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Comparison of the Frying Stability of Sunflower and Refined Olive Pomace Oils With/Without Adsorbent Treatment

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Abstract The aim of this study was to compare the frying behaviors of refined olive pomace (ROP) oil to sunflower oil in a 5-day trial, and to evaluate the refresh capacity of a new adsorbent mixture composed of diatomaceous earth, zeolite and lime. Frying trials were performed as control and adsorbent-treated groups. Oil samples collected after each day of frying were analyzed for physical characteristics (viscosity, turbidity, refractive index, smoke point), color values (*L*, *a** and *b**), and chemical properties (free acidity, peroxide value, conjugated dienoic acids, total polar materials). The amount of oil absorbed by the fried dough was measured. In general, results indicated that ROP oil had higher thermal stability. There were no significant differences between the quality parameters of control and adsorbent treated samples for either oil sample. Effectiveness of the new adsorbent mixture on frying oil refreshing was limited only to free acidity, viscosity, and color. Total polar materials measured with probe sensor were determined to be as accurate as the official technique, and can be recommended for quick, easy and cheap analysis. Also, there were some significant correlations between the measured oil quality parameters.

Keywords Refined olive pomace oil · Sunflower oil · Frying · Adsorbent · Comparison

Introduction

Deep-fat frying is one of the world's oldest and most common food preparation techniques. In the US, the economic value of the frying sector has been estimated to be $83 billion, and at least twice this amount for the rest of the world [1]. As a dynamic food preparation process, frying involves immersion of a food material in a fat or oil heated to a temperature sufficient (typically 150–190 °C) to achieve the desired cooking results. Over the course of time, and because of oil adsorption by the food being cooked, it is typically necessary to partially replenish the oil in the fryer. The frying oil may be reused several times before being discarded. Fried foods have desirable sensory characteristics, including crispy texture, golden brown color, desirable flavor and special fried aroma [2].

Deep-fat frying is accomplished through simultaneous heat and mass transfer of oil, food and air occurring during the process. Frying oil acts as a heat transfer medium and contributes to the development of texture and flavor of fried foods. During the process, the presence of oxygen, the moisture content of the food, high oil temperature and the leaching of components from the food cause a variety of reactions to occur including fat hydrolysis, fatty acid oxidation, dimer and polymer formation, and Maillard reactions, all of which contribute to degradation of the frying oil. Repeated reuse of frying oil results in the accumulation of degradation reaction products, which results in lower quality fried products and some health considerations. Hence, routine control of changes in frying oils and some techniques to extend the shelf-life of frying oils have been extensively studied [3].

The type of the oil used in the frying process is one of the most important factors affecting quality parameters. In general, fats and oils with very low free acidity and trace

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metals, higher oleic acid and lower linoleic/linolenic acid levels, very low peroxide value and moisture content, smoke points above 170 °C, and soft and milder flavor are preferred for frying [4]. In one study [5], it was shown that fatty acid composition of frying oils could account for half of the frying and storage stability. The other half was related to the amount and the kinds of minor components like tocopherols, sterols and phenols present in the oils. Commercial olive and sunflower oils were heated at high temperatures for long periods of time and the physical properties of the oils were monitored. Under these conditions, the viscosity of the oils increased very quickly, whereas the degree of unsaturation decreased noticeably. Of the two oils, sunflower oil underwent the greatest changes including a rapid increase in viscosity [6]. In another study, the frying performances of olive and corn oils were compared by frying potatoes and cod filets. It was shown that the lowest deterioration occurred in olive oil and the highest in corn oil. A 50:50 mixture of the two oils proved to be a good substitute for olive oil in domestic frying [7]. On the other hand, frying studies with refined olive pomace oil are scarce. In one study, olive pomace oil was used in preparation of an ideal frying oil mixture [8]. In another study, olive pomace oil mixed with other vegetable oils were tested for antioxidant capacity and found to be acceptable [9]. While virgin olive oil has been very well studied, refined olive pomace oil has not been studied thoroughly for frying.

Among other treatments to extend the frying life of oils and enhance fried product quality, adsorbent treatment with active filtration has been extensively studied. A number of adsorbents, including activated carbon, clay, aluminum hydroxide, charcoal, celite, silica gel, silicon dioxide, oyster shells, ceramic plate, aluminum oxide and others have been used to refresh frying oils for subsequent reuse [10]. A new adsorbent mixture composed of diatomaceous earth, zeolite and lime has recently been introduced as a new filtration aid for frying oils in our laboratory.

The objectives of the present study were to compare the frying performance of refined olive pomace oil to sunflower oil, the standard frying oil, under normal frying conditions and to measure the refreshing ability of the new adsorbent mixture in both of these oils.

Materials and Methods

Materials

Sunflower oil (Sole, Balıkesir, Turkey) and Refined Olive Pomace oil (Pitanea, Çandarlı, İzmir, Turkey) were purchased from the producers. The fatty acid composition and minor components composition of the oils were provided by the producers and shown in Table 1. Zeolite (10–50 µm) (Türkzeolit Madencilik Co, Balıkesir, Turkey) and Diatomaceous Earth (5–20 µm) (CMM Chemicals Co, Istanbul, Turkey) were gifts from the producers. Lime was purchased from local stores. All chemicals used for the analyses were of analytical grade and purchased from Merck Co. (Darmstadt, Germany).

Frying

In order to have a standard composition food for the frying studies, a dough with the following composition was prepared: 56% flour (Söke flour, Aydın), 42% water, and 0.5% each of dry yeast, baking soda and salt. After mixing the ingredients, the dough was fermented for 30 min at 40 °C, then cut and rolled into 35 g patties.

Utilizing 2 L Fryers (Fakir-Hausgeräte Nista, Enz, Germany), frying was continued for five consecutive days for both oils and treatment groups. At the beginning of the study, the fryers were filled with 2 L of fresh oil and heated to 180 °C. During the day, the fryers were kept open for 5–5.5 h at 180 °C. Each day in each oil sample, one fresh dough patty was fried for 10 min every half hour until a total of ten patties were fried. A total of 5–5.5 h was required to fry all ten samples. Frying studies were all

Table 1 Fatty acids and minor components composition of the oil samples used in this study

Fatty acid (%)	Sunflower oil	R. Olive Pomace oil
Myristic (C14:0)	0–0.2	≤0.05
Palmitic (C16:0)	5.1–7.5	7.5–20
Palmitoleic (C16:1)	0–0.3	0.3–3.5
Heptadecenoic (C17:1)	0–0.1	≤0.3
Stearic (C18:0)	2.7–6.3	0.5–5.00
Oleic (C18:1)	14.0–39.4	55–83
Linoleic (C18:2)	48.3–74.0	3.5–21
Linolenic (C18:3)	0–0.3	≤0.9
Arachidic (C20:0)	0.1–0.5	≤0.6
Gadoleic (C20:1)	0–0.3	≤0.4
Behenic (C22:0)	0.5–1.1	≤0.2
Lignoceric (C24:0)	0–0.5	≤0.2
Total sterols (mg/kg)	2,200–5,000	≥1,800
Cholesterol	n.a.	≤0.5
Brassicasterol	n.a.	≤0.2
Campesterol	n.a.	≤4.00
Stigmasterol	n.a.	<Campesterol
Total-*β*-Sitosterol	n.a.	≥93.0
Δ-7-Stigmastanol	n.a.	≤0.5
Total tocopherols (mg/kg)	400–1,500	n.a.

The data are provided by the producers

n.a. not available

conducted in duplicate. After each day, 200 ml of oil was collected from each fryer and stored in amber colored and capped glass bottles. The samples were refrigerated until and during the analyses.

Adsorbent treatment was performed after each day's frying was completed. The oil was cooled to 150 °C and treated by adding 10% (w/w) of the adsorbent mixture (diatomaceous earth:zeolite:lime = 1:1:1, w/w/w) directly into the frying oil, and mixing for 30 min. The mixture was then vacuum filtered through regular filter paper and the treated oil was put back into the fryer for the next day's frying. Sampling of oils was done in the same way after each day filtration.

The fried dough was put in refrigerator bags, labeled and kept frozen until absorbed fat analyses were performed.

Physical Analyses of Oil Samples

Oil viscosity was measured by placing 7.5 ml of the sample in a special sample holder, and directly measuring in centipoise (cP) with a Brookfield viscometer (model DV II + Pro with Rheocalc software, Brookfield Eng. Lab., Inc., MA, US) equipped with LV-SC4-18 spindle at 25 °C.

Turbidity was measured at 25 °C using a Micro T100 Lab Turbidimeter (HF Scientific Inc, US) calibrated with 0.2, 10 and 1,000 NTU calibration liquids, per manufactures's instructions.

Refractive indexes were measured in daylight with a 2WAJ model Abbe refractometer, calibrated against pure water at 25 °C.

Smoke points of the samples were measured following AOCS method Cc 9a-48 [11].

Instrumental color was measured with a Minolta CR-400 Chroma Meter (Osaka, Japan) by immersing the probe of the instrument into the oil sample placed in a Petri dish on the white tile. Readings of the *L*, *a** and *b** values were recorded.

Chemical Analyses of Oil Samples

Free fatty acid values were determined according to AOCS method Ca 5a-40 [11].

Peroxide values were determined according to AOCS method Cd 8-53 [11].

Conjugated dienoic acid contents were measured by a method based on AOCS Ti 1a-64 [11] with a UV Mini 1240 Spectrophotometer (Shimadzu Co, Japan).

Total polar materials analysis was accomplished by the column chromatography technique of AOCS method Cd 20-91 [11].

Quick estimated analyses of the total polar materials of the frying oil samples were made by sensor (probe) readings (Testo 265, Lenzkirch, Germany). The sensor was first calibrated with the calibration oil per the manufacturer's instructions, and direct readings of the percent total polar material estimates were taken by immersing the probe in hot oil (above 40 °C) and reading the value.

Measurement of Absorbed Fat

The amount of fat absorbed by the fried dough patties was determined with the Soxhlet technique described in AOAC method 920.39 [12].

Statistics

The study was replicated twice with all analyses performed twice. The statistical package programs of Minitab (ver. 14.1) and SPSS (ver. 10.1) were used for all analyses. Significant differences among the means of the samples for the measurements were determined by the general linear model with means separation by Duncan's test at a 95% level of confidence. In addition, correlation coefficients for the measured oil quality parameters were determined [13, 14].

Results and Discussion

The changes of measured physical properties for both sunflower oil (SFO) and refined olive pomace (ROP) oil used in the 'control' frying experiments are shown in Table 2. The viscosity of the oils increased from the beginning through the fifth day of frying. Fresh refined olive pomace oil's viscosity was higher than that of the fresh sunflower oil's, and this difference was maintained during the 5-day frying period. For both oil samples, the higher initial turbidity was decreased with the start of frying, and then increased gradually over consecutive days of frying. Similar to viscosity, the turbidity of ROP oil was higher than that of SFO for all days of frying. There was statistically no significant difference for the refractive index values of both oils and samples for different days of frying. It was most probable that there was not enough degradation to cause a difference in such a physical constant. Smoke points of both oils decreased gradually over the frying time. Also, the smoke point of ROP oil was significantly lower than that of SFO. Turkish regulations for the quality control criteria of frying oils [15] declares a min smoke point value of 170 °C for an oil to be utilized as a frying oil. Accordingly, there was no problem using the ROP oil as a frying oil.

For the control study of the oils, measured instrumental color (CIE, Commission Internationale d'Eclairage) values are shown in Table 3. *L** is the lightness or luminosity component ranging from 0 to 100. The values of *a** (from

Table 2 The measured physical properties of the sunflower and refined olive pomace oil samples for the control frying experiments

	Viscosity (cP, 25 °C) ($P = 0.023$)		Turbidity (NTU) ($P = 0.000$)		Refractive index (25 °C)		Smoke point (°C) ($P = 0.001$)	
	Sunflower	R. Olive Pomace	Sunflower	R. Olive Pomace	Sunflower	R. Olive Pomace	Sunflower	R. Olive Pomace
0 day	54.20 ± 0.09 Eb	64.80 ± 0.09 Ea	0.54 ± 0.01 ABb	3.35 ± 0.01 Aa	1.474 ± 0.0 Aa	1.470 ± 0.0 Aa	233.0 ± 0.0 Aa	185.0 ± 0.0 Ab
1 day	56.08 ± 0.13 Eb	65.85 ± 0.25 Ea	0.43 ± 0.01 Bb	1.02 ± 0.00 Ea	1.476 ± 0.0 Aa	1.471 ± 0.0 Aa	232.0 ± 0.99 Aa	182.3 ± 0.25 Ab
2 days	60.85 ± 0.90 Db	68.98 ± 0.22 Da	0.46 ± 0.00 Bb	1.08 ± 0.10 DEa	1.476 ± 0.0 Aa	1.471 ± 0.0 Aa	228.0 ± 0.0 Ba	177.1 ± 0.63 Bb
3 days	66.80 ± 0.15 Cb	72.53 ± 0.13 Ca	0.58 ± 0.02 ABb	1.32 ± 0.08 Da	1.476 ± 0.0 Aa	1.472 ± 0.0 Aa	225.5 ± 0.50 Ba	174.0 ± 0.99 Cb
4 days	73.68 ± 0.48 Bba	80.28 ± 0.63 Ba	0.69 ± 0.04 ABb	1.67 ± 0.14 Ca	1.477 ± 0.0 Aa	1.472 ± 0.0 Aa	221.5 ± 0.50 Ca	172.5 ± 0.50 Cb
5 days	82.13 ± 1.33 Ab	87.40 ± 1.95 Aa	0.82 ± 0.02 Ab	2.03 ± 0.25 Ba	1.477 ± 0.0 Aa	1.472 ± 0.0 Aa	216.3 ± 1.25 Da	172.3 ± 0.25 Cb

Capital letters shown in the same column compare the frying days for each of the frying oil samples

Small letters shown in the same rows compare the two oil samples per frying day

Table 3 Instrumental color values of the sunflower and refined olive pomace oil samples for the control frying experiments

	Instrumental color					
	L ($P = 0.603$)		a^* ($P = 0.387$)		b^* ($P = 0.500$)	
	Sunflower ($P = 0.008$)	R. Olive Pomace ($P = 0.001$)	Sunflower ($P = 0.017$)	R. Olive Pomace ($P = 0.016$)	Sunflower ($P = 0.204$)	R. Olive Pomace ($P = 0.002$)
0 day	54.26 ± 0.17 Ab	61.71 ± 0.15 Aa[1]	−0.150 ± 0.025 Ab	0.895 ± 0.009 Aa[2]	3.42 ± 0.04 Ab	9.66 ± 0.29 Ba[3]
1 day	46.38 ± 2.96 Ba	51.57 ± 0.04 Ba	−2.895 ± 0.320 Ba	−3.600 ± 0.015 Ba	6.97 ± 1.31 Ab	18.03 ± 0.47 Aa[4]
2 days	41.97 ± 0.74 Bb	51.70 ± 0.01 Ba[5]	−2.960 ± 0.225 Ba	−3.670 ± 0.475 Ba	9.23 ± 0.99 Ab	17.06 ± 0.44 Aa[6]
3 days	43.47 ± 1.50 Ba	50.97 ± 1.69 Ba	−4.210 ± 0.435 Ba	−3.575 ± 0.570 Ba	13.60 ± 0.30 Aa	16.15 ± 1.76 Aa
4 days	43.79 ± 0.67 Bb	51.63 ± 0.51 Ba[7]	−4.170 ± 1.235 Ba	−2.740 ± 1.115 Ba	14.28 ± 6.53 Aa	19.47 ± 1.21 Aa
5 days	44.97 ± 0.37 Bb	52.91 ± 1.26 Ba[8]	−3.420 ± 0.215 Ba	−2.465 ± 0.870 Ba	11.50 ± 2.27 Aa	19.92 ± 0.19 Aa

Capital letters shown in the same column compare the frying days for each of the frying oil samples

Small letters shown in the same rows compare the two oil samples per frying day

[1] $P < 0.01$, [2] $P < 0.01$, [3] $P < 0.01$, [4] $P < 0.05$, [5] $P < 0.01$, [6] $P < 0.05$, [7] $P < 0.05$, [8] $P < 0.05$

green to red) and b^* (from blue to yellow) are two chromatic components ranging from -120 to 120 [16]. For both oil samples there was no statistically significant difference in the L values during the 5 days of frying. L value for both oils decreased significantly only from fresh oil after the start of frying. When the two oils are compared, the luminosity of ROP oil was higher than SFO for all day's samples. For both oils, the chromatic component a^* increased in a negative direction, that is, the value of greenness increased over the course of the study. There was no significant difference between the a^* values of the two oils. After the first 3 days of frying, the yellowness values (positive b^* values) of ROP oil were higher than the yellowness values of SFO samples. Similarly, the frying time had not caused any significant changes in the b^* values. The color value changes of different soybean oil blends during frying have shown results consistent with this study [17].

Changes in the measured chemical properties in the control frying of SFO and ROP oils are shown in Table 4. Free acidity in both oils increased through the days of frying. Similarly, free acidity in the fresh samples and samples collected by the frying days of ROP oil were higher than those of SFO. It has been reported in the literature [3] that many studies of frying have shown that acidity increases with frying time. On the other hand, the peroxide value had a different route of change. For both oils, it increased from the beginning to the second day, and then gradually decreased for subsequent days. When the two oils are compared, an interesting fact becomes apparent. At the beginning, the peroxide value of ROP oil was higher, but at the end of the fifth day of frying, the peroxide value of SFO was significantly higher than the ROP oil samples. This result indicates that ROP oil is much more stable to the development of thermo oxidation than SFO. One reason for this might be that ROP oil is a high oleic oil, while SFO is a high linoleic oil (Table 1). Susceptibility to oxidation is much higher for fatty acids with more double bonds, as is well known [3]. There is no defined limitation for the peroxide value (PV) in Turkish regulations of the quality control criteria of frying oils. On the other hand, it is indicated that German Guidelines put a PV

Table 4 The measured chemical properties of the sunflower and refined olive pomace oil samples for the control frying experiments

	Free fatty acid (% Oleic acid) ($P = 0.000$)		Peroxide value (mequiv O_2/kg) ($P = 0.000$)		Conjugated dienoic acid (%) ($P = 0.000$)		Total polar materials-probe (%) ($P = 0.016$)		Total polar materials (%) ($P = 0.163$)	
	Sunflower	R. Olive Pomace	Sunflower	R. Olive Pomace	Sunflower	R. Olive Pomace	Sunflower	R. Olive Pomace	Sunflower ($P < 0.0001$)	R. Olive Pomace ($P < 0.0001$)
0 day	0.112 ± 0.000 Bb	0.265 ± 0.014 Ea	0.99 ± 0.00 Da	3.49 ± 0.49 Ba	0.279 ± 0.002 Ea	0.280 ± 0.004 Da	6.75 ± 0.25 Fa	4.75 ± 0.25 Ea	7.06 ± 0.12 Ea[1]	5.36 ± 0.37 Eb
1 day	0.115 ± 0.022 Bb	0.284 ± 0.006 DEa	17.97 ± 0.26 Aa	7.98 ± 1.02 Ab	0.816 ± 0.009 Da	0.427 ± 0.029 CDb	11.75 ± 0.49 Ea	6.75 ± 0.25 Eb	11.13 ± 0.13 Da[2]	6.59 ± 0.91 DEb
2 days	0.159 ± 0.02 ABb	0.342 ± 0.007 Da	18.26 ± 0.02 Aa	6.48 ± 0.53 ABb	1.604 ± 0.098 Ca	0.520 ± 0.03 BCDb	14.75 ± 0.49 Da	9.25 ± 0.25 Db	15.45 ± 0.35 Ca[3]	10.06 ± 0.40 Db
3 days	0.195 ± 0.028 ABb	0.430 ± 0.013 Ca	17.56 ± 1.73 ABa	5.98 ± 0.50 ABb	1.680 ± 0.042 BCa	0.660 ± 0.042 ABCb	18.75 ± 0.49 Ca	12.75 ± 0.25 Cb	18.69 ± 1.08 Ca	14.20 ± 0.60 Ca
4 days	0.208 ± 0.028 Ab	0.519 ± 0.015 Ba	12.10 ± 1.28 Ca	5.65 ± 0.67 ABb	1.944 ± 0.200 Ba	0.820 ± 0.065 ABb	21.50 ± 0.49 Ba	18.13 ± 0.16 Bb	23.83 ± 0.02 Ba[4]	18.64 ± 0.52 Bb
5 days	0.236 ± 0.000 Ab	0.592 ± 0.021 Aa	14.36 ± 0.05 BCa	4.79 ± 0.54 ABb	2.341 ± 0.002 Aa	0.957 ± 0.051 Ab	27.38 ± 0.87 Aa	21.63 ± 1.13 Ab	28.13 ± 1.03 Aa	24.87 ± 1.36 Aa

Capital letters shown in the same column compare the frying days for each of the frying oil samples

Small letters shown in the same rows compare the two oil samples per frying day

[1] $P \leq 0.05$, [2] $P < 0.05$, [3] $P < 0.01$, [4] $P \leq 0.01$

limit of 10 mequiv/kg for frying oils [15, 18]. A similar result is reported for sunflower and virgin olive oils in a frying experiment [19]. It was indicated that the increase in the amount of conjugated dienoic acids in frying operations is proportional to the uptake of oxygen and formation of peroxides during the early stages of oxidation, and to the thermal formation of oligomers and polymers [20]. Through the days of frying, conjugated dienoic acids gradually increased in both oils, but the total increase in SFO samples was significantly higher than ROP oil samples. This finding agrees with peroxide values, indicating that SFO is more sensitive to oxidation than ROP oil in frying. The Testo 265 (Lenzkirch, Germany) probe was developed for quick estimation of total polar materials (TPM) in frying oils. % TPM measured both by probe and by column chromatography technique [11] has yielded similar results for both oil samples. In general, accumulations of TPM in SFO samples were higher through the frying days than in the ROP oil samples. Also, for both oil samples % TPM increased constantly from fresh oil through days of frying. In one study, sunflower oil had 4% TPM at the beginning, 18.9% at the 30th and, 27.7% at the 60th frying operations [21]. According to the regulation [15], the TPM value of frying oils must be ≤25%. Since after 5 days of frying the SFO sample exceeded the limit value, it would need to be changed or refreshed. Another important finding is that a measurement of TPM by the quick probe technique was shown to be as accurate as the official technique employing column chromatography which takes hours of time per sample of analysis.

Fat absorption by the dough patties are shown in Table 5. There were no statistically significant differences either between the two oil samples or among the frying days.

Adsorbent treatment of frying fats and oils has long been in practice, and more effective adsorbents are continually being sought [10]. For this part of the study, a new adsorbent mixture composed of diatomaceous earth, zeolite and lime was used to treat both SFO and ROP oil after each days frying, as explained in the method section. The same measurements for these 'adsorbent treated' samples were

Table 5 Absorbed fat content of the dough fried in sunflower and refined olive pomace oil for the control frying experiments

	Absorbed fat (%) ($P = 0.430$)	
	Sunflower	R. Olive Pomace
1 day	24.24 ± 2.72	26.02 ± 4.24
2 days	22.55 ± 0.08	20.90 ± 1.66
3 days	21.31 ± 2.01	20.57 ± 1.34
4 days	31.26 ± 2.41	23.20 ± 0.61
5 days	25.23 ± 3.47	25.97 ± 4.31

performed. Results of the physical properties are shown in Table 6. Similar to the control frying, viscosity of the samples increased from fresh oil towards the fifth day of frying. It was indicated that the increase in viscosity of frying oils was due to accumulation of the products of oxidation and polymerization reactions [22]. There were no significant differences between the two oils and among the days for the turbidity values and refractive indices. In one study, it was shown that turbidity of frying oils was increased by frying time, but there was no adsorbent treatment in that study [23]. On the other hand, smoke points of the samples decreased with frying time, but after the first day, the decrease in the ROP oil was much lower than that of the control study. There were statistically insignificant differences between SFO and ROP oil samples for the L values. While the *a** values were higher in the greenness direction by frying time for SFO samples, there was no change in ROP oil samples. For both oil samples in the adsorbent treated groups, the *b** value increased with frying time (Table 7). The measured chemical properties of SFO and ROP oil samples treated by adsorbent mixture after each day's frying are shown in Table 8. Similar to the results of the control study, all measured chemical quality indices in the adsorbent treated samples increased as frying days increased. While free fatty acid content was higher in ROP oil, the peroxide value and conjugated dienoic acids were higher in SFO throughout the frying days. TPM measured by both probe and column chromatography have indicated the same trend that TPM increases by frying time for both oil samples. Under the defined frying conditions, both oils exceeded the TPM value limit [15] after the fourth day, although there is no statistically significant difference between the two oil samples. It was indicated [3] that the increase in TPM in frying oils is the most important phenomenon to show the degradation of oil, and also causes more oil absorption by the fried food items. The amounts of fat absorbed by the fried dough in these adsorbent treated oil samples are shown in Table 9. There were no significant differences between the frying days for each oil nor between the adsorbent treated SFO and ROP oil samples, except the fifth day in which ROP oil showed more oil absorption.

For both SFO and ROP oil samples, 'control' and 'adsorbent treated' samples are also compared by statistical analyses, but data are not shown in different tables in order to prevent data repetition. For the SFO samples, there were no significant differences between control and adsorbent treated samples for viscosity, turbidity, and refractive index values. Interestingly, adsorbent treatment caused the smoke point to decrease more slowly than that of the control samples. Similarly there were no significant differences among the color values for the two sets of SFO samples. On the other hand, dough fried in adsorbent treated SFO

Table 6 The measured physical properties of the sunflower and refined olive pomace oil samples for the adsorbent treated frying experiments

	Viscosity (cP, 25 °C) ($P = 0.732$)		Turbidity (NTU) ($P = 0.012$)		Refractive index (25 °C) ($P = 0.000$)		Smoke point (°C) ($P = 0.000$)	
	Sunflower ($P = 0.001$)	R. Olive Pomace ($P = 0.000$)	Sunflower	R. Olive Pomace	Sunflower	R. Olive Pomace	Sunflower	R. Olive Pomace
0 day	54.55 ± 0.05 Cb	64.95 ± 0.15 Ea^1	0.545 ± 0.005 Bb	3.280 ± 0.060 Aa	1.474 ± 0.000 Aa	1.470 ± 0.000 Ab	235.0 ± 0.0 Aa	184.0 ± 1.0 Ab
1 day	56.63 ± 0.48 Cb	67.25 ± 0.05 Ea^2	0.495 ± 0.165 Bb	1.460 ± 0.320 Ba	1.475 ± 0.000 Aa	1.470 ± 0.000 Ab	234.3 ± 0.25 Aa	172.3 ± 0.75 Bb
2 days	59.28 ± 0.33 BCb	70.43 ± 0.08 Da^3	0.390 ± 0.060 Bb	1.690 ± 0.370 Ba	1.475 ± 0.000 Aa	1.470 ± 0.000 Ab	230.5 ± 0.50 Ba	171.3 ± 1.25 Bb
3 days	69.00 ± 2.40 BCa	77.80 ± 0.20 Ca	0.395 ± 0.005 Bb	1.815 ± 0.565 Ba	1.476 ± 0.000 Aa	1.470 ± 0.000 Ab	229.0 ± 1.0 Ba	172.3 ± 1.25 Bb
4 days	80.08 ± 5.42 ABa	88.63 ± 0.28 Ba	0.595 ± 0.105 Ba	1.150 ± 0.280 Ba	1.476 ± 0.000 Aa	1.470 ± 0.000 Ab	225.4 ± 0.63 Ca	171.1 ± 0.13 Bb
5 days	100.43 ± 7.78 Aa	103.43 ± 1.18 Aa	1.060 ± 0.030 Aa	1.435 ± 0.455 Ba	1.477 ± 0.000 Aa	1.471 ± 0.000 Ab	221.3 ± 1.25 Da	171.5 ± 1.0 Bb

Capital letters shown in the same column compare the frying days for each of the frying oil samples

Small letters shown in the same rows compare the two oil samples per frying day

[1] $P < 0.0001$, $^2P < 0.01$, $^3P < 0.01$, $^4P < 0.0001$, $^5P < 0.05$, $^6P < 0.05$, $^7P < 0.05$

Table 7 Instrumental color values of the sunflower and refined olive pomace oil samples for the adsorbent treated frying experiments

	Instrumental Color					
	L ($P = 0.062$)		a* ($P = 0.447$)		b* ($P = 0.012$)	
	Sunflower ($P = 0.000$)	R. Olive Pomace ($P = 0.000$)	Sunflower ($P = 0.000$)	R. Olive Pomace ($P = 0.223$)	Sunflower	R. Olive Pomace
0 Gün	53.75 ± 0.06 Ab	60.41 ± 0.025 Aa[1]	−0.170 ± 0.015 Ab	0.840 ± 0.025 Aa[2]	3.93 ± 0.055 Bb	9.90 ± 0.15 Ba
1 Gün	41.22 ± 0.115 Bb	45.80 ± 0.45 Ba[3]	−2.485 ± 0.355 Ba	−2.165 ± 0.935 Aa	5.72 ± 1.35 ABb	28.30 ± 1.55 Aa
2 Gün	41.28 ± 0.39 Ba	47.73 ± 0.34 Bb[4]	−2.860 ± 0.305 Ba	−1.803 ± 1.127 Aa	6.59 ± 1.23 ABb	26.02 ± 2.04 Aa
3 Gün	42.04 ± 0.15 Ba	44.99 ± 0.54 Bb[5]	−2.968 ± 0.117 CBa	−3.768 ± 0.632 Aa	6.74 ± 0.56 ABb	25.37 ± 2.13 Aa
4 Gün	41.95 ± 0.50 Bb	46.32 ± 0.18 Ba[6]	−3.383 ± 0.262 CBa	−3.418 ± 0.967 Aa	8.20 ± 1.21 ABb	24.55 ± 4.73 Aa
5 Gün	41.56 ± 0.28 Ba	47.34 ± 1.74 Ba	−4.115 ± 0.015 Ca	−1.328 ± 2.242 Aa	11.54 ± 0.10 Ab	29.06 ± 1.13 Aa

Capital letters shown in the same column compare the frying days for each of the frying oil samples

Small letters shown in the same rows compare the two oil samples per frying day

[1] $P < 0.0001$, [2] $P \le 0.001$, [3] $P \le 0.01$, [4] $P < 0.01$, [5] $P < 0.05$, [6] $P < 0.05$

Table 8 The measured chemical properties of the sunflower and refined olive pomace oil samples for the adsorbent treated frying experiments

	Free fatty acid (% Oleic acid) ($P = 0.200$)		Peroxide value (mequiv O_2/kg) ($P = 0.013$)		Conjugated dienoic acid (%) ($P = 0.000$)		Total polar materials-probe (%) ($P = 0.448$)		Total polar materials (%) ($P = 0.041$)	
	Sunflower ($P = 0.009$)	R. Olive Pomace ($P = 0.000$)	Sunflower	R. Olive Pomace	Sunflower	R. Olive Pomace	Sunflower ($P = 0.000$)	R. Olive Pomace ($P = 0.000$)	Sunflower	R. Olive Pomace
0 day	0.116 ± 0.001 Bb	0.271 ± 0.006 Ba[1]	1.00 ± 0.01 Ca	3.12 ± 0.15 Ba	0.278 ± 0.019 Ca	0.287 ± 0.004 Ba	6.50 ± 0.00 Ea[6]	4.25 ± 0.25 Db	7.15 ± 0.17 Fa	4.96 ± 0.08 Fb
1 day	0.111 ± 0.000 Bb	0.220 ± 0.000 Ca[2]	17.42 ± 4.61 Ba	4.68 ± 0.74 Bb	0.785 ± 0.031 Ca	0.428 ± 0.009 Ba	9.25 ± 0.25 DEa[7]	5.88 ± 0.37 Db	10.11 ± 0.18 Ea	7.27 ± 0.66 Eb
2 days	0.091 ± 0.007 Bb	0.219 ± 0.001 Ca[3]	19.67 ± 0.03 ABa	4.67 ± 0.74 Bb	1.161 ± 0.122 Ba	0.585 ± 0.003 Bb	11.63 ± 0.63 CDa	8.50 ± 0.50 Da	13.93 ± 0.08 Da	11.27 ± 0.20 Db
3 days	0.111 ± 0.000 Bb	0.237 ± 0.001 BCa[4]	22.69 ± 0.99 ABa	8.16 ± 0.23 ABb	1.615 ± 0.122 Ba	0.795 ± 0.011 Bb	15.75 ± 0.50 Ca	13.00 ± 1.00 Ca	16.62 ± 0.41 Ca	16.11 ± 0.12 Ca
4 days	0.145 ± 0.035 ABa	0.263 ± 0.000 BCa	24.35 ± 4.21 ABa	11.58 ± 1.22 Ab	2.052 ± 0.214 Aa	1.043 ± 0.032 Ab	20.25 ± 1.75 Ba	18.75 ± 1.25 Ba	21.45 ± 1.51 Ba	21.69 ± 0.49 Ba
5 days	0.215 ± 0.007 Ab	0.382 ± 0.019 Aa[5]	26.51 ± 0.95 Aa	12.29 ± 3.48 Ab	2.571 ± 0.196 Aa	1.290 ± 0.020 Ab	26.75 ± 0.50 Aa	26.50 ± 1.00 Aa	28.73 ± 1.35 Aa	29.99 ± 0.39 Aa

Capital letters shown in the same column compare the frying days for each of the frying oil samples

Small letters shown in the same rows compare the two oil samples per frying day

[1] $P < 0.01$, [2] $P < 0.0001$, [3] $P < 0.01$, [4] $P < 0.0001$, [5] $P < 0.05$, [6] $P < 0.05$, [7] $P < 0.05$

Table 9 Absorbed fat content of the dough fried in sunflower and refined olive pomace oil for the adsorbent treated frying experiments

	Absorbed fat (%) ($P = 0.339$)	
	Sunflower ($P = 0.126$)	R. Olive Pomace ($P = 0.253$)
1 day	10.57 ± 0.12 Ab	13.48 ± 0.34 Aa[1]
2 days	10.62 ± 0.98 Aa	15.01 ± 0.33 Aa
3 days	13.12 ± 1.30 Aa	16.09 ± 0.60 Aa
4 days	13.86 ± 1.41 Aa	14.77 ± 1.29 Aa
5 days	10.13 ± 0.29 Ab	14.21 ± 0.53 Aa[2]

[1] $P < 0.05$, [2] $P < 0.05$

absorbed less fat than the control oil. Almost similar results are observed for the ROP oil samples when control and adsorbent treated groups are compared. Differences for the turbidity, refractive index, smoke point, and instrumental color values were not important. Adsorbent treatment of ROP oil resulted in a significant decrease in free acidity. On the other hand, adsorbent treatment increased the viscosity of ROP oils relative to the control samples. Also, no effect of the treatment on absorbed fat content of dough fried in ROP oil was observed. The whole findings of the new adsorbent mixture compared to the literature [2, 10, 20, 21] reports of significant enhancements of frying oil usage and frying life by other adsorbents (Hubersorb 600, Magnesol, Frypowder, Britesorb, etc.) are disappointing.

The correlations among the measured frying oil quality parameters were also analyzed. Instrumental color values were not included in the correlation analyses since there was no significant difference among the samples; the mathematical positive or negative signs only indicate the direction of the change on the color dimensions, but do not have any real meaning. Only one set of correlation data were selected for discussion, since all showed very similar results. Table 10 shows the correlation coefficients of the measured values with adsorbent treated ROP oil frying samples. The most significant correlations were between conjugated dienoic acids and TPM ($r^2 = 0.995$) and between TPM-probe and TPM ($r^2 = 0.993$). Interestingly, the smoke point was negatively correlated with almost all the parameters. The one unexpected significant correlation was between smoke point and turbidity. In a previous study [24] significant correlations among frying oil density, free acidity, alkaline contaminants and absorbed fat were

Table 10 Correlation coefficients of the measured properties for the absorbent treated frying of refined olive pomace oil

	Free fatty acid (% oleic acid)	Peroxide value (mequiv O_2/kg)	Conjugated dienoic acid (%)	Total polar material-prob (%)	Turbidity (NTU)	Viscosity (cP, 25 °C)	Refractive index (25 °C)	Smoke point (°C)	Total polar material (%)	Absorbed fat (%)
Free fatty acid (% oleic acid)	1	0.725*	0.690*	0.768**	−0.078	0.816**	0.926**	0.024	0.747**	−0.197
		0.008	0.013	0.004	0.810	0.001	0.000	0.941	0.005	0.585
Peroxide value (mequiv O_2/kg)	0.725**	1	0.956**	0.939**	−0.581*	0.962**	0.692*	−0.491	0.954**	0.046
	0.008		0.000	0.000	0.048	0.000	0.013	0.105	0.000	0.900
Conjugated dienoic acid (%)	0.690*	0.956**	1	0.985**	−0.576*	0.979**	0.710**	−0.597*	0.995**	0.064
	0.013	0.000		0.000	0.050	0.000	0.010	0.041	0.000	0.861
Total polar material-prob (%)	0.768**	0.939**	0.985**	1	−0.460	0.990**	0.783**	−0.522	0.993**	−0.011
	0.004	0.000	0.000		0.132	0.000	0.003	0.081	0.000	0.976
Turbidity (NTU)	−0.078	−0.581*	−0.576*	−0.460	1	−0.492	−0.210	0.782**	−0.524	0.124
	0.810	0.048	0.050	0.132		0.104	0.512	0.003	0.081	0.734
Viscosity (cP, 25 °C)	0.816**	0.962**	0.979**	0.990**	−0.492	1	0.815**	−0.475	0.990**	−0.026
	0.001	0.000	0.000	0.000	0.104		0.001	0.118	0.000	0.944
Refractive index (25 °C)	0.926**	0.692*	0.710**	0.783**	−0.210	0.815**	1	−0.211	0.767**	−0.226
	0.000	0.013	0.010	0.003	0.512	0.001		0.510	0.004	0.529
Smoke point (°C)	0.024	−0.491	−0.597*	−0.522	0.782**	−0.475	−0.211	1	−0.553	0.092
	0.941	0.105	0.041	0.081	0.003	0.118	0.510		0.062	0.800
Total polar material (%)	0.747**	0.954**	0.995**	0.993**	−0.524	0.990**	0.767**	−0.553	1	0.047
	0.005	0.000	0.000	0.000	0.081	0.000	0.004	0.062		0.897
Absorbed fat (%)	−0.197	0.046	0.064	−0.011	0.124	−0.026	−0.226	0.092	0.047	1
	0.585	0.900	0.861	0.976	0.734	0.944	0.529	0.800	0.897	

** $P < 0.01$, * $P < 0.05$

reported. Similarly, there were significant correlations between the important criteria of oil deterioration indices in this study.

Conclusions

The results of this study have indicated that ROP oil is a very good candidate for frying operations. It has demonstrably a better oxidative stability than SFO with comparable thermal behaviors. On the other hand, the new adsorbent mixture composed of diatomaceous earth, zeolite and lime was shown to have limited effects in refreshing the frying oils. Compared to the results of other adsorbents discussed in the literature, the performance of the new adsorbent mixture is disappointing in refreshing the frying oil and the ability to extend frying shelf life. Although the data are not presented here, previous studies in our laboratory to recover degraded frying oils with the new adsorbent mixture were promising. One of the significant effects of the new adsorbent mixture in this study was the reduction in the amount fat absorbed by the dough, which is quite important from a nutritional viewpoint. TPM measurements with the very cheap, easy and quick probe technique have produced very similar and highly correlated results in comparison to the time-consuming and laborious official column chromatography technique. Hence, for the routine control of frying oils the Testo 265 or similar probes can be used with good reliability. Except for the peroxide value, the correlation of other common physicochemical indices of frying oils were shown to be sufficient to monitor quality changes of frying oils during the process.

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References

1. Pedreschi F, Moyano P, Kaack K, Granby K (2005) Color changes and acrylamide formation in fried potato slices. Food Res Intl 38:1–9
2. Aladedunye FA, Przybylski R (2009) Degradation and nutritional quality changes of oil during frying. J Am Oil Chem Soc 86:149–156
3. Choe E, Min DB (2007) Chemistry of deep-fat frying oils. J Food Sci 72(5):77–84
4. Stevenson SG, Vaisey-Genser M, Eskin NAM (1984) Quality control in the use of deep frying oils. J Am Oil Chem Soc 61:1102–1108
5. Normand L, Eskin NAM, Przybylski R (2006) Comparison of the frying stability of regular and high-oleic acid sunflower oils. J Am Oil Chem Soc 83:331–334
6. Garcia AB, Valdes AF (2006) A study of the evolution of the physicochemical and structural characteristics of olive and sunflower oils after heating at frying temperatures. Food Chem 98:214–219
7. Tsaknis J, Chatzilazarou A, Gortzi O, Lalas S, Zoidis E (2006) Physicochemical changes of olive oil and selected vegetable oils during frying. J Food Lipids 13:27–35
8. Leonardi M (2005) New blends of frying oils. Rivista Ital Del Sus Grasse 82:71–81
9. Chantzos NV, Georgiou CA (2007) Monitoring lipid oxidation events at frying temperatures through radical scavenging assays. Chem Ind Chem Eng Quart 13:163–166
10. Singhal RS, Bhattacharya AB, Sajilata MG, Tiwari RS (2008) Regeneration of thermally polymerized frying oils with adsorbents. Food Chem 110:562–570
11. Firestone D (1998) Official methods and recommended practices of the AOCS, 5th edn. AOCS Press, Champaign
12. AOAC (1984) Official methods of analysis of the association of the official analytical chemists, 14th edn. Association of Official Analytical Chemists, Washington, DC
13. Minitab (2000) Minitab Statistical Software, Release 14.1, State College, PA
14. SPSS (1994) SPSS Professional Statistics 10.1. SPSS, Chicago, IL
15. TGK (2007) Official notification of the control criteria of frying fats/oils. Turkish Food Codex no: 2007/41
16. Yam KL, Papadakis SE (2004) A simple digital imaging method for measuring and analyzing color of food surfaces. J Food Eng 61:137–142
17. Su C, White P (2004) Frying stability of high-oleate and regular soybean oil blends. J Am Oil Chem Soc 81:783–788
18. Mariod A, Matthaeus B, Eichner K, Hussein IH (2006) Frying quality and oxidative stability of two unconventional oils. J Am Oil Chem Soc 83:529–538
19. Sanchez-Gimeno AC, Negueruela AI, Benito M, Vercet A, Oria R (2008) Some physical changes in bajo aragon extra virgin olive oil during the frying process. Food Chem 110:654–658
20. Ghazali HM, Abdulkarim SM, Long K, Lai OM, Muhammad SKS (2007) Frying quality and stability of high-oleic moringa oleifera seed oil in comparison with other vegetable oils. Food Chem 105:1382–1389
21. Arroyo R, Sánchez-Muniz FJ, Cuesta C, Burguillo FJ, Sánchez-Montero JM (1996) Hydrolysis of used frying palm olein and sunflower oil catalyzed by porcine pancreatic lipase. Lipids 31(11):1133–1139
22. Al-Harbi MM, Al-Kabtani HA (1993) Chemical and biologic evaluation of discarded frying palm oil commercial restaurants. Food Chem 48:395–401
23. Mittal GS, Paul S (1996) Dynamics of fat/oil degradation during frying based on optical properties. J Food Eng 30:389–403
24. Yılmaz E (2004) An oil dilution technique used in small-scale frying to reduce oil expenditure. Intl J Food Sci Tech 39:245–251