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Journal of Food Measurement and Characterization

ISSN 2193-4126
Volume 8
Number 3

Food Measure (2014) 8:171-179
DOI 10.1007/s11694-014-9178-3

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DOI 10.1007/s11694-014-9178-3

ORIGINAL PAPER

Rheological characteristics of vegetable oils as affected by deep frying of French fries

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Received: 1 January 2014 / Accepted: 30 March 2014 /

Abstract Fatty acid composition and rheological characteristics of sunflower oil (SO), cottonseed oil (CO) and palm olein (PO) during deep frying for 4–16 h were investigated. In the different oils, linoleic acid decreased while palmitic, stearic and oleic acids increased in the bath oil during frying. Total phenolic content (TPC) in different oils increased during frying and strongly correlated with frying time. As frying progressed, it was observed that the rate of increase in TPC was relatively slower in PO than in the SO and CO. The shear stress versus shear rate results was fitted to Newtonian, Bingham and Herschel–Bulkley rheological models. The flow behaviour of fresh and fried SO, CO and PO was recorded at 25 °C. Fresh oils showed Newtonian behaviour with correlation coefficients greater than 0.99 at 25 °C and slight non-Newtonian behaviour after frying. Palm olein showed higher increase in viscosity in comparison to CO and SO. Rheological parameters of vegetables 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_{0HB}, τ_{0B}, and η values, while the n values decreased with increasing the frying time. The viscosities of oils were plotted against the levels of C18:1 and C18:2 wherein highly positive correlations were found 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 viscosity to changes in temperature. It could be concluded that the rheological parameters can provide an overall estimate of oil quality during frying.

Keywords Rheological parameters · Viscosity · Fatty acids · Frying · Sunflower oil · Cottonseed oil · Palm oil

Introduction

Frying remains one of the most popular methods for food preparation. The importance of using a good quality frying oil becomes obvious when one considered that some of the oils is absorbed by food fried in it. The choice of frying oil depends on many factors such price, frying performance, flavour and stability of product during storage. It is necessary to examine some of the major changes which occur in the oils during deep frying [28]. As deep fat frying is normally carried out at high temperatures (between 160 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 [8, 22].

The overuse of frying oil causes adverse effects on flavour, stability, colour and texture of fried products and may be harmful to human health. The degradation products formed during frying include both volatile and non-volatile compounds, although most of the volatiles are lost during the frying process. The non-volatile de-compositional 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 public health [6, 24].

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Therefore,the quality of the frying medium is crucial to the nutritional quality and shelf-life of the final products.

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 [32]. 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 [18]. 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. 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 an overall estimate of frying oil quality [15]. The viscosity of oils is affected by a number of factors. These include the physical and chemical 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 [14]. 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.

Several methods for determinations of the degradation of deep frying oils were developed based on physical parameters (viscosity and dielectric changes, etc.) and on chemical parameters (free fatty acids and polymerized TAGs, etc.). Little information on the rheological characteristics of deep fried oils is available in research papers. Thus, the objectives of this study were to study and compare the changes in rheological parameters and fatty acid composition of SO, CO and PO during frying of French fries.

Materials and methods

Materials

Sunflower oil (SO), cottonseed oil (CO) and palm olein (PO) samples were obtained from the Misr Oil and Soap Company (Zagazig, Egypt). Potatoes (*Solanum tubersum*) were purchased from the local market (Zagazig, Egypt). Raw potatoes were peeled, washed and sliced (1.0 × 1.0 × 5.0 cm^3 sticks) immediately before frying. All solvents and reagents were of the highest purity needed for each application and used without further purification.

Frying process and oil sampling

Frying experiments were carried out using a electrical open pan fryer (Bosch, Germany) with pot of 5 kg capacity and equipped with an autolift stainless steel basket and automatic portable filter system. Oils (3 kg) were introduced into fryer. Each day, the oils were heated at 180 ± 2 °C and allowed to equilibrate at this temperature for 30 min. In total, 40 batches of the raw French fries, 300 gm 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 each day and the oil was allowed to cool to 60 °C. The oil in the fryer was filtered to remove debris using separate filters. The fryer oil was replenished with about 33.3 % (w/w) of the fresh oil (about 1 kg) after the 1st day and before starting frying operations. About 200 g of frying oils was withdrawn from the fryer and sampled into brown bottles after 8 (before replenishment) 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

Analysis of fatty acids

Samples ($n = 3$) of fresh oils and samples ($n = 3$) of the oils used in the 20th and 40th fryings were analyzed. Fatty acids were transesterified into methyl esters (FAME) using *N*-trimethylsulfoniumhydroxide (Macherey–Nagel, Düren, Germany) according to the procedure reported by Arens et al. [3]. 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 × 0.25 mm × 0.2 µm film thickness Supelco SP^{TM}-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.

Analysis of deterioration in bath oils

The progress of the deterioration of the oils during frying was followed by measuring total polar compound (TPC) using the column chromatography methods from American Oil Chemists' Society Official Methods and Recommended Practices [2].

Determination of the thiobarbituric acid value (TBA)

The thiobarbituric acid value (TBA) value was determined according to Grau et al. [11] with some modifications: sample weight (5 g of fresh or frying oil or fat) and homogenization step, which was carried out using a vortex instead of a high-speed homogenizer.

Rheological parameters

Measurement of viscosity 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. 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 (Eq. 1) by linear regression.

$$\tau = \eta\gamma \tag{1}$$

where τ is the shear stress (mPa), η is dynamic viscosity (mPa.s) and γ is the shear rate (s^{-1}).

Bingham plastic model

The Bingham equation is $\tau = \tau_{oB} + \eta_B\gamma$ (2)

where τ is the Shear stress (mPa), τ_{oB} is the Bingham yield stress, shear stress at zero shear rate, (mPa), η_B is the Bingham plastic viscosity (mPa.s) and γ is the Shear rate (sec^{-1}).

The calculated parameters for this model are plastic viscosity and yield stress according to [4].

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

$$\tau = \tau_0 + K\gamma^n \tag{3}$$

where τ is shear stress (mPa), τ_o is the yield stress (mPa), K is the consistency index (mPa s^n), γ 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 impact of temperature on viscosity

Activation energy was calculated using Arrhenius-type equation as mentioned by Kim et al. [17].

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

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 and T is the absolute temperature in °K.

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

Results and discussion

Effect of frying on the fatty acid composition

Table 1 presents the fatty acid compositions of the used 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 increase 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 [16]. In our investigation the amounts of PUFA tended to decrease, whereas that of SFA increased. However, because we have used an internal standard to quantify fatty acid changes, the slight increase in SFA during repeated frying may not be due to oxidative alteration but to interaction between the oil and the lipids of the fried food products. The increase observed throughout the 40 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 [24] to explain the increase in linoleic acid in high-oleic SO used 20 times for frying. It was reported that total lipids in various strains of potato is up to 0.5 % of dry tuber mass [20, 23]. 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 increased more rapidly in CO than in SO and PO. From 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. For unsaturated fatty acids, *trans* isomerization of a double bond can occur during frying of foods [25, 29]. However, the results obtained 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.

Impact of frying on total polar compounds (TPC) and TBA of vegetable oils

The TPC of the different oils used in the frying study are presented in Fig. 1. The figure shows the increase in TPC level for frying oils. Among different parameters, TPC content is one of the most objective and valid criteria for the evaluation of deterioration of oils during frying. During frying, as oil breaks down, peroxides, acids and other radicals are formed in the frying oil. These cause some molecules in the oil to become somewhat polar [34]. TPC in the oils increased during frying and were strongly correlated with frying time. As frying progressed, it was observed that the rate of increase in TPC was relatively slower in PO than in the SO and CO. The initial polar compounds contents were 0.91, 0.87 and 0.65 %, in CO, SO and PO, respectively. At the end of experiment, TPC level increased to 11.9, 10.7 and 10.1 %, for CO, SO and PO, respectively. Although the TPC level of CO was the highest compared to PO and SO at the end of frying, those oils were considered acceptable after 16 h of frying as many countries had set a maximum acceptable levels of 25–27 % for TPC contents [8].

The thiobarbituric acid values were very low for oils coming from continuous frying. Some TBA values expressed as µg of malondialdehyde (MDA)/kg of sample were below the detection limit (5.2 µg/kg) and others were below the quantification limit (17.4 µg/kg) (data not shown). This is due to the low concentrations of the frying oils in fatty acids with more than two double bonds (Table 1), which are the main precursors of the MDA. The oils used in this study showed a linolenic acid concentration under 1 %, which is common for frying oils, and several authors and institutions recommend a maximum linolenic acid concentration of 2–3 % [9, 12]. Sebedio et al. [30] have also reported very low TBA values for PO when it was subjected to continuous frying.

Rheological characteristics of oils during frying

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 [33] and Chatzilazarou et al. [5]. 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 [31]. 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 [5, 19].

In 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 [7]. 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

Table 1 Fatty acid composition (%) of different oils during frying

Fatty acid	Sunflower oil			Cottonseed oil			Palm Olein		
	Zero time	8 h	16 h	Zero time	8 h	16 h	Zero time	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			4.32	4.33
C18:1 *cis*	3.62	4.06	23.0	19.1	20.2			41.5	41.6
C18:1 *trans*	24.5	40.9	nd	nd	0.23			nd	0.22
C18:2 *cis*	0.41	nd	63.4	52.4	50.4	43.5	13.9	12.9	12.3
C18:2 *trans*	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
Σ SFA[b]	9.77	10.1	10.5	24.9	25.7	26.0	41.9	43.3	44.1
Σ MUFA[c]	22.5	23.2	23.9	19.7	21.1	25.4	41.0	41.6	41.9
Σ PUFA[d]	65.6	64.7	63.6	52.8	50.9	44.2	14.2	13.3	12.7
S/P[e]	0.14	0.15	0.16	0.47	0.50	0.58	2.95	3.25	3.47
Increase in saturation ratio × 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

nd not detected

[a] Values given are the mean of three replicates

[b] Total saturated fatty acids

[c] Total monounsaturated fatty acids

[d] Total polyunsaturated fatty acids

[e] The ratio of saturated to polyunsaturated fatty acids

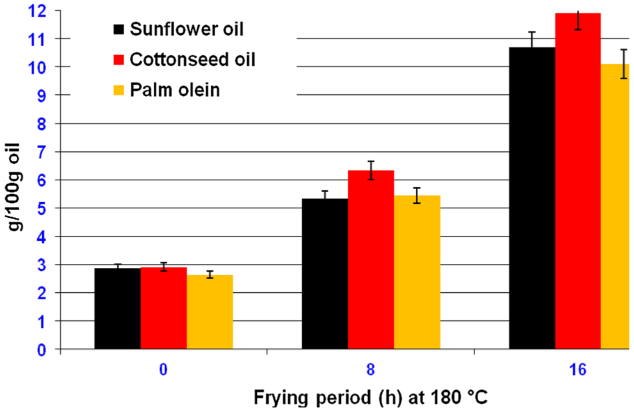

Fig. 1 Levels of total polar compounds (g/100 g oil) in different oils during frying of French fries. Values given are the mean of three replicates

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

Oil sample	Frying time (h)	Parameters for different rheological models				
		Newtonian Model		Bingham model		
		η Viscosity	r	τ_{0B}	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

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 [10]; Quinchia et al. [21] who found the flow behaviour of some edible oils behaved as non-Newtonian fluids. Also, the results are in agreement with Huang and Sathivel [13] 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 [10]. The increasing in viscosity indicates that polymers, which are the higher molecular weight fraction of the degradation products, are increased by

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

Oils sample	Frying time (h)	Parameters for Herschel–Bulkley rheological models			
		τ_{0HB}	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

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 [27].

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]. 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.

Effect of frying time on the rheological parameters

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 share rate-share stress curves and data in Tables 2 and 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 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. [26]. 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 Tables 2 and 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 [13]. 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 [19] whereas higher yield stress values were observed at longer frying time.

Palm olein had high flow behavior parameters than SO and 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. 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.

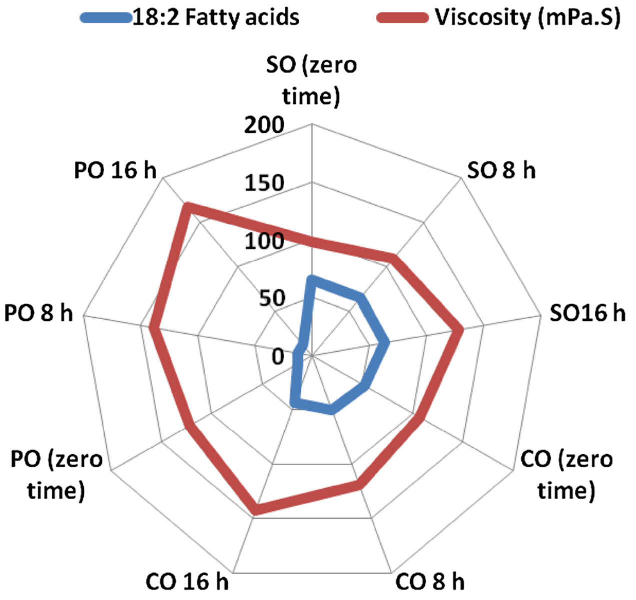

Fig. 2 Relation between the levels of C18:2 and viscosity in different oils

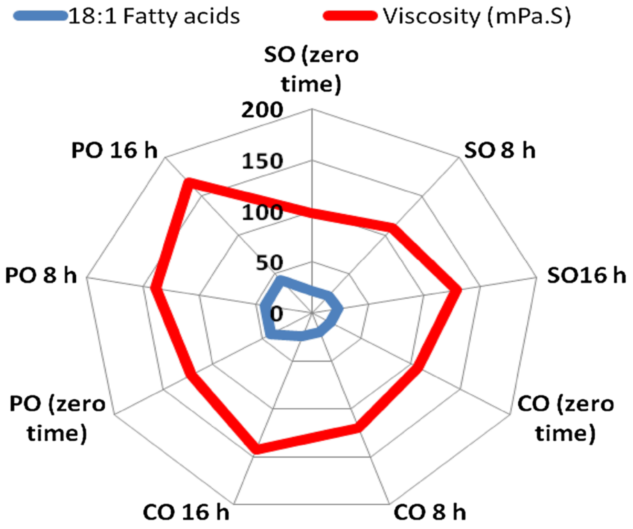

Fig. 3 Relation between the levels of C18:1 and viscosity in different oils

Relation between fatty acid profile and rheological parameters

The dependence of viscosity on the oil composition oils was investigated by correlating the oil viscosity with fatty acid 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 Figs. 2 and 3. The major fatty acids of the 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 [1, 17]. 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 impact of temperature on the 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 $\eta\infty$ and Ea parameters are determined by measuring η at different temperatures (5–100 °C) within 10 rpm (shear rate).

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 [14, 27]. A favorably good agreement was found when the results were compared with other studies [13, 19, 27]. 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 (Eq. 4). A linear relationship of ln (η) *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 Ea 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 increasing of the levels of C18:2 but decreased with increasing C18:1. Considering that vegetable oils viscosity depends on fatty acid composition, the activation energy increased with the decreasing double bonds in the fatty acid chain and temperature. Therefore, temperature had a great effect on the samples and this tendency is similar to the results of Huang and Sathivel [13].

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

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

Oils samples	Frying 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}	5–100
	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

3.708×10^{-3} to 1.742×10^{-3} mPa.s, respectively. 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, 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 [17]. 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 [19]. 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.

Conclusion

The impact of frying on the rheological characteristics of different vegetable oils was investigated. PO 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 acid 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.

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