

Impact of Frying on Fatty Acid Profile and Rheological Behaviour of Some Vegetable Oils

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Abstract

Rheological properties and fatty acid profile of sunflower oil (SO), cottonseed oil (CO) and palm olein (PO) during deep frying for 4, 8, 12 and 16 h were investigated. In the different systems, linoleic acid decreased while palmitic, stearic and oleic acids increased in the bath oil upon frying. The shear stress versus shear rate data was fitted to Newtonian, Bingham and Herschel-Bulkley rheological models. The flow behavior of fresh and used SO, CO and PO was measured at 25°C. All samples at zero time of frying (fresh oil) showed Newtonian behavior with correlation coefficients greater than 0.99 at 25°C and slight non-Newtonian behavior after 4, 8, 12 and 16 h of frying. Palm olein showed higher increase in viscosity in comparison to CO and SO. Rheological parameters of vegetable oils showed great changes, wherein the highest change in viscosity was recorded after 16 h of frying. Palm olein had higher flow behavior parameters than SO and CO. The increase in frying time caused an increase in K , η_B , τ_{0B} , and η values, while the n values decreased with increasing the frying time. The viscosities of the vegetable oils were plotted against either C18:1 or C18:2 and there were highly positive correlations between them ($R^2 = 0.99$). The temperature dependence of viscosity was studied by using the Arrhenius relationship and the activation energy indicates the sensitivity of the viscosity to the temperature change. The rheological parameters and viscosity measurements can provide a good overall estimate of frying oil quality.

Keywords: Sunflower oil; Cottonseed oil; Palm olein; Vegetable oils; Deep-frying; Rheological parameters; Frying time; Fatty acids composition

Introduction

The use of fat or oil for frying still remains one of the most popular methods for food preparation. The necessity of using a good quality frying medium becomes obvious when one considered that some of the fat is absorbed by every piece of food fried in it. The choice of frying fat depends on many factors such as price, frying performance, flavor and stability of product during storage. Before switching from oil to another, it is necessary to examine some of the major changes which occur in the oils during deep frying [1]. As deep fat frying is normally carried out at high temperatures (between 160°C and 180°C) and in the presence of air and moisture, the frying oils will undergo physicochemical deterioration which affect their frying performance and the storage stability of the fried products [2].

The overuse of deep frying oil causes adverse effects on flavour, stability, colour and texture of fried product and may be harmful to human health. The degradation products formed during deep frying include both volatile and non-volatile compounds, although most of the volatiles are lost during the frying process. The non-volatile decomposition products are produced primarily by thermal oxidation and polymerisation of unsaturated fatty acids. These compounds are of concern because they accumulate in the frying oil, promote further degradation, absorbed by the fried food, enter the diet and affect the public health [3-6]. Therefore, the quality of the frying medium is crucial to the nutritional quality and shelf-life of the final products.

It was recommended that analyses of frying oils should consider use of rapid tests for monitoring of oil quality that would reveal characteristics that would correlate with internationally recognized standard methods, show ease in application provide for safe use in food processing, give quantification of oil degradation, have field rugged properties, be independent of type of food and fat, and be

insensitive to water content (www.dgftt.de/material/recomm.htm). Several methods for determination of the degradation of deep frying oils have been developed based on physical parameters (viscosity and dielectric changes, etc.) and on chemical parameters (free fatty acids and polymerised triacylglycerols, etc.).

Oils play a dual role in the preparation of fried foods because they serve as a heat transfer medium between the food and the fryer, and they also contribute to the food's texture and flavor characteristics [7]. The oil rapidly changes from a light yellow to an orange brown color. This is the combined result of oxidation, polymerisation and other chemical changes which also result in an increase in viscosity of the frying oil. The changes in color and viscosity of frying oil are the signs of oil deterioration. The oil may thicken and become more viscous as it is heated. This seems to be due to the process of polymerisation and also to oxidation, hydrolysis and isomerization [8]. It is a serious performance fault because it causes a number of problems. In frying, the oil is really a heat transfer medium. Thickening reduces the rate of heat transfer and it takes longer to cook and color the food. It also increases oil absorption. This effect will carry over into the finished products, especially as oil content can comprise 30-40% of the product by weight. Viscosity measurements can provide a good overall estimate of frying fat or oil quality [9]. The viscosity of vegetable oils is affected by a number of factors. These include the physical and chemical

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properties of oils such as the density, molecular weight, melting point and degree of unsaturation. A factor that greatly affects the viscosity of oils is temperature. It has been reported that the viscosity of oils and fats decreased linearly with temperature [10]. In vegetable oils, viscosity increases with chain lengths of triglyceride fatty acids and decreases with unsaturation-in other words, increase with hydrogenation. So, viscosity is a function of molecules dimension and orientation [11]. Vegetable oils are multi-component systems containing different families of triacylglycerols (TAGs). In these systems the molecular relationships occurring among TAGs families determine the thermodynamic conditions (i.e., supercooling and supersaturation) that drive the formation of a solid in a liquid phase and the phase behavior of the solid phase. The resulting three-dimensional TAGs crystal network and the phase behavior of TAGs are major factors determining the physical and functional properties (i.e., rheology, liquid phase entrapment, mouth feel, appearance and spreadability) in products such as margarine, butter, confectionary coatings and fillings [12]. Additionally, crystallization conditions such as cooling rate and thermal history (i.e., crystallization temperature and tempering process) have significant effects on the kinetics and physical properties of the crystallized systems.

Very little information on oil viscosity is available in research papers and there is no detailed study on the rheological properties of frying oils in the literature. The objectives of this study were to study and compare the changes in physicochemical parameters and rheological properties of SO, CO and PO during frying of French fries.

Materials and Methods

Sunflower oil (SO), cottonseed oil (CO) and palm olein (PO) samples were obtained from the Misr Oil and Soap Company (Egypt). Potatoes (*Solanum tuberosum*) were purchased from the local market (Zagazig, Egypt). Raw potatoes were peeled, washed and sliced (1.0 x 1.0 x 5.0 cm sticks) immediately before frying. All solvents and reagents from various suppliers were of the highest purity needed for each application and used without further purification.

Frying protocol and oil sampling

Deep-frying experiments on the three oils were carried out simultaneously using a stainless steel electrical open pan fryer (Bosch, Germany) with pot of 5 kg capacity and equipped with an auto lift stainless steel basket and automatic portable filter system. Three kg of oil was introduced into fryer. Each day, the oils were heated at 180°C ± 2°C (Temperature was measured and controlled by a thermocouple) and allowed to equilibrate at this temperature for 30 min. In total, forty batches of the raw French fries, (300 g per batch), were intermittently fried for 6 min at intervals of 10 min, for 16 h during two consecutive days. The fryers were left uncovered during the frying period. The fryer was turned off at the end of the frying experiment for each day and the oil was allowed to cool to 60°C then stored at room temperature during the night till next day to continue the frying. The oil in the fryer was filtered to remove debris using separate filters. About 200 g of frying oils was withdrawn from the fryer and sampled into brown bottles after 8 h and 16 h after filtration. The oil samples including the fresh ones (zero time) were stored in brown bottles at -20°C for subsequent physical and chemical analyses. Frying experiments were conducted in two replicates on each system.

Methods

Gas chromatography analysis of fatty acids

Three samples of unused oils and three samples of the same oils after being used in the 20th and 40th fryings were analysed. Fatty acids were transesterified into methyl esters (FAME) using N-trimethylsulfoniumhydroxide (Macherey-Nagel, Düren, Germany) according to the procedure reported by Arens et al. (1994) [13]. FAME were identified on a Shimadzu GC-14A equipped with Flame Ionisation Detector (FID) and C-R4AX chromatopac integrator (Kyoto, Japan). The flow rate of the carrier gas helium was 0.6 mL/min and the split value with a ratio of 1:40. A sample of 1 µL was injected on a 30 m x 0.25 mm x 0.2 µm film thickness Supelco SPTM-2380 (Bellefonte, PA, USA) capillary column. The injector and FID temperature was set at 250°C. The initial column temperature was 100°C programmed by 5°C/min until 175°C and kept 10 min at 175°C, then 8°C/min until 220°C and kept 10 min at 220 °C. A comparison between the retention times of the samples with those of authentic standard mixture (Sigma, St. Louis, MO, USA; 99% purity specific for GLC), run on the same column under the same conditions, was made to facilitate identification.

Rheological measurements

Viscosity measurement was carried out by the Brookfield digital viscometer (model DV-III+) with 18 rotational speeds for comprehensive data gathering (0.3, 0.5, 0.6, 1.0, 1.5, 2.0, 2.5, 3, 4, 5, 6, 10, 12, 20,30,50,60 and 100 rpm). The Brookfield spindles used were: (a) UL adapter and (b) Brookfield small sample adapter (spindles Nr. 18 and 21). The test sample ranged between 8 to 16 ml oil for each treated samples according to kind of spindles. The temperature was kept constant using a thermostatically controlled water bath. All data were taken after 1 min between each 18 rotational speeds in each sample, with a resting in time between the measurements at the different spindle speeds. All experiments were replicated three times. The flow curves, shear stress vs. shear rate, of oil samples were plotted in the temperature range of 5-100°C by increasing (forward measurements) and decreasing (backward measurements) the speed rate. Average shear stresses and shear rates were calculated. The flow curves of oil samples were modeled by using the following models, which are the most frequently used for engineering applications:

Newton's model

The shear stress versus shear rate data was fitted to Newton's model (Equation. 1) by linear regression.

$$\tau = \eta \dot{\gamma} \quad (1)$$

Where τ is the shear stress (mPa), η is dynamic viscosity (mPa.s) and $\dot{\gamma}$ is the shear rate (s⁻¹).

Bingham plastic model

$$\text{The Bingham equation is } \tau = \tau_{OB} + \eta_B \dot{\gamma} \quad (2)$$

Where:

τ = Shear stress (mPa)

τ_{OB} = Bingham yield stress, shear stress at zero shear rate, (mPa)

η_B = Bingham plastic viscosity (mPa.s) $\dot{\gamma}$ = Shear rate (sec⁻¹)

The calculated parameters for this model are plastic viscosity and yield stress according to Bingham [14] and Malcolm [15].

Fatty Acids	Sunflower oil			Cottonseed oil			Palm Olein		
	time			time			time		
	Zero	8 h	16 h	Zero	8 h	16 h	Zero	8 h	16 h
C14:0	0.06 ^a	0.06	0.07	0.63	0.64	0.53	0.91	0.94	0.95
C16:0	6.12	6.34	6.58	21.8	22.5	21.9	37.0	38.1	38.9
C16:1	0.07	0.08	0.09	0.66	0.68	0.52	0.16	0.18	0.17
C18:0	3.59	3.71	3.85	2.56	2.62	3.62	4.06	4.32	4.33
C18:1 <i>cis</i>	21.8	22.4	23.0	19.1	20.2	24.5	40.9	41.5	41.6
C18:1 <i>trans</i>	nd ^b	nd	nd	nd	0.23	0.41	nd	nd	0.22
C18:2 <i>cis</i>	65.5	64.5	63.4	52.4	50.4	43.5	13.9	12.9	12.3
C18:2 <i>trans</i>	nd	0.06	0.09	0.30	0.40	0.60	0.20	0.25	0.28
C18:3	0.18	0.16	0.12	0.17	0.16	0.16	0.16	0.16	0.15
Others	2.68	2.65	2.70	2.38	2.17	4.32	2.71	1.63	1.45
∑ SFA ^c	9.77	10.1	10.5	24.9	25.7	26.0	41.9	43.3	44.1
∑ MUFA ^d	22.5	23.2	23.9	19.7	21.1	25.4	41.0	41.6	41.9
∑ PUFA ^e	65.6	64.7	63.6	52.8	50.9	44.2	14.2	13.3	12.7
S/P ^f	0.14	0.15	0.16	0.47	0.50	0.58	2.95	3.25	3.47
Increase in saturation ratio x 100		12.5			18.9			14.9	
C18:2/C16:0	10.7	10.1	9.63	2.40	2.24	1.98	0.37	0.33	0.31

^aValues given are the mean of three replicates. ^bnd, not detected. ^cTotal saturated fatty acids. ^dTotal monounsaturated fatty acids. ^eTotal polyunsaturated fatty acids. ^fThe ratio of saturated to polyunsaturated fatty acids.

Table 1: Changes in fatty acids composition (%) of different oils during frying of French fries.

Herschel-Bulkley model

The Herschel-Bulkley model describes the flow curve of a material with a yield stress and shear thinning or shear thickening behavior at stresses above the yield

$$\tau = \tau_0 + K \dot{\gamma}^n \quad (3)$$

Where:

τ is shear stress (mPa), τ_0 is the yield stress (mPa), K is the consistency index (mPa sn), $\dot{\gamma}$ is shear rate (s⁻¹) and n is the flow behavior index ($n = 1$ for Newtonian fluids, $n < 1$ for shear thinning fluids).

Data was analyzed by using Universal Software US200 (Physica, Germany), Bingham plastic and Herschel-Bulkley math models provide a numerically and graphically analyze for the behaviour of data sets. The coefficient of correlation (r) for all rheological models was calculated by using Universal Software US200.

Activation energy and the effect of temperature on viscosity

Activation energy was calculated using Arrhenius-type equation as mentioned by Kim et al.[16].

$$\eta = \eta_{\infty} \exp(E_a/RT) \quad (4)$$

Where:

η is the viscosity

η_{∞} is a constant (is the viscosity at infinite temperature) E_a is the activation energy of flows (J/mol)

R is the gas constant

T is the absolute temperature in °K.

Physicochemical parameters of oils

The progress of the deterioration of the oils during frying was followed by measuring changes in peroxide value (PV) and iodine value (IV) according to the official methods of the American Oil Chemists' Society (1998). Free fatty acid (FFA) content as percentage oleic acid was determined using AOCs Official Method Ca5a-40 (1998). Oil colour was measured in a 1" cell in a Lovibond Tintometer (model E, Salisbury, UK).

The physicochemical parameters were graphically plotted using Microsoft Excel software to obtain the regression coefficient of the variables to determine if there are significant differences.

All results presented are mean values of at least three experiments, wherein no statistically significant difference ($P > 0.05$) was found among the experiments.

Results and discussion

Deep frying is a very important method of cooking in the food services industry as it enhances the sensory properties of foods. Fried foods are desired for their distinctive flavor and odor. During frying, the oil is continuously and repeatedly used at elevated temperatures (160-180°C) in the presence of air and moisture. When foods are fried in heated oil, many complex chemical reactions occur resulting in the production of degradation products. As these reactions proceed, the functional, sensory and nutritional quality of the fat/oil changes and may eventually reach a point where it is no longer suitable for preparation of high quality fried products and the frying fat/oil will have to be discarded [17,18]

Impact of frying on the fatty acid profile of vegetable oils

Data in (Table 1) presents the fatty acid compositions of the used

Oil sample	Frying time (h)	Parameters for different rheological models				
		Newtonian Model		Bingham model		
		η Viscosity	r	τ_0 B	η B	r
Sunflower oil	0	97.73	0.995	8.691	67.12	0.984
	4	103.44	0.993	10.932	74.76	0.967
	8	109.12	0.997	13.357	85.24	0.961
	12	117.89	0.997	17.333	94.11	0.987
	16	128.73	0.999	20.098	103.65	0.989
Cottonseed oil	0	107.03	0.994	11.422	89.59	0.991
	4	113.09	0.996	13.621	98.17	0.986
	8	119.79	0.998	16.079	109.33	0.974
	12	131.05	0.999	19.868	123.26	0.981
	16	142.70	0.993	24.396	136.70	0.990
Palm olein	0	121.37	0.999	13.141	104.83	0.978
	4	128.96	0.995	15.038	112.59	0.961
	8	139.07	0.992	18.513	125.71	0.973
	12	149.93	0.994	20.208	137.42	0.968
	16	166.74	0.997	26.884	148.49	0.974

Table 2: Flow parameters of different oils during frying using the Newtonian model and Bingham model.

Oils sample	Frying Time (h)	Parameters for Herschel–Bulkley rheological models			
		τ_0 HB	K	n	r
Sunflower oil	0	5.11	57.00	0.977	0.999
	4	7.89	57.18	0.971	0.999
	8	12.07	59.34	0.966	0.997
	12	16.86	61.92	0.942	0.999
	16	22.63	65.09	0.916	0.996
Cottonseed oil	0	7.95	68.17	0.959	0.999
	4	11.83	69.86	0.943	0.998
	8	17.77	71.55	0.931	0.996
	12	23.98	73.24	0.917	0.997
	16	29.57	77.93	0.883	0.997
Palm olein	0	9.19	80.01	0.926	0.999
	4	13.59	81.70	0.905	0.996
	8	19.56	83.39	0.894	0.996
	12	27.75	85.09	0.869	0.998
	16	38.15	89.78	0.851	0.996

Table 3: Flow parameters for different oils during frying using the Herschel–Bulkley model.

oils across 2 days of frying. In all frying oils, there were decreases in linoleic acid (C18:2), whereas palmitic acid (C16:0), stearic acid (C18:0) and oleic acid (C18:1) were increased with frying time. During frying, polyunsaturated fatty acids (PUFA) were decreased and saturated fatty acids (SFA) were increased. It was reported that heat treatment of fats induces modifications of fatty acids with two or three double bonds [19,20]. In our study the level of PUFA tended to decrease, whereas that of SFA increased. However, because we have used an internal standard to quantify fatty acid changes, the increase in SFA during repeated frying may not due to oxidative alteration but to interaction between the bath oil and the lipids of the fried food products. The increase observed

throughout the frying in the oleic acid concentration is not easy to explain, but it could be due to the migration of this fatty acid from the food products into the bath oil. A similar hypothesis was suggested by Romero et al. [5] to explain the increase in linoleic acid in high-oleic SO used 20 times for frying. The results show that the decrease in C18:2 and the increase in C16:0, C18:0 and C18:1 across two consecutive days of frying was higher in CO than in the SO and PO. This shows that, the oxidation process progresses more rapidly in CO than in SO and PO. From data in Table 1, it could be noticed that the concentration of total SFA markedly increased after 8 h of frying being 10.1, 25.7 and 43.3% in SO, CO and PO, respectively. It was mainly due to the

increase in palmitic acid and stearic acid content. These increases were corresponding with reduction in total unsaturated fatty acids. However, as the frying time increased up to 16 h a slight effect on the percentage of total SFA and unsaturated fatty acids was observed. It means that the patterns of different frying oils slightly changed in small upward of palmitic, stearic, oleic and total SFA. In reverse relationship, PUFA had a small downward trend. On the other hand, the ratio of linoleic acid to palmitic acid tended to decrease at a diminishing rate by increasing frying period. In PO and SO, the drop in C18:2/C16:0 ratio was lower to a great extent than that of CO. Geometric isomers (*trans* fatty acids) from oleic and linoleic acids appeared after frying wherein the level remained relatively stable throughout successive frying. Unsaturated fatty acids, *trans* isomerization of a double bond can occur during frying of foods [21,22]. However, the obtained results suggest that *trans* fatty acids are minor constituents of oils used in frying French fries. These results indicated that PO is more stable than SO and CO with regards to changes in the fatty acid composition when the unsaturated fatty acids in the oil become oxidized during frying.

Rheological properties of vegetable oils

All oils samples showed great changes in viscosity and rheological parameters after frying for 16 h (Tables 2 and 3). As the oxidation accelerated by heat proceeded, the values of viscosity progressively increased and these results are in agreement with (Tyagi and Vasishtha [23] and Chatzilazarou et al. [24]). Palm olein showed higher increase in viscosity in comparison to the other oils. These results clearly indicate the deteriorative effect of oxidation and polymerization of fried oils compared to fresh oils. Viscosity of oil is strongly affected by its degradation products, increasing as a result of formation of dimers, trimers, polymers, epoxides, alcohols and hydrocarbons [3]. The increase in viscosity of oils was due to polymerization which resulted from the formation of high molecular weight compounds (carbon-to-carbon and/or carbon-to-oxygen-to-carbon bridges) between fatty acids [25,18,24]. In deep frying operations, the viscosity of the oil changes considerably with frying time and this change must be taken into consideration when designing frying operations so that product quality can be controlled.

Viscosity of the frying oil is an important factor in determining the total volume of oil sticking in the large cavities in the crust of the food product [26]. The shear stress versus shear rate data was fitted to Newtonian, Bingham and Herschel-Bulkley rheological models. The flow behaviour of fresh and used SO, CO and PO samples measured at 25°C. Fresh oils showed relative Newtonian behaviour with correlation coefficients greater than 0.99 at 25°C and slight non-Newtonian behaviour after 4, 8, 12 and 16 h of frying. These results are in agreement with those of Gloria and Aguilera [27]; Santos et al. [28] and Quinchia et al. [29] who found that the flow behaviour of some edible vegetable behaved as non-Newtonian fluids. Also, the results are in agreement with Huang and Sathivel [30] who reported that the crude salmon oil behaved as non-Newtonian fluids. The fresh oils are Newtonian liquids having high viscosity due to their long chain structure. Our results showed that repeated frying time processes change the rheological behaviour to non-Newtonian behaviour.

Viscosity of oils increased during frying and was influenced by frying time and the changes in viscosity indicate significant structural change. The tendency of viscosity to increase during frying of the oil has been found to correlate with formation of polymers [27]. The increasing in viscosity indicates that polymers, which are the higher molecular weight fraction of the degradation products, are increased by increasing frying time. Also, increasing in viscosity may be due

to a hidden effect of free fatty acids produced by hydrolysis reactions and other small molecular weight decomposition products during frying. This inverse relationship has been likened to the incidence of a freer molecule-to-molecule interaction at elevated temperatures. Since viscosity is an indication of the resistance to flow, such a freer interaction is expected to minimize the resistance. These results agree with the published studies [31,28].

Viscosity of PO had higher values than CO and SO either in fresh or during frying periods. These increases were attributed to thermal effect, the formation of polymeric compounds and a tendency toward foaming during frying [32,7]. It was also found that because of the high water content of fried products, the polymerization of frying oil increased within the frying process and the viscous materials were highly formed during the final stages of frying. Depending on viscosity profile, the obtained results indicated that CO and SO were more stable than PO as a frying medium. Monitoring changes in viscosity appear to be a good monitor to measure differences of frying fat deterioration.

Impact of frying time on the rheological parameters

The correlation coefficient was used to determine how good the models fit the data. Based on correlation coefficients and overall suitability of the models considered, the Newtonian, Bingham and Herschel-Bulkley rheological models were selected to describe the rheological behavior of SO, CO and PO. The flows of oils were characterized as nearly Newtonian at zero time of frying and non-Newtonian (pseudoplastic) after 4, 8, 12 and 16 h of frying and pseudoplasticity increased when frying time increased.

The rheological behavior of oils samples is of special importance when they are used to study the relation between the chemical properties and the flow behavior of oils. It is also well recognized that rheological properties play a role in process design, evaluation and modeling. These properties are sometimes measured as an indicator of product quality (e.g., indication of type of oil or change in molecular size). Rheological data are required for calculation in any process involving fluid flow (e.g., frying equipments, pump sizing, extraction, filtration, extrusion and purification) and play an important role in the analyses of flow conditions in food processes such as frying, evaporation, drying and aseptic processing. From the shear rate-shear stress curves and data in (Table 2 and Table 3), oils showed nearly Newtonian at zero time and a non-Newtonian pseudoplastic with yield stress fluids as the apparent viscosity decreases with increasing shear rate for all oils at 4, 8, 12 and 16 h of frying time.

Several models have been used to characterize the flow behavior of vegetable oils wherein Herschel-Bulkley model has been frequently used for determination of rheological properties of the vegetables oils according to San Martin-Gonzalez et al. [33]. In addition, Newtonian and Bingham models has been also used for the characterization of fluid foods such as vegetable oils. The parameters obtained for the Newtonian, Bingham and Herschel-Bulkely models are summarized in (Table 2 and Table 3). The correlation coefficients, for all cases, were higher than 0.961. K , n and η rheological parameters at zero time were similar to the range obtained by Huang and Sathivel [30], with longer frying time higher η , K , η_B , τ_{0HB} and τ_{0B} values were recorded. Increasing in frying time caused an increase in K , η_B , τ_{0HB} , τ_{0B} , and η values, while the n values decreased with increasing in frying time. This trend of results is in agreement with Maskan [18] and Steffe [34] whereas higher yield stress values were observed at longer frying time.

Palm olein had high flow behavior parameters than SO and

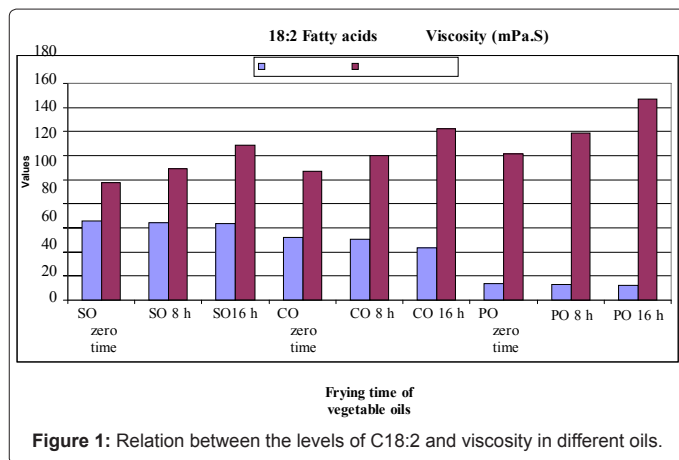


Figure 1: Relation between the levels of C18:2 and viscosity in different oils.

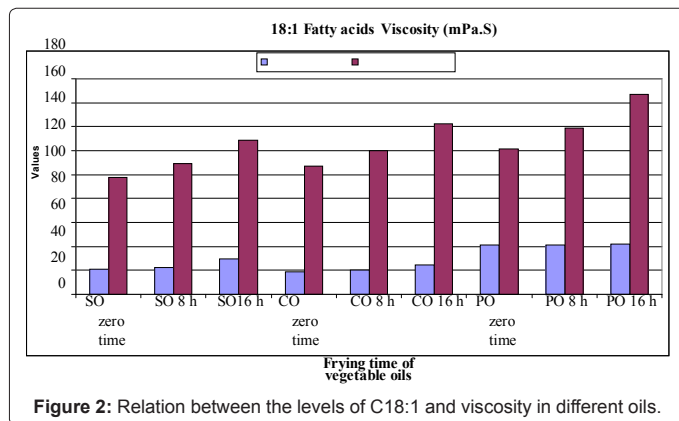


Figure 2: Relation between the levels of C18:1 and viscosity in different oils.

CO. It could be concluded in the view of the results that frying time particularly was more effective in increasing K values of all vegetable oils. Sunflower oil could be recommended for frying because it is fast in heat transfer, while PO might be not recommended for frying because they have high flow behavior parameters. Also blending SO and or CO with PO may be useful for attaining desired consistency. Vegetable oils under study are used in food industry for frying purpose since it is more economical compared to other oils, therefore blending those oils could be recommended in different frying oils formulations.

Relation between fatty acids profile and rheological properties

The dependence of viscosity on the oil composition was investigated by correlating the oil viscosity with fatty acids composition. An effort was made to investigate how the degree of unsaturation affected oil viscosity. Positive correlation was observed between viscosity and total SFA and PUFA. Also, when the viscosities of the oils were plotted against either C18:1 or C18:2 fatty acids, it was interesting to note that there were highly positive correlations between them ($R^2 = 0.99$) as shown in (Figure 1 and Figure 2), (this relationship was calculated by using Microsoft Office 2007 Excel). The major fatty acids of the vegetable oils (C18:1 and C18:2) appeared to make a great contribution to their flow behaviors. A decrease in the oil viscosity was distinctly observed with increasing the level of C18:2 and a decreasing the level of C18:1 fatty acid. Since each double bond with a *cis* configuration form causes a kink in the straight chain and the presence of double bond does not allow fatty acid molecules to stack closely together, consequently interfering with packing in the crystalline state [35,16]. Thus, fatty acids

with more double bonds do not have a rigid and fixed structure, being loosely packed and more fluid-like.

Activation energy and the effect of temperature on viscosity

The viscosity is depending upon the intermolecular distances. As the temperature increased, the intermolecular distances increase and therefore the viscosity will decrease for these reasons. In addition, the viscosity is a function of temperature and the dissolved solid concentration. The Arrhenius equation to a great extent explains the relationship between the temperature and viscosity. The η_{∞} and E_a parameters are determined by measuring η at different temperatures (5-100°C) within 10 round per minutes (RPM) as a shear rate, the RPM transform to the values of shear rate the by using special equations depend on the spindles type.

All oil samples exhibited the same viscosity pattern over temperature, which was a non-linear decrease in viscosity with high temperature. The temperature effect on oil viscosity has been attributed to the decrease in intermolecular interactions by great thermal molecular movement [10,28]. A favorably good agreement was found when the results were compared with other studies [18,28,30]. In addition, the effect of temperature on the oil viscosity was evaluated by means of the Arrhenius temperature model, which describes the exponential decrease of the viscosity over temperature. The dependence of viscosity was studied using the Arrhenius relationship (Equation 4). A linear relationship of $\ln(\eta)$ vs. $(1/T)$ was observed. The correlation coefficients (r) for each oil sample are presented in (Table 4). Activation energy indicates the sensitivity of the viscosity to the temperature change. Higher E_a means that the viscosity is relatively more sensitive to temperature change. Results presented in (Table 4) showed the parameters of Arrhenius equation. The activation energy increased with decreased of the levels of C18:1. Considering that vegetable oils viscosity depends on fatty acids composition, the activation energy increased with the decreasing double bonds in the fatty acids chain and temperature. Therefore, temperature had a great effect on the samples and this tendency is similar to the results of Huang and Sathivel [30].

As presented in Table 4, the calculated values of the activation energy and constant of the vegetable oils were ranged from 2.375×10^4 to 4.705×10^4 J/mol and from 3.708×10^{-3} to 1.742×10^{-3} mPa.s, respectively.

Oils samples	Time (h)	Coefficient correlation (r)	E_a (J/mol.)	η_{∞} (mPa.s)	Temperature range (°C)
Sunflower oil	0	0.993	2.745×10^4	3.533×10^{-3}	5-1000
	4	0.999	2.419×10^4	3.643×10^{-3}	5-100
	8	0.997	2.403×10^4	3.665×10^{-3}	5-100
	12	0.996	2.388×10^4	3.681×10^{-3}	5-100
	16	0.999	2.375×10^4	3.708×10^{-3}	5-100
Cottonseed oil	0	0.997	3.896×10^4	2.488×10^{-3}	5-100
	4	0.999	3.658×10^4	2.304×10^{-3}	5-100
	8	0.996	3.302×10^4	2.166×10^{-3}	5-100
	12	0.998	2.951×10^4	2.047×10^{-3}	5-100
	16	0.998	2.694×10^4	1.926×10^{-3}	5-100
Palm olein	0	0.999	4.705×10^4	2.061×10^{-3}	5-100
	4	0.997	4.589×10^4	1.917×10^{-3}	5-100
	8	0.999	4.277×10^4	1.863×10^{-3}	5-100
	12	0.999	4.094×10^4	1.808×10^{-3}	5-100
	16	0.994	3.850×10^4	1.742×10^{-3}	5-100

Table 4: Arrhenius-type constants relating the effect of temperature and viscosity at 10 RPM on oils.

Parameter	Sunflower oil			Cottonseed oil			Palm Olein		
	Zero	8 h	16 h	Zero	8 h	16 h	Zero	8 h	16 h
FFA (%)	0.050	0.152	0.190	0.052	0.220	0.241	0.069	0.27	0.343
Peroxide value (meq/kg)	1.7	23	28	1.9	29	33	1.6	5.5	10
Iodine value (IV)	128	127	125	107	105	103	87	79	77
Color (Lovibond)	0.9/11	3.9/31	8.8/35	3/30	9/35	11/38	3.7/31	7.9/35	10/35

Values given are the mean of three replicates

Table 5: Impact of frying on physicochemical characteristics of different frying oils during frying of French fries.

The highest value of the activation energy was observed in PO followed by CO and SO. Since the activation energy indicates the sensitivity of a material to temperature changes (Steffe [34]), the statistical results demonstrated that the flow behaviors of PO, CO and SO were highly dependent on temperature change. Also, when the activation energy value of each oil was plotted against the levels of C18:2 fatty acid (data not shown), there was a reasonable correlation suggesting that the oils containing more double bonds exhibit less activation energy and these results are agreed with (Kim et al.) [16]. It is generally recognized that the higher viscosity of frying oils, the greater the oil content in fried foods. This would be explained by the fact that high viscosity can allow the oils to be accumulated more easily on the surface of fried foods and enter inside during the cooling period [18]. It indicates that viscosity might not be the only factor to affect the oil content. Another possible explanation would be that a more substantial difference in the viscosity amongst the oils might be needed to cause a significant change in the oil uptake. Nonetheless, an overall increase in the oil content by high viscosity could be observed from the mean values of the oil content.

Impact of frying on physicochemical characteristics of different frying oils during frying of French fries

The characteristics of the different oils used in the frying study are presented in Table 5 by comparing these data, it can be considered that the quality of the starting oils in general were good and comparable. As expected in frying oils, the FFA, PV, colour of all the oils increased, while the IV, which is a measure of the degree of unsaturation, tended to decrease with frying time; the changes was generally least in palm olein. Continuous frying of French fries showed increasing in the levels of FFA of different oils versus time of experiments (Table 5).

It was observed that across 16 h of the frying experiment, FFA rise was slightly higher in palm olein than in sunflower and cottonseed oils. This higher value could be due to the fact that the initial FFA of palm olein (0.069%) was higher than that of sunflower oil (0.050%) and cottonseed oil (0.052%). At the second day of frying, the FFA of palm olein, cottonseed and sunflower oils were 0.34%, 0.24% and 0.19%, respectively. For all oils, these values were still below 0.5% which is the value normally used by snack food producers to discard the oil. However, the difference in FFA between the oils was found not to be significant. Generally, the increase in FFA levels were due to the cleavage and oxidation of double bonds to form carbonyl compounds which oxidized to low molecular fatty acids during frying treatments [36]. Furthermore, it is expected that water supplied from fried potato accelerated the hydrolysis cleavage of the oil. It was also noticed that the FFA values showed some decreases during frying periods (after 4 and 12 h, data not shown), it may be due to the loss of low molecular weight fatty acids through volatilisation. The determination of FFA by titration does not differentiate between acids formed by oxidation and

those formed by hydrolysis. For these reasons, the increase in FFA level is a poor measure of frying oils deterioration.

Peroxides are major initial reaction products of lipid oxidation that major for primary oxidation. The PV (Peroxide Value) of this study is shown in Table 5. The initial PV for all oils was lower than 2 meq/kg. Che Man and Wan Hussin (1998) [37] mentioned that a good-quality vegetable oils should have a PV of lower than 2 meq/kg. The PV during the frying operation of all systems was gradually increased. It is evident from Table 5 that frying the fresh oils up to 180°C for 8 h increased the PV of cottonseed oil more than sunflower oil and palm olein being 29, 23 and 5.5 meq/kg, respectively. A comparison of the data showing that the PV of cottonseed oil during deep frying were higher than those of sunflower oil and palm olein, indicating a greater extent of oxidation in cottonseed oil. The results also indicated that the PV of different oils after two days of frying were significantly different. It is well known that PV is useful as an indicator of oxidation at the initial stages. However, during frying the changes in PV were not related to duration of frying, but were dependent on rate of formation and breakdown of oxidation procedure. Another problem is that the peroxides may increase after the sample in taken from the fryer before analysis. This can be controlled but it is difficult. Therefore, the PV is not generally used to measure frying oil deterioration.

The higher the IV is, the greater is the unsaturation of a specific oil or fat. With regard to the effect on IV, the continuous frying affected regularly IV of the studied oils (Table 5). It was found that the stability of palm olein was higher than sunflower oil and cottonseed oil during frying of French fries. It could be noticed also that the deterioration in double bonds of cottonseed oil was outnumbered that of palm olein. This discrepancy in stability of palm olein compared to cottonseed oil is a consequence of its high oleic acid and low linoleic content.

Generally, intermittent frying of French fries 8 h daily for two consecutive days led to gradual reduction in the IV of the three oils reaching the minimal levels at the end of the frying periods. Replenishing the frying oils with fresh ones increased the IV but they were still lower than the initial values (data not shown). The oils IV decreased versus frying time due to consumption of double bonds by oxidation and polymerisation. These results could be considered as indication to the extent of thermal and oxidative degradation for the frying oils.

The colour value of vegetable oils increased simultaneously with increasing the frying time, due to brown pigments from the fried products dissolved into the frying oils and also a combined result of oxidation and polymerisation of the unsaturated fatty acids in the frying medium [38]. Table 5 shows the values of yellow and red colour of different oil systems. The increase in red and yellow colour values throughout the two consecutive days of frying were relatively similar for all systems, where the colour of all samples gradually darkened.

Fresh sunflower oil showed a lighter colour compared to those of palm olein and cottonseed oil, due to less carotenoid pigments presented in fresh sunflower oil. Although palm olein was darker before frying than cottonseed oil, the colour values of cottonseed oil rapidly increased and changed to a darker colour after frying for 16 h due to the oxidation. For the three oils, the higher the linolenic content, the darker the final oil colour. It is known that the colour increase in palm olein during heating or frying is relatively faster than in other oils. Palm olein also has a somewhat higher colour reading compared to the other oils. However, studies have shown that although palm olein may start with a higher colour value and darkens faster, this does not affect the colour of the fried products [39]. These results indicated that darkening is considered useful phenomenon as it prevent the continual use of edible oils which have undergone excessive deterioration.

Conclusion

The effect of deep-frying of French fries on the rheological characteristics of different oils was investigated. Palm olein appeared to be slightly more stable than SO and CO, but the difference was not as great as would be expected from the fatty acid compositions of the oils. The results demonstrated that there was a high correlation between oil viscosity and fatty acids composition of oil, suggesting that the oils with more double bonds appeared to have lower viscosity due to their loosely-packed structure. Also, their flow behaviours over temperature could be well characterised by the Arrhenius model. Since the quality, stability and rheological properties of oils over time could vary depending on the oil type. The rheological parameters and viscosity measurements can provide a good overall estimate of frying fat or oil quality.

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