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USE OF SAFFLOWER OIL MIXED WITH PALM OLEIN IN DEEP- FAT FRYING PROCESS

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ABSTRACT

The aim of the present study was to increase the stability of safflower oil during frying process. Therefore, safflower oil was mixed separately with palm olein at ratios (8: 2, 7: 3 and 5: 5, v/v). The frying process was conducted at 180˚C ± 5˚C for 20 hr, 5hr per day. Some physico-chemical properties (refractive index, viscosity, color, acid value, peroxide value, thiobarbituric acid, polar content, polymer content and oxidized fatty acids) of non-fried and fried oil mixtures were measured at various heating periods. The results demonstrate that mixing safflower oil with palm olein increased the stability and hence improved the quality of safflower oil during frying process.

Key words: Deep-fat frying, safflower oil, palm olein, hydroperoxids.

INTRODUCTION

Deep –fat frying is an ancient process that has grown exponentially over the last 50 years (Stier, 2004). This process of cooking consists in immersing food in edible oil that is heated to a temperature above the boiling point of water (Kochhar & Gertz, 2004). Edible fresh oils are, for 96 – 99 %, mixtures of triglycerides that undergo irreversible degradation during deep-fat frying, mainly due to heat, water, oxygen and light exposure. During the heating or the cooling of oil, at temperatures below 100˚C, the atmospheric oxygen reacts with the triacylglycerols, producing hydroperoxides (Achir *et al*, 2006). In the frying stage, at high temperatures, the oxidation of unsaturated fats is not accelerated as oxygen is limiting, but a free radical mechanism enhances hydroperoxide decomposition

into volatile and non-volatile secondary oxidation compounds as aldehydes, ketones, oxidative dimmers and polymers (Farag *et al*, 2008). Furthermore, during frying, water vapor escapes from the food and increases the moisture gives rise to hydrolytic reactions producing free fatty acids, mono and diacylglycerols and glycerol (Warner, 2001). Finally, the excess of energy provided to the oil forms chemical cross-likes causing polymer formation in the oil (Paul & Mittal, 1997). All these compounds may impair the nutritional value of the food, having adverse nutritional effects and potential hazards to human health (Matthaus, 2006, Velasco, 2004 & Gloria & Aguilera, 1988). On the other hand, investigations of commercial frying have generally indicated that these oils have no deleterious effects upon human health (Tyagi & Vasihtha, 1996). A part from this, the nutritional value of frying fats is affected by loss of polyunsaturated fatty acids, which supplement the essential fatty acids requirement in human metabolism (Katsuta, *et al*, 2008). Safflower oil, because of its high content of polyunsaturated fatty acids, is considered to be superior to many vegetable oils and hydrogenated fats from a nutritional standpoint, but it is inferior in thermal stability at high temperatures. Furthermore, partially hydrogenated fats and oils may have adverse nutritional effects due to the presence of trans isomers (Caponio, *et al*, 2003). Palm oil and palm olein are balanced fats containing about 50: 50 % saturated to unsaturated fatty acids (Razali & Badri, 2000). They have marginal amounts of linolenic acids and about 10 % linoleic acid (the essential fatty acid required by our body). They have a long induction period of more than 40 hr, low levels of polymer compound (< 1 %) and a high smoke point of over 200˚C (Marmesat, *et al*, 2005). These properties coupled with their competitive price and consistent supply, palm oil, olein and palm shortening have over the last 20 years or so been a popular choice for food manufactures in many countries, replacing (either totally or partially) traditional frying oils such as lard, tallow, peanut, sunflower or cotton seed oil (Masashi, et al, 1985 & Razali & Nor-Aini, 1992).

The main objective of this study was to assess the safflower oil mixed with palm olein (8: 2, 7: 3, and 5: 5 v/v) for deep-fat frying and to extend the shelf –life of oils.

MATERIALS AND METHODS

Source of safflower seed and palm olein:

Safflower seeds (*Carthamus tinctorius L.,*) Giza 1 variety was obtained from Agriculture Research Center, Oil Crops Department Giza, Egypt, and palm olein was obtained from Sila edible Oil Co. S.A.E., Kom Osheim, EL- Fayoum Governorate, Egypt.

Solvents:

All solvents used throughout the whole work were analytical grade and distilled before use.

Extraction of safflower oil:

The seeds were ground and packed in cheese cloth, pressed using hydraulic laboratory (Carver) press. The produced oil was filtered using Whatman filter paper No.1 and kept in brown glass bottle.

Preparation of oil blends:

System 1: safflower oil, system 2: palm olein, system 3: safflower oil and palm olein 80: 20 v/v, system 4: safflower oil and palm olein 70: 30 v/v, system 5: safflower oil and palm olein 50: 50 v/v.

Fatty acid composition determination:

Fatty acid composition was analyzed gas liquid chromatography (GLC). The oil was esterified before GLC analyses using the method described by (Stahl, 1967). The methyl esters of fatty acid were prepared using (benzene: methanol: concentrated sulphuric acid 86: 10: 4) and the methylation process was carried out for one hour at 80 – 90˚C. A pye Unicom PU 4550 equipped with dual flame ionization detector was used. The fractionation of fatty acid methyl esters was conducted using a coiled glass column (105 mm x 4 mm) packed with diatomite (100 – 120 mesh) and coated with 10 % polyethylene glycol adipate. The oven temperature was programmed at 8C / min. from 70C to 190C then isothermally at 190C for 10 min. with nitrogen at 30 ml / min as a carrier gas, the flow rates for hydrogen and air were 30 ml/ min. and 320 ml / min. respectively. Detector and injector temperature were 300C and 250C respectively. The chromatogram of the authentic fatty acids used to characterize the unknown fatty acids according to their retention times. Present normalization of each fatty

acid was calculated by the normalization with response factor method using the PU 4810 computing integration. The fatty acid composition was expressed as percentage of total fatty acid (Farag, *et al*, 1984).

Frying process:

Palm olein, safflower oil and their blends were used for frying potato chips as follows: A known amount (Ca. 2kg) of each system was placed separately in a stainless steel pan fryer (60 cm diameter x 30 cm height). The aforementioned oils and their mixtures were separately heated at 180˚C ± 5˚C, Then lot of potato chips (2 mm thickness) previously soaked in sodium chloride solution (10 %, w/v) were fried. After frying of potato chips and at end of each day, sample oils were withdrawn and stored in brown bottles at 20˚C until analysis.

Quality assurance methods for unfired and fried safflower oil and oil admixtures:

Refractive index, smoke point, viscosity, acid value, peroxide value, iodine value, and oxidized fatty acids were determined according to (A. O. A. C, 2005). Thiobarbiuric acid, polar content and insoluble polymer content for the unfired and fried oil samples were determined according to the methods of (Sidwell, 1954, Walking & Wessels, 1981 & Wu, & Nawar, 1986). The colour of the unfired and fried oil samples was estimated using a Lovibond tintometer. The yellow glass filter was fixed at 35 and the intensity of red glass colour was measured according to the method reported by (Nielson, 1998). Refractive flow time was measured as an indication of oil viscosity. The relative flow times of the various samples of oils were measured using an Ostwald viscometer according to (Joslyn, 1950).

Statistical analysis:

The present data were subjected to analysis of various and the least significant difference (LSD) test was calculated to allow comparison between the average values of the studied factors (Cochran & Cox, 1992).

RESULTS AND DISCUSSION

Several methods are used to prevent or delay oil oxidation and to improve the quality of fried oils. These methods include: additive of natural antioxidant (Basuny, 2004), blending or mixing oils (Basuny, *et al,* 2006), and ferrous sulfate (Farag & Basuny, 2004).

In the present study, the attention was focused on the prevention or delay oxidation and concomitantly obtains fried foods. Hence, safflower oil was mixed with palm olein at ratios of 8: 2, 7: 3 and 5: 5 (v/v) to delay safflower oxidation.

Characteristics of non-fried oils:

Physico-chemical properties of fresh safflower oil and palm olein are shown in Table (1). From the results, it could be noticed that refractive index of safflower oil and palm olein were 1.4741 and 1.4575, respectively. The smoke point of non-fried oils was 230˚C and 240˚C respectively. The color of fresh oils (at yellow 35) was 1.30 and 2.40 red. While the viscosity of safflower oil and palm olein was 5.50 min and 8.00 min. The data in Table (1) indicated that the safflower oil have higher iodine value than palm olein. This is mainly due to the type of oil as the safflower oil related to drying oils, besides safflower seed oil contains a high percent of unsaturated fatty acid. However the acid value, peroxide value and other chemical properties for fresh oils are within the limits permitted by the Egyptian Standard for oils (Egyptian Standard for Oils, 1993).

Fatty acid compositions of fresh oils (safflower and palm olein) were identified by gas liquid chromatography and the obtained data presented in Table (1). From the data it could be noticed that palmitic acid was presented as a major saturated fatty acid in oils as it amounted to 5.25 and 37.00 % in safflower oil and palm olein. Mean while, oleic acid ($C_{18:1}$) was present as a major unsaturated fatty acid as it reached 43.50 %in palm olein compared to 15.00% in safflower oil. On the other hand linoleic acid ($C_{18:2}$) was found in high content ratio in safflower oil (77.00 %) compared to minor concentrations in palm olein (10.50 %). The presence of linoleic acid in high percentage in safflower oil confirmed its higher iodine value as compared to that of palm olein. Similar results for the fatty acid composition of oils were also reported by (Baileys, 2006).

Table (1): Some physical, chemical and fatty acids composition of fresh oils (safflower and palm olein)

Characteristics		Safflower oil	Palm olein	LSD at P > 0.05
Refractive index (at 25°C)		1.4741	1.4575	0.0002
Smoke point (°C)		230.00	240.00	2.00
Viscosity (min)		1.300	8.00	1.50
Colour:	**Yellow**	35	35	-
	Red	1.30	2.40	0.30
Acid value (mg KoH / g oil)		0.15	0.02	0.03
Peroxide value (meq. O_2 / Kg oil)		0.61	0.30	0.10
TBA value (532 nm)		0.001	0.001	0.05
Iodine value (Hanus)		140.00	57.30	5.00
Polar content (%)		0.00	0.00	-
Polymer content (%)		0.00	0.00	-
Oxidized fatty acids (%)		0.00	0.00	-
Fatty acid composition:	**$C_{12:0}$**	1.00	0.50	0.20
	$C_{14:0}$	0.40	0.90	0.15
	$C_{16:0}$	5.25	37.00	2.00
	$C_{18:0}$	1.50	2.50	0.10
	$C_{18:1}$	15.00	43.50	0.45
	$C_{18:2}$	77.00	10.50	10.50
	$C_{18:3}$	0.60	0.20	0.10
	$C_{20:0}$	0.30	0.10	0.05

LSD demonstrates to least significant difference test at P > 0.05

Physico-chemical properties of non-fried and fried safflower, palm olein and their blends during frying:

Refractive index:

Table (2) shows the refractive index values for the non- fried and fried safflower oil, palm olein and their mixtures (8: 2, 7: 3 and 5: 5 v/v). The values demonstrate that safflower oil refractive index value

was higher than that of the refractive index of palm olein, and mixed oil samples. There is a strong relationship between the refractive index and iodine value, with higher iodine values would have higher refractive index and this fact is in line with data of the present work.

The value of refractive index of fried safflower oil, palm olein and mixtures of them indicate a linear relationship between their refractive indices and frying period. The increase of the refractive index values over frying time for the oil systems was in the order: safflower oil > safflower oil + palm olein mixture (5: 5 v/v) > palm olein + safflower oil mixture(7: 3 v/v) > palm olein + safflower oil mixture(8: 2, v/v) > palm olein. This sequence is in line index values for the conjugated compounds are higher than that of their non-conjugated isomers. It is established that during oil frying some of the non –conjugated double bonds are converted to conjugated ones and this process cause an increase in the refractive index value (Bailey's, 2006).

Smoke point:

Table (2) shows the changes in smoke point of fried oils and their blends at various periods compared with those at zero time. The value of smoke point of fried safflower oil was gradually decrease compared with palm olein. It is worth noting that the smoke points of fried safflower oil mixed with palm olein at various levels (8: 2, 7: 3, 5: 5, v/v) were generally higher than safflower oil alone.

Colour:

In most cases two types of colored glasses of Lovibond tintometer, i. e., yellow and red, were used to measure the color of the oils. The yellow glasses were fixed at a value of 35 and the variation in oil color was matched with red glasses. Table (2) illustrate that the initial red colors for safflower oil and palm olein were 2.00 and 1.80, respectively. As a general trend, the intensity of the red color in all oil systems was increased as the frying time increased. The darkness of oil color due to frying at 180˚C ± 5˚C was arranged according to the oil type in the following decreasing order: safflower oil > safflower oil + palm olein mixture (8: 2, v/v) > safflower oil +palm olein mixture (7: 3, v/v) > safflower oil + palm olein mixture (5'; 5, v/v) > palm olein. Accordingly blending safflower oil with palm olein produced lighter frying media.

Table (2): Changes in some physical properties of oils (safflower and palm Olien) and their blends during frying

Frying time (day)	Systems of frying oils				
	1	2	3	4	5
Refractive index (25˚C)					
0	1.4741a	1.4575a	1.4730a	1.4710a	1.4658a
1	1.4743a	1.4576a	1.4731a	1.4710a	1.4658a
2	1.4745b	1.4578b	1.4733b	1.4711b	1.4659b
3	1.4750c	1.4579c	1.4735c	1.4712c	1.4560c
4	1.4754d	1.4581d	1.4736d	1.4714d	1.4660d
LSD	0.0002				
Smoke point (˚C)					
0	230.00a	240.00a	232.00a	234.00a	236.00a
1	228.00b	238.00b	230.00b	232.00b	234.00b
2	224.00c	236.00c	227.00c	230.00c	233.00c
3	219.00d	230.00d	224.00d	229.00d	230.00d
4	215.00e	227.00e	221.00e	225.00e	226.00e
LSD	1.00				
Color (red) (yellow at 35)					
0	1.30a	2.40a	1.40a	1.65a	1.80a
1	2.70b	2.90b	1.90b	2.10b	2.30b
2	5.50c	4.50c	4.80c	4.80c	3.90c
3	9.40d	6.70d	7.80d	7.10d	7.00d
4	11.90e	8.12e	10.00e	9.50e	8.80e
LSD	0.30				
Viscosity (min)					
0	5.50a	8.00a	5.90a	6.00a	6.50a
1	6.70b	10.12b	7.00b	8.00b	8.10b
2	8.90c	13.50c	8.60c	10.30c	10.00c
3	9.40d	14.20d	10.11d	12.40d	10.90d
4	12.50e	15.30e	11.50e	13.50e	11.40e
LSD	1.50				

LSD demonstrates to least significant difference test $P > 0.05$

Viscosity:

Table (2) shows the changes in viscosity values of non –fried and fried safflower oil, palm olein and mixtures of them. The viscosity values of the non- fried safflower oil and palm olein were 4.5 min and

4.80 min, respectively. Frying the oil systems at 180˚C ± 5˚C for 5hr / 5 day heating caused a gradual increase in the viscosity values throughout the entire experiment. In other words, there were gradual and significant increases in the viscosity values of the oils and frying time.

Acid value:

Acid value is one of the indicators used to assess oil quality. Table (3) shows the changes of acid values for of fried oils under study. The acid value of fried oils showed gradually increase with frying time. Hence, the increase of the acid value was in the order: safflower oil > safflower oil + palm olien mixture (8: 2, v/v) > safflower oil + palm olein mixture (7: 3, v/v) > safflower oil + palm olein mixture (5: 5, v/v) > palm olein. These findings demonstrate the improvement in safflower oil quality during frying at 180˚C ± 5˚C when mixed with palm olein.

Peroxide value:

This fat constant indicates the primary oxidation products of the oils (hydroperoxides). Table (3) show the peroxide value of safflower oil and palm olein at the beginning of the experiment and were 0.61 and 0.31 meqO_2 / kg oil, respectively. The peroxide values of these oils were within the recommended values for human consumption. The changes in the peroxide values of fried safflower oil, palm olein and mixtures are shown in Table (3). The values of peroxide value of the fried oils were progressively and significantly increased during frying process. The values of peroxide values for the oils at the end of frying period indicate that the increase of peroxide value was in the order: safflower oil > safflower oil + palm olien mixture (8; 2, v/v) > safflower oil + palm olein mixture (7: 3, v/v) > safflower oil + palm olein mixture (5: 5, v/v) > palm olein. It's well known that the degree of oil oxidation is obviously dependent upon oil unsaturation and this order is in line with this fact. In other words, mixing safflower oil with palm olein lowered the peroxide value of safflower oil during frying and hence increases the stability of safflower oil during frying.

Thiobarbituric acid value (TBA):

The results of TBA test (Table 3) indicate the incidence of gradual and significant increase on the TBA values for fried safflower oil alone and mixed with different ratios of palm olein (8: 2, 7: 3, and 5: 5 , v/v).

Table (3): Changes in some chemical properties of oils (safflower and palm olein) and their blends during frying

Frying time (day)	Systems of frying oils				
	1	2	3	4	5
Acid value (mg KOH / g oil)					
0	0.15a	0.02a	0.13a	0.11a	0.08a
1	0.29a	0.16a	0.31a	0.21a	0.19a
2	0.45b	0.31b	0.47b	0.35b	0.25b
3	0.99c	0.79c	0.88c	0.73c	0.67c
4	1.90d	1.02d	1.71d	1.50d	1.20d
LSD	0.04				
Peroxide value (meq. / kg oil)					
0	0.61a	0.30a	0.55a	0.50a	0.45a
1	2.40	1.20b	2.10b	2.01b	1.91b
2	8.50	4.60c	7.00c	7.00c	6.50c
3	16.80	9.50d	14.30d	13.90d	12.55d
4	25.40	16.90e	23.50e	22.10e	18.10e
LSD	0.10				
Iodine value (g I2 / 100 g oil)					
0	140.00a	57.30a	130.00a	115.00a	99.00a
1	138.00b	56.00b	129.00b	114.00b	98.00b
2	135.00c	54.00c	124.00c	110.00c	96.00c
3	131.00d	50.00d	121.00d	107.00d	94.00d
4	127.00e	45.00e	117.00e	104.00e	91.00e
LSD	1.30				
Thiobarbituric acid (absorbance at 535 nm)					
0	0.001a	0.001a	0.0005a	0.0005a	0.0005a
1	0.01b	0.01b	0.001b	0.001b	0.001b
2	0.23c	0.18c	0.01c	0.01c	0.01c
3	0.64d	0.58d	0.20d	0.18d	0.15d
4	0.98e	0.84e	0.65e	0.50e	0.45e
LSD	0.05				

LSD demonstrates to least significant difference test $P > 0.05$

The results show that the production rate of TBA reacting substances was obviously dependent upon the degree of oil unsaturation. Consequently, mixing safflower oil with palm olein

resulted in depression of the production of secondary oxidation substances. Accordingly, the increase of the TBA value according to oil type was in the order: safflower oil > safflower oil + palm olien mixture (8; 2, v/v) > safflower oil + palm olein mixture (7: 3, v/v) > safflower oil + palm olein mixture (5: 5, v/v) > palm olein. These findings demonstrate that mixing safflower oil with palm olein decreased the formation rate of TBA reacting substances. This means that blending safflower oil with the other oil improved its quality during frying process.

Iodine value:

The iodine value indicates the degree of an oil unsaturation. Table (3) shows the changes of iodine values for fried safflower oil and palm olein during frying (180˚C) over time. The effect of frying time on the oils under study shows a gradual and significant decrease in the iodine values of the oils and these results may be expected because during oxidation process some of the non conjugated double bonds are converted to conjugated ones which preclude the complete addition of iodine to the double bonds (Caponio, *et al.,* 2003). The admixture of safflower oil with palm olein at ratios of 8: 2, 7: 3, and 5: 5, v/v) caused lowering the iodine value of safflower oil during frying.

Polar content:

Changes in polar content of safflower oil, palm olein and mixtures of them (8: 2, 7: 3, and 5: 5, v/v) are shown in Table (4). At zero time, non detectable polar compounds were found. Frying of safflower oil, palm olein and their mixture at 180˚C ± 5˚C for 5 hr / 5 day caused increase in the polar compounds content of all oil systems. The increases of polar compounds contents of the oil systems were in the order: safflower oil > safflower oil + palm olien mixture (8; 2, v/v) > safflower oil + palm olein mixture (7: 3, v/v) > safflower oil + palm olein mixture (5: 5, v/v) > palm olein. In addition blending safflower oil with palm olein induced lowering effect on the formation of polar content.

Polymer content:

At zero time, non detectable polymer compounds were found for safflower oil, palm olein and its admixtures were nil (Table 4). The changes in polymer contents of the fried oil systems showed increases with time. The increases of polymer contents of the oil systems were in the order: safflower oil > safflower oil + palm olien mixture (8; 2,

v/v) > safflower oil + palm olein mixture (7: 3, v/v) > safflower oil + palm olein mixture (5: 5, v/v) > palm olein. These results indicate that blending safflower oil with palm olein at different ratios possessed lower effect on the formation of polymers during process. It is well established that the degree of polymer formation is largely depends on the oil unsaturation.

Table (4): Changes in some chemical properties of oils (safflower and palm Olein) and their blends during frying

Frying time (day)	Systems of frying oils				
	1	2	3	4	5
Polar content (%)					
0	0.00a	0.00a	0.00a	0.00a	0.00a
1	0.72a	0.50a	0.65a	0.60a	0.52a
2	4.90b	3.80b	4.10b	3.90b	3.80b
3	11.80c	8.40c	10.40c	9.11c	9.00c
4	23.50d	11.30d	19.80d	15.10d	14.30d
LSD	1.70				
Polymer content (%)					
0	0.00a	0.00a	0.00a	0.00a	0.00a
1	0.30b	0.20b	0.30b	0.27b	0.25b
2	1.50c	1.05c	1.41c	1.32c	1.00c
3	2.11d	1.60d	1.90d	1.80d	1.70d
4	4.15e	2.50e	3.11e	2.90e	2.61e
LSD	0.30				
Oxidized fatty acids (%)					
0	0.00a	0.00a	0.00a	0.00a	0.00a
1	0.10b	0.05b	0.09b	0.09b	0.006b
2	0.30c	0.22c	0.28c	0.25c	0.23c
3	0.85d	0.56d	0.81d	0.78d	0.65d
4	1.41e	0.95e	1.31e	1.25e	1.00e
LSD	0.09				

LSD demonstrate to least significant difference test P > 0.05

Oxidized fatty acids:

The results in Table (4) showed the formation of oxidized fatty acids in all oil systems. The changes in oxidized fatty acids content of

the fried oil systems showed increases with time. Accordingly, the increase of the oxidized fatty acid contents of the oil systems were in the order: safflower oil > safflower oil + palm olien mixture (8; 2, v/v) > safflower oil + palm olein mixture (7: 3, v/v) > safflower oil + palm olein mixture (5: 5, v/v) > palm olein. These results showed that blending safflower oil with palm olein at different ratios led to the decrease of safflower oil oxidized fatty acid contents during frying a at180˚C ± 5˚C.

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استخدام خليط من زيت بذور القرطم وزيت اولين النخيل فى عملية التحمير

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يهدف هذا البحث الى زيادة ثبات زيت بذور القرطم اثناء عملية التحمير. وذلك بخلط زيت بذور القرطم مع زيت اولين النخيل بنسب مختلفة (8: 2، 7: 3 ، 5: 5 حجم /حجم). تم تقدير بعض الخواص الطبيعية والكيماوية (معامل الانكسار – اللزوجة – اللون – نقطة التدخين – رقم الحموضة – رقم البيروكسيد – رقم حامض الثيوباربيتيوريك – الرقم اليودى - محتوى المركبات القطبية – محتوى البوليمرات – محتوى الاحماض الدهنية المؤكسدة).

وقد اشارت النتائج المتحصل عليها الى ان خلط زيت بذور القرطم مع زيت اولين النخيل يؤدى الى زيادة الثبات الاكسيدى ويحسن من خصائص الجودة لزيت بذور القرطم اثناء التحمير.