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Frying Stability of Canola Oil Blended with Palm Olein, Olive, and Corn Oils

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Abstract The fatty acid composition, peroxide value (PV), acid value (AV), iodine value (IV), total tocopherols (TT) content, and total phenolics (TP) content of canola oil (CAO), palm olein oil (POO), olive oil (OLO), corn oil (COO), and the binary and ternary blends of the CAO with the POO, OLO, and COO were determined. The blends were prepared in the volume ratios of 75:25 (CAO/POO, CAO/OLO, CAO/COO) and 75:15:10 (CAO/POO/OLO, CAO/POO/COO). The CAO and its blends were used to fry potato pieces (7.0 × 0.5 × 0.3 cm) at 180 °C. During the frying process, the total polar compounds (TPC) content, AV, oil/oxidative stability index (OSI), and color index (CI) of the CAO/blends were measured. In general, frying stability of the CAO was significantly ($P < 0.05$) improved by the blending, and the frying performance of the ternary blends was found to be better than that of the binary blends.

Keywords Blending · Canola oil · Corn oil · Frying · Olive oil · Palm olein oil · Stability

Introduction

Canola is one of the most important oilseed crops in the world. Research indicates that the fatty acid composition of canola oil (CAO) is especially favorable in terms of health benefits when used as part of a nutritionally balanced diet. CAO is rich in 18 carbon fatty acids most notably the monounsaturated fatty acids (MUFA, 60%), oleic acid (18:1ω9), as well as the polyunsaturated fatty acids (PUFA, 30–37%), linoleic (18:2ω6, 22–25%) and linolenic (18:3ω3, 8–12%) acids. Moreover, it contains the lowest concentration of the saturated fatty acids (SFA, 7%) among vegetable oils. The other nutritionally favorable property of canola oil is a 2:1 ratio of ω6 and ω3 PUFA. CAO is also a rich source of antioxidant vitamin E [1].

Deep-frying is commonly used world-wide for the preparation and manufacture of foods. The nutritional value of frying oils is affected by the loss of essential PUFA. CAO, because of its high content of PUFA, is considered superior to many vegetable oils, but it is inferior in terms of thermal stability at high temperatures. The odor or flavor of fresh CAO is described as bland, slightly nutty and buttery, but during storage or upon heating, grassy, painty or rancid off-flavors develop. Flavor deterioration has been attributed mainly to secondary oxidation products of PUFA [2]. The most common method of stabilizing frying oils is modifying the fatty acid composition of the oil. This can be done by several methods, physically by fractionation or blending, chemically by hydrogenation or interesterification, or genetically by plant breeding [3–5]. Blending the polyunsaturated oils with more saturated or monounsaturated oils is a potential solution to improve oil stability [6].

Palm oil, the second most abundantly produced oil in the world, is not favored in many countries due to consumer concern about SFA. Palm oil contains approximately 50% SFA with 46.8% palmitic acid (C16:0). The second most abundant fatty acid in palm oil, however, is oleic acid at 37.6%. Palm olein oil (POO), a fraction obtained from palm oil during the production of stearin, is less saturated than palm oil and contains 38.3% palmitic acid, 42.1% oleic acid, and 10.6% linoleic acid. POO is being used increasingly in frying operations, and because of its

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inherent excellent frying properties, improves the frying quality of other vegetable oils when it is blended with them [7]. Olive oil (OLO) is an integral part of the cultural and culinary heritage of the Mediterranean countries and a product that is set apart by its organoleptic and nutritional qualities. OLO is an important cooking oil used extensively throughout the world, and recent studies have shown that it has high thermal oxidative stability. This has been attributed to its fatty acid composition, which is characterized by a high MUFA/PUFA ratio and the presence of minor compounds with powerful antioxidant activity, among which polyphenols particularly stand out [8]. Corn oil (COO) is widely used as an all-purpose cooking oil and for margarine because of its unique flavor attributes and because it is more stable to oxidation than linolenate-containing oils, such as soybean or canola [9].

There have been very limited reports on the frying performance of CAO in the presence of the vegetable oils mentioned above [6]. Therefore, the objective of this study was to determine the frying stability of CAO and their blends with POO, OLO, and COO during deep-frying.

Materials and Methods

Materials

Refined, bleached, and deodorized CAO, POO, COO, and OLO with no added antioxidants were supplied by Ghoncheh (in Sari), Behpak (in Behshahr), and Loyeh (in Roodbar) factories, respectively, and were stored at −18 °C until analysis. Their blends were prepared in the volume ratios of 75:25 (CAO/POO, CAO/OLO, CAO/COO) and 75:15:10 (CAO/POO/OLO, CAO/POO/COO). Fatty acid methyl ester (FAME) standards, and all chemicals and solvents used in this study were of analytical reagent grade and supplied by Merck and Sigma Chemical Companies.

Frying Process

Potatoes were peeled and cut into pieces (7.0 × 0.5 × 0.3 cm) and submerged in water until needed. Potato pieces were fried in the frying oils. The oil (2.5 L) was placed in a 2.5-L capacity bench-top deep-fryer (Tefal model 1250, France) and heated to 180 °C. Potato pieces were fried in 20-g batches at constant frying temperature. The batches were fried at 7-min intervals for 8 h per day for 2 consecutive days. At the end of each 4 h, about 10 g of the frying oil was filtered into a screw-cap vial and promptly stored in the dark at 4 °C until analyzed. The volume of oil was not replenished during the frying process. Frying experiments were conducted in duplicate on each frying medium [10].

Fatty Acid Composition

The fatty acid composition of the oils was determined by gas-liquid chromatography and was reported in relative area percentages. Fatty acids were transesterified into their corresponding FAMEs by vigorous shaking of a solution of oil in hexane (0.3 g in 7 mL) with 2 mL of 7 N methanolic potassium hydroxide at 50 °C for 10 min. The FAMEs were identified using an HP-5890 chromatograph (Hewlett-Packard, CA, USA) equipped with a CP-FIL 88 (Supel Co., Inc., Bellefonte, PA) capillary column of fused silica, 60 m in length × 0.22 mm I.D., 0.2 μm film thickness, and a flame ionization detector (FID). Nitrogen was used as carrier gas with a flow rate of 0.75 mL min^{-1}. The oven temperature was maintained at 198 °C, and that of the injector and the detector at 250 °C [11].

Peroxide Value (PV)

The spectrophotometric method of the International Dairy Federation as described by [12] was used to determine the PV.

Acid Value (AV)

The AV was determined according to the AOCS Official Method Cd 3d-63 [13].

Total Tocopherol (TT) Content

The TT content was determined according to the colorimetric method described in [14].

Total Phenolics (TP) Content

The TP content was determined spectrophotometrically using Folin-Ciocalteu's reagent according to the method described in [15]. A calibration curve of gallic acid in methanol was performed within a concentration range 0.04–0.40 mg mL^{-1}.

Total Polar Compounds (TPC) Content

The TPC content was determined according to the economical micro method developed by Schulte [16].

Oil/Oxidative Stability Index (OSI)

A Metrohm Rancimat model 743 (Herisau, Switzerland) was used for the OSI analysis. The tests were done with 3-g oil samples at temperatures of 120 °C at an airflow rate of 15 L h^{-1} [17].

Color Index (CI)

Absorption of the oil samples at 420 nm was determined, the CI was read against water as a blank [18].

Statistical Analysis

All experiments and measurements were carried out in triplicate, and the data were subjected to analysis of variance (ANOVA). Analysis of variance and regression analyses were performed according to the MStatC and Excel software. Significant differences between means were determined by Duncan's multiple range tests. *P* values less than 0.05 were considered statistically significant.

Results and Discussion

The fatty acid composition and chemical characteristics of the CAO, POO, OLO and COO, and also those of the CAO blended with the three other oils are shown in Table 1. It can be observed that the oils are distinguished from each other mainly due to the significant differences in the percentages of palmitic (C16:0), oleic (C18:1), linoleic (C18:2), and linolenic (C18:3) acids. Due to the high level of C16:0, the POO showed the highest significant percentage of SFA. The %SFA for the OLO and COO was significantly higher than that of the CAO. There was no significantly difference between the %MUFA of the CAO and OLO whereas these amounts were significantly higher than those of the POO and COO, respectively. The COO had the highest significant %PUFA, followed by the CAO, OLO, and POO. From information stated above, the PUFA/SFA ratio (also known as polyene index) was the greatest for the CAO and COO with no significant difference between them, followed by the OLO and POO. The PUFA/SFA ratio is usually taken as a measure of the extent of polyunsaturation of an oil and, obviously, of its tendency to undergo autoxidation [19]. As can be seen in Table 1, the blending of the CAO with the other three oils, especially with the POO, led to an increase in its %SFA. The blends consisting of more contributions of the POO and COO showed lower levels of MUFA. Except for the blends containing the COO, the %PUFA of the blends was lower than that of the CAO. Consequently, the blends prepared had the polyene indices of nearly the same as the CAO or better than that.

The PV and AV of the vegetable oils and their blends were all less than 2 mequiv kg^{-1} and 0.3 mg g^{-1}, respectively, indicating that they were unoxidized and of high initial quality (Table 1). The IV, which is considered as a measure of the oil unsaturation, for the oils and their blends was in very good accordance with their polyene index. The TT content of the COO (1192.8 ppm) was significantly higher than that of the CAO (750.4 ppm), which was in turn significantly higher than those of the OLO (362.6 ppm) and POO (332.3 ppm). The highest significant TP content was found in the CAO (53.8 ppm), and the other oils showed lesser amounts with no significant differences. It was interesting to find that there was no considerable difference between the TP content of the blends and that of the CAO.

The changes in the TPC content of the CAO and their blends with the vegetable oils examined in this study during the frying process at 180 °C are shown in Fig. 1. There was no statistically significant difference between the initial TPC content of the CAO and those of their blends. The TPC contents linearly increased with the high determination coefficients. Research has shown that the fraction of polar compounds isolated from oxidized oils is the most toxic to laboratory animals [20]. Therefore, it has been recommended that frying oils containing more than 24–27% of the TPC content should be discarded [21]. Within different lengths of time during the frying process, the oil/blends studied reached the discarding range of the TPC content. Assuming that the limit of acceptance for the TPC content is 24%, the time required to reach this limit was considered as a measure of frying stability. As shown in Fig. 1, the CAO showed a frying stability significantly lower (7.3 h) than those of its blends (8.2–15.8 h). The similar contributions of the POO, OLO, and COO in the binary blends significantly increased the frying stability of the CAO (15.9, 13.7, and 8.2 h, respectively). As can be seen in Table 1, the CAO/POO and CAO/OLO blends had polyene indices considerably better but TT contents significantly lower than that of the CAO. On the contrary, the CAO/COO blend showed a polyene index slightly worse but a TT content significantly higher than that of the CAO. Therefore, the quite obvious superiority of the binaries containing the POO and OLO rather than the COO can be attributed to a greater effect of the polyene index than antioxidative tocopherols on the frying stability. However, the relatively higher frying stability of the binary blend containing the COO than the CAO is due to its markedly higher TT content. The ternary blends also significantly improved the frying stability of the CAO, so that the ternary blend containing the OLO was statistically the same as the CAO/POO blend but the ternary blend containing the COO was significantly less stable than the CAO/POO blend.

The AV, which is used to assess frying oil degradation, increases during the frying process due to progressive hydrolytic reactions [22–24]. This quantity could be used as an indicator to show whether the hydrolysis process is under control [18]. The high AV is not accepted in any commercial product because of the strong off-flavor caused

Table 1 The fatty acid composition (%) and chemical characteristics of the canola (*CAO*), palm olein (*POO*), olive (*OLO*) and corn (*COO*) oils, and the blends examined in this study

Parameter	CAO	POO	OLO	COO	CAO/ POO	CAO/ OLO	CAO/ COO	CAO/POO/ OLO	CAO/POO/ COO
Fatty acids									
12:0	–	0.31 ± 0.01 a	–	0.18 ± 0.01 a	0.08	–	0.05	0.05	0.06
14:0	–	0.96 ± 0.01 a	–	0.24 ± 0.04 b	0.24	–	0.06	0.14	0.17
16:0	5.02 ± 0.45 d	42.88 ± 0.25 a	13.17 ± 0.26 b	12.07 ± 0.70 c	14.49	7.06	6.78	11.51	11.40
16:1	0.66 ± 0.32 b	0.53 ± 0.03 b	1.91 ± 0.26 a	0.44 ± 0.02 b	0.63	0.97	0.61	0.77	0.62
18:0	2.60 ± 0.05 c	4.39 ± 0.12 a	3.03 ± 0.25 b	1.22 ± 0.12 d	3.05	2.71	2.26	2.91	2.73
18:1	62.51 ± 0.92 a	44.47 ± 1.07 b	64.08 ± 0.59 a	26.73 ± 1.40 c	58.00	62.90	53.57	59.96	56.23
18:2	19.46 ± 0.41 b	5.78 ± 0.84 d	15.53 ± 0.29 c	56.59 ± 1.15 a	16.04	18.48	28.74	17.02	21.12
18:3	7.29 ± 0.58 a	0.25 ± 0.03 d	2.14 ± 0.11 b	1.51 ± 0.19 c	5.53	6.00	5.85	5.72	5.66
20:0	–	0.36 ± 0.02 b	–	0.62 ± 0.04 a	0.09	–	0.16	0.05	0.12
SFA	7.62 ± 0.45 c	48.8 ± 0.24 a	16.21 ± 0.21 b	14.91 ± 14.91 b	17.92	9.77	9.44	14.66	14.53
MUFA	65.50 ± 0.50 a	44.99 ± 1.06 b	65.99 ± 0.34 a	27.17 ± 1.38 c	60.37	65.62	55.92	62.47	58.59
PUFA	26.75 ± 0.36 b	6.03 ± 0.82 d	17.67 ± 0.19 c	58.10 ± 1.01 a	21.57	24.48	34.59	22.73	26.78
PUFA/SFA	3.51 ± 0.18 a	0.12 ± 0.02 c	1.09 ± 0.01 b	3.93 ± 0.46 a	2.66	2.91	3.62	2.76	3.04
PV	0.22 ± 0.11 c	0.26 ± 0.04 c	0.74 ± 0.07 b	1.95 ± 0.23 a	0.23	0.35	0.65	0.28	0.40
AV	0.31 ± 0.01 a	0.18 ± 0.01 b	0.28 ± 0.01 a	0.29 ± 0.01 a	0.28	0.30	0.31	0.29	0.29
IV	108.98 ± 0.91 b	49.62 ± 0.64 d	89.41 ± 0.08 c	125.37 ± 1.46 a	94.14	104.09	113.08	98.12	101.72
TT content	750.4 ± 12.9 b	332.3 ± 13.3 c	362.6 ± 10.4 c	1192.8 ± 28.7 a	645.9	653.4	861.0	648.9	731.9
TP content	53.8 ± 2.4 a	40.3 ± 2.1 b	38.4 ± 1.4 b	35.3 ± 2.5 b	50.4	50.0	49.2	50.2	49.9

Means ± SD (standard deviation) within a row with the same lowercase letters are not significantly different at $P < 0.05$. The fatty acid composition and chemical characteristics of the blends were calculated from the data of the corresponding oils

SFA saturated fatty acids, *MUFA* monounsaturated fatty acids, *PUFA* polyunsaturated fatty acid, *PV* peroxide value (meq O_2 per kg oil), *AV* acid value (mg KOH per g oil), *IV* iodine value (g of I_2 per 100 g oil), *TT* total tocopherols (mg α-tocopherol per kg oil), *TP* total phenolics (mg gallic acid per kg oil)

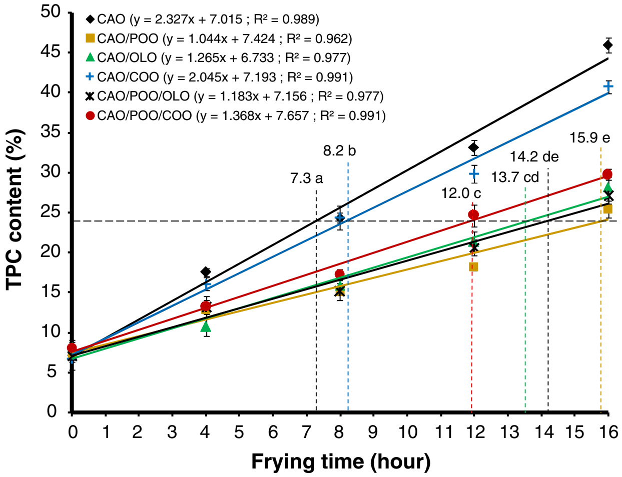

Fig. 1 The TPC content of the canola oil (CAO) and their blends with the palm olein (POO), olive (OLO) and corn (COO) oils during the frying process at 180 °C. The quantities with the same lowercase letters are not significantly different at $P < 0.05$

Table 2 The results calculated from the linear relationship between the acid value (*AV*) and the frying time for the canola oil (*CAO*) and their blends with the palm olein (*POO*), olive (*OLO*) and corn (*COO*) oils during the frying process at 180 °C

	AV = *a* (time) + *b*		
	a	*b*	R^2
CAO	0.025 ± 0.002 bc	0.313 ± 0.018 a	0.986
CAO/POO	0.021 ± 0.002 cd	0.188 ± 0.023 b	0.971
CAO/OLO	0.022 ± 0.002 cd	0.198 ± 0.019 b	0.979
CAO/COO	0.035 ± 0.003 a	0.317 ± 0.031 a	0.978
CAO/POO/OLO	0.017 ± 0.001 e	0.113 ± 0.017 c	0.976
CAO/POO/COO	0.020 ± 0.002 d	0.134 ± 0.026 c	0.963

Mean ± SE (standard error) within a column with the same lowercase letters are not significantly different at $P < 0.05$

by the degradation products (volatile and non-volatile compounds) of the free fatty acids during deep-frying [23, 24]. The results calculated from the linear relationship between the AV and the frying time for the CAO and their blends with the vegetable oils studied during the frying process at 180 °C are shown in Table 2. The slopes of the linear equations (*a* values), which were considered to be a measure of the rate of AV increase during the frying process, was significantly different for the oil/blends. In the binary blends, the POO and OLO could not significantly decrease the *a* value of the CAO during the frying process; meanwhile, the COO significantly increased it. It was interesting to find that, however, the ternary blends showed *a* values significantly lower than that of the CAO. The *a* value for the ternary blend containing the OLO (0.017) was significantly better than that of the ternary blend containing the COO (0.020).

The OSI is a direct evidence for changes in oxidation resistance [25]. Using this criterion for oils used in deep-frying, it is possible to compare the degree of deterioration of these oils resulting from the deep-frying process. The fresh CAO and its blend with the POO had OSIs (6.3 and 6.5 h, respectively) markedly greater than those of the other blends (5.2–5.5 h) (Fig. 2). During the frying process, the OSIs decreased with different rates. While the CAO showed a decrease of 79% of the initial OSI, for the CAO blended with the same contributions of the POO, OLO, and COO decreases of 64, 78 and 85%, respectively, were found after 16 h of frying. This indicates that the POO positively changed the OSI whereas the OLO showed no considerable effect and the COO had a negative effect on the OSI. It was interesting to find that the CAO/POO/OLO and CAO/POO/COO blends with decreases of 21 and 39% of the initial OSI, respectively, were more stable than the others. In a previous research [26], it was characterized if the OSI of a used frying oil is ≥2.3 h, the oil will still be considered as being safe and acceptable flavorwise. After 16 h of frying at 180 °C, only the CAO/POO/OLO and CAO/POO/COO had OSIs considerably greater than 2.3 h (4.3 and 3.2 h, respectively). The final OSIs for the CAO and its binary blends with the POO, OLO, and COO were 1.3, 2.3, 1.2, and 0.8 h, respectively.

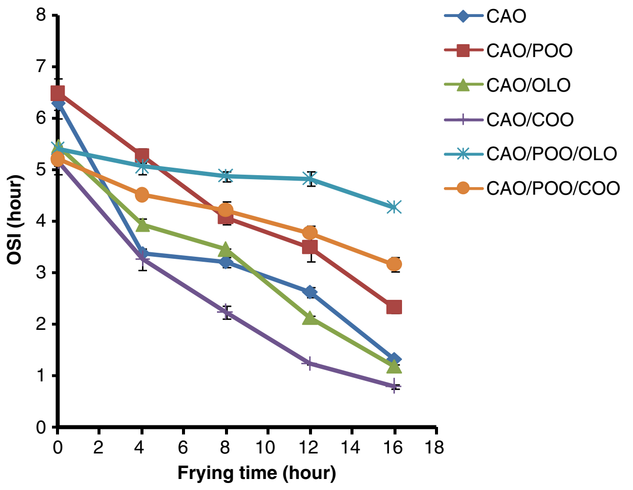

Fig. 2 The oil/oxidative stability index (OSI) of the canola oil (CAO) and their blends with the palm olein (POO), olive (OLO) and corn (COO) oils during the frying process at 180 °C

The changes in the CI of the CAO and its blends with the POO, OLO, and COO during the frying process at 180 °C are shown in Table 3. It was observed that the CI (reflecting an overall chemical degradation and polymerization) increased with the frying time. Darkening of the oil during deep-frying is due to the polymer formation of unsaturated carbonyl compounds and non-polar compounds of foodstuff solubilized in the oil [27]. The initial CI for the CAO was 0.10 and it gained 0.99 units to a value of 1.09 after 16 h of frying. The CI of the CAO/POO, CAO/OLO, and CAO/COO blends significantly changed from 0.24, 0.24, and 0.19 to 1.10, 1.25, and 1.22, respectively; they gained 0.86, 1.01, and 1.03 units, respectively, during the frying process. The initial CIs for the ternary blends containing the OLO and COO were 0.27 and 0.21, respectively, and they significantly gained 0.46 and 0.41 units during the frying process. The color change is related to the degradative processes such as formation of hydroperoxides, conjugated dienoic acids, ketones, and hydroxides [22, 23]. Additional cause for a color change in deep-frying might be the presence of pigments in the commercial oils together with the solubilization of browning pigments from the potatoes during the frying [23, 24, 28].

Table 3 The color index (*CI*) of the canola oil (*CAO*) and their blends with the palm olein (*POO*), olive (*OLO*) and corn (*COO*) oils during the frying process at 180 °C

Time (h)	CAO	CAO/POO	CAO/OLO	CAO/COO	CAO/POO/OLO	CAO/POO/COO
0	0.10 ± 0.00 c^{E}	0.24 ± 0.00 b^{B}	0.24 ± 0.00 b^{B}	0.19 ± 0.00 c^{D}	0.27 ± 0.00 b^{A}	0.21 ± 0.00 b^{C}
4	0.22 ± 0.06 c^{C}	0.41 ± 0.01 ab^{A}	0.38 ± 0.02 b^{A}	0.30 ± 0.02 c^{B}	0.31 ± 0.00 b^{B}	0.24 ± 0.00 b^{C}
8	0.56 ± 0.02 b^{A}	0.50 ± 0.02 ab^{A}	0.64 ± 0.09 ab^{A}	0.54 ± 0.03 bc^{A}	0.34 ± 0.02 b^{A}	0.35 ± 0.02 ab^{A}
12	0.96 ± 0.01 a^{A}	0.72 ± 0.14 ab^{B}	0.91 ± 0.08 ab^{A}	0.88 ± 0.04 ab^{A}	0.45 ± 0.08 b^{C}	0.49 ± 0.04 ab^{C}
16	1.09 ± 0.05 a^{A}	1.10 ± 0.22 a^{A}	1.25 ± 0.25 a^{A}	1.22 ± 0.12 a^{A}	0.73 ± 0.07 a^{B}	0.62 ± 0.11 a^{B}

Means ± SD (standard deviation) within a column with the same lowercase letters are not significantly different at $P < 0.05$. Mean ± SD within a row with the same uppercase letters are not significantly different at $P < 0.05$

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