deterioration processes such as hydrolysis, oxidation and thermal alteration, which generate a large number of compounds including free fatty acids, monoacylglycerols, diacylglycerols,volatile compounds, cyclic compounds, geometric isomers of unsaturated fatty acids, *etc*. Oxidised monomeric, dimeric and oligomeric triacylglycerols formed from the native triacylglycerols may have negative effects on human health (Dobarganes and Marquez-Ruiz, 2003; 2006).

The different vegetable oils used for frying are characterised by different fatty acid profiles (Erickson, 2006). Oils with a high content of saturated fatty acids are more stable in the frying process but because of the negative health attributions associated with these, the interest in using monounsaturated oils in frying has increased (McDonald and Eskin, 2006). The quality of the products from deep-fat frying depends not only on the frying conditions but also on the type of oils and foods used during the process (Chen and Moreira, 1997, Debnath *et al.,* 2012). Many different types of edible fats and oils are available for frying purposes. These include the animal fats (*i.e.* lard and tallow) and vegetable oils such as palm oil, rapeseed oil (low erucic acid), olive oil, soybean oil, sunflower oil, cottonseed oil, corn oil, *etc*. (Rossell, 2001). The choice of frying oil depends on many factors such as availability, price, flavour and stability. Resistance to oxidation during prolonged exposure to high temperature is one of the main properties that industrial frying oil should possess (Kochhar, 2001).

Olive oil can be another choice for frying purposes. Olive oil is typically the main lipid source in the Mediterranean diet, being used as salad dressing and for frying purposes. Its beneficial properties are associated with the richness in monounsaturated fatty acids, but other minor compounds (Casal *et al.,* 2010).

In addition, the high content of monounsaturated fatty acids, low concentrations of linoleic (C18:2) and linolenic (C18:3) acids and content of antioxidants are considered valuable properties of olive oil (Quaglia and Bucarelli, 2001). Consuming flaxseed oil is one good way to increase the n-3 fatty acids in the diet as most societies nowadays are known to generally consume plenty of n-6 fatty acids in processed foods (Choo *et al.,* 2007).

Hydrolysis is one of the major reactions occurring during deep frying due to the presence of moisture introduced with the food and the relatively high temperatures used. Hydrolysis of ester bonds in the lipids results in the formation of free fatty acids (FFA), mono- and di-acylglycerols and glycerols (Perkins, 2006). Lipid oxidation is one of the important causes of food spoilage.

Oxidation, which is accelerated at the high temperature used in deep frying, creates rancid flavours and reduces the organoleptic characteristics of fried food. Hydroperoxides are the major initial reaction products of lipid oxidation. However, they are not stable and decompose spontaneously to form other compounds such as aldehydes, ketones, alcohols, acids, hydrocarbons, *etc*. (Nawar, 1996). In the high temperatures during the frying process, triacyglycerols undergo decomposition reactions such as isomerisation, cyclisation and polymerisation (Saguy and Dana, 2003; Sebedio and Juaneda, 2006). Dimeric and polymeric glycerides acids also can be formed by the thermal and oxidative combination of free radicals (Dobarganes and Marquez-Ruiz, 2003).

The ratio of polyunsaturated to saturated fatty acids (P/S) is considered to be a major factor affecting oil oxidation. The presence of a high content of polyunsaturated fatty acids increases the susceptibility of oil to oxidation (Quaglia and Bucarelli, 2001). Oil resistance to oxidation in the frying process depends mainly on the fatty acid composition and antioxidant content of the oil (Rossell, 2001; Sanches-Silva *et al*., 2003; Nogala-Kalucka *et al.,* 2005 and Przybylski and Eskin, 2006).

A number of methods such as peroxide value (PV), *p*-anisidine value (*p*-AV), viscosity, colour, free fatty acids (FFA), sensory analysis, smoke point, foaming and total polar compounds (TPC) have been used to test the quality of frying oils and fried products (Stier, 2001). Peroxide value (PV) is one of the methods for determination of hydroperoxides as the initial lipid oxidation products. The PV is expressed as milliequivalents oxygen per kg of fat/oil (Nawar, 1996). Since hydroperoxides do not accumulate due to their instability at frying temperature, PV determination is not suitable for assessment of used frying oils (Matthaus, 2006; Suleiman *et al.,* 2006). *p*-Anisidine value (*p*-AV) is a method for measuring secondary decomposition products such as aldehydes (Mariod *et al.,* 2006). Aldehydes are the carbonyl compounds formed by decomposition of hydroperoxides and can be used as markers to determine degradation of peroxidised materials produced by the heating process (Stier, 2001).

The FFA level determines the quality of oil, because the presences of high FFA result in poor quality oil (Makky and Soni, 2013a, 2013b, 2014). Free fatty acids (FFA) are a measure of the amount of fatty acids hydrolysed on the triacylglycerol backbone. They are used as a chemical marker for monitoring the quality of frying operations (Stier, 2001; Barthet *et al.,* 2008). This parameter is often used for assessment of the suitability of frying oils for human consumption and a value of 2% is defined as the limit for oil rejection (Matthaus, 2006). Therefore the aim of this work was to study the effects of deep frying on the quality changes of some vegetable oils and the sensory properties of the fried product.

MATERIALS AND METHODS

1. Materials

1.1. Vegetable oils:

Virgin olive oil: (5 kg) was obtained from EL Quorum Company .Alexandria, Egypt. Olive oil was selected as it is high in oleic acid (18:1) content. Refined, bleached, and deodorized (RBD) sunflower oil (5 kg) was obtained from SAVOLA, Egypt. Sunflower oil is selected as high in linoleic acid (18:2) content.

Edible fresh flaxseed oil (5 kg) was obtained from a private oil company in Tanta, Egypt. Flaxseed oil was selected as high in linolenic acid (18:3) content.

1.2. Potatoes

Potatoes (*Solanum Tuberosum*) (18 kg) were purchased from a local market, Alexandria, Egypt.

2. Experimental procedures

2.1. Preparation of potato chips

Potatoes were peeled, cut into 2 mm thick slices using a rotary slicer (Edelstahl, Rostfrel, England), washed and dewatered prior to frying.

2.2. Determination of frying optimum temperature and time

The optimum temperature and time of frying of potato chips were determined according to (Barbary *et al*., 1999). The optimum temperature and frying time obtained for all oils to produce the best quality of potato chips were 180 °C and 10 min., respectively.

3. Thermal behavior of oils during frying process:

Thermal behaviors of oils during deep frying were conducted according to the method performed by Barbary *et al.* (2000**).** Oil (2.5 kg each) was initially heated in an electrical deep-fat fryer (Moulinex, France) until reached 180°C. The time required to reach that temperature was recorded during the frying process and assigned as the initial time. Potato chips were (250 g) introduced to the heated oil at 180° C and the oil temperatures were recorded using a metal sensor (Hanna instruments, Highland Industrial Park Woonsocket RI 02895) every minute during frying process. This time was considered as a zero time of frying process. This frying process was repeated on the heated oils every 30 minutes for 16 hours (8 hours /day ,total of frying cycle 32) in order to study the effect of heating time on the thermal behavior of the oil during deep frying of potato chips. The process was reported twice for each oil.

Potato chips as well as the heated oils were sensory evaluated every 2 hour. Oil samples (80g.each) were collected every 2 hours and analyzed for their physicochemical characteristics including: peroxide value(PV), free fatty acid content (FFA), thiobarbituric acid number (TBA), iodine value (IV), and Ansidine Value (An-V).

3.2. Sensory evaluation of fried potato chips:

Potato chips fried up to 16 hours were sensory evaluated every (2) hours of frying. Group of arbitrators analytical sensory-trained panels ranked the fried potato chips for their sensory attributes of visual appearance in terms of colour; texture in terms of crispness; greasiness; flavour in terms of flavour by mouth (taste) and odour (smell); and overall acceptability.

There are 10-point hedonic scale was used according to Warner (1989) where:

2- Light yellow; not crispy (soft); most greasy; bitter taste; rancid soapy flavour; and unaccepted potato chips.
4- Pale yellow; weak crispy; more greasy; no taste; no flavouur; and just accepted potato chips.
6- Bright yellow; slight crispy; moderate greasy; moderate taste; moderate flavour; and accepted potato chips.
8- Brownish yellow; moderate crispy; slight greasy; good taste; good flavour; and good overall acceptability.
10- Golden colour; crispy; not greasy; best taste; best flavour; and best overall acceptability.

4. Chemical Analysis of heated oils (Quality Parameters):

2.4. 1. Peroxide value (PV)

Peroxide value (PV) was determined according to AOCS (2010); (Method Cd8-53) by titration with standard sodium thiosulphate (0.1 N) and was calculated as milliequivalent peroxides per kilogram oil (meq/kg oil).

4. 2.Iodine Value (IV)

Iodine value was determined using Hans method as described by (AOCS, 2010).

4. 3. Free fatty acids (FFA %)

The free fatty acid content was determined by titration with standard potassium hydroxide solution 0.1 N in presence of ph.ph as indicator and calculated as oleic acid percentage according to the AOCS (2010) (Method Cd 3a-94).

4. 4. Anisidine Value (An-V)

Anisidine value was determined colorimetry as described by Egan,*et al.,*(1981) using a spectrophotometer model safas Monaco1900.

The anisidine value was calculated using the following equation:

$$\text{Anisidine value} = \frac{25\ (1.2\ A2 - A1)}{W}$$

Where
A1= is the absorbance of oil solution.
A2= is the absorbance of reaction product of oil with p-anisidine.
W= is gram of oil present in the 25ml of test solution.

4.5. Thiobarbituric acid number (TBA)

TBA number was determined according to Allen and Hamilton (1989). The resultant solutions were measured at 538 nm using spectrophotometer . The TBA number was calculated from the following equation:

TBA number = 7.8 D mg malonaldehyde per kg oil

Where: D is the absorbency against blank at 538 nm.

5. Analysis of fatty acid methyl esters

Esterification (Methylation)

Preparation of Fatty Acid Methylation Ester (FAME) of lipids samples were performed according to the procedure of Radwan (1978) . A sample of (50 mg) was transferred into screw-cap vial, 2 ml beuzene and 10 ml 1% H2S04 in absolute methanol were added. The vial was covered under a stream of nitrogen before heating in an oven 90 °C for 90 minutes. Then 1 ml of distilled water were added to the cooled vial and the methyl esters in each vial were extracted with 5 ml of petroleum ether for three times. The three petroleum ether extracts were combined and concentrate to its minimum volume by using a stream of nitrogen.

Analysis of fatty acids was carried out using a gas chromatography (GC) (Shimadzu GC-4CM-PFE) equipped with stainless steel column packed with 3 % diethylene glycol succinate on chromosorb W 80/100 and flame ionization detector (FID). The oven and detector temperatures were 180°C isothermal and 270°C, respectively. N2 gas was used as a carrier gas at a flow rate of 20 ml/min.

5.1. Analysis of composition of fatty acids isomers:

Contents of individual isomeric FA were determined by capillary gas chromatography (Agilent Technology, 6890N) with flame ionisation detection (CGC/FID) according to ISO 15304:2002. Fatty acid methyl esters (FAME) were prepared by standard method (ISO 5509:2000), pentadecanoic acid was used as internal standard to obtain content of FA in absolute values (% w/w). For analysis the capillary column SPTM 2560 (Supelco, Bellefonte), 0.25 mm × 100 m, film thickness 0.2 µm was used. The conditions of analysis were: hexane solution of FAME (1%) was used for the injection (1 µl), split injection (1:50) at 220°C; flow of carrier gas (He) 1 ml/min; analysis at 175°C for 120 min; FID detection at 250°C, flow of H2 40 ml/min, air flow 450 ml/min and make-up gas (N2) flow 45 ml/min. (Cihelkova *et al.*, 2009).

RESULTS AND DISCUSSION

1. Thermal behaviour of oils during frying process:

Frying oils were studied to learn how to control both the process and the resulting quality of the fried food simultaneously. Thermal behaviour (Temperature changes) of three types of vegetable oils during deep frying at 180°C (at zero time) .

This thermal behavior curve could be classified into five stages. (Stage1), represented the time required to heat the oil to reach the required temperature (180°C) and to keep it constant at this temperature this initial time, Table (1) varied among the three oils used. It was 9, 10 and 8 minutes for olive, sunflower and flaxseed oils, respectively. (Stage2) represented the introducing potato chips at zero time. After only one minute of frying time, the temperature suddenly decreased from 180°C to 142° C , 141° C and 140°C for olive, sunflower and flaxseed oils, respectively. The temperature continued to decrease up to 5-6 minutes of frying time according to the type of oil and reached the minimal temperature (stage 3) at 125, 128 and 130 °C for the same oils, respectively. This decrease could be attributed to water evaporation from potato chips. The temperature then started to increase again (Stage 4). It increased to 153, 152 and 155°C for olive, sunflower and flaxseed oils, respectively. However the rate of increment differed according to the type of oil used. Temperature increase is possibly because of the absorption of oil by potato chips and lower water evaporation. Finally, in (stage5), end of frying operation, where potato chips had the optimum sensory quality.

Oil oxidizes faster at higher temperatures. For example, increasing the frying temperature from 163 to 180° C more than doubles the oxidation reaction rate; therefore, frying temperature, even within the normal range, should be selected very carefully. An increase in temperature dramatically raises the rate at which fatty acids react with oxygen, promoting rancidity, and therefore increasing the peroxide value. Increasing the frying oil temperature tends to decrease oil uptake because the product spends less time in the fryer. It might be that this process is aided by the formation of a crust that acts as a barrier to further oil uptake. In addition, it might prevent water from leaving the food to an extent and consequently hinder the ingress of oil. However, it is important to find the optimum frying temperature to prevent a semi-raw and oily product as a result of too low a cooking temperature and a burnt and only partially cooked product from too high a frying temperature (Gertz, 2000).

Table (1): Effect of heating time (hrs) on the initial time (min) and frying time (min) of different oils at 180°c up to 8 hrs.

	Olive oil		Sunflower oil		Flaxseed oil	
Heating time(hrs)	Initial time(min)	Frying time (min)	Initial time(min)	Frying time (min)	Initial time(min)	Frying time (min)
0	9	10	10	10	8	9
8	10	11	11	12	10	11
16	12	15	14	15	14	16

Frying involves heat and mass transfer as well as interaction between the food and the frying medium. Only few studies offer some partial explanation of the mechanism (s) of oil uptake during frying (Saguy and Pinthus, 1995). During immersion frying of foods, there are two distinct modes of heat transfer, conduction and convection.

Convective heat transfer occurs between a solid food and the surrounding oil. The surface interactions between the oil and the food material are complicated because of the vigorous movement of water vapour bubbles escaping from the food into the oil. Conductive heat transfer, however, occurs within a solid food. The rate of heat transfer is influenced by the thermal properties of the food, including thermal diffusivity, thermal conductivity, specific heat, and density (Singh, 1995). The magnitude of these properties changes during the frying process.

These increases observed in both initial time required to reach 180°C and frying time as the heating continued up to 8 hours could be attributed to many factors:

(1) As the high heat capacity of oils is diminished by the prolonged heating, the oil would loss its functional properties as a heat transfer medium (Blumenthal, 1991) and as a result the time required to achieve the best frying will increase.

(2) Formation of soap and soap-like materials will cause excessive foaming in oil forming a soapy layer on the surface of potato chips preventing the oil to reach potato surface hence increasing the frying time (Gil and Handel, 1995).

(3) As saturation increases during frying, viscosity and melting points of oils will increase causing oil to need longer time reaching there required, temperature, (Hemandez, 1989.; and Tyagi and Vasishtha, 1996) .

(4) Frying process causes the formation of fatty acids with trans configuration (Hu *et al.,* 1997; Tyagi and Vasishtha, 1996), which have higher melting points than cis configuration fatty acids (i.e., C18:I cis melts at 14°C while C18 : 1 trans melts at 51 °C) (Nawar, 1996).

These trans fatty acids will increase viscosity and melting points. At the same time, variation differences existed in both initial heating time and frying time observed in the three oils could be due to the deterioration rate for oleic: linoleic : linolenic acids, which is 1: 10 : 20-30 (Warner, 1995).

Olive oil containing oleic acid, as a major constituent, was the least deteriorated among the oils because it has not yet been possible to find an easy, reliable, practical analytical solution to predict when to discard the oil (Chang *et al.,* 1978; Fritsch, 1981; Nawar, 1986; Firestone *et al.,* 1991).

2. Sensory quality of potato chips:

Warner *et al.,* (1994) found that the initial fatty acid composition of the oils significantly affected the overall flavor quality scores of the chips. They found that the quality scores decreased linearly with the increase of linolenic acid, while the relationship of linoleic acid to overall flavour quality was not linear. They suggested that there may be an optimum amount of oleic acid, and, too little or too much may contribute to decreased quality.

Results revealed that potato chips fried in the three oils gave the best colour (golden colour) at the beginning of heating time then gradually deteriorated as the frying time for 16 hours. Colour of potato chips fried in flaxseed oil after 2 hours and same in all oils, Colour of potato chips fried in olive oil and sunflower oil steadily decreased as the frying time increased.

Effect of heating time on texture of potato chips in terms of crispness is shown in Table (2). Data revealed that the potato chips fried in olive oil the best and the most stable crispness in 2 hours of frying then slightly became moderate crispy of frying as compared to those fried in flaxseed and sunflower. However, showed stable crispness. Same results oils frying up to 16 hours, texture of potato chips decreased as the heating time increased.

Sensory results of flavour by mouth (taste) revealed that potato chips fried in sunflower oil had the best taste up to 2 hours and same in other oils of frying. The taste of potato chips was affected by increasing the frying time.

Table (2): Effect of f time on the quality of potato chips fried in different oils at 180°c up to 16 hrs.

Frying time (hrs.)	Flaxseed oil				Sunflower oil				Olive oil			
	colour	flavor	texture	Overall acceptabity	colour	flavor	texture	Overall acceptabity	colour	flavor	texture	Overall acceptabity
After 2 hrs.	9± 0.31	8± 0.52	8.5± 0.47	8.5± 0.45	9± 0.47	9± 0.47	9± 0.18	9± 0.43	9± 0.56	8± 0.78	8.5± 0.80	8.5± 0.78
After 4 hrs.	8.5± 0.20	7.5± 0.45	8± 0.75	8± 0.34	8.5± 0.57	8.5± 0.47	8.5± 0.78	8.5± 0.35	8.5± 0.78	8± 0.75	8± 0.46	8.5± 0.75
After 6 hrs.	8± 0.36	7.5± 0.65	7.5± 0.94	7.5± 0.78	8± 0.19	8± 0.78	8± 0.42	8± 0.72	8± 0.65	8± 0.76	8± 0.59	8± 0.47
After 8 hrs.	7.5± 0.46	7± 0.45	7.5± 0.74	7.5± 0.47	8± 0.43	8± 0.48	8± 0.81	8± 0.52	8± 0.37	7.5± 0.42	8± 0.82	8± 0.83
After 10 hrs.	7.5± 0.65	6± 0.75	7± 0.26	7± 0.18	7.5± 0.18	7± 0.19	7± 0.74	7± 0.43	7± 0.63	7± 0.67	7.5± 0.56	7.5± 0.68
After12 hrs.	7± 0.14	5.5± 0.43	6± 0.74	6± 0.47	7.5± 0.75	6.5± 0.72	6.5± 0.65	7± 0.62	6.5± 0.84	6± 0.43	7± 0.74	6.5± 0.91
After 14 hrs.	6± 0.54	5± 0.74	5.5± 0.25	5± 0.49	7± 0.49	6± 0.65	6± 0.71	6.5± 0.54	6± 0.47	5.5± 0.36	6± 0.55	5± 0.85
After 16 hrs.	5± 0.82	4.5± 0.18	5± 0.78	5± 0.78	6± 0.73	5.5± 0.71	5.5± 0.91	5.5± 0.65	5± 0.64	5± 0.52	5± 0.73	5± 0.53

Values are means ±SD.

They concluded that potato chips fried in sunflower oil had a higher flavour quality and stability. The selection of frying oil used in frying process is based on price, quality, flavor, oxidation susceptibility, functionality, and availability (Blumenthal, 1991). Warner and Knowlton (1997) found that, the composition of 16-42% oleic acid and 37-55% linoleic acid produced fresh fried-food with moderate fried food flavour intensity, good overall flavour quality and low to moderate Total Polar Compounds (TPC) levels. However, in aged food or food fried in deteriorated oil, composition of 42-63% oleic and 23-37% linoleic provided the best flavour stability.

3.Quality parameters of frying oils:

The high temperatures used during frying, in the presence of oxygen and water, induce important chemical changes of the oils, namely by oxidation, polymerization, cyclization, and hydrolysis (Paul and Mittal, 1997; Saguy and Dana, 2003), inevitably reducing their shelf life and affecting directly the quality of the final fried food (Kochhar, 2001). These chemical reactions are influenced by the type and quality of the oil, the food properties, and the food/oil ratio, among other parameters (Saguy and Dana, 2003), altogether determining the frying oil performance (Andrikopoulos *et al.,* 2002). Each vegetable oil is characterized by typical stabilities against oxidation, dependent on the fatty acids composition, particularly the unsaturation degree, and the content and composition of minor compounds such as tocopherols (particularly **c**-tocopherol), certain sterols, hydrocarbons (squalene), carotenoids, polyphenols, and trace metals (Kochhar, 2001).

3. 1. Peroxide value (PV)

Peroxide value (PV) is one of the methods for determination of hydroperoxides as the initial lipid oxidation products. The PV is expressed as milliequivalents oxygen per kg of fat/oil (Nawar, 1996). Since hydroperoxides do not accumulate due to their instability at frying temperature, PV determination is not suitable for assessment of used frying oils (Matthaus, 2006; Suleiman *et al.,* 2006). Lipid oxidation involves the continuous formation of hydroperoxides as primary oxidation products that may break down to a variety of nonvolatile and volatile secondary products. (Dobarganes., *et al*., 2000).

Figure (1) shows the effect of Frying time on the PV (meq/kg oil) of the three oils during frying process at 180°C for 16 hours continually. Generally, the PV increased with increasing the heating time up to 8 hours, however all PV values were below 10 meq/kg oil. Results also revealed that the sunflower oil showed the highest PV value during the heating process as the initial PV of this oil was the highest (2.3 meq/kg oil). The PV reached 7.2 for sunflower oil after 16 hrs of heating as compared to other oils. Results also revealed that the longer the heating time, the higher the PV observed. The PV continued to increase as the heating time increased up to 8 hrs. The higher ramp rate, however, observed for sunflower and flaxseed oils that could be attributed to their high content of $C_{18:2}$ in sunflower oil and the high content of $C_{18:3}$ in flaxseed oil. These acids provided more active methylene groups, which were more prone to oxidative deterioration (Tyagi and Vasishtha, 1996). Data also showed that the PV represented the total hydroperoxide content and was one of the most common quality indicators of fats and oils during production and storage (Matthaus, 2006; and Suleiman *et al.,* 2006).

Data of PV also revealed that the oxidation process is affected by the degree of unsaturation. Both sunflower oil and flaxseed oil containing 18:2 and 18:3, respectively showed the highest PV. Meanwhile, the olive oil containing 18:1 showed lower PV. These results indicated that the oxidation stages of oils and frying were resulted a free radical from initiation, propagation and termination stages. The primary products of lipid oxidation are hydroperoxides. Hydroperoxides ROOH are the major initial reaction products of fatty acid with oxygen (Burcham1998). More recently, Skufca *et al,* (2003) determined the peroxide value of blend oil (sunflower with palm oil 89:11w/w) used in frying process was 682 meq O_2/Kg after frying period for 5 weeks.

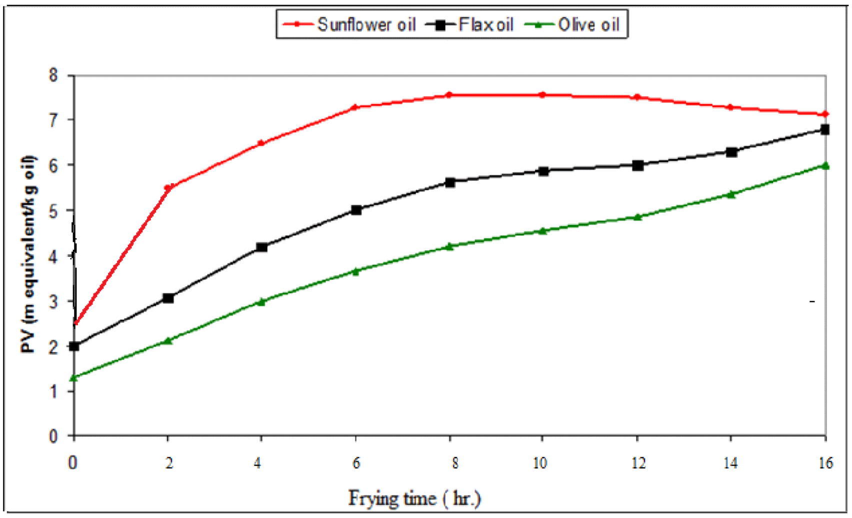

Figure (1). Effect of frying time on peroxide value of different oils during frying potato chips at 180ºC up to 16 hrs.

3. 2 . Anisidine value (An-V)

p-Anisidine value (An-V) is a method for measuring the secondary decomposition products such as aldehydes (Mariod *et al.,* 2006). Aldehydes are the carbonyl compounds formed by decomposition of hydroperoxides and can be used as markers to determine degradation of peroxidised materials produced by the heating process (Stier, 2001).

Figure (2) shows the effect of heating time on the *p*-Anisidine value (An-V) of the three oils during frying process at 180°C for 16 hours continuously. Generally, the (An-V) increased with increasing the heating time up to 8 hours, however all values were below 10. Results again revealed that the sunflower oil showed the highest (*p*-AV) value during the heating process as the initial (An-V) of this oil was the highest. The (An-V) reached 9.5 for sunflower oil after 16 hrs of heating as compared to other oils. Results also revealed that the longer the heating time, the higher the (An-V) observed.

Flaxseed oil, on the other hand, showed the lowest (An-V) as compared to other oils, however, olive oil showed close (An-V) values. The present results revealed that despite flaxseed oil contained 18:3 n-3 and sunflower oil contained 18:2 n-6 as a major fatty acid, the flaxseed oil showed lower (An-V) than the sunflower oil. This could be due to the high oxidation stability of flaxseed oil compared to the sunflower oil. In other words, sunflower oil deteriorated faster than flaxseed oil during frying process. However, the oxidation stability of these oils were close to each other and showed (An-V) values between sunflower oil and flaxseed oil (Barbary, 2000).

The oxidative deterioration of lipids involves primary autoxidative reaction which is accompanied by various secondary reactions having oxidative and non-oxidative reaction. The primary products of lipid oxidation are hydroeroxides. The secondary products were Ansidine value. The increased consumption of food fried by deep-fat frying entails the necessity of knowledge of the thermoxidative transformation occurring in the frying medium. Oxidation and polymerization reaction were predominated happen during deep-fat frying and in frying medium. Monitory Ansidine value (An-V) and polar compound fractions in the frying medium were excellent indicators to evaluate frying fat qualities Gertz (2000).

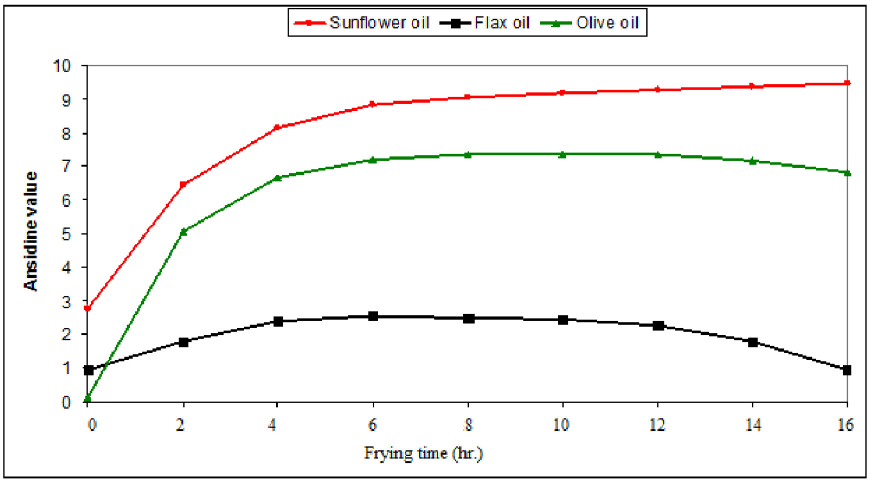

Figure (2). Effect of frying time on anisidine value of different oils during frying potato chips at 180°C up to 16 hrs.

The present study also confirmed that there was good correlation between PV and (An-V) as well as oil stability to establish the deterioration that happened in frying oils (Kajimato *et al.*, 1996). These statements agree with those found by Hansen *et al.,* (1994) who confirmed the increase of both peroxide and Ansidine value during frying process.

3. 3.Free fatty acids (FFA)

The free fatty acids (FFA) content and peroxide value (PV) of the oil were shown as general indicators for deterioration of frying oils. Free fatty acids or acid value was used as a measure of the effect oxidation and hydrolysis in triglycerides (Fritsch 1981 and Lopez-Varela. *et al.,* 1995). The acid value determination does not necessarily correlate with sensory evaluation (Handel *et al.,* 1984). During deep –fat frying, the level of fatty acids in the oil affected on acid value by shifting and evaporation rate equilibrium with addition of 5% fatty acid was decreased to evaporation (Handel and Guerrieri 1990). Both color index and free fatty acid values were highly correlated with frying time (Mazza and Qi 1992).

Figure (3) shows the effect of frying time on the free fatty acids (FFA) of the three oils during frying process at 180°C for 16 hours continuously. Generally, the FFA % increased with increasing the heating time up to 16 hours, however all values were below 2.0. This parameter is often used for assessment of the suitability of frying oils for human consumption and a value of 2% was defined as the limit for oil rejection (Matthaus, 2006). Results revealed that the flaxseed oil showed the highest FFA% (1.8%) during the heating process, however, sunflower oil showed the lowest FFA (0.2%), followed by olive oil. Free fatty acids (FFA) are a measure of the amount of fatty acids hydrolysed on the triacylglycerol backbone. They are used as a chemical marker for monitoring the quality of frying operations (Stier, 2001). Frying oil will break down during food processing. Free fatty acids (FFA) are normally measured to determine the relative stabilities of oil towards oxidative and thermal deterioration under deep frying conditions.

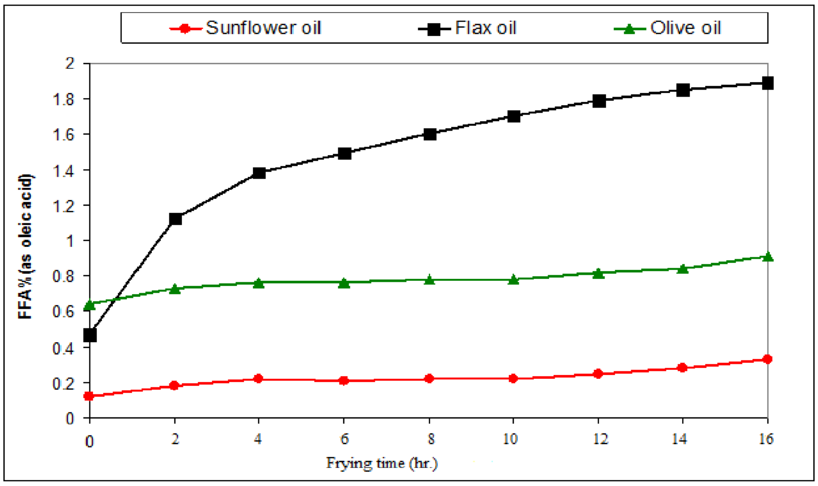

Figure (3). Effect of frying time on free fatty acids of different oils during frying potato chips at 180°C up to 16 hrs.

3. 4. Thiobarbituric Acid (TBA)

The thiobarbituric acid (TBA) test was proposed over 40 years ago and is now one of the most extensively used methods to detect oxidative deterioration of fat-containing foods (Kishida, *et al.,* 1993). During lipid oxidation, malonaldehyde (MA), a minor component of fatty acids with 3 or more double bonds, is formed as a result of the degradation of polyunsaturated fatty acids. It is usually used as an indicator of the lipid oxidation process, both for the early and later appearance as oxidation occurs and for the sensitivity of the analytical method.

Figure (4) shows the effect of frying time on the TBA number of the three oils during frying process at 180°C for 16 hours continuously. Generally, the TBA (mg malonaldehyde/kg oil) increased with increasing the heating time up to 16hours. Flaxseed oil showed the highest TBA value followed by sunflower oil and olive oil. As the TBA value is a measure of oxidation, these results were expected. Flaxseed oil that had the highest oxidation rate among the three studied oils also had the highest TBA values. Since oil undergoes a variety of chemical changes during cooking and frying, chemical changes brought about by heating are extremely important to both the consumer and process from nutritional and toxicological points of view (Chung and shu-yueh 1993).

3. 5. Iodine Value (IV)

Heating of fats and oil caused a corresponding chemical deterioration. This deterioration decreased the degree of unsaturation (iodine vaule) in addition to the physical changes including increases in color and viscosity (Paradis and Nawar1981 and Mounts *et al.* 1994). Such chemical changes are not only influenced the quality of frying oil and fried foods product but also are extremely important for both the consumers nutritional and toxicological.

Figure (5) shows the effect of heating time on the iodine value (IV) of the three oils during frying process at 180°C for 16 hours continuously. Generally, the IV decreased with increasing the heating time up to 8 hours. Flaxseed oil showed the highest decrease value followed by sunflower oil and finally the olive oil. As the IV value is a measure of degree of unsaturation, these results were expected. Flaxseed oil contained the most unsaturated fatty acid (linolenic 18:3) and sunflower oil contained linoleic acid (18:2) and finally the olive oil that contained 18:1. Moreover, this decrease in IV could be attributed to the destruction of double bonds by thermal oxidation. Data also revealed that there was a progressive decrease in the IV observed so confirming the loss of unsaturated fatty acids.

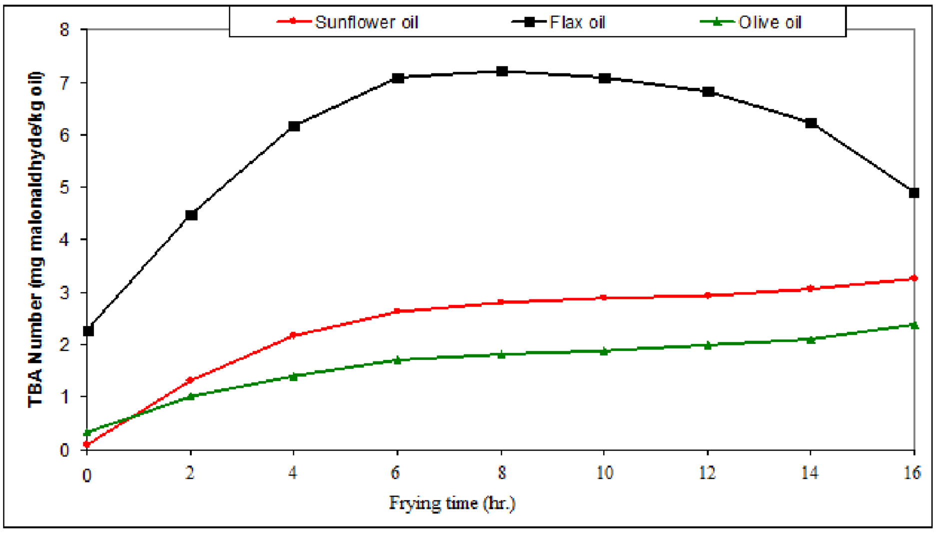

Figure (4). Effect of frying time on the thiobarbituric acid of different oils during frying potato chips at 180ºC up to 16 hrs.

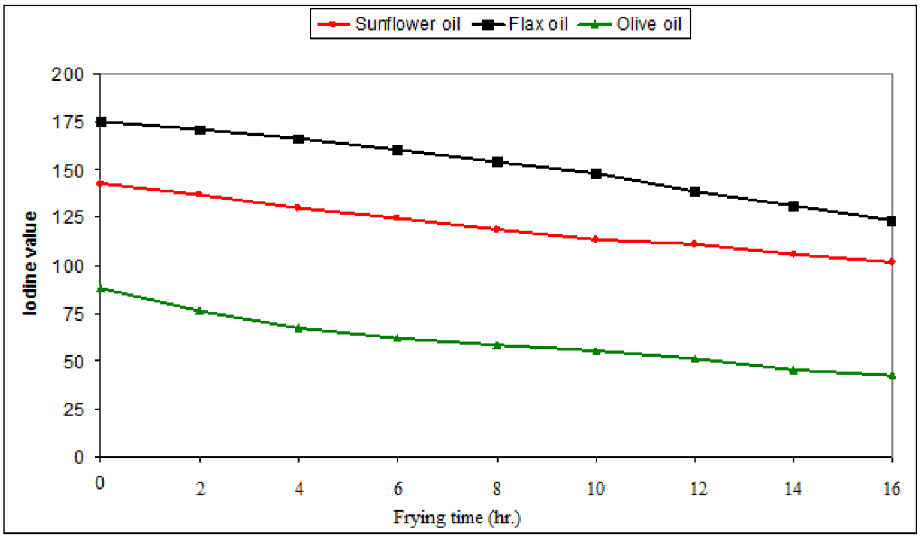

Figure (5). Effect of frying time on the iodine value of different oils during frying potato chips at 180ºC up to 16 hrs.

3 6. Fatty acid composition

As deep fat frying is normally carried out at high temperatures (between 160°C and 180°C) and in the presence of air and moisture, these frying oils and fats will undergo physical and chemical deterioration which will affect their frying performance and the storage stability of the fried products (Fauziah, *et al.,* 2000 **).**

The fatty acid compositions of three fresh vegetable oils were determined and are shown in Table (3). Data revealed that fresh olive oil composed of 16:0 (9.60 %); 16:1 (1.40 %); 18:0 (3.0 %); 18:1 (70.00 %); 18:2 (12.50 %) and 18:3 (3.50 %). These values are typical range of olive oil and are in agreement with those reported by Kiritsakis (1983).

Table (3): Fatty acid composition of different oils during frying potato chips at 180°c for 16 hrs.

Fatty acid	Flaxseed oil			Sunflower oil			Olive oil		
	Fresh	After 8 hours	After 16 hours	Fresh	After 8 hours	After 16 hours	Fresh	After 8 hours	After 16 hours
C 12:0	0	0	0.20	0	0	0	0	0	0
C 13:0	0.21	0.23	0.27	0	0.51	0.95	0	0	0.56
C 14:0	0.22	0.25	0.63	0	0.25	1.14	0	0	0.72
C 16:0	5.58	8.93	14.76	6.24	7	7.77	9.60	11.45	15.01
C 16:1	0	0	0	0	0	0	1.40	0	0
C 18:0	3.64	5.76	7.17	4.62	4.62	5.09	3.0	3.11	2.80
C 18:1	31.72	30.81	26.90	33.01	32.92	31.82	70.00	69.95	69.53
C 18:2	26.32	23.88	21.65	56.12	54.70	53.23	12.50	12.38	11.38
C 18:3	32.65	30.50	28.66	0	0	0	3.50	3.10	0
T. Saturated	9.31	14.81	22.79	10.86	12.38	14.95	12.6	14.56	19.09
T.Unsaturated	90.69	85.19	77.21	89.14	87.62	85.05	87.4	85.44	80.91

Fresh composition of flaxseed oil was 13:0 (0.04 %); 14:0 (0.05 %); 16:0 (5.58 %); 18:0 (3.64 %); 18:1(31.72 %); 18:2(26.32 %); and 18:3 (32.65 %).

Fresh sunflower oil composition was 16:0 (6.24 %); 18:0 (4.62 %); 18:1 (33.01); and 18:2 (56.12 %).

The total saturated fatty acids of fresh olive, flaxseeds and sunflower oils were 12.6; 9.31, and 10.86 %, respectively. The total unsaturated fatty acids in these fresh oils, however, were 87.4; 90.69; and 89.14 % for the same oils, respectively.

Therefore, the main constituent of olive oil was the oleic acid 18:1 (70.0%) with total unsaturated of 87.40 %. The main constituents of sunflower oil were the oleic acid 18:1 (33.01%) and linoleic acid 18:2 (56.12%) with total unsaturated of (89.14%). The main constituents of flaxseed oil were the oleic acid 18:1 (31.72 %); linoleic acid 18:2 (26.32 %) and linolenic18:3 (32.65 %) with total unsaturated of 92.56 %.

The effect of frying time on the fatty acid composition of the three oils was investigated during frying potato chips at 180°C up to 16 hours is also shown in Table (3). Results revealed that the fatty acids composition of the three heated oils was markedly affected by increasing the time of heating. Progressive decreases in unsaturation were observed in all oils. The total unsaturation of olive, flaxseed and sunflower oil after 4 hours decreased from 87.4, 90.69, and 89.14 % to 85.44; 85.19, and 87.62%, respectively. These decreases could be attributed to the destruction of double bonds by oxidation, scission, and polymerization (Cuesta, *et al.,* 1991).

The lowest decrease in the total unsaturation was in olive oil as compared to those of the other oils could be attributed mainly to the presence of natural tocopherols and other polyphenolic compounds in the olive oil (Fedeli, 1988). Olive oil also has a relatively high quantity of oleic acid (70.00) % and decreased to (69.96) % after 4 hours.

The total saturation, on the other hand, increased progressively in all oils with increasing the heating time up to 8 hours.

They increased from 12.6; 9.31 and **10.86** to 19.09; 22.79 and 14.95 for olive, flaxseed and sunflower oils, respectively. Afte 8 hours, increases in saturated fatty acid such as palmitic and stearic is probably due to linolenic, linoleic and oleic acid degradation. The different vegetable oils used for frying are characterized by different fatty acid profiles (Erickson, 2006). Oils with a high content of saturated fatty acids are more stable in the frying process but because of the negative health attributions associated with these, the interest in using monounsaturated oils in frying has increased (McDonald and Eskin, 2006).

The oil is quite stable to oxidation because of the small amount of linoliec acid present. Olive oil remains clear at lower temperature than most other liquid oils, Kiritsakis, (1983) found that higher oxidation rates were stimulated by chlorophyll. The occurrence of phenols in virgin olive oil is an important factor in oil stability and sensory quality. Natural phenols provide high resistance to oxidation, and a relationship between polyphenols content and oxidative stability has been reported for virgin olive oil (Vazquez, 1978).

Refined sunflower oil is a bale yellow colour with a pleasant flavour and with a fairly good resistance to oxidation. It is used as a salad oil, for frying, and as a component of margarines and shortenings. Sunflower oil has a rather high linoliec acid content than corn oil and is therefore, like corn oil, advocated as a suitable dietary fat in conditions of heart disease and high blood cholesterol levels.

Flaxseed oil is derived from the seeds of the flax plant and has been proposed as a more aesthetically pleasing alternative to fish oil supplements. Flaxseed oil contains higher levels of alpha-linolenic acid (ALA) than fish oil, and also contains omega-6 fatty acids. ALA is an omega-3 fatty acid that is ultimately converted to eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) in some species. EPA and DHA are of significant benefit in the management of chronic inflammatory and immune disorders. Flaxseed (*Linum usitatissimum*) is an oilseed produced mainly in Canada and, to a lesser extent, in other parts of the globe.

Despite being existed in the three oils, (C 18:2) decreased differently by 11.38, 21.65, and 53.23% for olive, flaxseed and sunflower oils, respectively after 8 hours. During oil heating in deep-fat frying the content of trans fatty acids is increased. Tyagi and Vasishtha (1996). The lowest percentage for olive oil is most probably due to the antioxidative effect of the natural tocopherols and phenolic compounds present in olive oil. Disappearance palmitoleic acid (C16:1) content in olive oil after 4 hours and be in blend oil after 8 hours as follows (1.73) %.

Free fatty acids increase the thermal oxidation of oils, and their unsaturation rather than chain length led to significant effects on thermo oxidative degeneration. Stevenson, *et al.* (1984) and Warner *et al.,* (1994) reported that the oxidation rate of oil increased as the content of unsaturated fatty acids of frying oil increased. This explains why corn oil with less unsaturated fatty acid is better frying oil than soybean or canola oils with more unsaturated fatty acids (Warner and Nelsen 1996). The content of linolenic acid is critical to the frying performance, the stability of oil, and the flavor quality of fried food (Liu and White 1992; Xu *et al.,* 1999). Total polar compounds contents of sunflower oil (C16:0, 5.3%; C18:0, 4.8%; C18:1, 55.4%; C18:2, 32.4%) and high linolenic canola oil (C16:0, 4.1%; C18:0, 2.2%; C18:1, 69.3%; C18:2, 13.8%; C18:3, 6.8%) after 80- h frying at 190°C were 44.6% and 47.5%, respectively (Xu *et al.,* 1999). The oil containing linolenic acid at 8.5% produced extremely undesirable acid and fishy odors when heated above 190° C (Frankel *et al.,* 1985). Low linolenic acid (2.5%) canola oil produced less free fatty acids and less polar compounds during deep-fat frying of potato chips at 190° C (Xu *et al.,* 1999). (Warner and Knowltor 1997) reported that polar compounds formation in cottonseed oil during deep-fat frying of potato chips increased proportionally with the linoleic acid content in the oil.

On the other hand , trans fatty acids of all samples were less than 1%,the same results were obtained by (Kemeny *et al*., 2001).Also (Henon *et al*., 1999) reported the rate and the degree of *cis-trans* isomerisation increase with the heating time and temperature.

Conclusion:

The time need for oil to reach the optimum temperature of 180 °C for frying increased with the number of frying process for vegetables oil of different omega fatty acids.

The degree of colour darkness increased by increase the number of frying process due to formation of polymers and polar compounds. The flaxseed oil recorde high value of colour up to 16 hours of frying followed by sunflower oil and finally olive oil. The frying process increased the saturated fatty acids in the vegetable oil and decreased of unsaturated fatty acids by increasing of the number of frying process due to the thermal oxidative and double bounds breakage in the unsaturated fatty acids which lead to change in the chemical composition of the oil.

It is concluded that potato chips fried in sunflower oil had a higher quality and stability. The selection of frying oil used in frying process is based on price, quality, flavor, oxidation susceptibility, functionality, and market availability.

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تأثير التحمير العميق على خصائص بعض الزيوت النباتيه

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الملخص العربى

عملية التحمير من العمليات الهامه و التى فيها يتم وضع الغذاء فى الزيت الساخن حيث يتم ذلك فى وجود الزيت والهواء و الغذاء معا على درجة حراره عاليه تصل مابين١٦٠-١٨٠ درجه مئويه. وتحفز درجات الحراره العاليه المستخدمه اثناء التحمير وفى وجود الاوكسجين تغيرات كيمائيه هامه للزيت ومن اهمها الاكسده والتحلل المائي. وقد وجد ان الزيوت يوجد بها اختلافا فى كل من الجوده والخصائص الوظيفيه ومعدل التدهور الذى يعتمد على مصدر الزيت والعمليات التصنيعيه. ولذلك كان هدف البحث دراسة السلوك الحرارى للزيوت النباتيه المختلفة فى محتواها من الاحماض الدهنيه من نوع الاوميجا.

ولتحقيق هدا الهدف ثم اختيار ثلاث زيوت نباتيه مختلفة فى محتواها من الاحماض الدهنيه (الاوميجا) واستخدمت فى عمليات التحميروهى زيت الزيتون وعباد الشمس والكتان.

وقد ثم اجراء ٣٢ دورة تحمير لكل زيت وتم اجراء تقيم حسى لشبسى البطاطس المحمره وقد تم تقدير كلا من رقم البيروكسيد و رقم الانسيدين و الرقم اليودى و قيمة (TBA) والنسبه المئويه للاحماض الدهنيه الحره تم ثم تحليل تركيب الاحماض الدهنيه لتلك الزيوت.

أوضحت النتائج التى تم الحصول عليها ان كلا من البيروكسيد و رقم الانسيدين والرقم اليودى و قيمة (TBA) والنسبه المئويه للاحماض الدهنيه الحره زادت بزيادة عدد مرات التحميربينما انخفض الرقم اليودى.و أوضحت النتائج التى تم الحصول عليها ايضا ان الاحماض الدهنيه المشبعه فى كل زيوت التحميرزادت بزيادة عدد مرات التحمير بينما انخفضت نسبة الاحماض الدهنيه الغير مشبعه.وأيضا خلال التقيم الحسى تم تفضيل شبسى البطاطس المحمره فى زيت عباد الشمس عن الزيوت الاخرى .