Frying Performance of Genetically Modified Canola Oils

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ABSTRACT: The frying performance of low linolenic and high oleic canola oils was compared to regular and hydrogenated canola oils. The antifoaming agent dimethylpolysiloxane (2 ppm) was added to all frying oils. Potato chips were fried in the four oils over a 5-d period for a total of 40 h of frying. Oil samples were collected each day and analyzed for conjugated dienoic acids, free fatty acids, polymers, oxidation products, and polar components. Polar components were determined by the gravimetric method and by thin-layer chromatography with flame-ionization detection. The initial quality of the four oils was similar except in the amount of tocopherols present. All oils deteriorated after 5 d of frying but differences were not as anticipated, possibly as a result of observed differences in tocopherol levels.

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KEY WORDS: Canola oil, frying stability, high oleic, hydrogenated oil, low linolenic, polar materials.

During frying, changes take place in an oil as a result of thermal degradation, oxidation, and hydrolysis. The rate of decomposition depends on the composition of the oil, the temperature and length of frying, continuous or intermittent frying, type of food fried, and fresh oil replenishment (1–6). Among these factors, the degree of unsaturation of the oil is an important factor influencing the frying stability of the oil. Canola oil has high levels (9–11%) of linolenic acid (18:3) and therefore has limited frying stability. Reduction of the linolenic acid content in canola oil by genetic modification should result in a more stable frying oil.

Studies undertaken to examine modified canola oils have found a lower intensity of "heated room odor" for low-linolenic canola oil (LLCO) compared to regular canola oil (RCO) (7–9). Higher odor and flavor quality scores were found for french fries fried in LLCO than fries fried in RCO and hydrogenated canola oil (HYCO) (9). Potato chips fried in LLCO and high-oleic canola oil (HOCO) had improved flavor quality scores as compared to chips fried in RCO (10). Reduction in the linolenic acid content in canola oil resulted in significantly lower levels of free fatty acids, carbonyls, and dienals in oils heated 10 min at 185°C (8). Lower accumulation of free fatty acids and a lower foam height were found in LLCO compared to RCO over 45 h of frying of french fries, but the amount of polar materials was not found to be significantly different between the two oils (9). In contrast, a study by Warner *et al.* (10) using continuous frying rather than batch frying found the amount of polar compounds in LLCO and HOCO was significantly lower than in RCO, but free fatty acid levels were significantly lower in RCO compared to the other two oils. Thus, although there is evidence that there is improved frying stability with genetically modified canola oils, the results are not consistent, suggesting a need for further investigation. Therefore the objective of this study was to compare the frying performance of LLCO and HOCO with RCO and HYCO. A second objective was to evaluate two different methods for the determination of polar components in the frying oils. Polar components are considered by regulators in most European countries to be a good measure of frying oil deterioration (11). The classical method for determining polar compounds involves the elution of the nonpolar fraction from a silica column using solvents (12). A less time-consuming gravimetric procedure introduced by Sebedio *et al.* (12) uses silica gel Sep-Pak cartridges. A high correlation was found between this method and the classical method (12). Components of different polarity can also be separated by thin-layer chromatography with flame-ionization detection (TLC–FID) (13,14). The advantage of the TLC–FID procedure is that polar (monoglycerides, diglycerides, free fatty acids, and highly polar components) and nonpolar (triglycerides) components can be separated and their respective amounts determined in one step. Thus, the gravimetric and the TLC–FID procedures for measuring polar components in frying oils were evaluated.

EXPERIMENTAL PROCEDURES

Materials. Commercially refined, bleached and deodorized RCO and LLCO were obtained from CanAmera Foods Ltd. (Altona, Manitoba, Canada). Citric acid had been added to the oils during processing. Commercially processed HYCO was obtained from CanAmera Foods Ltd. (Nipawin, Saskatchewan, Canada). Laboratory refined, bleached and deodorized HOCO was obtained from Anderson Clayton/Humko (Memphis, TN). Norchip variety potatoes were obtained from the Southern Potato Company (Winkler, Manitoba, Canada).

Frying protocol. The antifoaming agent dimethylpolysiloxane (Dow Corning, Toronto, Ontario, Canada) was added to RCO, LLCO, and HOCO in the amount of 2 ppm (15). To

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achieve the required concentration, a mix of silicone in oil was prepared as follows: 0.17 g of silicone was added to 20 g of oil, and 1 g of this mixture was added to 4.25 kg of oil. Dimethylpolysiloxane (2 ppm) was added to HYCO by the manufacturer.

Unpeeled potatoes were washed and sliced to a thickness of 1.2–1.3 mm (16). The slices were washed under cold running water to remove surface starch and placed in a pan of cold water until required for frying. Potato slices (approximately 60–70 g) were removed from the pan, blotted with paper towels, and spread in a single layer on the wire frying rack. A model 611 mini fryer (Belshaw Bros., Inc., Seattle, WA) with 5-kg capacity was used. The initial amount of oil used was 4.25 kg. On the first day of frying, the oil was conditioned by heating to 185 ± 5°C and held at this temperature for 30 min. Potato slices were lowered into the oil, and chips were fried until bubbling of the oil ceased (approximately 2 min). After frying, the chips were allowed to drain for 5 min and were then transferred to paper towels and blotted to remove excess oil. Thirty-two batches of potato chips were fried each day, 15 min apart for a total of 8 h of frying. Chips were fried in each oil for 5 d (40 h of frying).

On the second and consecutive frying days, the oil was weighed prior to frying to determine the amount of fresh oil needed to replenish the oil in the fryer. The antifoaming agent/oil mixture was added to achieve 2 ppm of silicone in the make-up oil. The oil was then heated to 185 ± 5°C before frying of the first batch of chips.

Sampling of oil for analyses. Samples of oils for analyses were taken each morning after the oil had cooled overnight at 20°C and before it was measured and replenished with fresh oil. The 0 h time oil was collected after the oil was conditioned for 30 min at 185 ± 5°C. For each oil, six samples of oil were gathered (0 h, day 1, day 2, day 3, day 4, and day 5).

Chemical and instrumental analyses. The initial quality of the fresh, nonheated oils was determined by peroxide value (PV) and free fatty acids (FFA) using AOCS methods Cd 8-53 and Ca 5a-40, respectively (17). Tests were performed in duplicate. Fatty acid composition was determined by gas chromatography of methylated samples. A Hewlett-Packard 5890A (Palo Alto, CA) gas chromatograph (GC) with fused-silica capillary column 30 m × 0.25 mm i.d. coated with polar phase Supelcowax 10 (Supelco Inc., Bellefonte, PA) was used. The GC was equipped with autosampler, 3392A Integrator, and a flame-ionization detector. The temperature of the detector and the injection port was held at 250°C. The carrier gas was hydrogen. The column temperature was programmed from 195 to 235°C at a rate 2°C/min and was held at lower and upper temperatures for 3 and 4 min, respectively. The injected amount was 3 µL. The amounts of individual fatty acids were quantitated using an internal standard, $C_{21:0}$ (heneicosanoic acid).

Frying performance of the oils was determined by measuring conjugated dienoic acids (CDA) by AOCS method Ti 1a-64 (17), FFA by AOCS method Ca 5a-40 (17), and polymers and oxidation products by quantification of noneluted materials according to AOAC method 977.17 (18). The levels of unsaturated fatty acids (18:1, 18:2, 18:3) were monitored in the oils over the 5 d of frying using gas chromatography of methylated samples described previously. The amounts of each of these fatty acids were expressed as ratios to the amount of 18:0 present in the oil. This acid (18:0) was used since saturated fatty acids experience the least amount of change during high-temperature exposure (19). Polar components were determined gravimetrically using Sep-Pak Vac 6 cartridge (Waters Co. Division of Millipore Corp., Milford, MA) containing 1 g of silica. The separation of the nonpolar fraction was done using a 20-mL mixture of petroleum ether/diethyl ether (90:10, vol/vol). The polar fraction was eluted with 30 mL of methanol. Polar components were also determined by TLC–FID by adapting the method of Sebedio *et al.* (13). Developing solvents were prepared according to Przybylski and Eskin (20). An Iatroscan TH-10 analyzer (Iatron, Tokyo, Japan) was used in conjunction with the ChromPerfect Direct software (Justice Innovations Inc., Mountain View, CA). The hydrogen and air flow rates were constant at 190 mL/min and 2.15 L/min, respectively. Thin layer consisted of quartz rods covered with a layer of silica—Chromarods S III. The scan speed was set at 35 s per rod. The quantification of the individual polar compounds present was based on individual calibration curves for triglycerides, free fatty acids, diglycerides, and highly polar compounds. The total amount of polar components was determined as a sum of FFA, 1,2- and 1,3-diglycerides, and highly polar compounds.

Statistical analyses. Analysis of covariance was used to analyze the data using the general linear model procedure (21). The model included type of oil, frying day, and their interaction term. A *t*-test (with 16 degrees of freedom, $\alpha = 0.05$) was used to estimate the difference in slopes and intercepts, above and beyond error variability. When the distribution of the residuals lacked normality a natural logarithm data transformation was used in the model. Pearson's correlation coefficients (21) were used to determine the relationship between the two methods used to measure polar components.

RESULTS

Initial quality of the oils. The fresh oils were of good quality with PV of 0.2, 0.4, 1.0, and 0.4 meq/kg for RCO, HYCO, LLCO, and HOCO, respectively. Hawrysh (22) reported that a PV of less than 2 meq/kg is an indication of a high-quality canola oil. The level of FFA in the four oils was no higher than 0.03% oleic.

The fatty acid composition of the four oils revealed that RCO had expected levels of oleic, linoleic, and linolenic fatty acids (Table 1). HYCO had no linolenic acid present, but had some linoleic and considerable amounts of oleic acid present. LLCO had smaller amounts of linolenic acid and slightly higher levels of oleic and linoleic fatty acids than RCO. HOCO had higher levels of oleic acid compared to RCO, which was similar to the amounts found in HYCO. HOCO also had a reduction in linolenic acid content compared to

TABLE 1
Fatty Acid Composition of Canola Oils

Oil	18:1	18:2	18:3[a]	SFA[b]	MUFA[b]	PUFA[b]
Regular	56.5	22.3	10.8	7.3	58.4	33.1
Hydrogenated	73.7	8.0	—	16.0	75.8	8.0
Low linolenic	58.2	27.9	3.7	6.4	60.0	31.6
High oleic	75.2	8.0	5.5	6.6	76.9	13.5

[a]Combined *cis* and *trans* isomers.
[b]SFA, saturated fatty acids; MUFA, monounsaturated fatty acids; PUFA, polyunsaturated fatty acids.

RCO, which was closer to the amount found in LLCO. Increased levels of linolenic acid *trans* isomers were also found in the HOCO, which may indicate that elevated temperatures were used during deodorization of the oil (23,24). The content of linoleic acid in HOCO was similar to that of HYCO.

Stability of the oils during frying. The accumulation of FFA increased over frying days for all four oils (Fig. 1). RCO had higher initial amounts of FFA compared to HOCO ($t_{16} = -2.35$, $P = 0.032$). HYCO had a significantly higher rate of FFA accumulation than LLCO ($t_{16} = -2.65$, $P = 0.018$).

As the days of frying increased, there was an increase in CDA in all oils except HYCO (Fig. 2). Lower levels of CDA were found initially in the LLCO than the other three oils (HYCO $t_{16} = 5.59$, $P < 0.001$; RCO $t_{16} = 3.91$, $P = 0.001$; HOCO $t_{16} = -5.06$, $P < 0.001$). HYCO had a significantly lower rate of accumulation of CDA compared to the other three oils (LLCO $t_{16} = 6.29$, $P < 0.001$; RCO $t_{16} = 4.88$, $P < 0.001$; HOCO $t_{16} = 2.73$, $P = 0.015$). LLCO and RCO had significantly greater rates of CDA accumulation than HOCO and HYCO ($t_{16} = 3.55$, $P = 0.003$; $t_{16} = 2.15$, $P = 0.047$, respectively). It is possible that the levels of polyunsaturated fatty acids (PUFA) may be influencing the accumulation of CDA. Liu and White (25) found canola oil, which had the lowest level of PUFA compared to several samples of soybean oil, exhibited the lowest accumulation of CDA during 40 h of frying of bread cubes. In the present study HOCO and HYCO, which had low levels of PUFA (Table 1), exhibited the lowest accumulation of CDA.

The rate of disappearance of 18:1 was not very pronounced over the 5 d of frying for all four oils, although LLCO showed a slight drop at frying day 5 (data not shown). LLCO and RCO showed a gradual decrease in 18:2, and RCO exhibited a gradual decrease in 18:3 over the 5-d frying period (data not shown).

The amount of polymers and oxidation products increased in all four oils over the 5 d of frying (Fig. 3), but the rates of

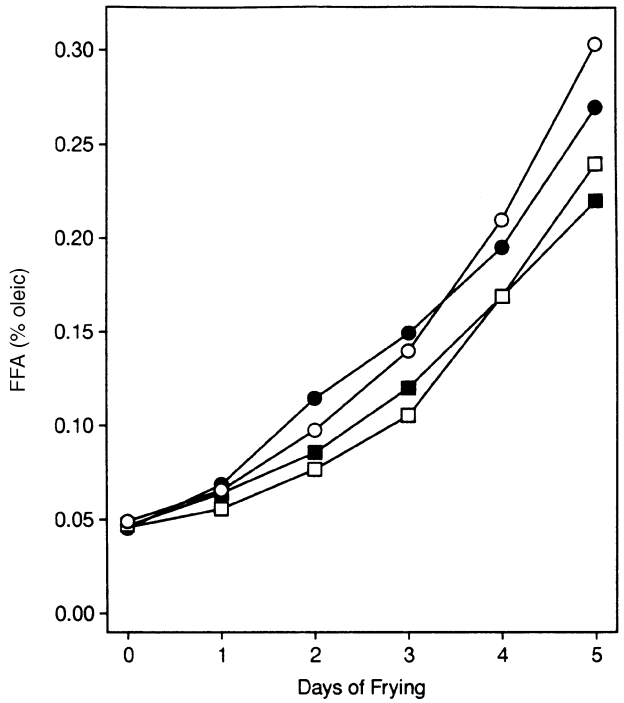

FIG. 1. Accumulation of free fatty acids (FFA) over 5 d of frying: ●, regular; ■, low linolenic; □, high oleic; and ○, hydrogenated canola oils.

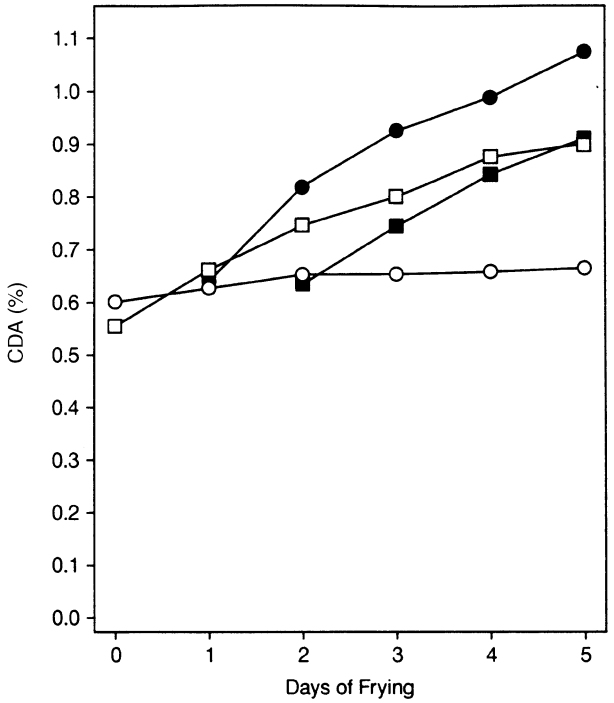

FIG. 2. Content of conjugated dienoic acids (CDA) over 5 d of frying: ●, regular; ■, low linolenic; □, high oleic; ○, hydrogenated canola oils. For 0 day low linolenic and 0 and 1 day regular canola oil 0% CDA was detected.

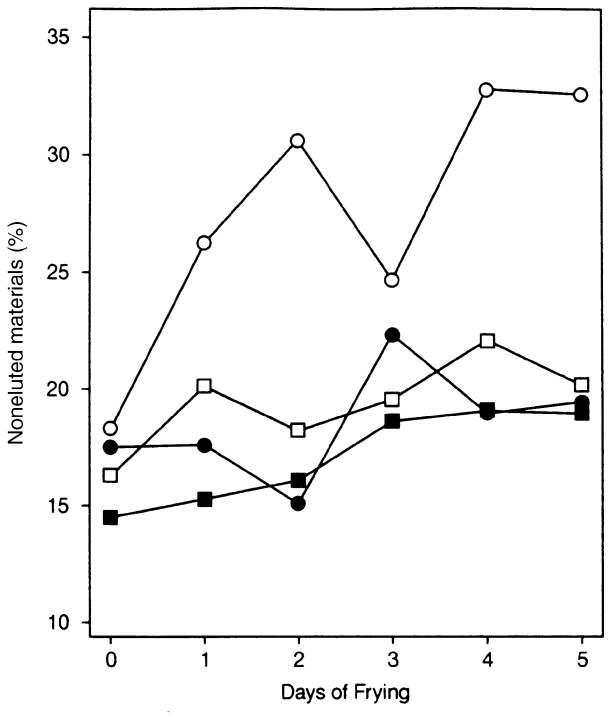

FIG. 3. Content of polymers and oxidation products (noneluted materials) over 5 d of frying: ●, regular; ■, low linolenic; □, high oleic; ○, hydrogenated canola oils.

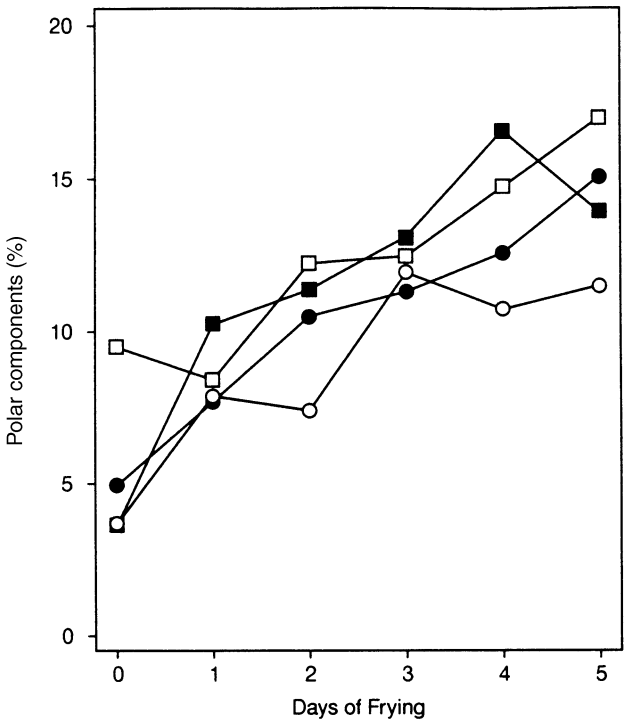

FIG. 4. Content of polar components as measured by gravimetric method over 5 d of frying: ●, regular; ■, low linolenic; □, high oleic; ○, hydrogenated canola oils.

accumulation were not significantly different among the oils. The initial amount of polymers was significantly higher in the HYCO than in the LLCO ($t_{16} = -3.58$, $P = 0.003$). These observations contradict Lumley (26) who reported that fats high in unsaturated fatty acids yield more polymers than fats low in unsaturated fatty acids.

Both the gravimetric and the TLC–FID determinations of polar components revealed an increase in polar components in the four oils with increasing frying days (Figs. 4 and 5). For both methods there was no significant difference in the rate of accumulation of polar compounds among the four oils. According to the gravimetric method, HOCO had a significantly higher level of polar compounds initially than HYCO ($t_{16} = -2.34$, $P = 0.032$). When polars were determined by TLC–FID, RCO had significantly higher initial levels of polar materials than LLCO ($t_{16} = -2.79$, $P = 0.013$) and HYCO ($t_{16} = -1.98$, $P = 0.065$), whereas HOCO had higher initial levels of polar compounds than RCO ($t_{16} = -3.23$, $P = 0.005$). The high initial amount of polar compounds present in HOCO may have been caused by the use of high temperatures during deodorization (23) as suggested by the high levels of 18:3 positional isomers. A correlation coefficient of 0.77 was found between the TLC–FID and the gravimetric methods, indicating that TLC–FID can be used with some confidence to determine the amount of polar components present in frying oils. This value was smaller than the correlation coeffient reported by Sebedio *et al.* (13) (0.77 vs. 0.95) likely owing to a difference in how the amount of polar materials were calculated in the two studies. Sebedio *et al.* (13) calculated the amount of polar compounds for both methods based on the amount of nonpolar fractions. In this study, the levels of polar

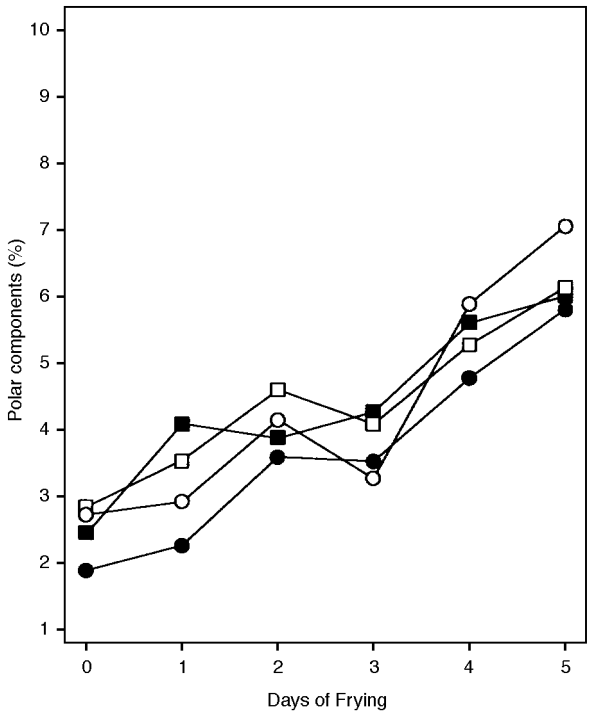

FIG. 5. Content of polar components as measured by thin-layer chromatography–flame-ionization detection over 5 d of frying: ●, regular; ■, low linolenic; □, high oleic; ○, hydrogenated canola oils.

materials in the TLC–FID method were calculated as a sum of FFA, diglycerides, and highly polar compounds, thus taking into account differences in chemical structures between newly formed degradation products.

DISCUSSION

No one oil had consistently lower initial amounts and/or rates of accumulation of the degradation products. All oils deteriorated after 5 d of frying (40 h of frying). LLCO and HOCO, the two genetically modified canola oils, showed a slight improvement in frying performance over RCO. HOCO had a lower rate of accumulation of CDA than RCO and had lower initial levels of FFA. LLCO had lower initial levels of CDA and polar materials than RCO. LLCO also showed some improvement in frying performance over HYCO as demonstrated by a lower rate of FFA accumulation and lower initial levels of CDA and polymers. Similar to this study, other researchers have not been able to show any consistent trends in the frying performance of canola oils. Warner *et al.* (10) found that RCO used for continuous frying of potato chips over two 9-h periods had significantly lower accumulation of FFA and intermediate amounts of polar compounds compared to genetically modified and hydrogenated canola oils. HOCO had significantly higher accumulation of FFA and lower amount of polar materials; HYCO had intermediate amounts of FFA and significantly higher amounts of polar substances; LLCO had amounts of FFA similar to that of HYCO, and the second-highest accumulation of polar materials after HYCO. In contrast, Warner and Mounts (9) found that RCO had higher amounts of FFA than LLCO after 45 h of batch-frying french fries. Accumulation of polar substances did not differ among the oils, although measurement of foam height (an indirect measure of polymers) singled out RCO as having the highest foam height after 20 h of frying. Eskin *et al.* (8) found that LLCO had significantly lower thiobarbituric acid and dienals than RCO after heating both oils for 10 min without frying at 185°C. The amounts of FFA and carbonyls were significantly lower in LLCO than in one of two RCO included in the study.

Studies undertaken to compare the frying performance of modified soybean oils have also not shown any consistent trend. Mounts *et al.* (28) found that regular and low-linolenic soybean oils did not differ significantly in the accumulation of FFA and polar compounds during heating and frying of french fries (20 h). No significant differences in the accumulation of CDA were found by Liu and White (24) for two regular and three low-linolenic soybean oils during heating and frying of bread cubes for 40 h. Dobarganes *et al.* (29) showed that high-oleic sunflower oils had lower initial amounts and lower accumulation of polar materials than regular sunflower oil during frying of 15 batches of french fries over a period of 5 h.

In the present study, there are several explanations as to why the observed differences were not as pronounced between the genetically modified canola oils and the regular canola oil as might be expected. Analysis of the tocopherol levels in the oils revealed that RCO and HYCO had twice as much total tocopherols as LLCO and HOCO had at the beginning of the frying period. After 5 d of frying, the initial level of tocopherols was reduced in LLCO and RCO by a factor of 2 and by a factor of 2.5 and 16.5 in HOCO and HYCO, respectively (30).

Another factor which may have slowed down the degradation of the oils could be the use of the antifoaming agent. Antifoaming agents added to soybean frying oils have been reported to exhibit a substantial antioxidant effect (31). Citric acid, a metal-chelating agent, was also added to the regular and low-linolenic canola oils which may have improved their stability to oxidation (27). Finally, the addition of fresh oil every morning to maintain the level of oil for frying likely slowed down the accumulation of degradation products (4,5). In the present study, 10–15% of fresh oil was added to the used oil each morning prior to frying.

Thus, the evaluation of the frying performance of an oil is a complicated task suggesting that more than one parameter should be measured to follow the changes that take place in the oil. Although the present study indicates a slight improvement in the frying stability of genetically modified canola oils the results are not convincing. Clearly, the fatty acid composition of the oil is not the only factor determining the frying stability of an oil. The presence of minor components such as tocopherols in the oil as well as processing effects (processing temperatures, addition of citric acid) and the frying practices used (addition of antifoaming agent, replenishing of the oil) all play an important role in influencing the stability of an oil.

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