

Frying Stability of Soybean and Canola Oils with Modified Fatty Acid Compositions

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Pilot plant-processed samples of soybean and canola (low-erucic acid rapeseed) oil with fatty acid compositions modified by mutation breeding and/or hydrogenation were evaluated for frying stability. Linolenic acid contents were 6.2% for standard soybean oil, 3.7% for low-linolenic soybean oil and 0.4% for the hydrogenated low-linolenic soybean oil. The linolenic acid contents were 10.1% for standard canola oil, 1.7% for canola modified by breeding and 0.8% and 0.6% for oils modified by breeding and hydrogenation. All modified oils had significantly ($P < 0.05$) less room odor intensity after initial heating tests at 190°C than the standard oils, as judged by a sensory panel. Panelists also judged standard oils to have significantly higher intensities for fishy, burnt, rubbery, smoky and acrid odors than the modified oils. Free fatty acids, polar compounds and foam heights during frying were significantly ($P < 0.05$) less in the low-linolenic soy and canola oils than the corresponding unmodified oils after 5 h of frying. The flavor quality of french-fried potatoes was significantly ($P < 0.05$) better for potatoes fried in modified oils than those fried in standard oils. The potatoes fried in standard canola oil were described by the sensory panel as fishy.

KEY WORDS: Canola oil, flavor, free fatty acids, frying, low-erucic acid rapeseed oil, oils, polar compounds, sensory, soybean oil.

The lack of frying stability and the poor frying oil performance of soybean and canola (low-erucic acid rapeseed) oils have been well documented (1-6). Linolenic acid (Ln) has been identified by various researchers as the primary factor contributing to deterioration of these oils during high-temperature use. Previous research at our Center has shown that oils with high Ln contents have typical acrid and fishy odors when heated to frying temperatures above 150°C (4-5). Foods fried in these oils and consumed soon after preparation have an unacceptable fishy flavor, whereas foods fried and aged before consumption, such as snack-type foods, have decreased shelf life because of the development of rancid and painty flavors. In the late 1960s, research on oil stability showed that hydrogenating soy oil or blending soy oil with nonlinolenate oils increased stability because of the decrease in Ln (6-8). Oil blending is effective and is used depending on the price of the other oils (cottonseed oil is often used). However, hydrogenation imparts an unpleasant characteristic odor/flavor to the oil. This "hydrogenation" odor is really a compound odor, consisting of several individual odors, such as fruity, flowery or waxy. This complex odor/flavor decreases the quality of the oil and the foods fried in it. An alternative to blending and hydrogenation to decrease Ln is modification of oils by breeding (9). Researchers have shown that stabil-

ity of the frying oil is increased with decreased levels of this fatty acid (10-12).

This report continues efforts to provide more information on frying stability and frying performance of new modified oils as they are developed. Effects of lowering Ln first by breeding, followed by further decreases with hydrogenation, were investigated. Hydrogenation of oils with reduced Ln may not have the characteristic off-odor/flavor found in oils hydrogenated from Ln levels at 8-10% (13). This current research reports on studies with soybean and canola oils modified by breeding or breeding/hydrogenation. The purpose of this work was to identify characteristic odors and flavors of heated oils and fried food and to determine frying stabilities and frying performances of modified soybean and canola oils.

EXPERIMENTAL PROCEDURES

Materials. Unmodified soybean (SBO) and canola oils (CAO) were obtained from commercial processors as refined, bleached, deodorized oils with only citric acid added. Both oils were processed according to accepted commercial practices. The modified oils were processed from soybeans and canola bred for lower Ln levels in programs by InterMountain Canola Company (Cinnaminson, NJ). The altered oils were processed to finished oils under pilot plant conditions, and portions of the oils were further modified by various levels of hydrogenation and then deodorized (POS Pilot Plant, Saskatoon, Saskatchewan, Canada).

Methods. The frying protocol for the oils included intermittent frying of potatoes at 190°C with total heating/frying time of 40 h. Six thousand grams of each oil was heated in 14-L capacity fryers (Model 250 EL; Cecilware, West Palm Beach, FL). Oils were heated for 8 h each day for 5 d. Fresh Idaho russet potatoes were cut into 8-cm lengths of shoestring size (0.5 cm × 0.5 cm) and fried in 150-g batches. A total of sixteen batches of potatoes were fried each day for 5 min/batch with the exception of par-frying and finish frying potatoes. Oil temperature was held at 190°C; however, this decreased to 160°C as potatoes were initially added. Each day, 300 g of fresh oil was added as makeup oil to each sample.

Sensory evaluation. The fryers were placed in small laboratory hoods in a room odor facility as previously described (5,10). The odor intensity of the heated oil was evaluated by a trained, experienced 16-member panel after 1, 10, 20 and 30 h of oil heating and frying. Panelists rated the oil odor for overall intensity and for individual odor intensities on a 10-point intensity scale with 0 = no odor and 10 = strong intensity (14). The french fries used for sensory testing were parfried in 150-g batches for 2 min on Day 1, frozen and then finish-fried for 2 min prior to panel sessions on Days 2, 3, 4 and 5 after 10, 20, 30 and 40 h of oil use, respectively. A 15-member panel trained and experienced in evaluating fried foods rated the potatoes on a 10-point quality scale with 1 = bad quality and 10 = excellent quality (14).

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Oil characterization. Fatty acid compositions of the initial oils were determined by capillary gas chromatographic (GC) analysis with a Varian 3400 GC (Palo Alto, CA) equipped with a SP2330 column (30 m, 0.25 mm i.d., 0.20 μ m film thickness) (Supelco, Bellefonte, PA). After sample injection, the column temperature was held at 170°C for 10 min. The temperature was programmed to increase at 3°C/min to 220°C, with a final hold of 10 min. Free fatty acid (FFA) contents were measured in duplicate by the AOCS Method Ca 5a-40 (15). The percent polar compounds were determined in duplicate by the Association of Official Analytical Chemists' column chromatography method (16). Foam height (in cm) was measured in duplicate in the fryers after 10, 20, 30 and 40 h of heating and frying at 190°C. A 15-cm stainless-steel measure with 10-mm gradations was held in the center of the fryer, and a reading was taken 30 s after a 150-g batch of fresh shoestring potatoes was placed in the fryer. The height of oil prior to each frying was subtracted from the measurement to determine exact foam height.

Statistical analysis. Data were interpreted by analysis of variance (17). Statistical significance was expressed at the $P < 0.05$ level unless otherwise indicated.

RESULTS AND DISCUSSION

Fatty acid composition. The fatty acid composition of the SBOs showed a range of iodine values from 131 for SBO to 92 for an oil modified by breeding to a Ln content of 3.7 (Lo Ln), followed by hydrogenation to a Ln value of 0.4 (Lo Ln-Hyd) (Table 1). The SBO had a 6.2% Ln content.

The CAOs ranged in iodine value from 114 for CAO to 77 for an oil modified to a Ln level of 1.7% (Lo Ln), with a further reduction in Ln to 0.7% (Lo Ln-Hyd) by hydrogenation (Table 2). A brush hydrogenation process decreased the Lo Ln sample from 1.7 to 0.8% Ln (Lo Ln-Br Hyd). By these procedures, *trans* C18:3 was not detected in any of the oils.

Oil deterioration measurements. FFAs, which measure oil hydrolysis, increased in the SBOs with increasing oil usage as expected (Fig. 1). The SBO had the highest FFA levels, followed by the Lo Ln-Hyd soy and the Lo Ln soy. The FFA values after 45 h of heating and frying were 0.24 for soy, 0.23 for Lo Ln-Hyd soy and 0.21 for Lo Ln soy.

TABLE 1

Fatty Acid Composition of Soybean Oils

Fatty acid composition	Oils		
	SBO ^a	Lo Ln ^b	Lo Ln ^c -Hyd
C16:0	11.4	11.4	9.9
C18:0	3.9	4.4	4.0
C18:1- <i>cis</i>	24.2	25.0	48.1
C18:1- <i>trans</i>			16.3
C18:2- <i>cis</i>	54.4	55.3	17.6
C18:2- <i>trans</i>			3.0
C18:3	6.2	3.7	0.4
Iodine value	131	126	92

^aStandard soybean oil.

^bLow-linolenic acid soybean oil.

^cHydrogenated, low-linolenic acid soybean oil.

TABLE 2

Fatty Acid Composition of Canola Oils^a

Fatty acid composition	Oils			
	CAO ^b	Lo Ln ^c	Lo Ln ^d -Br Hyd	Lo Ln ^e -Hyd
C16:0	4.3	5.1	5.3	5.3
C18:0	1.7	1.9	2.6	5.1
C18:1- <i>cis</i>	60.5	65.6	69.0	39.7
C18:1- <i>trans</i>			3.9	46.6
C18:2- <i>cis</i>	20.8	24.0	16.5	0.5
C18:2- <i>trans</i>			0.3	1.1
C18:3	10.1	1.7	0.8	0.7
C20:1	1.3	0.8	0.8	0.6
C22:1	0.5	0	0	0
Iodine value	114	91	91	77

^aLow-erucic acid rapeseed oil.

^bStandard canola oil.

^cLow-linolenic acid canola oil.

^dBrush hydrogenated, low-linolenic acid canola oil.

^eHydrogenated low-linolenic acid canola oil.

The FFA levels in the CAOs showed no significant differences between the Lo Ln and the Lo Ln-Br Hyd CAOs at any of the evaluation times (Fig. 1). The FFA levels in the CAO and Lo Ln-Hyd oils were significantly higher than the other two CAOs. After 45 h of usage, oils had FFA of .34 for Lo Ln; .37 for Lo Ln-Br Hyd; .48 for Lo Ln-Hyd; and .66 for CAO.

The decreased levels of Ln in the modified SBOs resulting from either breeding or breeding/hydrogenation helped contribute to significantly lower amounts of polar compounds compared to the SBO (Fig. 2). The SBO

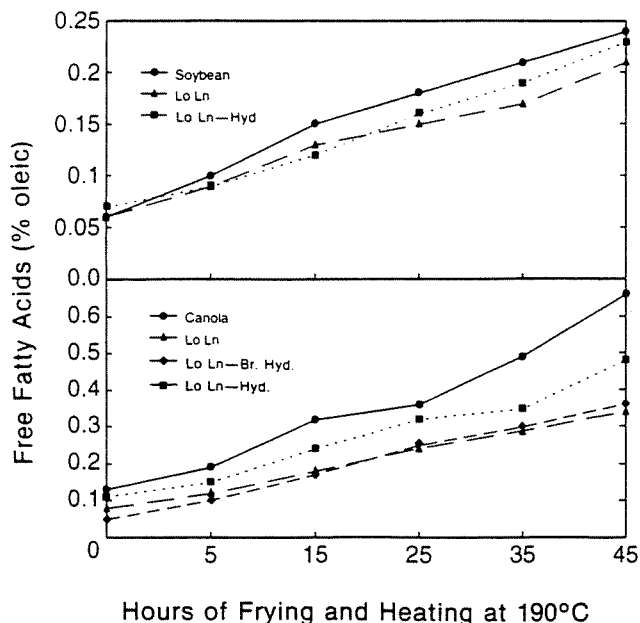


FIG. 1. Free fatty acids in soybean and canola oils. Lo Ln, low linolenic; Lo Ln-Hyd, low linolenic, hydrogenated; Lo Ln-Br Hyd, low linolenic, brush hydrogenated.

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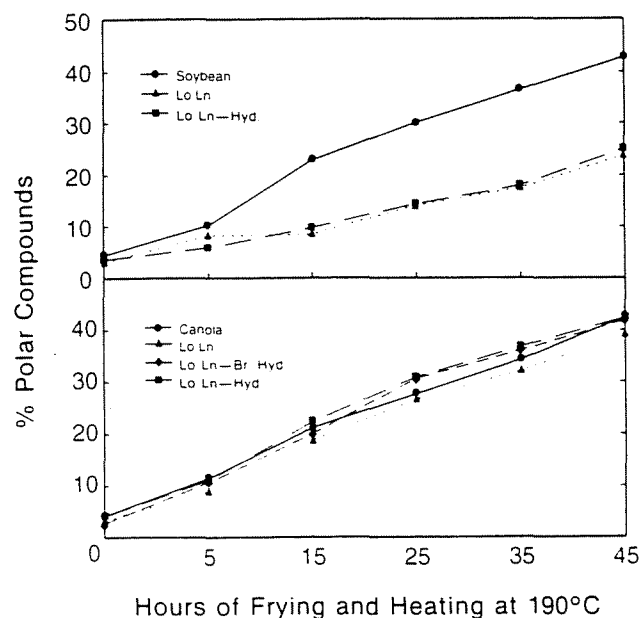


FIG. 2. Percentage polar compounds in soybean and canola oils. See Figure 1 for abbreviations.

contained 42% polar compounds after 45 h of heating and frying, whereas both modified SBOs only had 25% polar compounds. A standard level of 27% polar compounds is used in Europe to indicate severely deteriorated oil. The SD for polar compounds in the soybean varieties ranged from 0 to 1.6 with an average deviation of 0.9.

The amount of polar compounds formed in the modified CAOs and CAO were similar at all evaluation times (average SD = 0.7) (Fig. 2). The Lo Ln CAO had the least amount of polar compounds of all the CAOs at each frying time; however, the levels were high—27%—even after only 25 h of oil usage.

It is well known that unsaturated fatty acids are more susceptible than saturated ones to oxygen attack during thermal oxidation, and this can result in higher levels of polar compounds. Therefore, the level of polar compounds in the frying oils should be related to the degree of unsaturation of the oil. However, previous reports in the literature are not consistent in finding high correlations of unsaturation and polar compounds. Dobarganes and Perez-Camino (18) reported a trend toward higher polar compounds as unsaturation increases. In their study, palm oil with 56% unsaturates was heated for 100 h at 195°C and had a polar compound level of 58%. Olive oil with 86% unsaturation was treated under the same conditions and had a polar content of 66%. On the other hand, they found that olive oil and SBO with similar unsaturation (86%) had polar compounds of 66 and 71%, respectively. Sebedio and co-workers (19) found similar results for peanut and SBOs. They reported that the percentages of polar compounds in the oils were equivalent after up to 30 h of frying french fries. Work by Chu (20) supports the findings that unsaturation is not always a good predictor of polar compound formation. In that study, a blend of palm olein:SBO with an iodine value (IV) of 101 and a sesame:SBO blend with an IV of 122 were used for frying for 16 h. Total polar compounds in the blends were

similar at 14 and 15%, respectively. In this present study, both the Lo Ln SBO and Lo Ln-Hyd SBO had significantly less total polar compounds than SBO or any of the CAOs after 15 to 45 h of heating and frying. We observed these results even though the three SBOs had similar levels of unsaturation (84–85%). Unsaturation of the oil is probably only one of many compositional factors affecting the formation of total polar compounds.

The amount of foaming in a used frying oil is another measure of fat deterioration. The values in this study represent the level of foam above the surface of the oil as fresh potatoes were fried. There were no significant differences between the two modified SBOs; however, the SBO had significantly higher foam height than the other two oils at the 20-, 30- and 40-h testing periods (Fig. 3). In addition, the foam height in the modified SBOs was less than 1.0 cm at every sampling time.

The variations in foam heights of CAOs were not significantly different until 20 h of oil usage (Fig. 3). The CAO had significantly more foam development than the modified CAOs at the 20-, 30- and 40-h times.

Foam height measurement was the most sensitive test for differences between modified and unmodified oils of both oil types. Polar-compound analysis was sensitive to the differences in modification in SBO but not CAO, whereas FFA was a better indicator of differences for CAOs than for SBOs.

Room odor. The overall room odor intensities of the SBOs showed that reducing the Ln content to 3.7% significantly decreased the odor score at all evaluation times compared to the standard SBO with 6.2% Ln (Table 3). The overall odor intensity for the Lo Ln-Hyd soy sample was significantly less than the SBO after only the 1- and 10-h testing periods, but significantly stronger than the Lo Ln soy oil at all times except the 1-h test. The fishy odor, which is characteristic of heated linolenate-containing oils, was present in all three oils for the initial 1-h

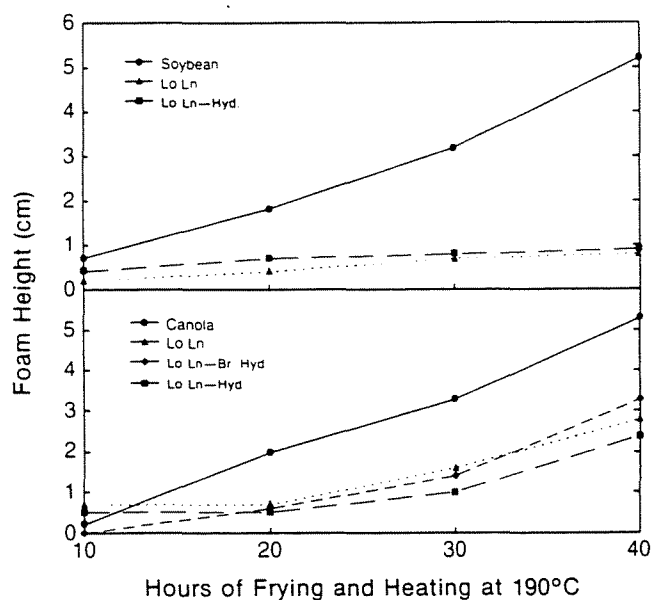


FIG. 3. Foam heights in soybean and canola oils. See Figure 1 for abbreviations.

TABLE 3

Sensory Analyses of Soybean Oils and Food Fried in Soybean Oils

Oils	Heat/fry at 190°C (h)	Analyses		
		Room odor ^a intensity scores	Fishy odor ^b intensity scores	French fries ^c quality scores
Soybean	1	6.6	2.8	—
	10	6.2	1.0	5.8
	20	6.1	0.5	5.9
	30	5.8	0.7	6.1
	40	5.8	0.8	5.9
Lo Ln	1	5.1	0.3	—
	10	4.2	0.5	7.4
	20	4.5	0.7	7.2
	30	4.1	0.6	7.1
	40	4.2	0.8	6.9
Lo Ln-Hyd	1	5.6	1.7	—
	10	5.2	0.2	7.0
	20	5.5	0.0	6.9
	30	5.8	0.1	6.8
	40	5.9	0.0	6.7

^aRoom odor intensity: 0 = none; 10 = strong.

^bFishy odor (of frying oils) intensity: 0 = none; 10 = strong.

^cFrench-fried potato quality: 10 = excellent; 1 = bad; LSD = 1.0 ($P < 0.05$). See Table 1 for abbreviations.

evaluation but was significantly lower in the Lo Ln sample (Table 3). The intensity of this odor decreased in the SBO as heating and frying time increased and disappeared in the Lo Ln-Hyd soy sample after 20 and 40 h of heating and frying. The fishy odor intensity increased slightly in the Lo Ln SBO as frying time increased. Other off-odors contributing to the overall odor intensity were acrid in all oils and hydrogenation in the Lo Ln-Hyd oil. The SBO had high intensity levels of acrid odor, ranging from 2.9 for the 1-h sample to 2.0 for the 40-h oil. The Lo Ln and Lo Ln-Hyd SBOs had initial acrid scores of 1.6 and 1.3, respectively. These values decreased slightly over the 40-h test. The hydrogenation odor increased with increased heating and frying of the Lo Ln-Hyd from a low of 1.9 at 1 h to a high of 3.4 after 40 h, but was not present in either the SBO or the Lo Ln SBO.

The CAO had significantly more overall room odor intensity than the modified CAOs only at the initial 1 h evaluation period (Table 4). In subsequent tests at 10, 20, 30 and 40 h, no significant differences were noted. The off-odors in the unmodified oil were predominantly fishy and acrid. The fishy odor intensity in the CAO was significantly higher than in the other CAO samples at 1 and 10 h (Table 4). The acrid ratings for the CAO ranged from 2.4 for the 1-h sample to 3.0 for the 40-h oil. The fishy odor intensity of the hydrogenated oils increased slightly over time—0.1 to 0.6. The Lo Ln CAO had low levels of fishy odor intensity (0.5–1.2) at all evaluation times. Hydrogenation odor was present in both the Lo Ln Br Hyd CAO and the Lo Ln Hyd CAO but not in the CAO or the Lo Ln CAO.

Fried food. The quality of french fries fried in both of the modified SBOs were significantly better than the potatoes fried in the SBO (Table 3). The potatoes fried in the SBO had less fried-food and potato flavors and stronger fishy flavor than the potatoes fried in the modified oils. In the SBO french fries, the fishy flavor intensity was highest at 10 h with a score of 2.0, which decreased

to 0.5 after 40 h. Both modified oils produced french fries with slight (0.2) to no fishy flavor. Potatoes fried in Lo Ln-Hyd SBO had a slight hydrogenation flavor at all frying times.

The quality of the french fries in all modified CAOs were significantly better than those fried in CAO (Table 4). The potatoes fried in CAO had stronger flavor intensities of fishy than the potatoes fried in the modified oils. This finding is in contrast to that of Dobbs *et al.* (2) who reported that the fishy odor of CAO did not transfer to the flavor of donuts fried in the same oil. The potatoes fried in the hydrogenated oils had a slight hydrogenation flavor.

Characteristic odors/flavors. Introduction of these newly modified oils as frying oils has generated interest in the types of odors and flavors characteristic of the oils and the resulting fried foods. Standard soy and canola oil odors formed during high-temperature heating—acrid, fishy, burnt and rubbery—are characteristic of any Ln-containing oil (Table 5). As the Ln content is decreased, the fishy odor is less evident, although the rubbery odor may still be detected. Predominant odors in the Lo Ln oils, modified by breeding only, were fried food and acrid. Use of hydrogenation to further reduce Ln content produced hydrogenation odors and flavors, although at less intense levels than found in oils hydrogenated from 8% Ln (4). The hydrogenation off-odor was still detectable, even when the initial Ln content of the oil to be hydrogenated was 1.7%.

In summary, most sensory and physical/chemical analyses showed that the quality and stability of Lo Ln SBO were equal to the Lo Ln-Hyd SBO. Both modified SBOs were better than the SBO in all tests (Table 6). The Lo Ln CAO was significantly better than the hydrogenated Lo Ln CAOs for only polar compounds (Table 6). All modified CAOs had better quality and stability than the CAO in all analyses except polar compounds.

Modification of fatty acid composition by breeding to reduce the Ln content produced soy and canola oils of

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TABLE 4

Sensory Analyses of Canola Oils and Food Fried in Canola Oils

Oils	Heat/fry at 190°C (h)	Analyses		
		Room odor ^a intensity scores	Fishy odor ^b intensity scores	French fries ^c quality scores
Canola	1	7.0	2.9	—
	10	6.3	1.6	3.4
	20	6.2	1.6	4.8
	30	6.1	1.5	4.0
	40	5.7	0.5	5.3
Lo Ln	1	5.9	1.0	—
	10	5.7	0.5	6.6
	20	5.6	0.9	6.7
	30	5.3	1.2	6.9
	40	5.4	0.9	6.7
Lo Ln-Br Hyd	1	6.0	0.1	—
	10	6.2	0.6	6.7
	20	5.6	0.3	6.4
	30	5.4	0.5	7.1
	40	5.1	0.6	7.0
Lo Ln-Hyd	1	6.0	0.1	—
	10	6.3	0.6	7.1
	20	5.7	0.2	6.7
	30	5.5	0.3	6.4
	40	5.4	0.4	6.4

^aRoom odor intensity: 0 = none; 10 = strong.

^bFishy odor (of frying oils) intensity: 0 = none; 10 = strong.

^cFrench-fry potato quality: 10 = excellent; 1 = bad. LSD = 1.0 ($P < 0.05$). See Table 2 for abbreviations.

TABLE 5

Characteristic Odors and Flavors of Heated Fats/Oils^a

Oil	Heated oil odors	Fried-food flavors
Soybean		
SBO	Acrid, fried food, fishy, burnt, rubbery	Fried food, fishy
Lo Ln	Fried food, acrid	Fried food
Lo Ln-Hyd	Hydrogenated, fried food, fruity	Fried food, hydrogenated
Canola		
CAO	Acrid, burnt, fried food, fishy, rubbery	Fried food, fishy
Lo Ln	Fried food, acrid, burnt, woody	Fried food
Lo Ln-Br Hyd	Fried food, fruity, hydrogenated	Fried food, hydrogenated
Lo Ln-Hyd	Hydrogenated, fried food, fruity	Fried food, hydrogenated

^aSee Table 2 for abbreviations.

TABLE 6

Frying Stability of Soybean Oils and Canola Oils with Modified Fatty Acid Compositions

	Soybean oils	Canola oils
Sensory analyses		
Room odor intensity	Lo Ln = Lo Ln-Hyd < SBO	Lo Ln = Lo Ln-Br Hyd = Lo Ln-Hyd < CAO
French-fry quality	SBO < Lo Ln = Lo Ln-Hyd	CAO < Lo Ln = Lo Ln-Br Hyd = Lo Ln-Hyd
Physical/chemical analyses (oils)		
Foam height	Lo Ln = Lo Ln-Hyd < SBO	Lo Ln = Lo Ln-Br Hyd = Lo Ln-Hyd < CAO
Polar compounds	Lo Ln = Lo Ln-Hyd < SBO	Lo Ln < Lo Ln-Br Hyd = Lo Ln-Hyd = CAO
Free fatty acids	Lo Ln < Lo Ln-Hyd < SBO	Lo Ln = Lo Ln-Br Hyd < Lo Ln-Hyd < CAO

significantly improved quality and stability compared to unmodified oils. Hydrogenation of low-Ln oils did not improve the oil quality further, and with the CAOs it even decreased quality because of the hydrogenation off-odors/flavors.

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