

# Evaluation of Oxidative Stability of Vegetable Oils during Deep Frying

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## ABSTRACT

The oxidative degradation of the used oils were evaluated by monitoring total polar compound (TPC), Iodine value (IV), Peroxide value (Pv), specific extinction E1% at 233nm and 269nm, and changes in the fatty acids profile. Three different types of edible oils, namely, corn oil, soybean, and palm oil, were used in deep fat frying at 180 °C ± 5°C for 5 h/d for three consecutive days. The result of this study indicates that palm oil showed significantly ( $P < 0.05$ ) lower in all measured parameters than the other oils used. For PV, the rate of increase was not constant as frying progressed. The extent of oil deterioration was best reflected in the changes in percent TPC, IV, E1%cm at 233nm.

**Keywords:** *Frying potato, chicken, frying deterioration, oxidation, Polymerization*

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## Introduction

Deep-fat frying of food is considered everywhere in the world to be the most common unit operation used in food preparation (Rossan *et al.*, 1999). For decades, consumers have desired deep-fat fried products because of their unique flavor-texture combination, ranging from potato chips, French fries, doughnuts, extruded snacks, fish sticks, and the traditional fried chicken products. The aim of deep-fat frying is to seal the food by immersing it in hot oil so that all the flavors and the juices are retained in a crisp crust. Many foods may be deep-fat fried. If they have a soft, rich texture that contrasts with the crispy outside (for example, scallops and eggplant), so much the better.

During deep-fat frying, the frying fat or oil is continuously or repeatedly used at high temperatures in the presence of air and hence suffers oxidative and thermal abuse such as unavoidable chemical reaction which cause formation of range volatile and non-volatile decomposition products such as peroxides, ketones, dimeric, polymeric and cyclic compounds and can lead to changes in functional, sensory and nutritive values and even safety of the fried food (Chu *et al.*, 2001). The main causes of oil degradation are oxidation, thermal treatment, and oil-food interaction at high temperature (Gary *et al.*, 1996). The rate of decomposition depends on the composition of the oil, the temperature and the length of frying, continuous or intermittent frying, type of fried food, and fresh oil replenishment. Among these factors, the degree of unsaturation of oil is an important factor influencing the frying stability of the oil (Abdulkarim *et al.*, 2007).

Oxidative stability is very important factor in oil quality especially for these used for frying because of the high temperature applied. Frying oil must have high oxidative stability during use. From a nutritional point of view, it should be taken into account that oils with high amounts of saturated fatty acids and fats containing trans fatty acids are less desirable for good health. During frying Triacylglycerol are subject to chemical reactions (oxidation, hydrolysis, and polymerization) which can occur particularly during deep fat frying. The extent of these reactions, which may be reflected by a decrease in iodine value of the fat and an increase in free fatty acids, depends on the frying conditions (principally the temperature, aeration, and duration). The composition of a frying fat also may be affected by the kind of food being fried. For example, when frying foods such as chicken, some fat from the food will be rendered and blend with the frying fat while some of the frying fat will be absorbed by the food. In this manner the fatty acid composition of the frying fat will change as frying progresses (Dennis *et al.*, 2006). Therefore, the main objective of the present study was to assess the stability of Corn, soybean and palm oil during deep frying of the most common fried products, namely potato and chicken.

## **2. Material and methods**

### **2.1 Material**

All the used vegetable oils were obtained from the local supermarkets and kept at 10°C until frying. Potato and chicken were purchased from a local grocery store, 1 h before frying and were washed, peeled and sliced into 4 wedges. High-performance liquid chromatography-grade solvents were used throughout the experiments. All solvents and reagents got from various suppliers and were of the highest purity needed for each application.

### **2.2. Methods**

#### **2.2.1 Frying protocol**

Laboratory scale frying test was carried out on the four selected commercial oils. The frying protocol used was intermittent frying at intervals of 15 min at  $185 \pm 5^\circ\text{C}$  with a total heating/frying time of 15h (5 h per day for a total of 3 days). One and half kilograms of each oil sample to be tested were used for the frying (Abdulkarim., *et al* 2007). Fresh potato and chicken were cut into uniform wedges and fried 150g in a 2 L Philips fryer model HD 6121 (Philips Malaysia Sdn. Bhd) for 5 h each day. On the first day of frying, the oils were conditioned by heating to  $185 \pm 5^\circ\text{C}$  and held for 30 min and the product was fried until bubbling of the oil ceased. Each day, fresh oil was added to replenish the oil to its initial level in the fryer (Petuchov *et al.*, 1999; Warner and Knowlton, 1997).

#### **2.2.2 Standard chemical and physical analysis**

The PORIM test methods (PORIM, 1995), were used to determine the P<sub>v</sub>, IV, and specific extinction at 233 and 269nm values. TPC were determined using the standardized IUPAC methods (IUPAC 2000). FFA was determined as an Oleic acid. The fatty acid composition was determined by conversion of oil into fatty acid methyl esters prepared by adding 950 µL of n-hexane to 50 mg of oil followed by 50 µL of sodium methoxide using the method of Cocks and Rede 1996. The mixture was vortex for 5Sec, and allowed to settle for 5min. The top layer (1 µL) was injected into a gas chromatograph ( Model GC-14A, Shimadzu Corporation, Kyoto, Japan) equipped with a flame-ionization detector and a polar capillary column BPX70 0.25 ( 0.32 mm internal diameter, 60 m length and 0.25 µm film thickness), ( SGE Incorporated, Austin, Texas USA) to obtain FA methyl ester peaks. The detector temperature was 240°C and column temperature was 110°C held for 1 min and increased at the rate 8°C/min to 220°C and held for 1 min and run time of 32 min. Individual peaks of FA methyl ester was identified by comparing their retention times with those of standards. Individual FA compositions were calculated using the peak areas of the FA species that appear in the chromatogram as a relative percentage of the total peak areas of all the FA in the oil sample (AOCS, 1989).

### 2.3. Statistical Analyses

All experiments were performed in three replicates in order to ensure better statistical analysis of the data. The data were subjected to the analysis of variance (ANOVA). Significance was based on 5% level in all cases.

## 3. Result and discussion

### Changes in Peroxide Value (PV)

Storage of used oils leads to increase in Pv. Peak values for the PV (meqO<sub>2</sub>/kg oil) was attained. a follows; soybean oil; 23.16 and 22.48 after the second day of frying potato and first day of frying chicken respectively. Corn oil; 25.81 after the second of frying potato and 22.80 after the first day of frying of chicken, and palm olein; 17.20 during frying potato and 15.16 during frying of chicken. Comparison of the data shows that the PV of soybean and corn oil during deep frying were higher than palm olein, indicating a greater extent of oxidation in soybean and corn For peroxides, the data confirms the results showed in early studies (Tsaknis and Lalas, 2002; Abdulkarim *et al.*, 2007; Ali *et al* 2014), with an increase in the peroxides until a maximum is reached, followed by a decrease of those compounds due to their reactions and degradations to other compounds such as aldehydes and ketones, as secondary compounds derived from the oxidation of oils. The results also indicate that the PV of different oils with different types of food after three days of frying was significantly different. In the case of chicken, no conclusion can be drawn, because one can tentatively assume the oil was past the peroxide formation stage and was not fit for consumption. A significant decrease ( $P < 0.05$ ) in PV was observed with frying time. The increase in PV during frying potato could be as a result of substantial amount of unsaturated linoleic acid and the very unstable linoleic acid, which are rapidly oxidized to produce. The obtained result indicates that the PV is only useful an indicator of oxidation during the initial stages and is not representative for changes occurring with oil samples during heating at 180 °C.

### Changes in IV

Decrease in IV (Table 2), over the 3 days frying period from the initial values to the end of frying period for corn oil; 120.83 to 111.03, 104.39, and soybean oil from 128.50 to 112.34, 113.19 were significantly greater ( $P < 0.05$ ) than those of and palm olein oil; 82.73 to, 70.10, 70.00 during frying , sweet potato and chicken respectively. Significant difference ( $P < 0.05$ ) was found between the oils used to fry potato and chicken, where the rate of decreasing was fastest during frying chicken. This can be only explained by the natural and the composition of the products. Chicken fat has 20-25%, palmitic acid 5-10% stearic, and 40-45% oleic acid (one double bond), and 20% linoleic acid. These are mostly unsaturated fatty acids and during frying, these fats will melt and leach out into the frying medium, where they are rapidly oxidized to form saturated fatty acids. The level of saturation increases at a faster rate in the oil, leading to a faster decrease in IV (Daya, 2000). This is the main reason for the higher rate of oxidation and polymerization occurs in the oil, which lead to a faster decrease in IV. The decrease of iodine value correlated well with the decrease of unsaturated fatty acids of soybean oil ( $r = 0.950, 0.930, 0.900$ ) during frying of, potato and chicken respectively. Moreover, this analysis confirmed that less oxidation of unsaturated fatty acids took place in palm olein and the highest occurred in corn oil due to the high contain of oleic acid and low contain of linoleic acids . With regard to the changes in IV of the studies oils, it was found that the stability of palm oil was higher than the other oils.

### Changes in TPC

The content of total polar components (TPC) in used deep frying fats is until today an important parameter for assessing the deterioration of frying oil quality. TPC are considered to be nonvolatile compounds having a higher polarity than triacylglycerol, resulting from thermal, hydrolytic and oxidative alteration (Sibel and Sebnem, 2011). In several European countries the maximum value for TPC is between 24 and 27% for commercial frying oils. The results of the TPC show that TPC linearly increased with increase in the frying time. As frying progressed, the rate of increase in TPC was relatively slower in palm olein than in the other oil samples. The initial polar compounds contents were 4.71%, 3.36%, and 3.83%, in, soybean oil, palm olein and corn oil respectively. At the end of frying days, the corresponding TPC level increased to 24.65%, 12.49%, 25.22%, during frying potato and, to 25.19%, 35.73% 22.33%, 37.41% and to 30.55%, 27.62 %, 16.42% during frying chicken. Although the TPC content of corn and soybean oil were the highest during frying of potato, and chicken compared with the rest of the oils at the end of frying period. It is observed all oils had highest TPC during frying of chicken with lower values during frying potatoes. A similar trend was found by Enríquez-Fernández *et al.* (2011). This is an indication of the changes in TAG contents during frying of chicken as a result of oil leach from chicken fat which also lead to changes in the fatty acids profile. These have adverse effect on the formation of TPC (Kalogianni *et al.*, 2010; Lioumbas *et al.*, 2012).

### Changes in Specific Extinction (E233nm & E269nm)

The absorbance at 233nm which measures the content of conjugated dienes and the degree of primary oxidation increased with progress in heating and frying times. These differences arise mainly because hydroperoxides thermally degrade at the temperature of heating and frying. The obtained results were closely related to the PV. For all samples, both E at 233nm and 269nm increased throughout the frying days and their changes paralleled each other. Results also showed that the absorbance of the used oil used to fry chicken was higher than the oil used to fry potato. Specific extinction value at 233nm during frying was significantly ( $P < 0.05$ ) higher in soybean and corn oil, followed by palm olein during frying of chicken, sweet potato respectively. The high absorbance of soybean oil and corn oil during frying could be attributed to its higher PV, which led to a greater degree of primary oxidation. Generally, the variation of absorptivity at 269nm, attributed to the formation of conjugated trienes as well as unsaturated ketones and aldehydes, showed a pattern similar to that of absorptivity at 233nm. Meanwhile, the longer frying time, the higher the absorbance at 269nm. The small changes in absorbance may be a result of the low concentration of linoleic acid in palm olein and subsequently low relative rates of formation of ketonic and aldehydic oxidation products (Frankel, 1998).. This is coupled with the possibility of volatilization of these products as well as low formation of conjugated trienes. The level of conjugated diene was much higher than conjugated triene in all samples. This is mainly because the samples contained higher levels of linoleic acid than linolenic acid. (Chu, *et al.*, 2001).

### Changes in fatty acid composition

The most prominent fatty acids in the oils were palmitic (13.53, 12.42, 38.30%), oleic (30.03, 22.63, 45.40%) and linoleic (53.00, 54.04, 11.61%) for corn, soybean, and palm olein, respectively. High amounts of unsaturated fatty acids in corn, and soybean oils are the cause of deterioration during high temperature application and storage because of their high susceptibility to oxidation. Linoleic acid containing in vegetable oils such as soybean have been reported to produce off-flavors and odors when they are oxidized (Warner and Gupta 2003).

In general, the results show that, in all the frying systems, there were decreases in the amount of polyunsaturated fatty acids, (C18:2, C18:3, ) from day 0 to day 3 during frying potato and chicken respectively, whereas palmitic acid (C16:0), stearic acid (C18:0) and oleic acid (C18:1) increased with frying time. These increases were corresponding to a reduction in total unsaturated fatty

acids. In particular, during frying, polyunsaturated fatty acids (PUFAs) decreased and total saturated fatty acids (SFAs) increased (Orthoefer and Cooper 1996). In the current study, the level of PUFAs tended to decrease, whereas that of SFAs increased. The increase observed throughout the frying time in the oleic acid concentration is not easy to explain, but it could be attributed to the migration of this fatty acid from the food products into the bath oil. A similar hypothesis was suggested by Romero *et al.* (1998) and Sebedio *et al.* (1990) to explain the increase in linoleic acid in high-oleic sunflower oil used 20 times for frying frozen foods. The change in fatty acids composition of oils used can be an indication of extent of deterioration. Their composition has a major effect on the volatile compound detected in the oil and on flavor of fried food. Although frying oils are complex mixtures of triacylglycerols, a wide variety of degradation compounds are primarily from fatty acids (Pokorny, 1989).

**Table (1) Parameters for fresh oil**

	<b>Corn</b>	<b>Soyabean</b>	<b>Palm Olien</b>
<b>Pv (meq/Kg)</b>	2.12	2.24	1.64
<b>IV</b>	120.83	128.50	60.99
<b>E 233</b>	2.35	2.72	2.15
<b>E269</b>	0.067	0.042	0.037
<b>TPC %</b>	3.83	4.71	3.36
<b>C16:0</b>	13.72	12.42	38.30
<b>C18:0</b>	2.43	4.56	3.87
<b>C18:1</b>	30.03	22.63	45.40
<b>C18:2</b>	53.00	54.04	11.61
<b>C18:3</b>	0.56	5.86	0.20

**Table 2 changing in some parameters during deep frying of potato and chicken**

**Parameters changes during frying potato/hr**

Oil Time/hr	Corn oil			Soybean oil			Palm oil		
	1	2	3	1	2	3	1	2	3
<b>PV (meq/kg)</b>	18.5±0.05 <sup>a</sup>	25.81±0.02 <sup>b</sup>	20.15±0.05 <sup>b</sup>	19.30±0.06 <sup>b</sup>	27.81±0.04 <sup>b</sup>	23.16±0.03 <sup>c</sup>	6.86±0.02 <sup>a</sup>	14.34±0.05 <sup>b</sup>	17.20±0.02 <sup>b</sup>
<b>IV</b>	119.84±1.04 <sup>a</sup>	116.24±0.65 <sup>b</sup>	114.44±0.78 <sup>b</sup>	126.73±0.65 <sup>a</sup>	124.19±0.63 <sup>b</sup>	123.37±0.63 <sup>b</sup>	58.00±1.50 <sup>a</sup>	56.58±1.20 <sup>b</sup>	55.18±1.78 <sup>b</sup>
<b>E233 nm</b>	12.99±0.01 <sup>a</sup>	15.20±0.01 <sup>b</sup>	20.20±0.07 <sup>c</sup>	15.51±0.15 <sup>a</sup>	19.21±0.02 <sup>b</sup>	25.02±0.01 <sup>c</sup>	7.10±0.01 <sup>a</sup>	7.89±0.05 <sup>b</sup>	8.65±0.05 <sup>c</sup>
<b>E 269 nm</b>	0.63±0.01 <sup>a</sup>	1.18±0.02 <sup>b</sup>	1.30±0.02 <sup>b</sup>	0.65±0.01 <sup>a</sup>	1.07±0.05 <sup>b</sup>	1.45±0.01 <sup>b</sup>	0.45 ±0.02 <sup>a</sup>	1.00 ±0.03 <sup>b</sup>	1.24±0.04 <sup>c</sup>
<b>TPC</b>	12.07±0.02 <sup>a</sup>	18.30±1.11 <sup>b</sup>	25.22±0.96 <sup>c</sup>	12.32±0.75 <sup>a</sup>	18.21±0.48 <sup>b</sup>	24.65±1.10 <sup>c</sup>	6.50±0.44 <sup>a</sup>	10.07±0.73 <sup>b</sup>	12.49±0.55 <sup>b</sup>
<b>C16:0</b>	14.53	15.56	15.71	13.46	13.48	14.49	39.60	43.79	40.29
<b>C18:1</b>	31.74	31.10	31.99	24.48	25.11	25.47	44.04	42.35	43.74
<b>C18:2</b>	50.19	49.88	48.54	52.93	52.38	50.98	11.43	9.25	11.00
<b>C18:3</b>	0.51	0.45	0.41	3.87	3.60	3.39	0.22	0.19	0.20

**Parameters changes during frying chicken/hr**

Oil Time/hr	Corn oil			Soybean oil			Palm oil		
	1	2	3	1	2	3	1	2	3
<b>PV (meq/kg)</b>	22.80±0.02 <sup>a</sup>	18.50±0.09 <sup>b</sup>	16.00±0.04 <sup>c</sup>	22.48±0.02 <sup>c</sup>	19.70±0.04 <sup>b</sup>	15.2±0.03 <sup>c</sup>	15.16±0.06 <sup>a</sup>	13.22±0.02 <sup>b</sup>	10.80±0.02 <sup>c</sup>
<b>IV</b>	116.00±1.25 <sup>a</sup>	114.44±0.67 <sup>b</sup>	111.17±1.00 <sup>c</sup>	125.02±0.6	123.31±0.55 <sup>a</sup>	122.07±0.01 <sup>b</sup>	59.57±2.55 <sup>a</sup>	57.98±1.68 <sup>a</sup>	56.98±1.52 <sup>a</sup>
<b>E233 nm</b>	11.21±0.12 <sup>a</sup>	19.19±0.05 <sup>b</sup>	22.49±0.12 <sup>b</sup>	14.86±0.09 <sup>a</sup>	19.33±0.04 <sup>b</sup>	24.69±0.02 <sup>c</sup>	7.13±0.02 <sup>a</sup>	8.89±0.02 <sup>b</sup>	9.25±0.01 <sup>ab</sup>
<b>E 269 nm</b>	0.7±0.01 <sup>a</sup>	1.38±0.07 <sup>b</sup>	1.73±0.01 <sup>b</sup>	0.63±0.02 <sup>a</sup>	1.22±0.07 <sup>b</sup>	1.63±0.01 <sup>b</sup>	1.05±0.07 <sup>a</sup>	1.20±0.02 <sup>b</sup>	1.35±0.07 <sup>a</sup>
<b>TPC</b>	12.74±0.72 <sup>a</sup>	23.27±0.83 <sup>b</sup>	27.62±1.24 <sup>b</sup>	13.43±0.99 <sup>a</sup>	21.65±0.82 <sup>b</sup>	30.55±0.63 <sup>b</sup>	8.61±0.69 <sup>a</sup>	11.98±0.63 <sup>b</sup>	16.42±0.0
<b>C16:0</b>	13.28	13.88	14.67	13.64	13.69	14.79	36.05	38.14	38.76
<b>C18:1</b>	33.98	34.63	35.43	24.84	25.99	27.22	43.57	43.21	43.94
<b>C18:2</b>	48.38	46.86	44.89	51.61	50.24	48.27	14.78	13.09	11.63
<b>C18:3</b>	1.08	0.92	0.84	4.85	4.71	4.25	0.55	0.43	0.31

Each value in the table represents the mean ± standard deviation of triplicate analysis, for each fried foods, mean value with columns (a,b,c) followed by different superscript are significantly different ( $P<0.05$ )

#### 4. Conclusion

The results revealed that Palm Olien has better stability against thermal oxidation when compared to polyunsaturated oils, which is due to fatty acid composition. On the other hand, the stability of frying oil is also influenced by the kind of food being fried; unlike different products have different composition. Results also indicated that the frying of chicken increased the concentration of decomposition products compared to oils with potato. All the parameters (except PV) showed that the corn and soybean oils used to fry potato and Chicken were abused after 15 hours of frying, where palm olien still usable.

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