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Anti-Rancidity Effects of Sesame and Rice Bran Oils on Canola Oil During Deep Frying

Reza Farhoosh · Reza Esmaeilzadeh Kenari

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Abstract In this study, the effect of sesame oil (SEO) and rice bran oil (RBO) on the rancidity of canola oil (CAO) during the process of frying potato pieces at 180 °C was investigated. The SEO and RBO were added to the CAO at levels of 3 and 6%. Frying stability of the oil samples during the frying process was measured on the basis of total polar compounds (TPC) content, conjugated diene value (CDV), acid value (AV), and carbonyl value (CV). In general, frying stability of the CAO significantly ($P < 0.05$) improved in the presence of the SEO and RBO. The positive effect of the SEO on the stability of the CAO was more than that of the RBO. Increasing the amounts of SEO and RBO from 3 to 6% led to decreases in the TPC and AV, and increases in the CDV and CV of the CAO during the frying process. The best frying performance for the CAO was obtained by use of 3% of both SEO and RBO together (CAO/SEO/RBO, 94:3:3 *w*/*w*/*w*).

Keywords Canola oil · Frying · Rice bran oil · Sesame oil · Stability

Introduction

Deep frying is commonly used world-wide as a method for the preparation of foodstuffs. During this process, the oil is exposed to elevated temperatures over a long period of time, in the presence of water from the frying product and of atmospheric oxygen. Under these extreme conditions, a number of chemical reactions occur in the oil, including oxidation, hydrolysis, and polymerization of unsaturated fatty acids, which change the composition of the frying medium and produce volatile oxidation products, non-volatile oxidized derivatives, and dimeric, polymeric, or cyclic substances [1]. In this process, not only desired components are formed but also compounds with adverse nutritional effects and potential hazards to human health [2].

Canola oil, because of its high content of polyunsaturated fatty acids (PUFA), is considered superior to many vegetable oils, but it is inferior in thermal stability at high temperatures [3]. Addition of antioxidants to the oils is considered as one of the most conventional ways to inhibit the development of off-flavors arising from the alterations of unsaturated fatty acids. Normally, synthetic antioxidants, for example butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and tertiary butyl hydroquinone (TBHQ), are used to reduce the rancidity of fats and oils. However, adverse effects of synthetic antioxidants, for example toxicity and carcinogenicity [4–6], and increasing consumer demand for natural products have directed our attention toward sesame oil (SEO) and rice bran oil (RBO) as sources of safer and more effective natural antioxidants [7, 8].

There have been very limited reports on the frying performance of canola oil in the presence of natural antioxidants. Recent studies have been focused on determination of the frying stability of canola oils reduced in linolenic acid by genetic modification [9]. In this study, the effects of SEO and/or RBO on the rancidity of canola oil during deep frying of potatoes were investigated.

R. Farhoosh (✉) · R. Esmaeilzadeh Kenari
Food Science and Technology Department,
Faculty of Agriculture, Ferdowsi University of Mashhad,
P.O. Box 91775-1163, Mashhad, Iran
e-mail: rfarhoosh@um.ac.ir

Materials and Methods

Materials

Refined, bleached, and deodorized CAO with no added antioxidants was supplied by Ghoncheh (Sari, Iran). The SEO and RBO were purchased from a local shop. The oil samples were stored at −18 °C until analysis. The SEO and RBO were added to the CAO in weight percentages of 3 and 6. Fatty acid methyl ester (FAME) standards and other 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 cm × 0.5 cm × 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 three consecutive days. At the end of each 4 h, approximately 10 g of the frying oil was filtered into a screw-cap vial and promptly stored in the dark at 4 °C until use. The volume of oil was not replenished during the frying process. Frying experiments were conducted in duplicate on each frying medium [10].

Chemical Analyses

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 7 M 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-Sil 88 (Supelco, Bellefonte, PA, USA) fused silica capillary column, 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 at a flow rate of 0.75 mL/min. The oven temperature was maintained at 198 °C, and that of the injector and the detector at 250 °C [11].

The spectrophotometric method of the International Dairy Federation, as described by Shantha and Decker [12], was used to determine peroxide value (PV). Acid value (AV) was determined according to AOCS Official Method Cd 3d-63 [13]. Total polar compounds (TPC) content was determined according to the economical micro method developed by Schulte [14]. For the conjugated diene value (CDV) the oil samples were diluted to 1:600 with hexane and measured spectrophotometrically at 234 nm and read against HPLC-grade hexane as a blank. An extinction coefficient of 29,000 mol/L was used to quantify the concentration of conjugated dienes formed during oxidation [15]. The carbonyl value (CV) of the oils was measured according to the method developed by Endo et al. [16] using 2-propanol and 2,4-decadienal as solvent and standard, respectively, [17].

Statistical Analysis

All determinations were carried out in triplicate, and data were subjected to analysis of variance (ANOVA). ANOVA and regression analysis were performed using MStatC and SlideWrite 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 PV and AV of the original oils examined in this study were all less than 1.00 meq/kg and 0.30 mg/g, respectively, as shown in Table 1, indicating that they were unoxidized and of high initial quality. As can be seen in Table 1, the oils are distinguished from each other mainly by the

Table 1 Initial characteristics of the canola, sesame, and rice bran oils examined in this study

Property	CAO	SEO	RBO
Fatty acids (%)			
16:0	5.02 ± 0.45 c	9.98 ± 0.25 b	15.34 ± 0.59 a
16:1	0.66 ± 0.32 a	0.05 ± 0.01 b	0.24 ± 0.03 b
18:0	2.60 ± 0.05 b	5.81 ± 0.14 a	2.13 ± 0.30 b
18:1	62.51 ± 0.92 a	40.15 ± 0.62 c	43.34 ± 0.82 b
18:2	19.46 ± 0.41 c	41.74 ± 0.76 a	36.55 ± 1.53 b
18:3	7.29 ± 0.58 a	0.36 ± 0.02 c	1.10 ± 0.11 b
SFA	7.62 ± 0.45 c	15.79 ± 0.15 b	17.34 ± 0.36 a
MUFA	63.17 ± 0.50 a	40.20 ± 0.50 c	43.58 ± 0.85 b
PUFA	26.75 ± 0.36 c	42.10 ± 0.75 a	37.65 ± 1.43 b
PUFA/SFA	3.51 ± 0.18 a	2.67 ± 0.02 b	2.16 ± 0.04 c
PV (meq O_2/kg oil)	0.22 ± 0.11 c	0.60 ± 0.11 b	0.90 ± 0.04 a
AV (mg KOH/g oil)	0.27 ± 0.03 a	0.17 ± 0.01 c	0.23 ± 0.03 b

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

CAO, canola oil; SEO, sesame oil; RBO, rice bran oil; SFA, saturated fatty acids; MUFA, monounsaturated fatty acids; PUFA, polyunsaturated fatty acid; PV, peroxide value; AV, acid value significant differences in the percentages of palmitic (C16:0), oleic (C18:1), linoleic (C18:2), and linolenic (C18:3) acids. The RBO and SEO had percentages of saturated fatty acids (SFA) more than twofold that of the CAO. Because of the high level of C18:1, the percentage of monounsaturated fatty acids (MUFA) in the CAO was much higher than those of the RBO and SEO. The SEO had the highest percentage of polyunsaturated fatty acids (PUFA), followed by the RBO and CAO. Accordingly, the PUFA/SFA ratio (also known as the polyene index) was greatest for the CAO, followed by the SEO and RBO. The PUFA/SFA ratio is usually taken as a measure of the extent of polyunsaturation of an oil, and of its tendency to undergo autoxidation [18].

Figure 1 shows the TPC content of the CAO as affected by the SEO and RBO during the frying process at 180 °C. There was no statistically significant difference between the initial TPC content of the CAO and those of the CAOs containing the SEO and RBO. The TPC contents increased linearly with high correlation coefficients. Research has shown that the fraction of polar compounds isolated from oxidized oils are toxic to laboratory animals [19]. Therefore, it has been recommended that frying oils containing more than 24–27% of TPC content should be discarded [20]. Except for the CAO/SEO/RBO (94:3:3 *w*/*w*/*w*), all the oils studied reached the discarding range of TPC content during the frying process. 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 (7.57 h) than that of CAOs containing the SEO and RBO (13.15–29.56 h). The frying stability of the CAO significantly increased as the percentage of the SEO and RBO increased from 3% to 6%. However, at the same levels (3% and 6%), the frying stability of the CAO increased more in the presence of the SEO (15.70 and 22.62 h) than in the presence of the RBO (13.15 and 19.30 h). It was interesting to find that the CAO/SEO/RBO (94:3:3 *w*/*w*/*w*) mixture had the highest frying stability (29.56 h) among the CAOs containing the SEO and RBO.

Table 2 shows the CDV of the CAO as affected by the SEO and RBO during the frying process at 180 °C. Measurement of the CDV is a good method of determination of oxidative stability of the oils [21]. Lipids containing methylene-interrupted dienes or polyenes show a shift in their double bond position during oxidation. This is accompanied by increased UV absorption at 234 nm. The increase in CDV is proportional to the uptake of oxygen. Greater the levels of CDV will lower the oxidative stability of the oils [22]. In this study, the CDVs increased parallel to an increase of frying time (0–24 h) with a greater rate for the CAO (an percentage increase of 207). The CAOs stabilized with the SEO and RBO showed lower levels of the CDV after 24 h of frying (increases of 70–160%), indicating the antioxidant potential of the SEO and RBO components. Lignans and tocopherols are well known naturally occurring antioxidant components present in SEO, with sesamin and sesamolin being the predominant sesame lignans [7]. It is also well known that γ-oryzanol

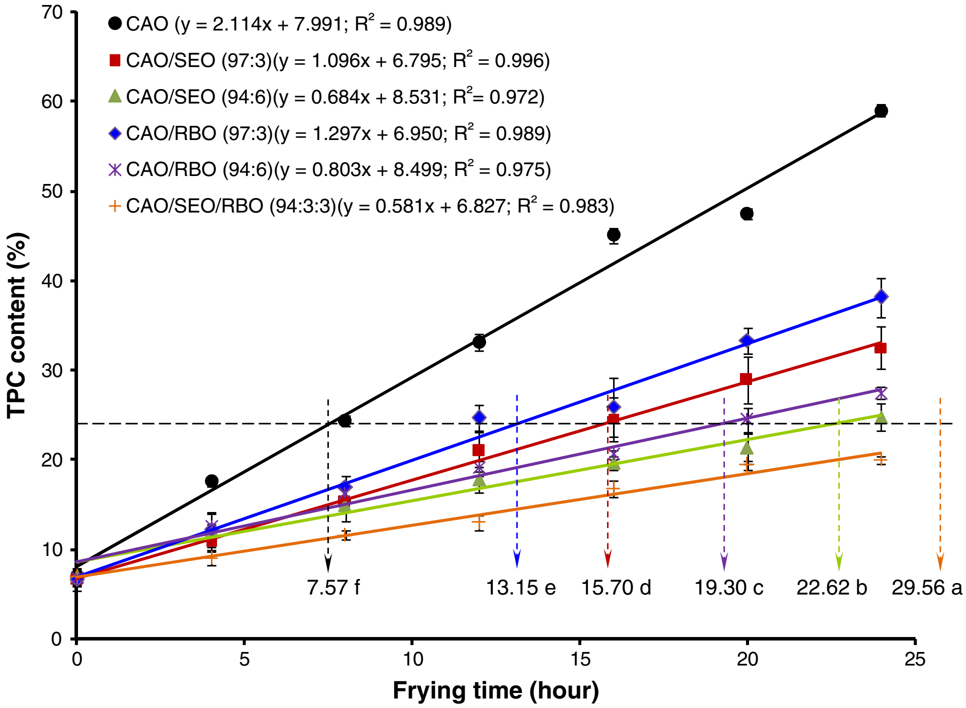

Fig. 1 Total polar compounds (TPC) content of canola oil (CAO) as affected by sesame oil (SEO) and rice bran oil (RBO) during frying at 180 °C. Quantities (times required to reach a TPC content of 24%) with the same lowercase letters are not significantly different at $P < 0.05$

Table 2 Conjugated diene value (CDV) of canola oil (CAO) as affected by sesame oil (SEO) and rice bran oil (RBO) during frying at 180 °C

Time (h)	CAO	CAO/SEO		CAO/RBO		CAO/SEO/RBO
		97:3	94:6	97:3	94:6	94:3:3
0	20.50 ± 1.29 f A	20.76 ± 1.16 e A	21.40 ± 1.07 f A	21.20 ± 1.96 f A	21.79 ± 1.63 g A	21.49 ± 0.74 d A
4	21.25 ± 1.26 f D	27.01 ± 1.01 d A	25.47 ± 2.09 e AB	26.58 ± 2.20 e A	24.00 ± 0.93 f BC	22.70 ± 1.63 d CD
8	24.75 ± 1.71 e D	28.71 ± 1.45 d C	32.51 ± 1.37 d AB	31.00 ± 1.38 d BC	33.73 ± 1.54 e A	25.99 ± 1.80 c D
12	36.85 ± 1.94 d AB	35.04 ± 1.59 c BC	33.50 ± 1.29 d CD	32.00 ± 1.83 d D	38.85 ± 1.19 d A	31.44 ± 1.99 b D
16	55.50 ± 1.29 c A	40.78 ± 1.58 b BC	39.00 ± 1.41 c CD	37.55 ± 1.32 c D	42.25 ± 1.71 c B	29.75 ± 1.71 b E
20	60.30 ± 1.70 b A	41.69 ± 1.43 b D	45.36 ± 1.07 b C	48.24 ± 1.83 b B	49.55 ± 1.62 b B	35.50 ± 1.73 a E
24	63.00 ± 1.82 a A	44.50 ± 2.52 a E	49.50 ± 1.29 a D	52.50 ± 1.29 a C	56.75 ± 1.71 a B	36.50 ± 1.29 a F

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

together with tocopherols are responsible for the high antioxidative strength of the RBO [8]. At the experimented levels of 3% and 6%, the SEO showed antioxidant potential higher than that of the RBO (increases of 114% and 131% vs 148% and 160%, respectively, in the CDV after 24 h of frying). It should be noted that both the antioxidative oils at the level of 6% exerted pro-oxidant effects to some extent, whereas their similar levels together (CAO/SEO/RBO, 94:3:3 *w*/*w*/*w*) had a marked synergistic effect (an increase of 70% in the CDV after 24 h of frying).

Changes in the AV of the CAO in the presence of the SEO and RBO during the frying process at 180 °C are shown in Table 3. AV, which is used to assess degradation of the frying oil, increased gradually for all treatments from hour 0 to hour 24 of frying. The steady rise in the AV can be attributed partly to hydrolysis of triacylglycerols and partly to the component carboxyl groups present in oxidative and/or polymeric products of frying [9, 23, 24]. It can be seen that the change in AV for the CAO was higher (1.18 units) than that for CAOs containing the SEO and RBO (0.57–0.89 units) after 24 h of frying. This indicates that the SEO and RBO could significantly reduce the oxidative and thermal degradation taking place in unsaturated fatty acids. At the end of the frying process, an increase of 0.86 units was observed in the AV of CAOs containing 3% SEO or RBO. Samples containing 6% SEO had a higher protective effect on the CAO (an increase of 0.63 units in the AV), whereas the same percentage of RBO showed an increase of 0.89 units in the initial AV of the CAO after 24 h of frying. Gopala Krishna et al. [25] concluded that the RBO's oryzanol may contribute to the formation of free fatty acids; thus, the increased AV observed in RBO-treated oils might be because of oryzanols. The AV changed the least in the CAO/SEO/RBO (94:3:3 *w*/*w*/*w*) frying oil.

Changes in the CV of the CAO affected by the SEO and RBO during the frying process at 180 °C are shown in Table 4. The CV does not measure primary products of oxidation (hydroperoxides), but secondary decomposition products such as aldehydes and ketones [26]. According to Woyewoda et al. [27], peroxides are transformed into secondary products that contain carbonyl groups. These compounds are more stable than peroxides and the CV is considered to be a good index of oxidative changes in lipids. The determination of carbonyl compounds in frying oils is very important for evaluating the quality of frying fats and oils, because these compounds often contribute to

Table 3 Acid value (AV) of canola oil (CAO) as affected by sesame oil (SEO) and rice bran oil (RBO) during frying at 180 °C

Time (h)	CAO	CAO/SEO		CAO/RBO		CAO/SEO/RBO
		97:3	94:6	97:3	94:6	94:3:3
0	0.274 ± 0.029 g A	0.260 ± 0.009 g C	0.239 ± 0.014 g E	0.261 ± 0.002 f B	0.238 ± 0.007 g F	0.250 ± 0.003 g D
4	0.528 ± 0.070 f A	0.345 ± 0.028 f B	0.315 ± 0.013 f BC	0.325 ± 0.010 f BC	0.283 ± 0.007 f C	0.291 ± 0.003 f C
8	0.620 ± 0.091 e A	0.556 ± 0.027 e AB	0.511 ± 0.013 e B	0.430 ± 0.018 e C	0.398 ± 0.011 e C	0.328 ± 0.006 e D
12	0.773 ± 0.053 d A	0.718 ± 0.021 d B	0.628 ± 0.013 d C	0.670 ± 0.043 d BC	0.684 ± 0.008 d B	0.446 ± 0.013 d D
16	0.988 ± 0.084 c A	0.860 ± 0.021 c B	0.725 ± 0.013 c D	0.852 ± 0.026 c B	0.774 ± 0.020 c C	0.547 ± 0.013 c E
20	1.153 ± 0.021 b A	0.927 ± 0.008 b D	0.774 ± 0.021 b E	0.952 ± 0.020 b C	0.979 ± 0.007 b B	0.677 ± 0.007 b F
24	1.450 ± 0.061 a A	1.120 ± 0.073 a B	0.868 ± 0.027 a C	1.118 ± 0.103 a B	1.131 ± 0.006 a B	0.821 ± 0.006 a C

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

Table 4 Carbonyl value (CV) of canola oil (CAO) as affected by sesame oil (SEO) and rice bran oil (RBO) during frying at 180 °C

Time (h)	CAO	CAO/SEO		CAO/RBO		CAO/SEO/RBO
		97:3	94:6	97:3	94:6	94:3:3
0	4.85 ± 0.91 d A	6.50 ± 1.78 g A	6.32 ± 1.19 e A	6.32 ± 1.05 e A	6.37 ± 0.98 e A	6.31 ± 1.21 e A
4	33.29 ± 1.68 a A	13.06 ± 1.55 f BC	15.09 ± 0.94 d B	13.58 ± 1.15 d BC	14.71 ± 2.38 d B	11.29 ± 1.44 d C
8	29.82 ± 1.83 b A	19.00 ± 1.40 e C	25.40 ± 1.57 c B	25.08 ± 2.04 c B	28.01 ± 1.04 c A	16.60 ± 1.65 c C
12	26.28 ± 2.07 c CD	24.64 ± 1.43 d D	29.51 ± 2.10 b B	27.56 ± 1.27 b BC	39.84 ± 1.20 a A	22.00 ± 1.15 b E
16	28.35 ± 1.68 bc C	38.39 ± 1.95 a B	39.63 ± 1.11 a B	43.20 ± 1.98 a A	30.17 ± 1.59 bc C	22.75 ± 1.50 b D
20	34.28 ± 1.70 a A	31.83 ± 1.08 b B	26.95 ± 1.09 c C	30.00 ± 1.38 b B	32.18 ± 2.40 b AB	31.65 ± 1.17 a B
24	33.00 ± 1.70 a A	29.25 ± 1.71 c B	25.25 ± 2.22 c C	28.17 ± 1.97 b B	29.94 ± 0.95 bc B	24.04 ± 1.59 b C

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

rancid and unpleasant flavors, and reduce the nutritional value of fried foods [16]. In previous research, the CV of a set of frying oils increased and reached a maximum value during the frying process, and then decreased as a result of further heat treatment [28]. This was attributed to the decomposition of carbonyl compounds during the prolonged heating period and the formation of new compounds which were not detectable by the CV assay. Such a trend was observed for the oil samples examined in this study during the frying process. There were no significant differences among the initial CV of the oil samples, which ranged from 4.85 to 6.50 μmol/g. The CAO, with an increase of 586%, reached the maximum CV (33.29 μmol/g) after 4 h of frying, whereas the CAO/SEO (97:3 *w*/*w*), CAO/SEO (94:6 *w*/*w*), CAO/RBO (97:3 *w*/*w*), CAO/RBO (94:6 *w*/*w*), and CAO/SEO/RBO (94:3:3 *w*/*w*/*w*) with increases of 491, 527, 583, 525, and 402%, respectively, reached the maximum CVs (38.39, 39.63, 43.20, 39.84, and 31.65 μmol/g, respectively) after 16, 16, 16, 12, and 20 h, respectively. As can be seen, these results are well in accordance with those of the CDV test, so the same order of stability can be observed for these oil samples.

Conclusions

The results of this study indicated that the SEO and RBO can be used as potent natural anti-rancidity additives in CAO during deep frying. The anti-rancidity effect of the SEO on the CAO was significantly better than that of the RBO. Increasing the percentages of SEO and RBO from 3 to 6% promoted primary (CDV) and secondary (CV) oxidation of the CAO during the frying process (pro-oxidant effect). A marked synergistic effect was observed when 3% of both SEO and RBO were added to the CAO (CAO/SEO/RBO, 94:3:3 *w*/*w*/*w*).

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