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The Effect of Frying Conditions on Sunflower Oil Attributes

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A B S T R A C T

A sample of sunflower oil, produced from Homs Sugar Company, was used in this study to fry local potato by frying under air at household conditions, and frying under pressure (at 150-180ºC, pressure 10-15kg/cm²) for 12 continuous hours without adding new oil. The results were estimated statistically by using Minitab program version 17.0 at level 0.01. The results showed, in both cases of frying, an increase in the physical properties (density, viscosity, refractive index, and coloring degree) of used oil by increasing frying time. A decrease Iodine Number, increase Peroxide Number, increase the percentage of free fatty acids, increase of $C_{16:0}$ and $C_{18:1}$ acids percentage, and decrease of $C_{18:2}$ and $C_{18:3}$ acids percentage, associated by increasing frying time. But when frying under pressure we noticed that these changes were slow because of the unadequated oxygen presence during frying under pressure. So we can say that the oil was still usable for frying for a long time when frying under pressure more than when frying under air with the vessel is open.

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تأثير ظروف القلي على خصائص زيت عباد الشمس

الخلاصة

تمت الدراسة على عينة من زيت زهرة الشمس (إنتاج شركة سكر حمص) استخدمت في قلي البطاطا المحلية، بتطبيق القلي تحت الهواء في ظروف منزلية، والقلي تحت الضغط (عند درجة حرارة 150-180 °م ، وضغط 10-15 كغم/سم) لمدة 12 ساعة متواصلة من دون إضافة زيت. عولجت النتائج إحصائياً باستخدام برنامج Minitab الإصدار17.0، عند مستوى 0.01 أظهرت النتائج، في كل من حالتي القلي تحت الهواء والقلي تحت الضغط، زيادة في الخواص الفيزيائية للزيت (كثافة، لزوجة، قرينة الانكسار، والدرجة اللونية) مع زيادة زمن القلي. وانخفاض قرينة اليود، زيادة قرينة البيروكسيد، زيادة نسبة الأحماض الدسمة الحرة، زيادة في نسبة الأحماض $C_{16:0}$ و $C_{18:1}$, وانخفاض في نسبة الأحماض $C_{18:2}$ و $C_{18:3}$ مع زيادة زمن القلي، ولكن عند القلي تحت الضغط لاحظنا أن هذه التغيرات كانت بطيئة بسبب وجود الاوكسجين بنسبة غير كافية. وبذلك يمكننا القول بأن الزيت بقي صالحاً للقلي لمدة أطول عند القلي تحت الضغط مقارنة مع القلي تحت الهواء والإناء مفتوح.

1. INTRODUCTION

Frying process is defined as food immersion in hot oil with contact between oil, food, and air at high temperature 150-190 ºC. Synchronization heat, oil transmission, foodstuff, and air during frying process produce unique desirable fried foods, also frying oil act as heat transfer contribute the frying food texture and flavor. Frying temperature and humidity of foodstuff affect the properties of oil and fat using in frying process that lead up to decrease its quality and change its chemical composition, this is related with frying time and chemical composition of used oil, because frying process decrease the unsaturation of fatty acids in oil by increasing polymerization, and increase foam, density, viscosity, coloring degree of used oil, also its content of free fatty acids, functional materials, and polymeric compounds [1].

During frying process set of chemical reactions occur to used oil, one of them is oil hydrolysis. As foods fried in hot oil, a vapor is formed because of moisture that evaporated with bubbles then decrease gradually during frying. Water, vapor, and oxygen are lead the chemical reactions in food and frying oil to begin. Water and weak nucleophyl attack the ester bond in tri-acid acyl glycerol and produce mono and diacyl glycerol, glycerol, and free fatty acids [2,3].

Large amounts of water hydrolyze the oil rapidly, and water hydrolyzes the oil faster than steam, and the large

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contact between the oil and the aqueous phase of food increases hydrolysis of oil [4-6].

The chemical mechanization of thermal oxidation is similar to autoxidation mechanism, but thermal oxidation average is faster than autoxidation. Thermal oxidation includes three stages, which are: initiation, propagation, and termination, illustrated in Fig. 1 [7,3]. Oil should be in a radical state to react with radical oxygen for oil oxidation reaction, the hydrogen with the weakest bond on the carbon of oil will be removed first to become radical [8-10].

Oxidation hydrolysis reactions range is increased when hydrogen and free radicals concentration increase. The amount of mono and diacyl glycerol at the beginning of frying process is little. And because of high surface tension in frying system, the vapor bubbles will break and a layer of vapor formed at oil surface which lower the rubbing between oil and oxygen so the oil oxidation will be decreased [11,12].

The chemical reactions that occur during the oxidation process contribute to the formation of both volatile and nonvolatile decomposition products, the volatile degradation products are usually saturated and monounsaturated hydroxyl, aldehydic, keto, and dicarboxylic acids; hydrocarbons; alcohols; aldehydes; ketones; and aromatic compounds are primarily responsible for undesirable oxidized (rancid) flavors, so, we can say that the autoxidation is an important degradation reaction which is attributed to the rancidity of oil and fat. Thermal oxidation, which is accelerated at the high temperature used in deep frying, creats rancid flavors and reduces the organoleptic characteristics of fried food [13-15]. The hydroperoxides are not generally stable during the deep-fat frying, they are decomposed to alkoxy radicals and hydroxyl radicals by homolysis of the peroxide bond [16].

Volatile compounds in frying oil suffer another reaction such as oxidation, dimerization, and polymerization. Volatile compounds also support the frying oil flavor quality, and consequently the fried foods. Many nonvolatile polar compounds and tri-acylglycerol dimmers and polymers are produced in thermal oxidized oil by radical reactions. Dimerization and polymerization are major reactions in the thermal oxidation in oil [17,18].

Polymerization occurs more easily in oil with high linoleic acid than in high oleic acid oil contents. As polymerized products increase in the frying oil, viscosity of the oil and undesirable color of food also increases. During frying, oils with polyunsaturated fatty acids, such as linoleic acid, have a distinct induction period of hydroperoxides followed by a rapid increase in peroxide values, then a rapid destruction of peroxides [19,20].

Sunflower oil is considered as one of the best oils used in frying because of its low smoking point, slight color and taste, low level of saturated fats found in, and its firmness at high cooking degrees, also, it is an excellent oil for household using such as backing preparing, frying, and salads. Foodstuff frying by using vegetable oils is done in open vessels contacted with air as for household frying, or under pressure by using closed household frying devices, small and large, for restaurants and factories [21-23].

This research is aimed to study the effect of frying time on physical and chemical sunflower oil attributes while potato frying without adding new oil throughout frying, and frying is done in contact with air and under pressure in an electric frying pan, and determine the period can use this oil in frying with keeping its quality.

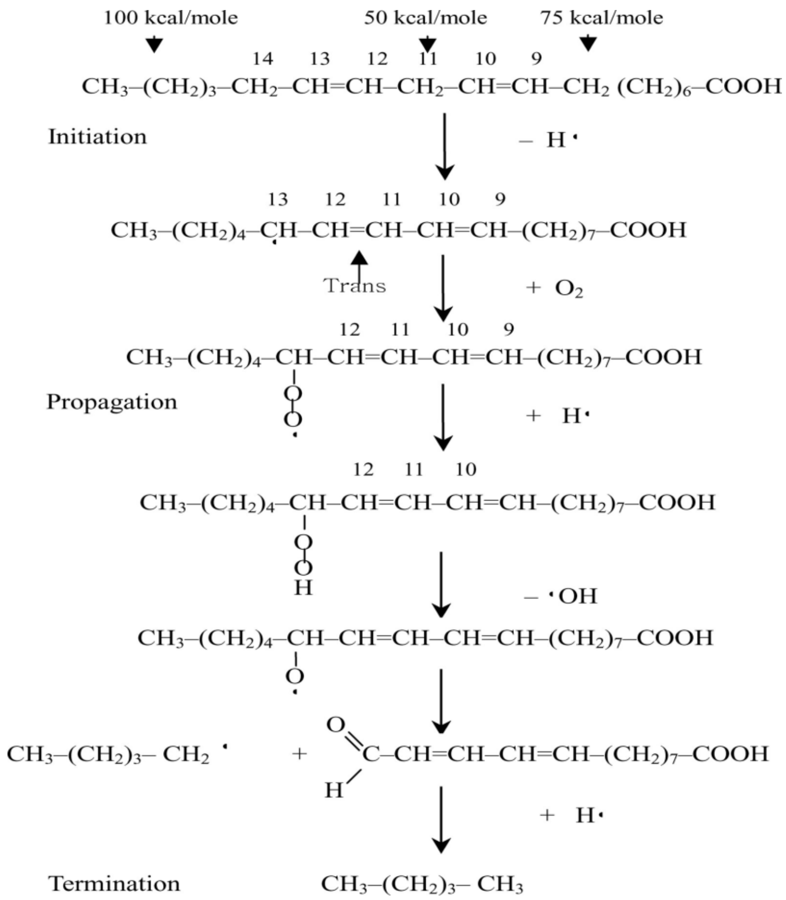


Fig. 1. The initiation, propagation, and termination of thermal oxidation of oil [3].

2. MATERIAL AND METHODS

2.1. Materials

Sunflower oil produced from Homs Sugar Company, was used in frying local potato in household conditions in an open vessel for frying under air, and for frying under pressure we used a tightly closed electric frying pan under pressure 15 kg/cm², and temperature about 180 ºC. The electric pan depth wasn't large, so the height of added oil was enough to let a little space between surface oil and pan cover, in this way we reduced the amount of air, and thus, oxygen as possible as we could. The frying process was continued for 12 hours without adding new oil.

2.2. Methods

Physical Tests

Density, viscosity, refractive index, and coloring degree for used oil were measured before and during frying. Density (g/cm^3) was measured at 20 ºC by using density flask according to AOAC (1990) [24], viscosity (Poise) is measured according to Stocks Method, refractive index was measured by refractometer at 20 ºC, and coloring degree was measured by using Lyvipond colorometer.

Chemical Tests

Iodine number, peroxide value, and percent of free fatty acids were measured for used oil before and during frying. Iodine number indicates the iodine grams that absorbed by 100 gr of oil, (g I_2/100 gr Oil). Peroxide number was evaluated as (ml eq. peroxide/1kg Oil). While free fatty acids were calculated as a percentage on account of oleic acid.

Chromatographical Test

The used oil was tested before and at the end of frying process by using Gas Chromatogrphy, that for qualitative and quantitative tests of fatty acids found in glycerides forming the test sample. The apparatus is of the model Shimadzu 1998, supplied with injection system (spilt/splitless), with gas insert, flame ioned detector FID, hydrogen generation device (Shimadzu-OPGU-2200S), air pump, nitrogen gas from nitrogen generation device (Peak-series, 600A), capillary column of trademark Teknokorma was used, Spanish origin, have the symbol TR-140533 and sequential number 2056295, column length 30 meter and with diameter 0.32 mm, painted with stable phase of kind TRB-WAX. Work conditions was controlled as follows: column temp. 195 ºC, injection temp. 250 ºC, detector temp. 250 ºC, holder gas flow 0.7, and partition percent 10:1.

3. RESULTS AND DISCUSSION

3.1. Frying Under Air

Physical properties of oil samples taken during frying process under air, presented in Table 1, showed an increase of density, viscosity, and refractive index. This is because of the thermal oxidation of oil having unsaturated fatty acids and accumulation of high molecular weight compounds and polymerization occurrence, the results we found were agreed with what was found by Marmesat et al. [22] and Hasson [25]. As for coloring degree, it was increased as frying time increased, because of polymerization and forming the free radicals as a result of thermal oxidation which oxidize the pigments found in oil, also from transmission food pigments into frying oil, this increase in coloring degree was agreed with what was found by Melton et al. [26] and Yunsheng [27]

From chemical analysis of oil samples taken during frying process under air, shown in Table 2, we noticed decreasing of iodine number, and increasing of peroxide number and percent of free fatty acids accomplished by increasing frying time. This is because of glycerides hydrolysis and thermal oxidation which lead to accumulation of free fatty acids, breaking down the double bonds of unsaturated fatty acids, and forming free radicals that produce peroxides and hydroperoxides. As for peroxide number, after increasing, it decreases because of the dissociation of peroxides and hydroperoxides to ketones and aldehydes. The results we found were similar to what was found by Farag et al. [28], Bangash and Khattak [29], Farhoosh and Moosovi [30]. Statistically, significant differences were found at level 0.01.

Table 1
Physical properties of oil samples before and during potato frying under air.

Frying Time (hour)	Density at 20 ºC (g/cm³)	Viscosity at 20 ºC (Poise)	Refractive index at 20 ºC	Coloring degree (Lyvipond) Red	Yellow
Before frying	^{D}0.9180	^{G}3.4862	^{A} 1.4748	^{A} 0.6	^{A} 4
2	^{CD}0.9184	^{F}3.7352	^{A} 1.4750	^{A} 0.6	^{A} 4
4	^{C}0.9187	^{E}4.1086	^{A} 1.4751	^{A} 0.7	^{A} 4
6	^{BC}0.9190	^{D}4.3574	^{A} 1.4752	^{A} 0.7	^{A} 5
8	^{AB}0.9194	^{C}4.6063	^{A} 1.4754	^{A} 0.7	^{A} 5
10	^{AB}0.9196	^{B}4.7307	^{A} 1.4755	^{A} 0.7	^{A} 5
12	^{A}0.9199	^{A}4.9796	^{A} 1.4757	^{A} 0.7	^{A} 5

*Duplicate tests were done for everyone of studied samples
*Different letters in the same column indicate presence of significant differences at level 0.01

Table 2
Chemical analysis of oil samples before and during potato frying under air.

Frying Time (hour)	Iodine number ($g\ I_2/100\ g$ oil)	Peroxide number (ml eq.peroxide/1 kg oil)	Free fatty acids (%)
Before frying	^{A}127.4	^{G}0.98	^{D}0.0705
2	^{B}121.7	^{F}6.37	^{D}0.0705
4	^{B}119.7	^{E}15.98	^{D}0.0705
6	^{BC}117.9	^{D}34.16	^{D}0.0705
8	^{CD}115.5	^{C}23.91	^{C}0.0846
10	^{DE}113.4	^{B}45.98	^{A}0.1410
12	^{E}110.0	^{A}67.00	^{B}0.1551

*Duplicate tests were done for everyone of studied samples.
*Different letters in the same column indicate presence of significant differences at level 0.01.

3.2. Frying Under Pressure

From physical properties of oil samples taken during frying process under pressure, shown in Table 3, we noticed an increase of density, viscosity, and refractive index because of the high frying temperature which lead to polymerization occurrence and oil oxidation that cause to accumulate free fatty acids, mono, and diacylglycerols. The results we found were correspondent to what was found by Yan [31], Tseng et al. [32]. Also we found an increase of coloring degree accomplished by increasing frying time because of thermal oxidation of oil, breaking down the pigments found in oil by high frying temperature, and pigments transmission from food to oil. This result was similar to what was found by Smouse [33] and Verela et al. [34].

Also, through the chemical analysis taken during frying process under pressure, presented in Table 4, we noticed a decrease in iodine number, and increase in peroxide number and percent of free fatty acids accomplished by increasing frying time. This is because of oil hydrolysis at high frying temperature and oil oxidation that lead to accumulation of unsaturated free fatty acids and forming peroxides and hydroperoxides, as for peroxide number, it was decreased after increasing because of the dissociation of peroxides and hydroperoxides to ketones and aldehydes. These changes were slow because of inadequate oxygen during frying under pressure. The results we found were correspondent to what was found by Abdel-Rahman [35], Orthoefer [1] and Masson et al. [5]. Statistically, significant differences were found al level 0.01.

Table 3
Physical properties of oil samples before and during potato frying under pressure.

Frying Time (hour)	Density at 20 °C (g/cm^3)	Viscosity at 20 °C (Poise)	Refractive index at 20 °C	Coloring degree (Lyvipond) Red	Coloring degree (Lyvipond) Yellow
Before frying	^{D}0.9152	^{A}3.1180	^{A} 1.4749	^{A} 0.6	^{B} 3
2	^{CD}0.9158	^{B}3.2595	^{A} 1.4745	^{A} 0.6	^{B} 3
4	^{C}0.9166	^{C}3.4011	^{A} 1.4742	^{A} 0.7	^{AB} 4
6	^{B}0.9192	^{D}3.5422	^{A} 1.4741	^{A} 0.7	^{AB} 4
8	^{A}0.9204	^{E}3.8253	^{A} 1.4739	^{A} 0.7	^{AB} 4
10	^{AB}0.9197	^{F}3.9665	^{A} 1.4736	^{A} 0.8	^{A} 5
12	^{AB}0.9197	^{G}4.1085	^{A} 1.4733	^{A} 0.8	^{A} 5

*Duplicate tests were done for everyone of studied samples
*Different letters in the same column indicate presence of significant differences at level 0.01.

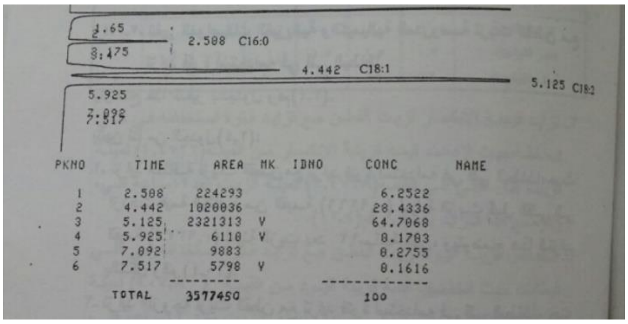
Table 4
Chemical analysis of oil samples before and during potato frying under pressure.

Frying Time (hour)	Iodine number ($g\ I_2/100\ g$ oil)	Peroxide number (ml eq.peroxide/1kg oil)	Free fatty acids (%)
Before frying	^{A}129.7	^{C}0.77	^{D}0.1692
2	^{B}122.4	^{BC}0.98	^{D}0.1833
4	^{C}116.4	^{B}1.08	^{D}0.1974
6	^{D}112.5	^{AB}1.26	^{D}0.2256
8	^{E}108.2	^{A}1.44	^{C}0.3948
10	^{EF}105.3	^{AB}1.15	^{B}0.5358
12	^{F}103.7	^{A}1.39	^{A}1.2690

*Duplicate tests were done for everyone of studied samples.
*Different letters in the same column indicate presence of significant differences at level 0.01.

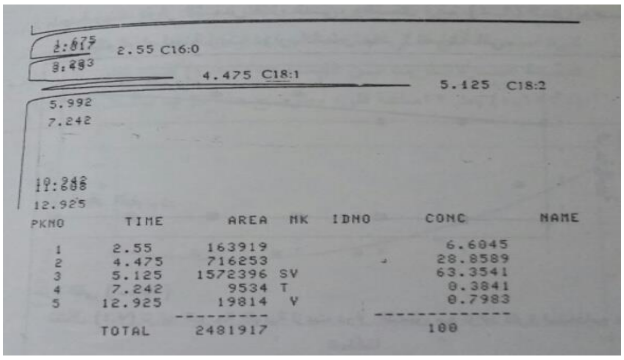
3.3. Chromatographical Test

When compared chromatographical test results for used oil, before and at the end of frying time, when frying under air and under pressure, which illustrated in Figs. 2-5, respectively, we noticed an increase of $C_{16:0}$ and $C_{18:1}$ acids percentage, and decrease of $C_{18:2}$ and $C_{18:3}$ acids percentage at the end of frying time. The decrease in unsaturated fatty acids percentage was accomplished by iodine number decrease, and it was because of the oxidation of double bonds found in unsaturated fatty acids by high frying temperature. This result was similar to was found by Orthoefer and Cooper [36] and Suliman et al. [37].



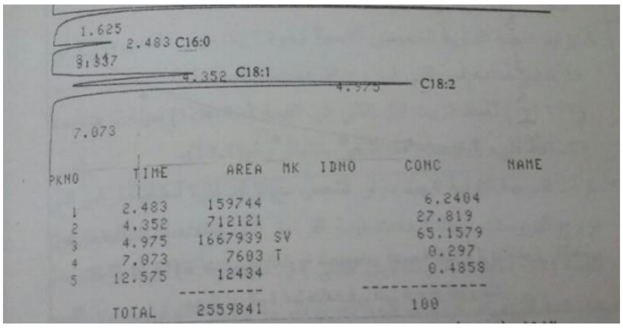
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	2.508	224293			6.2522	
2	4.442	1020036			28.4336	
3	5.125	2321313	V		64.7068	
4	5.925	6110	V		0.1703	
5	7.092	9883			0.2755	
6	7.517	5798	V		0.1616	
TOTAL		3577450			100	

Fig. 2. Chromatogram of sunflower oil sample before frying under air.



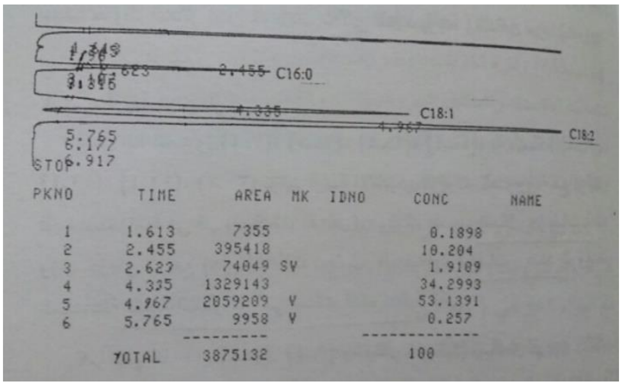
PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	2.55	163919			6.6045	
2	4.475	716253			28.8589	
3	5.125	1572396	SV		63.3541	
4	7.242	9534	T		0.3841	
5	12.925	19814	V		0.7983	
TOTAL		2481917			100	

Fig. 3. Chromatogram of sunflower oil sample after 12 hours of frying under air.



PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	2.483	159744			6.2404	
2	4.352	712121			27.819	
3	4.975	1667939	SV		65.1579	
4	7.073	7603	T		0.297	
5	12.575	12434			0.4858	
TOTAL		2559841			100	

Fig. 4. Chromatogram of sunflower oil sample before frying under pressure.



PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	1.613	7355			0.1898	
2	2.455	395418			10.204	
3	2.627	74049	SV		1.9109	
4	4.335	1329143			34.2993	
5	4.967	2059209	V		53.1391	
6	5.765	9958	V		0.257	
TOTAL		3875132			100	

Fig. 5. Chromatogram of sunflower oil sample after 12 hours of frying under pressure.

4. CONCLUSIONS

Increase sunflower oil density, viscosity, and refractive index while increase frying time, in both frying cases, (frying under air and frying under pressure), is because of the high frying temperature that lead to polymerization and thermal oxidation of oil having unsaturated fatty acids that increase mono, diacylglycerols, and free fatty acids. Also increasing frying time lead to increase coloring degree of frying oil because of thermal oxidation, polymerization, breaking down the pigments found in oil, and transmission of food pigments to frying oil. As for chemical analysis, during frying process under air and under pressure, we found decreasing of iodine number, increasing of peroxide number, and percent of free fatty acids accomplished by increasing frying time. This is because of glycerides hydrolysis and thermal oxidation which lead to accumulation of free fatty acids, breaking down the double bonds of unsaturated fatty acids, and forming free radicals that produce peroxides and hydroperoxides. As for peroxide number, after increasing, it decreases because of the dissociation of peroxides and hydroperoxides to ketones and aldehydes. But, in case of frying under pressure, we noticed that these changes were slow because of the inadequate oxygen presence during frying under pressure. Also we found, in both cases of frying, increase of $C_{16:0}$ and $C_{18:1}$ acids percentage, and decrease of $C_{18:2}$ and $C_{18:3}$ acids percentage at the end of frying time. The decrease in unsaturated fatty acids percentage was accomplished by iodine number decrease, and it was because of the oxidation of double bonds found in unsaturated fatty acids by high frying temperature. The results we found were similar to many researches were done in this scale of study.

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