EFFECT OF HEATING PROCESS ON THE STABILITY OF SOYBEAN AND SUNFLOWER OIL MIXTURE TREATED WITH SOME DIFFERENT NATURAL ANTIOXIDANTS.

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ABSTRACT

Soybean oil is the most popular types of edible oils in Egypt. It is characterized by rapidly due to oxidation and rancidity processes. This study has been conducted to study the various transactions mixing and heating on the stability of soybean oil. And has been mixing soybean oil to sunflower oil by ratio (1: 1) and has been conducting the process of primary heating at 50°C for 3 hours and then was treated with natural antioxidants extracted from waste of fruits and grains factories for example mango peels, apple pomace and wheat bran with concentrations (200, 400 and 600 ppm) and TBHQ as synthetic antioxidants with concentration (200 ppm).

Results for the identification and separation of phenolic compounds of the antioxidants using HPLC being as follows: chlorogenic, salicylic, vannillic, benzoic and ellagic acids were the predominant obtained phenolics compounds. also the results obtained from total phenolic compounds as gallic acid being (14.53: 144.13 mg / g) and 2,2 diphenyl1-picrylhydrazyl(DPPH) results showed that mango peel extract gave the highest antioxidant activity(96.59%) compared to other extracts.

Treated oil were thermally heated at 65°C for 96 hours and some chemical properties (acid number, peroxide value and TBA value) were evaluated , our results showed an observed increase in acid value of untreated oil samples compared with treated samples with different antioxidants extracts , whereas high gradual increase in the constants of oxidation and rancidity (peroxide and TBA values). Peroxide and TBA values were reached a maximum values which peroxide values being 22.57 ml.eqv./Kg oil for untreated oil sample and 12.96ml.eqv./Kg oil for treated oil sample with mango peels extract, while TBA values being 2.330 mg malonaldhyde/Kg oil for untreated oil sample compared with and 0.700 mg malonaldhyde/Kg oil in oil samples treated mango peel extract after 96 hours of heating.

From then evident from the previous results that the additions of mango peel extract concentration of 600 ppm led to the improvement of the qualities of soybean oil mixture and thermally laboratories (chemical and natural) and delay rancidity and oxidation processes.

INTRODUCTION

Oxidative stability is one of the most important indications for maintaining the quality of the vegetable oils. The resistance to oxidation is recognized as oxidative stability under different conditions and is expressed as the period of time necessary to accomplish an end point which can be selected according to diverse criteria, but typically leads to rapid increase in the rate of lipid oxidation is a measure of oxidative stability and is known as induction time (Arain *et al*., 2009).

Thermo-oxidation process subjects oils or fats to high temperature, similar to the frying process, but without the presence of food. Therefore, the

temperature and the oxygen content are the variable that determines thermo-oxidation rates (Ramalho and Jorge 2008).

At high temperatures the formation of new compounds is very rapid, the oxygen pressure is reduced and the hydro-peroxides decompose rapidly and are practically absent above 150°C indicating that the decomposition of hydro-peroxides becomes faster than their formation (Marmesat *et al*., 2010).

Sunflower oil is the non-volatile oil compressed from sunflower seeds. It is commonly used in food as frying oil and cooking. It is a monounsaturated (MUFA) \ polyunsaturated (PUFA) mixture of mostly oleic (omega-9), linoleic (omega-6) group of oil. The oil content of the seed range from 22 to 36 % (average 29 %). It contains appreciable quantities of vitamin E, sterols, squalene and other aliphatic hydrocarbons, terpene and methyl ketones (Chowdhury *et al*., 2007).

Soybean oil of typical composition performs well as a salad oil, but it is usually hydrogenated for use as a margarine stock or as frying oil. Soybean oil's stability to oxidation also is limited by its content of linoleic acid (Hammond *et al*., 2005).

It is known that soybean oil contains triglycerides, free fatty acids, pigments, phospholipids and other constituents. Recently, as public concern for health problems caused by consuming animal fat has grown, consumption of vegetable oils has become more and more popular, thus being increased at an average annual rate of 4.2% over the last decade (Yuan, 2006).

Some agricultural wastes from the fruit can industry such as mango peels have been found to be a rich source of antioxidants phenolic compounds. The major phenolic compounds of mango peels were gallic acid, syringic acid, gentisyl-protocatechuic, mangiferin, ellagic acid and quercetin that these phenolic compounds could be a good source of natural antioxidant and can used in food, pharmaceutical and cosmetics industry (Tunchaiyaphum *et al*., 2013).

Apple pomace is the main by-product obtained by crushing and pressing apple during the clear juice process recovery. It represents approximately 30% of the original fruits and it's highly susceptible to biodegradation. Therefore, apple pomace is a real problem for manufacturers who have to manage extremely volume of waste generated daily. Apple pomace can be evaluated according to the compounds initially present in the fruit and which remain in the pomace after the pressing step. Among the components contained in the apple fruit, the polyphenolic ones are widely studied in recent years and are well known for their beneficial effects on human health and their ability to limit damage from oxidative stress due to radical species. These compounds have many interesting properties such as anti-inflammatory, antimicrobial, antimitotic, antioxidant, liver protective, antiviral, immunomod-ulatory, hemolytic or cytostatic effects (Grigoras *et al*., 2013).

Wheat bran is a source of various natural antioxidants that possess health benefits for humans such as preventing cardiovascular disease and certain cancers. Phenolic, tocopherols and fiber in wheat bran are generally believed to be primarily responsible for its positive effects on cardiovascular disease; undesirable lipid oxidation reactions in the body also contribute to these disease conditions. Recent studies have suggested that these

compounds of wheat bran exhibited significant capabilities in scavenging free radicals and reducing lipid oxidation at different conditions. Similar to other cereal grains, wheat bran contains many different types of phenolic antioxidant compounds such as ferulic, vanillic, caffeic, coumaric and syringic acids (Oufnac *et al*., 2007).

This research was investigated to study the effect of heating process at 65°C for 96 hours on the stability of (soybean: sunflower) oil mixture treated with some different natural antioxidants from industrial wastes namely mango peels, apple pomace and wheat bran.

MATERIALS AND METHODS

Materials:

Raw materials:.

Refined, bleached, and deodorized sunflower oil was purchased from Tanta Oil and Soup Company, El-Mhala El-Kobra city, El-Gharbia government, Egypt. Refined, bleached, and deodorized Soybean oil was obtained from Misr Company for Oil and Soup, El-Mansoura city, El-Dakahlia government, Egypt.

Natural and synthetic antioxidants:.

Mango peels and apple pomace were obtained from Egyptian Canning Company (Best), Meanyt samanoud city, El-Dakahlia government, Egypt. Wheat bran was obtained from Local Milling Flour of Mohammed Fahmi El-Sheikh, Aaga city, El-Dakahlia government, Egypt.

TertiaryButylhydroxy Quinone (TBHQ) was purchased from Tanta Oil and Soup Company, El-Mhala El-Kobra city, El-Gharbia government, Egypt.

Chemicals:.

All chemicals were purchased from El-Gomhouria Pharmaceutical Company and Chemicals Company, El-Mansoura city, El-Dakahlia government, Egypt.

Methods:

Preparation of antioxidants extracts:.

Both of mango peels (MP) and apple pomace (AP) were dried at 65°C for 24 hours in oven (model TREVISO) Italy then the dried materials were powdered using BRAWN Mixer (model MR120 HC plus), Japan. Then the extraction of antioxidants extracts packed in polyethylene bags and stored at deep freezer at -18°C until the extraction was prepared in Research in Food Industries Dept. Fac. of Agric. Mans. Univ. according to the method described by (Semnani *et al*., 2006).

The final extracts were as follows: Mango peels (MP), and mixture (2Apple pomace (AP): 1wheat bran (WB) [V/V]).

Determination of total phenolic compounds:.

The Folin-Ciocalteu method was used for determining of total phenolic compounds (as gallic acid equivalent) using standardized spectrophotometric at Agricultural Research Center, El-Giza, Egypt according to (Ivanova *et al*., 2006).

Determination of antioxidant activity:.

2,2 diphenyl1-picrylhydrazyl(DPPH %)assay was carried out according to the method of Brand-Williams *et al*.,(1995)at Food Tech. Res. Institute, Agric. Res. Center El-Giza, Egypt.

Determination of phenolic compounds:.

Phenolic compounds were determined as using HPLC and the data were analyzed at Food Technology Research Institute, El-Giza, Egypt by Hewlett packaged software according to (Goupy *et al*., 1999).

Stability of oil:

Preparation of oil blends:.

The mixture of vegetable oils (soybean oil "SBO" and sunflower oil "SFO") was prepared after determining the fatty acid composition of native oils SFO and SBO. The oils containing SBO with SFO were mixed in the ratio of 1:1[V/V] then preheated at 50°C for 3 hours at laboratory oven(model WT binder Typ: B 15), Italy(Chandrasheker *et al*., 2010).

Heating of treated oil with different antioxidants:

Each ethanolic extract from the mixture of apple pomace (AP) and wheat bran (WB) with (2:1) and mango peels (MP) were added to preheated mixture oils at concentrations of 200,400and600 ppm in transparent opeaned glass flask. Then oil mixture was heated for (96 hours at 65°C) in the same oven at Food Industries Dept. Research Lab. Fac. of Agric. Mans. Univ. Synthetic one (TBHQ) was added at the legal limit 200 ppm to the same blends according to (Iqbal *et al*., 2008).

Physical properties:

Specific gravity, smoke point and colour of oils were determined according to the method described by (A.O.A.C. 2000).

Chemical properties:.

Acid value (AV), Free fatty acids (FFA %) and peroxide value (PV) were determined according to the A.O.A.C (2000)

-Thiobarbituric acid value(TBA):

Thiobarbituric acid (TBA) value was determined as using spectrophotometer. TBA value was expressed as mg/malonaldhyde/kg. The method described by (A.O.A.C. 2000) by using the following equation:

TBA = 7.8 x O.D.

O.D. = Optical density at 530 nm

Fatty acids composition of oils and oil mixture:

Fatty acids methyl esters (FAMS) of oils and oil mixture were performed according to the procedure of Radwan ss (1978), at Higher Institute of Public Health, Alex. Univ. Alexandria, Egypt.

RESULTS AND DISCUSSION

Total phenolic compounds(TPC) content (mg/g) and antioxidants activity (DPPH %) of mango peels, apple pomace and wheat bran:

Plant phenolics constitute one of the major groups of the compounds acting as primary antioxidants or free radicals terminator it was reasonable to determine their total phenolics content.

TPC were determined and expressed as gallic acid equivalents (Zeyada *et al*., 2007) and (El-Gammal., 2012). Results in Table (1) showed the percentage of each total phenolic content in different extracts namely mango peels, apple pomace and wheat bran.

Data in Table (1) was noted that mango peels had the highest phenolic content compared with the other extracts, it was 144.13 mg/g as gallic acid, followed by apple pomace and wheat bran mixture was 90.37 mg/g as gallic acid and apple pomace was 37.92 mg/g as gallic acid. While wheat bran extract was the lowest one recorded 14.53 mg/ gas gallic acid compare to other extracts (Table 1).

Table1:Total phenolic compounds (TPC) content (mg/g) and antioxidants activity (DPPH %) of mango peels, apple pomace and wheat bran:

Samples	TPC(mg/g)as gallic acid	Antioxidants activity (DPPH %)
Mango peels	144.13	96.59
Apple pomace	37.92	19.21
Wheat bran	14.53	8.00
2 Apple pomace : 1 wheat bran	90.37	81.35

In the same table the radical scavenging activity of natural extracts was evaluated by DPPH technique which depend on donate hydrogen to free radical and inhibiting the propagation stage in lipids oxidation pathway(Picerno *et al*., 2003) and (El-Gammal, 2012).

The results in Table(1) showed that highest scavenging activity as DPPH% was detected for mango peels extract which reached to 96.59% followed by apple pomace 19.21%. Results in the same table indicated that the lowest scavenging effect detected in wheat bran extract 8.00%.

In the same table, it showed that the antioxidants activity (DPPH %) of the mixture of apple pomace extract and wheat bran extract for ratio (2:1)[V/V] was 81.35%.And have been using this mixture as a result of increasing the efficiency of the antioxidant extract of this mixture than all separately.

Phenolic compounds content (ppm) in different ethanolic extract of mango peels, apple pomace and wheat bran.

The amount of phenolic compounds is an important factor when evaluating the quality of different extracts, it involved for their resistance to oxidation and the properties attributed to these antioxidants (Moure *et al*., 2001) and (El-Gammal, 2012) Results in Table (2) indicated that there was a great variation among the components identified in the ethanolic extracts of each material.

Data in Table (2) showed that mango peels contained 9 compounds of phenolic compounds, the most abundant one being salicylic comprised about 6015.28 ppm concerning to the derivatives with the chlorogenic and benzoic being 2485.44 ppm and 2390.23 ppm, respectively while the lowest

compounds were protocatchoic, vannillic, gallic, catechin and catechol being 37.49, 132.68, 137.30 and 189.58 ppm, respectively .

Data in the same table showed that apple pomace extract contained 10 compounds which could be arranged ascending as follows: gallic, protocatchoic, coumaric acid, vannillic acid, caffeic acid, catechin, ferrullic acid, ellagic, chlorogenic acid and salicylic acid. The lowest compounds were gallic, protocatchoic, coumaric acid, and vannillic being 2.50, 3.18, 4.92 and 7.04 ppm, respectively. While the highest compounds were salicylic acid and chlorogenic acid being 201.99 and 99.06 ppm, respectively.

Table 2: Phenolic compounds content (ppm) in different ethanolic extract of mango peels, apple pomace and wheat bran.

Phenolic compounds	Mango peels	Apple pomace	Wheat bran
-Chlorogenic acid	2485.44	99.06	161.04
Caffeic acid-	……	7.94	8.20
-Coumaric acid	……	4.92	6.27
Ferrullic acid-	……	19.78	11.08
-Cinnamic acid	……	……	5.47
-Vannillic acid	124.46	7.04	6.27
-Salicylic acid	6015.28	201.99	43.91
-Benzoic acid	2390.23	……	557.80
-Protocatchoic	37.49	3.18	……
-Catechin	137.30	16.33	18.36
-Catechol	189.58	……	15.60
-Gallic	132.68	2.50	2.42
-Ellagic	640.10	32.16	68.17
-Caffiene	……	……	6.13

While results in the same table showed that wheat bran had 13 compounds which the highest one was benzoic acid recorded 557ppm followed by chlorogenic acid being 161.04ppm while ellagic and salicylic acid were 68.17 and 43.91ppm, respectively. The other compounds were nearly except catechin and catechol were 18.36 and 15.60ppm, respectively.

The variation of phenolic compounds could be due to the concentration of these compounds which varied between the examined extracts (El-Gammal, 2012).

Physical and chemical properties of refined, bleached, and deodorized (RBD) sunflower, soybean oils and soybean oil: sunflower oil mixture "A" [V/V]:

In this study, there were two types of vegetable oils used namely sunflower and soybean oils. Physical and chemical properties of these oils were determined and the results were tabulated in Table (3).

Acid value (AV) and free fatty acids (FFA %) value were used as a measure of the formation of acidic compounds and secondary products dissent formed during oxidation (Chavan *et al*.1992). Data presented in Table (3) could be observed that AV and FFA% of both of (RBD) sunflower and soybean oil were (0.6488, 0.8630 mg KOH/ gm oil 0.2256 and 0.4028 %)

respectively while the mixture of two oils being (1.0014 and 0.5035%) for mixture A. These results may be due to the formation of fatty acids composition of oils. The results were nearly accordance with those found by Oladiji *et al*. (2010) who reported that AV of soybean oil was (0.933) and FFA% was ranged from (0.3:1.01%) and Lamas *et al*. (2014)who found that AV of sunflower oil was (0.654) and FFA% ranged from (0.5:1.8%).

Peroxide value (PV) used as an index for the degree of lipid oxidation rancidity and the formation of hydro-peroxides (Chavan *et al*., 1992). Results in Table 3 indicated that PV were (8.73, 9.71 and 7.25ml.eqv/ Kg oil) for sunflower, soybean oil and there mixture respectively. These findings were in line with result for (Chowdhury *et al*., 2007).

Thiobarbituric acid (TBA) value was used to determine secondary oxidation products namely aldehydes and ketones. Results in the same table showed that TBA values were (0.272, 0.288 and0.343mg malonaldhyde/ Kg oil) for sunflower, soybean oil and their mixture respectively.

Table 3: Physico-chemical properties of sunflower oil (SFO), soybean oil (SBO) and soybean oil: sunflower oil mixture "A":

Properties	SFO	SBO	Mixture "A"
Acid value(AV)(mg KOH/gm oil)	0.6488	0.8630	1.0014
Free fatty acids (F.F.A %) (as oleic acid)	0.2256	0.4028	0.5035
Peroxide value(PV) (ml.eqv./kg oil)	8.73	9.71	7.25
Thiobarbituric acid(TBA) (mg malonaldhyde/Kg oil)	0.272	0.288	0.343
Specific gravity(SG)(25°C)	0.722	0.725	0.866
Smoke point(SP)	230°C/4min	210°C/4min	190°C/5min
Colour	1.1	1.2	1.5

Mixture "A": (1soybean oil: 1sunflower oil)

From the same table it could be seen that specific gravity (SG) of sun flower and soybean oil were (0.722 and 0.725) respectively, while the mixture of oils "A" was(0.866).No obvious variation was detected in the colour of all investigated oils and mixture "A" which results were ranged between (1.1: 1.5) (Table 3).

Also results in Table 3 indicated that smoke point (SP) were 230°C/4 min, 210°C/4 min and 190°C/5 min respectively, for SFO, SBO and mixture "A". These values are fairly close to Hammond *et al*., (2005) and Nimet *et al*., (2011).

Fatty acids composition of refined, bleached, and deodorized (RBD) sunflower, soybean oils and soybean oil: sunflower oil mixture "A"[V/V]:

Results of the GLC analysis of methyl esters of saturated (SFA) and unsaturated fatty acids (USFA) of SFO, SBO oils and their mixture "A" indicated in Table (4). From these results saturated and unsaturated fatty acids could be specified in SFO, SBO oils and their mixture. Elevation level of unsaturated fatty acids in all samples is a major prominence for nutritional estimation.

In general, it is well demonstrated fact now that increasing the suitability of unsaturated fatty acids in a diet will reduce the level of blood cholesterol which relate the infected of coronary heart diseases(Ulbricht and Southgate 1991).

From our obtained results in Table(4) it could be observed that palmitic acid ($C_{16:0}$) was the major saturated short chain fatty acid observed in all oil samples under investigation being (18.56, 25.42 and 22.21%) for SFO, SBO and Mixture A respectively, following by stearic acid ($C_{18:0}$)being (15.91, 17.10 and 17.19%)in the same oil sample, respectively.

The epidemic unsaturated fatty acid in all oil samples was oleic acids. Data in the same table showed that levels of the values of oleic acids ($C_{18:1}$) were (56.64, 51.7and50.44%) for SFO, SBO oils and their mixture, respectively, but the lowest one was Linoleic acid ($C_{18:2}$)which results were (0.02, 0.01and0.02%) for SFO, SBO oils and their mixtures, respectively.

The concentration of oleic acid found in oils makes these useful for the food industry as a frying or salad oil. Sunflower and soybean oils are good sources of linoleic acid. Linoleic acid is essential oil in human nutrition because it represents a group of essential fatty acids, omega three and six (Pardauil *et al*., 2011).

Table 4: Fatty acids composition of soybean oil (SBO), sunflower oil (SFO) and their mixture "A" [V/V].

Samples / Fatty acids	SFO	SBO	Mixture "A"
	%	%	%
Saturated fatty acids (SFA)			
Caproic acid ($C_{6:0}$)	0.08	0.03	0.04
Caprylic acid ($C_{8:0}$)	0.24	0.18	0.46
Capric acid ($C_{10:0}$)	0.32	0.24	0.66
Undecylic acid ($C_{11:0}$)	……	0.23	0.64
Lauric acid ($C_{12:0}$)	0.23	0.10	0.33
Tridecylic acid ($C_{13:0}$)	0.33	0.49	0.45
Myristic acid ($C_{14:0}$)	0.17	0.75	0.69
Pentadecylic acid ($C_{15:0}$)	0.35	0.28	0.48
Palmitic acid ($C_{16:0}$)	18.56	25.42	22.21
Margaric acid ($C_{17:0}$)	……	0.15	…….....
Stearic acid ($C_{18:0}$)	15.91	17.10	17.19
Arachidic acid ($C_{20:0}$)	0.64	0.71	0.65
Heneicoylic acid ($C_{21:0}$)	0.48	……	0.76
Lignoceric acid ($C_{24:0}$)	0.73	……	…….....
Total(SFA)	38.04	45.68	44.56
Unsaturated fatty acids (USFA)			
Myristoleic acid (C14:1)	0.16	0.16	0.17
Ginkgolic acid (C15:1)	0.28	0.37	0.35
Palmitoleic acid (C16:1)	0.21	0.16	0.13
Heptadecenoic acid (C17:1)	……	0.13	0.87
Oleic acid (C18:1)	56.64	51.7	50.44
Linoleic acid (C18:2)	0.02	0.01	0.02
Eicosadienoic acid (C20:2)	1.00	1.01	1.57
Brassic acid (C22:2)	2.30	1.11	1.56
Total(USFA)	61.66	55.02	54.43
USFA/SFA	1.62	1.20	1.22

From the abovementioned data it was clear that the mixing of both oils (SFO and SBO) enhance the physical and chemical properties during heating process.

Effect of pre-heating (50°C for 3 hours) on physical and chemical properties of mixture oil "A" [V/V]:

The results of physical and chemical properties of pre-heated mixtures oils were shown in Table (5).

Data illustrated in Table (5) indicated that all physical and chemical properties were increased during heating process. Acid value was increased to 2.1mg KOH/gm oil and this increase in acid value is confirmed with an increase in free fatty acid (0.793%).

Peroxide value (PV) was also increased to (10.7meq/Kg oil).This increase in peroxide value is attributed to the formation of hydro-peroxides, i.e. primary oxidation products (Jaswir *et al*., 2002) and (Iqbal *et al*., 2008).

On the other hand, TBA value was increased during pre-heating process to (0.7098 mg malonaldhyde/ Kg oil). This increasing for TBA value due to the formation of secondary oxidation products.

From data presented in Table (5), it could be observed that all physical properties namely specific gravity value at25°C was (1.222),smoke point (190°C/4 min) and colour was changed after pre-heating process from 1.5 to 2.8 Table (5)

Table 5: Effect of pre-heating process (50°C for 3 hours) on oil mixture "A" (SBO/SFO) [V/V] properties.

Properties	Mixture "A"
Acid value(AV)(mg KOH/gm oil)	2.1
Free Fatty Acids (F.F.A%)(as oleic acid)	0.793
Peroxide value(PV) (ml.eqv./Kg oil)	10.7
Thiobarbituric acid value(TBA) (mg malonaldhyde/Kg oil)	0.7098
Specific gravity (SG)(25°C)	1.222
Smoke point (SP)	190°C/ 4 min
Colour	2.8

Effect of heating process (65°C for 96 hours)on acid value (AV) in preheated mixture oil "A" treated with antioxidants:

Results in Table (6) showed the effect of heating process (65° C for 96 hours) on the A.V of the mixture treated oil with natural antioxidants(MP and 2AP:1WB)with the concentrations (200,400 and 600 PPM) compared with synthetic antioxidants TBHQ (200).

From data presented in Table (6), it could be seen that the A.V of the control sample increases sharply up to 2.019 after 96 hours. But the A.V of treated samples being increasing sharply after 96 hours to 0.887, 0.860 and 0.892 mgKOH/gm oil respectively for treated oil with (MP)at the concentrations (200, 400 and 600 PPM) and 0.963, 0.948 and 0.915 mg KOH/gm oil respectively for the other treated oil samples with (2 AP : 1 WB) after 96 hours.

The increasing of A.V may be due to occurrence hydrolysis in oils result to heating.

Table 6: Effect of heating process (65°C for 96 hours) on acid value (AV) (mg KOH/gm oil) in preheated mixture oil "A" treated with antioxidants.

Heating time (hr)	Control	TBHQ 200ppm	MP 200ppm	MP 400ppm	MP 600ppm	2 AP:1WB 200ppm	2 AP:1WB 400ppm	2 AP:1WB 600ppm
24	1.840	0.431	0.681	0.626	0.583	0.821	0.802	0.788
48	1.922	0.483	0.730	0.712	0.697	0.850	0.846	0.803
72	1.987	0.582	0.792	0.812	0.840	0.914	0.902	0.897
96	2.019	0.698	0.887	0.860	0.892	0.963	0.948	0.915

Effect of heating (65°C for 96 hours) on peroxide value (PV) in preheated mixture oil "A" treated with antioxidants:

Peroxide formation is a major concern from the point of view of rancidity and toxicology Chowdhury *et al*. (2007).From data in table (7) it could be noticed the peroxide values of control sample increased with extending heating time reached to 22.57ml.eqv/Kg oil after 96 hours. Addition of antioxidants retarded the oxidation process in all treated oil samples while P.V of treated samples was lower than those of the control one.

Table 7: Effect of heating (65°C for 96 hours) on peroxide value (PV) (ml.eqv/ /Kg oil) in preheated mixture oil "A" treated with antioxidants:

Heating time (hr)	Control	TBHQ 200ppm	MP 200ppm	MP 400ppm	MP 600ppm	2 AP:1WB 200ppm	2 AP:1WB 400ppm	2 AP:1WB 600ppm
24	16.86	9.20	10.86	10.22	10.15	11.53	11.30	11.05
48	18.97	9.68	11.35	11.15	11.01	11.96	11.83	11.74
72	19.64	10.75	13.02	12.67	12.54	13.32	13.54	13.43
96	22.57	12.34	14.68	13.88	12.96	15.84	14.86	13.83

P.V for treated samples was increased gradually prolonged heating process. It was shown, these results for treated oil samples with (MP) with the concentration (600PPM) was nearly from results comparing for those obtained by TBHQ as synthetic one.

Bensmira *et al*. (2007) reported that there is a significant difference between P.V values of treated (sunflower oil with lavender and sunflower oil with thyme and P.V of untreated) samples and during heating process. The amount of peroxides found in untreated sample was higher than that of peroxides contained in treated samples. Moreover, peroxides increased from 4.13 to 10.37 ml eqv /Kg oil for untreated oil, from 3.43 to 5.57 ml eqv. /Kg oil for sunflower oil with lavender and from 3.53 to 5.83 ml eqv. /Kg oil for sunflower oil with thyme. However, others have reported an increasing in P.V of oil during heating and/or frying.

Effect of heating process (65°C for 96 hours) on Thiobarbituric acid value (TBA) in preheated mixture oil "A" treated with antioxidants:

The most common method for measuring oxidative changes in the biological samples and food products is the TBA test Che and Tan (1999) and El-Gammal (2001). In fact, TBA test is more reliable than P.V in determining oil deterioration as it measures the secondary stages of oxidation or accumulation of secondary products. It was assumed that these products are accumulated during heating Ramadan (1998) and El-Gammal (2001).

Results in Table (8) mentioned that TBA values of samples were increased during heating process. For control sample, TBA value was increased sharply from 0.936 mg malonaldhyde/Kg oil to 2.330 mg malonaldhyde/Kg oil after 96 hours at 65°C, but TBA values for treated samples were increased gradually. Oil samples which treated with (MP) at concentration of (600PPM) was more effective than other treated oil samples with antioxidants (2AP: 1WB). On the other hand, the results of MP at concentration of (600PPM) were nearly close to the other treated oil with TBHQ.

Table 8: Effect of heating process (65°C for 96 hours) on Thiobarbituric acid value (TBA) (mg malonaldhyde / Kg oil) in preheated mixture oil "A" treated with antioxidants.

Heating time (hr)	Control	TBHQ	MP			2 AP:1WB		
		200ppm	200ppm	400ppm	600ppm	200ppm	400ppm	600ppm
24	0.936	0.461	0.531	0.552	0.579	0.598	0.591	0.579
48	0.986	0.599	0.681	0.650	0.659	0.690	0.698	0.698
72	1.530	0.630	0.701	0.691	0.687	0.713	0.707	0.700
96	2.330	0.696	0.728	0.711	0.700	0.816	0.800	0.791

It could be concluded that addition of mango peels extract (MP) could reduce the oxidative changes and enhancing the physical and chemical properties of oil mixture (1soybean oil: 1sunflower oil) during heating process at 65°C for 96 hours.

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تأثير عملية التسخين على ثبات مخلوط زيت فول الصويا و عباد الشمس المعامل ببعض مضادات الأكسدة الطبيعية المختلفة .

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يعتبر زيت فول الصويا من أشهر أنواع الزيوت الغذائية فى مصر. و يتميز بسرعة تعرضه لعمليات الأكسدة و التزنخ. و قد أجريت هذه الدراسة بغرض دراسة المعاملات المختلفة كالخلط و التسخين على ثبات زيت فول الصويا. و قد تم خلط زيت فول الصويا مع زيت عباد الشمس بنسبة (١:١) و تم إجراء عملية التسخين الإبتدائي على درجة ٥٠°م لمدة ٣ ساعات ثم تمت معاملة مخلوط الزيت بمضادات الأكسدة الطبيعية المستخلصة من مخلفات مصانع الفواكه والحبوب و هى قشور المانجو و تفل التفاح و نخالة القمح بتركيزات (٤٠٠,٢٠٠و ٦٠٠ جزء فى المليون) و مضاد أكسدة صناعى TBHQ بتركيز (٢٠٠ جزء فى المليون).

اوضحت نتائج تقدير و فصل المركبات الفينولية للمستخلصات الثلاثة بإستخدام جهاز HPLC و وجود المركبات الفينولية التالية : Chlorogenic, Salicylic, Vannillic, Benzoic and Ellagic acids . ومن النتائج المتحصل عليها المركبات الفينولية الكلية مقدرة كحمض جاليك (١٤,٥٣ : ١٤٤,١٣ ملجم/ جم) و أظهرت نتائج DPPH أن مستخلص قشور المانجو أعطى أعلى نشاط كمضاد للأكسدة (٩٦,٥٩%) مقارنة بالمستخلصات الأخرى .

تمت معاملة الزيت حراريا على درجة ٦٥°م لمدة ٩٦ ساعة و تم إجراء بعض الإختبارات الكيميائية (رقم الحموضة, رقم البيروكسيد و TBA) وكانت أهم النتائج المتحصل عليها حدوث ارتفاع ملحوظ فى رقم الحموضة فى عينات الزيت الغير معاملة مقارنة بالعينات المعاملة بمضادات الأكسدة كما حدث ارتفاع تدريجى فى ثوابت الأكسدة و التزنخ(رقم البيروكسيد و TBA).وقد وصلت نتائج رقم البيروكسيد و TBA أقصاها حيث كانت نتائج رقم البيروكسيد ٢٢,٥٧ ملليمكافئ/ كجم زيت لعينات الزيت الغير معاملة و ١٢,٩٦ملليمكافئ / كجم زيت للعينات المعاملة بمستخلص قشور المانجو بينما كانت نتائج TBA ٢,٣٣٠ ملليجم مالونألدهيد/كجم زيت للعينات الغير معاملة مقارنة مع العينات المعاملة بمستخلص قشور المانجو و التى كانت نتيجتها ٠,٧٠٠ملليجم مالونألدهيد/كجم زيت بعد ٩٦ ساعة من التسخين.

ومن ثم يتضح من النتائج السابقة أن إضافة مستخلص قشور المانجو بتركيز ٦٠٠ جزء فى المليون أدى إلى تحسين الصفات الكيميائية و الطبيعية و تأخير عمليات الأكسدة و التزنخ لمخلوط زيت فول الصويا وعباد الشمس.