Frying Stability of High-Oleate and Regular Soybean Oil Blends

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ABSTRACT: The objective of this work was to study the frying stability of soybean oil (SBO) with reduced linoleate (18:2) and linolenate (18:3) and elevated oleate (18:1) contents. Higholeate SBO [HO SBO, 79% oleic acid (OA)] and a control (conventional SBO, 21.5% OA) were tested as is, as well as blended in different ratios to make three blended oils containing 36.9, 50.7, and 64.7% OA, abbreviated as 37%OA, 51%OA, and 65%OA, respectively. In addition, a low-linolenate (LL) SBO containing 1.4% 18:3 and 25.3% 18:1 was tested. Bread cubes (8.19 cm^3) were fried in each of 18 oils (6 treatments \times 3 replicates). We hypothesized that stability indicators would be indirectly related to the total 18:2 plus 18:3 percentages and/or the calculated oxidizability. In general, the results were fairly predictable based on total 18:2 and 18:3 concentrations. The overall frying stability of the six oil treatments, from the best to the poorest, was: 79%OA, 65%OA, 51%OA, LL \geq 37%OA, and the control, with respective total compositions for 18:2 plus 18:3 of 10.3, 23.6, 36.3, 59.6, 48.9, and 62.8%. The greatly reduced concentration of 18:3 in the LL SBO made it more stable than the 37%OA, even though the combined composition of 18:2 and 18:3 of LL was greater than that of the 37%OA. Blending conventional SBO with HO SBO had a profound effect on the oxidative stability index and color of the blended oils, but the values were not linearly predictable by the percentage of control in the blended oil. Other stability indices, including calculated oxidizability, calculated iodine value, conjugated dienoic acid value, and viscosity, changed in linear response to an increased proportion of the control in the blends.

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KEY WORDS: Conjugated dienoic acid, free fatty acids, fried bread cubes, frying oil stability, high-oleate soybean oil, low-linoleate soybean oil, low-linolenate soybean oil, oxidative stability, polar compounds, viscosity.

Soybean oil (SBO) has a good nutritional profile because of its high proportion of unsaturated FA, but the oil has poor oxidative stability and is prone to flavor deterioration. The FAME of linoleic (18:2) and linolenic acids (18:3) in SBO oxidize quickly and are the major contributors to the poor stability of SBO (1). To improve oxidative and flavor stability, SBO may be hydrogenated to reduce the concentration of PUFA and increase the content of saturated FA; however, *trans* FA (*t*FA) are formed and saturated FA are increased during this process. Unfortunately, consumption of a diet high in *t*FA has been reported to raise total and LDL cholesterol and lower HDL cholesterol levels (2), and a diet having a high ratio of saturated FA to PUFA has been shown to increase serum total cholesterol (3), all of which are indicators of increased risk for cardiovascular diseases. Thus, lowering the 18:3 content to a level similar to that obtained by partial hydrogenation, but without *trans* formation, has been an objective of plant breeders.

Various SBO with different lowered levels of 18:3 have been developed and studied (4,5). The oxidative and flavor stabilities of SBO containing as little as 1.0% 18:3 were compared to SBO containing 2.2% 18:3 in previous studies (4,5). The 1.0% 18:3 oil was slightly more stable than the 2.2% 18:3 oil by oxidative and flavor stability indices. On the other hand, 18:3 is an essential FA belonging to a group called omega-3 (or n-3) FA, which reduce or help prevent certain chronic diseases (6). Thus, reducing 18:3 to a minimal level may diminish the health benefits of SBO. Therefore, developing SBO with enhanced stability, but still retaining some 18:3, with no formation of *t*FA and with a maximal amount of total unsaturated FA is desirable.

Studies have shown that the oxidation rate of oleate (18:1) is much slower than that of the PUFA, 18:2 and 18:3 (7). A diet high in monounsaturates may also help to reduce elevated levels of total plasma cholesterol without reducing the HDL cholesterol level (8). Therefore, the incentive to breed HO soybeans (reducing, but not eliminating 18:2 and 18:3, reducing total saturated FA, and eliminating *t*FA) becomes obvious. Also, such an oil would require no or minimal additional processing and thus could result in more profit for farmers and processors (9).

We hypothesized that values for stability tests would be indirectly related to the total 18:2 and 18:3 and/or the calculated oxidizability. The main objective of this project, then, was to study the frying stability of SBO with reduced 18:2 and 18:3 and elevated 18:1 concentrations, as is and blended with regular SBO, to obtain mixtures with various FA compositions. A secondary objective was to compare a low 18:3 SBO with these oils and their blends during frying.

MATERIALS AND METHODS

SBO and design. Soybeans (*Glycine max*) containing oil with high-oleate [HO, 79% oleic acid (OA)], low-linolenate (LL, 1.4% with 25.3% OA), and conventional (control, 21.3% OA)

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FAME compositions were grown in the summer of 1998 in Iowa (weather zone 4). The soybeans were crushed and the oils were hexane-extracted, in triplicate, in the Pilot Plant of the Center for Crops Utilization Research, Iowa State University (ISU), Ames, Iowa, by following a previously published method (9). All the oils were refined and bleached as described in AOCS official methods Ca 9a-52 and Cc 8a-52, respectively (10), and deodorized by following the procedure described by Stone and Hammond (11). Triplicate sets of each oil were refined, bleached, and deodorized separately. Citric acid (100 ppm) was added to the oils during the cool-down stage of deodorization before placement in high-density polyethylene plastic bottles. The bottles were sparged with nitrogen, then sealed and stored at -10° C until used for testing.

Six SBO treatments were evaluated for frying stability, including the three SBO just mentioned (control, LL, 79%OA), which were tested as is, as well as three oil blends prepared as follows: (i) 75% of the control (by weight) and 25% of the HO (37%OA), (ii) 50% of the control and 50% of the HO (51%OA), and (iii) 25% of the control and 75% of the HO (65%OA).

Frying. Eighteen frying sessions of six oil treatments evaluated in triplicate, as three simultaneous sessions per day, were carried out. At each frying session, 220 g of an oil treatment was weighed into a Teflon-coated 473-mL electric baby fryer (National Presto Industries Inc., Eau Claire, WI), and the oil was then heated to 185°C within 10 min. The oil was held at $185 \pm 5^{\circ}$ C for 2.5 h before frying. Eight 5-piece batches of crust-free bread cubes $(2.54 \times 2.54 \times 1.27 \text{ cm})$ were fried for 1 min per batch at 3-min intervals. Therefore, the actual frying of the cubes was completed within 0.5 h. The fried bread cubes were then drained and cooled to room temperature. Half of the bread cubes was used immediately for testing, including evaluating PV of the extracted oil. The other half of the bread cubes were stored, loosely covered, at 60°C in the dark for 3 d before evaluating PV of the extracted oil by the same procedure used on fresh bread cubes. The oil remaining in the fryer was maintained at $185 \pm 5^{\circ}C$ for another 7 h for a total of 10 h heating on day 1, then cooled to 25°C. The oil was heated at 185 ± 5 °C for another 10 h on day 2. Aliquots from each oil were taken before heating, immediately after frying, at the end of day 1 heating (10 h), and at the end of day 2 heating (20 h).

FAME composition by GC, tocopherol contents by HPLC, oil stability indices (OSI), and polar compounds. FAME compositions of SBO before frying were determined according to a method described by Hammond (12). The GC conditions were the same as described by Shen *et al.* (9). Calculated oxidizability (7) and iodine value (IV) (10) of the oils were determined according to formulas based on the FAME composition of the oils. Tocopherol contents and OSI of the oils before frying and the percentage of polar compounds were determined according to AOCS Official Methods Ce 8-89, Cd 12b-92, and Cd 20-91, respectively (10). The HPLC conditions for tocopherol contents were the same as described elsewhere (4). *Viscosity*. Viscosity of the oils before and after frying and heating was measured by using a Brookfield DV–II+ viscometer (Brookfield Engineering Laboratories Inc., Stoughton, MA). One milliliter of oil was placed on the plate of the viscometer with cone spindle CP-42; the viscosity of the sample was read in cP (1 cP = 1 mPa·s) directly from the viscometer, which was maintained at 40°C by a circulating water bath.

Conjugated dienoic acid (CDA). The percentage of CDA of the frying oils was determined according to AOCS Official Method Ti 1a-64 (10) as a measurement of the diene conjugation of unsaturated linkages present in the fatty esters.

Colors. Colors of the frying oils were measured with a HunterLab colorimeter (Hunter Associate Laboratory, Inc., Reston, VA) at a 10° field of vision with illuminant D65. Oil (13.0 g) was placed in a 60×15 cm standard disposable petri dish and the measurements were recorded in Hunter units of L [L = 0 (black), L = 100 (white)], a (+a = red, -a = green), and b (+b = yellow, -b = blue).

PV of the SBO before frying and of the oil extracted from bread cubes. The PV of the oils before frying was determined by the Stamm test as modified by Hamm *et al.* (14). Commercially available tetrachloroethane was purified as described elsewhere (4).

Oil from the fried bread cubes (3.0 g) was hexane-extracted as previously described (15). The extracted oil was used to determine the PV of the fried bread cubes by the same procedure as just mentioned.

Statistical analysis. There were 6 treatments \times 3 replicates. The SAS general linear model procedure was used to analyze the data (16). Differences in mean values among treatments were determined by the least significant differences test at α = 0.05, unless listed otherwise.

RESULTS AND DISCUSSION

FAME composition, calculated oxidizability, and calculated IV (*Table 1*). The control oil had much greater palmitate (16:0), 18:2, and 18:3 concentrations than did the 79%OA. The blended treatments were intermediate in these FA levels, based on the ratios of each oil percentage. The LL was similar in FA composition to the control, except for its greatly reduced 18:3 level. Clearly, the calculated oxidizability and IV increased in the order: 79%OA, 65%OA, 51%OA, 37%OA, LL (25.3% OA), and control (21.5% OA). The combined concentrations of 18:2 and 18:3 in the oils were: 10.3, 23.6, 36.3, 48.9, 59.6, and 62.8%, respectively. That is, the lower the combined concentration of 18:2 and 18:3 in the oils, the lower the calculated oxidizability and IV.

To copherols (Table 1). The concentrations of α -to copherol of the oil treatments increased as the combined concentration of 18:2 and 18:3 in the oils increased. The concentrations of δ -to copherol of the oil treatments decreased as the combined concentration of 18:2 and 18:3 in the oils increased, except for the LL treatment, which had the least amount of δ -to copherol even though

	FAME ^d							Tocopherols (µg/g) ^f				
Oils ^c	16:0	18:0	18:1	18:2	18:3	Oxidizability ^e	lodine value	α	γ	δ	Total	OSI
79%OA	6.9	3.8	79.0	6.5	3.8	2.3 ^e	89 ^f	113 ^e	722 ^a	495 ^a	1329 ^a	31.74 ^a
65%OA	7.8	3.9	64.7	18.7	4.9	3.6 ^d	101 ^e	156 ^d	722 ^a	457 ^{a,b}	1335 ^a	13.02 ^b
51%OA	9.0	4.1	50.7	30.3	6.0	4.9 ^c	112 ^d	199 ^c	722 ^a	419 ^{b,c}	1340 ^a	8.63 ^{b,c}
37%OA	9.9	4.3	36.9	41.8	7.1	6.2 ^b	123 ^c	242 ^b	723 ^a	381 ^{d,c}	1346 ^a	6.48 ^{b,c}
Control	11.2	4.4	21.5	54.8	8.0	7.6 ^a	134 ^a	285 ^a	723 ^a	343 ^d	1352 ^a	5.25 ^c
LL	10.6	4.5	25.3	58.2	1.4	6.6 ^b	126 ^b	274 ^a	731 ^a	286 ^e	1290 ^a	8.13 ^{b,c}

TABLE 1 FAME Composition (area %), Calculated Oxidizability^a, Calculated Iodine Value^b, Tocopherols, and Oil Stability Indices (OSI) of Soybean Oil (SBO) Treatments

^aOxidizability = [oleate% + 10.3 (linoleate%) + 21.6 (linolenate%)]/100 (Ref. 9).

^blodine values were calculated from the FAME profile, according to AOCS Official Method Cd 1c-85 (Ref. 12).

^c79.1%OA = high-oleate (OA) SBO. The 65%OA, 51%OA, 37%OA = three blends of control and 79%OA SBO. Control = conventional SBO. LL = low-linolenate SBO.

^dMethyl palmitate (16:0), stearate (18:0), oleate (18:1), linoleate (18:2), and linolenate (18:3).

^eValues in the same column for each test with superscripts in common were not significantly different (P < 0.05).

¹Tocopherol concentrations in 79%OA, control, and LL SBO were determined. Tocopherol concentrations in the three blended oils were calculated.

its combined concentration of 18:2 and 18:3 was intermediate between those of 37%OA and the control. There were no differences in the concentrations of γ -tocopherol and total tocopherol among 79%OA, the control and LL SBO, and any of the blends.

OSI (Table 1). The OSI of all SBO treatments suggested an order of heat stability from greatest to lowest as: 79%OA, 65%OA, 51%OA, LL, 37%OA, and the control. These values are consistent with the predicted order by calculated oxidizability (also, combined total of 18:2 and 18:3 concentrations) and IV, except for the LL treatment, which tended to be more stable than the 37%OA treatment as indicated by OSI, instead of just slightly more stable than the control as predicted by calculated oxidizability and IV. The 65%OA (with 25% by weight of the control blended in) had a greatly reduced OSI compared with 79%OA, but there were no significant differences in OSI values among 51%OA, 37%OA, control, and LL treatments, showing a trend of OSI that was not linearly predictable by the 18:2 and 18:3 concentrations or calculated oxidizability. The presence of a poor-stability oil, the control in this study, may have greatly shortened the induction period of the blended oils, causing them to have OSI values that were close to that of the control. Thus, for the OSI test results, the common belief in the oil industry that a blended oil is only as stable as the "poorest" oil held true.

FFA (Table 2). The FFA of all oil treatments increased with heating time. There were no significant differences in FFA among the fresh SBO and among the oils immediately after frying the bread cubes, except that the control had greater FFA than did LL immediately after frying. Even though the difference was significant, it was small. At 10 and 20 h of heating, greater FFA tended to develop as the combined concentration of 18:2 and 18:3 and/or calculated oxidizability decreased, except for LL at 20 h. The greater the reduction of 18:2 and 18:3, the greater the FFA. Previous researchers found the same trend when frying potato chips using high-oleate canola oil (17). These findings were quite different from those of the OSI test. Perhaps this paradox was the result of a limitation of the FFA method. Generally, the oils that had less 18:2 and 18:3 were less viscous (see section immediately following) after 20 h of frying, so the FFA may have been better dissolved in the alcohol used for titration of the FFA, resulting in a greater measured content than for the other, more viscous oils. FFA content is an important marker for oil quality. The recommended FFA content in fresh refined, bleached, and deodorized oils is 0.05% maximum (18).

Viscosity (Table 2). Similar to the changes of FFA in the frying oil treatments, the differences in viscosity were small among fresh SBO and among the oils immediately after frying the bread cubes. At 20 h of heating, however, the oil viscosity increased with increasing 18:2 and 18:3 concentrations, except for the LL. This viscosity order suggests that the lower the 18:2 plus 18:3 content, the more stable the oil during frying, except for the LL treatment, whose very low 18:3 concentration elevated its stability above that of the 37%OA, instead of just above that of the control, as would be predicted solely by the combined 18:2 and 18:3 concentration order, and also by calculated oxidizability.

CDA (*Table 2*). There were no differences in CDA among the fresh oils. Immediately after frying, and at 10 and 20 h of heating, the lower the 18:2 and 18:3 concentrations in the oils, the less the CDA formed during frying and heating, except that the LL treatment, with 59.6% 18:2 and 18:3, had less CDA than did the 37%OA treatment (with 48.9% 18:2 and 18:3). Again, the very low 18:3 concentration of the LL treatment elevated its stability above that of the 37%OA.

Polar compounds. There were differences among oils in polar compound percentages only at 10 h of heating, with the lower the 18:2 and 18:3 concentration, the lower the polar compounds formed during frying. Again, the LL was very close in polar compound percentage to that of the 37%OA and the control. At 10 h of heating, the polar compound percentages in all oils exceeded the upper limit for used frying fats based on the German standard of 27% total polar compounds (19). At 20 h of heating, the values were all similarly high, likely because the extensive breakdown in all oils had reached a plateau. In this frying study, relatively small quantities of oil were used in each baby fryer, and only a small quantity of food was fried. Thus, the polar materials were formed abundantly, and very little was carried away by the fried food, which probably contributed to the great quantity of polar compounds in all the frying oils in this study.

TABLE 2 FFA (% oleic), Viscosity (cP), Conjugated Dienoic Acid (%), Polar Compounds (%), HunterLab Colors (L, a, b) and PV (mequiv/kg) of SBO^{*a*} and Fried Bread Cubes^{*b*}

		Frying time								
Analysis	Soybean oil	0 h	Immediately after frying	10 h of heating	20 h of heating					
FFA	79%OA 65%OA 51%OA	0.04 ^a 0.04 ^a 0.04 ^a	$0.18^{a,b}$ $0.18^{a,b}$ $0.18^{a,b}$ $0.17^{a,b}$	0.57 ^a 0.45 ^b 0.33 ^c	1.10 ^a 1.06 ^{a,b} 0.90 ^{b,c}					
	Control LL	0.04 ^a 0.03 ^a 0.04 ^a	0.17 ^a 0.19 ^a 0.16 ^b	0.27° 0.31° 0.25°	0.43 ^d 0.77 ^c					
Viscosity ^C	79%OA 65%OA 51%OA 37%OA Control LL	31.9 ^a 29.1 ^b 28.8 ^b 27.4 ^{b,c} 24.8 ^d 26.7 ^{c,d}	33.9^{a} $32.1^{a,b}$ $31.9^{a,b}$ $32.2^{a,b}$ 30.0^{b} 29.3^{b}		$189.9^{d} \\ 235.2^{c,d} \\ 271.0^{c} \\ 295.4^{b,c} \\ 358.2^{a,b} \\ 289.5^{b,c} \\$					
Conjugated dienoic acid	79%OA 65%OA 51%OA 37%OA Control LL	0.10^{a} 0.10^{a} 0.10^{a} 0.10^{a} 0.10^{a} 0.10^{a}	0.44^{c} $0.65^{b,c}$ $0.84^{a,b}$ 1.09^{a} 1.15^{a} $0.91^{a,b}$	0.97 ^e 1.69 ^d 2.34 ^c 2.90 ^b 3.41 ^a 3.33 ^a	1.49 ^e 2.07 ^d 2.57 ^c 3.06 ^b 3.62 ^a 3.60 ^a					
Polar compounds	79%OA 65%OA 51%OA 37%OA Control LL	1.9 ^a 1.9 ^a 1.6 ^a 1.8 ^a 2.0 ^a 2.2 ^a	10.2 ^a 12.6 ^a 11.7 ^a 13.9 ^a 14.0 ^a 12.6 ^a	47.5^{c} 55.7^{b} 53.9^{b} 53.8^{b} 67.4^{a} 62.5^{a}	70.5 ^a 70.7 ^a 72.2 ^a 73.1 ^a 76.0 ^a 73.1 ^a					
HunterLab color (L) ^C	79%OA 65%OA 51%OA 37%OA Control LL	75.7 ^a 75.5 ^{a,b} 75.7 ^a 75.9 ^a 75.0 ^b 75.2 ^{a,b}	72.2 ^c 73.5 ^b 73.7 ^b 74.1 ^{a,b} 74.3 ^{a,b} 74.8 ^a		63.3^{a} 55.7 ^b 52.8 ^b 54.7 ^b 54.8 ^b 59.8 ^{a,b}					
HunterLab color (a)	79%OA 65%OA 51%OA 37%OA Control LL	-2.4 ^a -2.5 ^a -2.6 ^a -2.4 ^a -4.0 ^b	$-5.4^{a,b}$ -5.8^{b} -5.8^{b} -6.1^{b} $-5.6^{a,b}$ -4.4^{a}		4.3 ^b 15.7 ^a 19.5 ^a 16.8 ^a 16.3 ^a 16.8 ^a					
HunterLab color (b)	79%OA 65%OA 51%OA 37%OA Control LL	6.8^{b} 6.5^{b} 7.0^{b} 7.2^{b} 6.4^{b} 12.0^{a}	24.3 ^a 21.2 ^{a,b} 20.0 ^{a,b} 18.5 ^{a,b,c} 16.5 ^{b,c} 13.2 ^c		39.1 ^a 36.0 ^b 34.4 ^b 35.4 ^b 35.5 ^b 35.4 ^b					
		Fresh SBO	Fresh fried bread		Stored fried bread					
P√ ^d	79%OA 65%OA 51%OA 37%OA Control	$\begin{array}{c} 0.08^{d} \\ 0.10^{d,c} \\ 0.12^{b,c} \\ 0.15^{a} \\ 0.16^{a} \\ 0.14^{a,b} \end{array}$	$5.45^{b} \\ 5.60^{b} \\ 5.60^{b} \\ 5.80^{b} \\ 6.60^{a} \\ 6.00^{a,b} \\ \end{cases}$		$7.30^{d} \\ 11.37^{d} \\ 14.27^{d,c} \\ 29.47^{a,b} \\ 38.27^{a} \\ 22.03^{b,c} \\ $					

^aSee footnote *c* in Table 1 for definitions of SBO treatments. ^bValues in the same column for each test with superscripts in common were not significantly different (P < 0.05).

^cViscosity and color of the oils at the end of the first 10 h of heating were not measured. ^dPV of fresh SBO used in frying, of SBO extracted from fresh fried bread cubes, and of SBO extracted from stored fried bread cubes. For abbreviations see Table 1.

Colors. Darkness, redness, and yellowness in all oils increased as the length of heat treatment increased. The 79%OA was significantly less dark, red, and yellow than the other oils at the end of 20 h of heating, and there were no differences in darkness, redness, and yellowness among the other treatments, indicating the 79%OA had less polymerization and other related reactions and therefore was the most heat-stable oil among all treatments.

PV of the fresh oils and of the oils extracted from the fried bread cubes. The PV from the least to the greatest in the fresh oils and in the oils extracted from fresh fried and stored fried bread generally was directly related to the combined 18:2 and 18:3 concentrations in the oils and to the calculated oxidizability, except for the LL treatment. As with some of the previous tests, the reduced 18:3 concentrations of the LL treatment elevated its stability above the predicted order. The 79%OA tended to be the most stable oil, and the control tended to be the least stable oil during storage of the fried bread cubes according to the PV.

A common perception of professionals working with edible oils is that the quality of a blended oil is only as stable as the poorest oil present. In this study, however, the impact of blending on oil stability indices was generally directly and linearly related to the percentage of control oil present and furthermore to the combined concentration of 18:2 and 18:3, and to the calculated oxidizability, IV, CDA content, and viscosity (Figs. 1A-D). Values at 20 h of heating were selected in Figure 1 to demonstrate this finding visually. The impact of blending oils on the PV and polar compounds was not linearly related to the percentage of the control in the blended oils, but the values actually were better than would be predicted based on the percentage of the control and/or the total 18:2 and 18:3 concentrations (Figs. 2A, B). The OSI and HunterLab color values for the oils at 20 h of heating showed that the presence of a small amount of the control in the blended oils greatly reduced the stability (Figs. 2C–F).



FIG. 1. The impact of the percentage of control oil present in oil blends on the stability indices at 20 h of heating. The low-linolenate (LL) soybean oil (SBO) values are also reported, even though this oil was not blended with the control. The vertical (*y*) axes are (A) calculated oxidizability, (B) iodine value of fresh oil, (C) conjugated dienoic acid content (%), and (D) viscosity (cP). The horizontal (*x*) axis—0, 25, 50, 75, and 100—represents the percentage of the control (by weight) in the oil, and LL represents the LL SBO treatment.



FIG. 2. The impact of the percentage of the control oil present in oil blends on the stability indices at 20 h of heating. The LL oil values are also reported, even though this oil was not blended with the control. The vertical (*y*) axes are (A) PV (mequiv/kg), (B) polar compounds (%), (C) oil stability index of fresh oil (h), and (D–F) Hunter-Lab color values. The horizontal (*x*) axis—0, 25, 50, 75, and 100—represents the percentage of the control (by weight) in the oil. For abbreviations see Figure 1.

Overall, the 79%OA was the most stable oil treatment. In general, the lower the 18:2 and 18:3 concentrations, the greater the stability of the oil treatment, except that the greatly reduced 18:3 concentration in the LL treatment elevated its stability to be greater than or equal to that of the 37%OA, making it more stable than its predicted stability. Blending a poor-stability oil, such as conventional SBO, with a high-stability oil had a profound effect on the OSI and color of the blended oils, but not on other stability indicators. The evaluation of sensory characteristics and volatile compounds of the fried bread cubes in the oils is presented in a related paper (20).

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