Pan-Frying Stability of NuSun Oil, a Mid-Oleic Sunflower Oil

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ABSTRACT: Pan-frying is a popular frying method at home and in many restaurants. Pan-frying stabilities of two frying oils with similar iodine values (IV)—mid-oleic sunflower oil (NuSun oil; IV = 103.9) and a commercial canola oil (IV = 103.4)—were compared. Each oil sample was heated as a thin film on a Teflon-coated frying pan at ~180°C to a target end point of ≥20% polymer. High-performance size-exclusion chromatography analysis of the mid-oleic sunflower and canola oil samples indicated that the heated samples contained 20% polymer after approximately 18 and 22 min of heating, respectively. The food oil sensor values increased from zero to 19.9 for the canola sample and from zero to 19.8 for the mid-oleic sunflower sample after 24 min of heating. The apparent first-order degradation rate for the mid-oleic sunflower sample was 0.102 ± 0.008 min^{-1}, whereas the rate for the canola sample was 0.092 ± 0.010 min^{-1}. The acid value increased from approximately zero prior to heating to 1.3 for the canola sample and from zero to 1.0 for the mid-oleic sunflower sample after 24 min of heating. In addition, sensory and volatile analyses of the fried hash browns obtained from both oils indicated there were no significant differences between the two fried potato samples.

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KEY WORDS: Mid-oleic acid sunflower oil, NuSun oil, oil stability, pan-frying.

Pan- or griddle-frying is a popular cooking method in the home and in many restaurants. Even with the emphasis on low-fat diets, people are still fond of fried foods because of their crispy texture and desirable fried food flavor. The FA composition of the frying oil is a key factor influencing fried food flavor and oil stability. Ideally, frying oil should have a long frying life and good organoleptic attributes, and it should be low in saturated and *trans* FA (1) and relatively low in PUFA.

NuSun oil is a mid-oleic acid sunflower oil that was developed by plant geneticist Jerry F. Miller and biochemist Brady A. Vick in 1995 at the Northern Crop Science Laboratory of the (USDA-ARS in Fargo, North Dakota, using conventional breeding (2,3). Commercial production began in 1997–1998. The two main advantages of mid-oleic acid sunflower oil over regular frying oil ARE that it does not require hydrogenation for industrial frying applications and that it is produced from a non-genetically-modified plant.

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The purpose of this study was to compare the pan-frying stability of mid-oleic acid sunflower oil (NuSun) to a commercial frying oil with a comparable iodine value (IV). Our hypothesis was that oils with comparable IV should have the same pan-frying stability. The study was divided into two parts and included both heating and frying experiments.

EXPERIMENTAL PROCEDURES

Materials and methods. Two oils—mid-oleic acid sunflower oil (NuSun oil; ADM Packaged Oils, Decatur, IL) and commercial pure canola oil (Wesson, Fullerton, CA)—were compared. IV were determined according to AOCS Official Method Cd 1d-92 (4). FA profiles of the oil samples were determined by FAME analysis according to AOCS Official Method Ce 2-66 (4). Triheptadecanoin (Nu-Chek-Prep, Inc., Elysian, MN) was used as the internal standard. The column used was an Omegawax 250 [30 m, 0.25 mm i.d., film depth (d_f) = 0.25 μm (Supelco, Bellefonte, PA)] for the FA separation. The initial temperature was 180°C (2 min), and the temperature was ramped at 2°C/min to a final temperature of 230°C (10 min). Helium was used as the carrier gas (1 mL/min); and the injector split ratio was 1:80.

Heating. The pan-heating procedure was conducted according to the method of Soheili *et al.* (5). The heating operation was conducted in a square Teflon-coated frying pan (679 cm^2 surface area, 26.0 × 26.0 cm; Ultra-base; T-FAL, Rumilly, France) using an electric hot plate (30.5 × 30.5 cm; Thermolyne, Dubuque, IA) as the heating source. Oil temperatures were monitored with an IR thermometer (Model HP A2235M; Cole-Parmer, Vernon Hills, IL). To collect sufficient material for all analyses, heated oil from four identical heating replications was combined into a single pooled sample. Oil samples were heated for varying lengths of time (6, 12, 18, and 24 min of heating) to produce triplicate pooled samples. All analyses were conducted in duplicate.

Physicochemical analysis. The acid value (AV) of each oil sample was determined based on AOCS Official Method Cd 3d-63 (4). A food oil sensor (FOS) Model NI-21A (Northern Instruments Corporation, Lino Lakes, MN) was used to measure the dielectric constants of the oil samples.

Chromatographic analysis. Supercritical fluid chromatographic (SFC) and high-performance size-exclusion chromatography (HPSEC) analyses were accomplished as described by Artz *et al*. (6). The capillary column used for SFC analysis was a 14-m SB-cyano-25 (50 μm i.d., d_f = 0.25 μm) column. SFC-grade CO_2 (MG Industries, Malvern, PA) was used as the mobile phase. The HPSEC system consisted of five

Phenogel columns containing 5-µm particles with pore sizes of 500 (600 mm, 7.8 mm i.d.), 100, 100, 100, and 50 Å (each 300 mm in length and 7.8 mm i.d.; Phenomenex, Torrance, CA) connected to an ELSD (ELSD IIA; Varex Corp., Burtonsville, MD). THF was used as the mobile phase.

Frying. The frozen hash brown potato patties were stored at approximately −23°C. After warming to approximately 0°C, the patties (100 g per potato patty, approximately 8 cm in width and 10 cm in length; Ore-Ida, Boise, ID) were fried on an electric griddle (Model 515 TG; Star Manufacturing International Inc., St. Louis, MO) using each oil sample. Package labeling recommended frying at 177°C with 15 mL of oil. The griddle was preheated at 177°C for 30 min. The oil sample (15 mL) was measured and separated into three 5-mL samples. The first 5-mL sample was applied to the griddle and heated to 177°C. A hash brown patty was placed in the heated oil. Every 5 min, the patty was turned or flipped for uniform frying, and 5 mL of oil was added until the entire 15 mL of oil was used. The total frying time was 25 min.

Sensory evaluation of fried hash browns. Four men and six women were selected to participate as sensory panelists. All panelists were under 55 years old, nonsmokers, and under no current medical treatment. The panelists were trained during three 1-h sessions using standards and score cards. Panelists were required to evaluate samples using two tests: a descriptive analysis and a difference test. Each test was conducted four times. Scaled (intensity) evaluations were based on standards. A 15-cm semiunstructured line-scale (0 = none and 15 = intense) was used to evaluate attributes. Standards used for training and during the intensity test included canola oil (Wesson) spiked with 60 ppm of hexanal for "grassy" (= 11); canola oil (Wesson) aged 14 d at 60°C for "rancidity" (= 8); burnt toast for "burnt" (= 11), a 2.5 × 2.5 cm square of cardboard immerged in 5 mL of distilled water overnight for "cardboard" (= 7.5); instant rehydrated mashed potatoes (Preferred Product Inc., Eden Prairie, MN) for "potato" (= 8); butter (grade AA; Prairie Farms Dairy, Inc., Carlinville, IL) for "buttery" (= 9.5); 10% sucrose in distilled water for "sweet" (= 11); 2.5% vinegar in distilled water for "sour" (= 11); and 5% coffee in distilled water for "bitter" (= 11). High numbers (i.e., close to the reference value) indicated that the flavor in question in the product was intense, whereas low numbers (near zero) indicated a flavor of much lower intensity (7).

The difference test was conducted as a triangle test in which three samples were served at a time. The panelists were notified that two samples were the same and one was different. They were asked to identify the different sample.

The fried hash browns were coded with three-digit random numbers. Each sample (approximately one-fourth of a patty) was served individually immediately after frying. Panelists received distilled water and apple juice at room temperature to cleanse their palates between samples. All panelists received samples in a random order, with approximately 5 min between samples (7).

Volatile analysis of fried hash browns. Approximately 1 mm of crust surface from the fried hash browns was ground through a 6.3-mm inlet sieve to form a homogeneous sample. Ground crust (10 g) was weighed into a 300-mL round-bottomed flask. Ten grams of NaCl was added to the flask, and the sample was spiked with 5 µL of an internal standard (2-methyl-3-heptanone at approximately 0.1 mg/mL in methanol). The sample was purged with nitrogen gas at 100 mL/min *via* a Pasteur pipette inserted through an adapter fitting into a 300-mL round-bottomed flask while heating at 60°C for 10 min. Volatile compounds were collected on a Tenax TA trap (Supelco). After the purge and trap process, the trap was removed and immediately transferred to a thermal desorption system (TDS2; Gerstel, Mülheim au der Ruhr, Germany) connected to the injection port of an HP 6890 Series gas chromatograph (Hewlett-Packard Co., Naperville, IL) interfaced to an HP 5973 mass selective detector (Hewlett-Packard). A capillary column (DB-FFAP; 30 m, 0.25 mm, d_f = 0.25 µm; J&W Scientific, Folsom, CA) was used for the separation. The thermal desorption system temperature was held at 30°C (5 min), ramped at 60°C/min to 210°C, and held for 10 min. The cold inlet system (cryotrap) temperature was started at −120°C, increased 12°C/s to 250°C, held for 5 min, increased 12°C/s to 280°C, and held for 10 min. The column temperature was held at 35°C for 5 min, then increased at 4°C/min to 225°C and held for 10 min. Helium was used as the carrier gas.

The total ion signal from the mass spectrometer was integrated using Hewlett-Packard ChemStation software to determine the relative amounts of each of the volatile compounds. The relative concentration of each volatile compound was calculated based on the concentration of the internal standard.

Statistical analysis. The mid-oleic acid sunflower oil and canola oil results were analyzed using Statistical Analysis System software (SAS, 2001; Cary, NC). A two (oil types) by five (heating times) factorial design was used, and data were subjected to ANOVA for main effects and interactions. Least squares means for significant ($P < 0.05$) effects were separated using the General Linear Model (GLM) program. The TAG substrate concentrations of the two oils were subjected to a regression analysis to determine degradation rates (SAS, 2001).

Sensory data from the difference test were analyzed as a three-alternative forced choice (3-AFC) test (8). Scaled (intensity) data were evaluated using ANOVA to determine treatment (oil type) effects on various sensory attributes. Means for significant effects ($P < 0.05$) were separated using Fisher's protected LSD (7). Means from volatile analysis data were calculated and separated using Fisher's protected LSD, expressed at a confidence level of 0.05.

RESULTS AND DISCUSSION

The IV of the mid-oleic acid sunflower and canola oil samples were 103.9 and 103.4, respectively. The FA profiles of both oils are shown in Table 1. NuSun, or mid-oleic acid sunflower oil, contained approximately 58% oleic acid and 32% combined linoleic and linolenic acids, whereas the canola oil sample had approximately 65% oleic acid and 28% combined linoleic and

TABLE 1
FA Composition of NuSun and Canola Oil

FA	NuSun oil[a]	Canola oil[a]
16:0	4.4 ± 0.2	4.6 ± 0.1
18:0	3.7 ± 0.0	0.2 ± 0.2
18:1	58.2 ± 0.1	65.1 ± 0.1
18:2	32.2 ± 0.0	21.5 ± 0.0
18:3	0.2 ± 0.0	6.5 ± 0.2
Other saturated FA	1.1 ± 0.1[b]	0.9 ± 0.0[c]
Other unsaturated FA	0.2 ± 0.0[d]	1.3 ± 0.1[e]

[a]Values are the average of three replicates. NuSun oil was obtained from ADM Packaged Oils (Decatur, IL), and canola oil was obtained from Wesson (Fullerton, CA).
[b]Includes 20:0, 22:0, and 24:0.
[c]Includes 20:0 and 22:0.
[d]Includes 20:1.
[e]Includes 20:1, 20:2, and 22:1.

linolenic acids. The similar IV and the relative amounts of monounsaturated FA and PUFA suggest that the two oils would be expected to have similar oxidative stabilities.

The average amount of mid-oleic acid sunflower oil and canola oil recovered per pan was 2.91 ± 0.20 g and 2.84 ± 0.15 g, respectively. Five milliliters of each oil sample was sprayed on the Teflon-coated pan. During heating, there was a decrease in the unaltered TAG content as a function of heating time as the percentage of polymer increased. The concentration of unaltered TAG in the unheated samples was calculated based on the relative concentration of internal standard as determined by capillary SFC. Data (natural log of the ratio of the unaltered TAG concentration at any time, *t,* to the initial TAG concentration) from all of the heating intervals were plotted to calculate the degradation rate of each oil sample. A linear regression analysis (Fig. 1) was used to determine the slope. The apparent first-order degradation rate constant, which was based on the slope of the line, for mid-oleic acid sunflower oil was 0.102 ± 0.008 min^{-1} (R^2 = 0.92), whereas the degradation rate for canola oil was 0.092 ± 0.010 min^{-1} (R^2 = 0.95). Degradation rates of the oils were compared using the Student *t*-test. At a confidence level of 0.05, there was no significant difference between the degradation rates of the two oils.

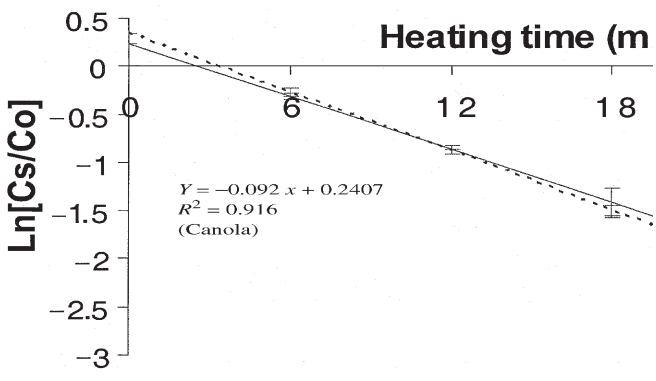

FIG. 1. Degradation rates of NuSun (·····) and canola oil (——) after heating based on the unaltered TAG content. Cs, TAG concentration at any time; Co, initial TAG concentration. Error bars indicate SD.

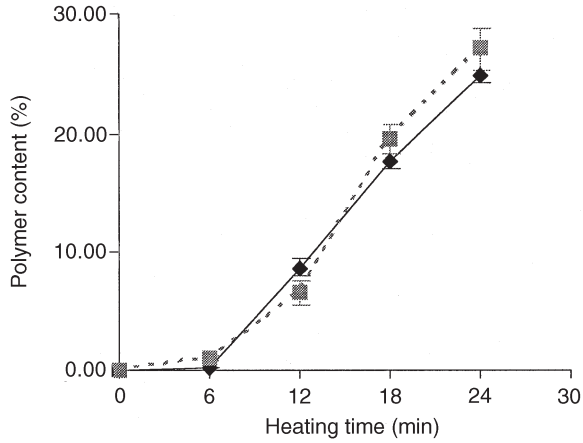

FIG. 2. Polymer contents for heated NuSun (·····) and canola oil (——). Error bars indicate SD.

The polymer contents of NuSun and canola oil after heating are shown in Figure 2. After 6 min of heating, polymer formation increased substantially, and there was a significant difference among the samples heated for 12, 18, and 24 min. The AV increased because of FA hydrolysis during heating in both NuSun oil and canola oil (Fig. 3). The FOS readings for both oils, shown in Figure 4, appeared to follow a pattern similar to that of the polymer content. Both the FOS values and the polymer content correlated well with the polar compound content, a result that was not unexpected. There was a significant difference between samples for the FOS values at the heating intervals; however, the general trend was an increase over time regardless of sample type.

In the sensory evaluation, data from two panelists were eliminated based on overall performance with actual samples. Hence, the statistical evaluation data presented were based on the evaluations of eight panelists. Table 2 contains data from the descriptive analysis. Hash browns had similar scores for all attributes, regardless of the frying oil used. After conducting four replications of the triangle test for overall differences, nine correct answers were obtained out of 32 responses. To conclude that there was a significant difference between the oils at a 95% confidence interval, at least 16

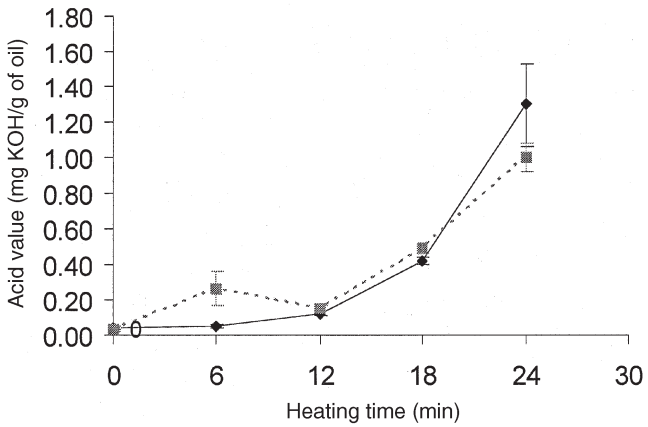

FIG. 3. Acid values for heated NuSun (·····) and canola oil (——). Error bars indicate SD.

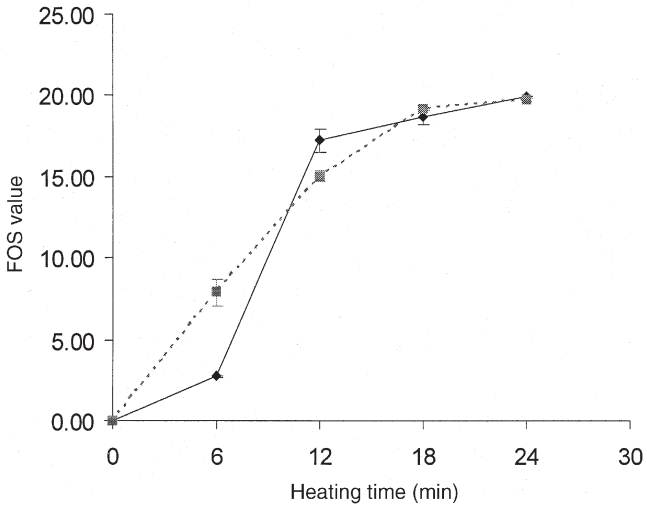

FIG. 4. Food oil sensor (FOS) readings for heated NuSun (·····) and canola oil (——). Error bars indicate SD.

correct answers must have been received (8). These results indicate that the panelists could not detect any difference in terms of odor or flavor between the fried hash brown samples.

The relative concentrations of volatiles in the unheated hash browns, as well as the hash browns fried in mid-oleic acid sunflower and canola oils, are shown in Table 3. The unheated hash browns were investigated to identify the volatiles present in the potatoes prior to frying. All volatiles were lipid oxidation products and/or Maillard browning reaction products.

Some of the volatile compounds detected included pentanal, hexanal, heptanal, octanal, nonanal, decanal, *trans*-2-hexenal, *trans*-2-octenal, 2-nonenal, 2-undecenal, *trans,trans*-2,4-heptadienal, *trans,trans*-2,4-decadienal, 2,3-butanedione, and 2-pentylfuran, all of which are lipid oxidation products. These compounds have been reported in used frying oil in

TABLE 2
Descriptive Analysis of Fried Hash Browns Fried in NuSun and Canola Oil[a]

Attribute	Hash browns fried with Nusun oil[a]	Hash browns fried with canola oil[a]
Grassy	1.8 ± 1.3[b]	2.0 ± 1.6[b]
Rancid	1.5 ± 1.5[b]	1.3 ± 1.2[b]
Burnt	1.0 ± 1.1[b]	1.0 ± 0.9[b]
Buttery	1.3 ± 0.9[b]	1.4 ± 1.2[b]
Bitter	0.6 ± 0.8[b]	0.9 ± 1.2[b]
Sour	1.7 ± 1.4[b]	1.5 ± 1.1[b]
Cardboard	1.3 ± 1.3[b]	1.0 ± 0.9[b]
Potato	6.2 ± 2.0[b]	6.2 ± 2.0[b]
Sweet	1.0 ± 0.9[b]	1.0 ± 0.9[b]

[a]Values represent the average of eight panelists in four replicate analyses ± SD. Values within the same row with the same superscript do not differ ($P < 0.05$).

TABLE 3
Relative Concentration of Selected Volatile Compounds (>10 ng/g) in Hash Browns[a]

Compound group	Compound name	Unfried hash browns[a]	Hash browns fried in NuSun oil[a]	Hash browns fried in canola oil[a]
Aldehydes	2-Methylpropanal	—[b]	395 ± 173[c]	362 ± 58.8[c]
	2-/3-Methylbutanal	7.04 ± 2.47[b]	454 ± 233[c]	382 ± 64.8[c]
	Pentanal	12.6 ± 0.79[b]	10.5 ± 6.51[b]	5.14 ± 1.69[b]
	Hexanal	57.0 ± 4.25[b]	29.9 ± 16.5c	14.4 ± 4.08[c]
	Nonanal	38.8 ± 13.2[b]	11.3 ± 11.8[c]	18.4 ± 4.48[b]
	Trans-2-hexenal	—[b]	12.7 ± 7.39[c]	0.66 ± 1.15[b]
	Trans,trans-2,4-heptadienal	—[b]	—[b]	12.8 ± 5.58[c]
	Trans,trans-2,4-decadienal	10.8 ± 12.8[b]	19.5 ± 6.65[b]	5.37 ± 2.70[b]
	Benzene acetaldehyde	5.74 ± 9.94[c]	29.2 ± 14.8[b]	21.8 ± 2.49[b,c]
Ketones	2,3-Butanedione (diacetyl)	11.2 ± 2.34[b]	18.4 ± 8.96[b]	11.3 ± 1.91[b]
Sulfur compounds	Dimethyl disulfide	—[b]	10.1 ± 6.75[c]	7.68 ± 0.58[b,c]
	Methional	Trace[b]	28.0 ± 16.2[c]	6.79 ± 5.93[b,c]
Nitrogen heterocycles	Methylpyrazine	—[b]	69.7 ± 47.1[c]	69.1 ± 9.53[c]
	2,5-Dimethylpyrazine	—[b]	72.5 ± 58.2[b,c]	105 ± 10.8[c]
	2,6-Dimethylpyrazine	—[b]	35.3 ± 19.1[c]	29.1 ± 3.86[c]
	Ethylpyrazine	—[b]	22.7 ± 15.6[c]	17.1 ± 3.22[b,c]
	2,3-Dimethylpyrazine	—[b]	13.3 ± 7.99[c]	9.62 ± 1.96[b,c]
	2-Ethyl-6-methylpyrazine	—[b]	16.4 ± 10.7[c]	13.9 ± 3.11[c]
	2-Ethyl-5-methylpyrazine	—[b]	55.8 ± 43.8[c]	24.7 ± 4.31c
	Trimethylpyrazine	—[b]	30.4 ± 15.2[c]	23.3 ± 4.22[c]
	3-Ethyl-2,5-dimethylpyrazine	—[b]	25.5 ± 13.8[c]	13.7 ± 9.33[b,c]
Total aldehydes		132 ± 11.4[b]	964 ± 438[c]	823 ± 132[c]
Total nitrogen compounds		—[b]	341 ± 157[c]	306 ± 41.2[c]

[a]Values represent the average of triplicate fryings ± SD. Values within the same row with like superscripts do not differ significantly ($P < 0.05$). —, not detected.

previous studies (9–11). Various nitrogenous heterocyclic compounds, such as pyrazine, methylpyrazine, 2,6-dimethylpyrazine, and 2,3-dimethylpyrazine, have been found in fried food and are considered Maillard browning–lipid interaction products by some investigators (12).

Data in Table 3 indicate that heterocyclic compounds with one or more nitrogen or sulfur atoms were found only in fried hash browns. This was expected since nitrogen containing heterocyclic compounds can be formed by the lipid-derived carbonyl compounds formed during the thermal oxidation of the frying oil and because of the free amino group formed from amino acids contained in potato proteins (13).

In addition, the flavor profile of fried hash browns in our study had a pattern similar to that reported by Wagner and Grosch (14) for french fries. Methional was suggested as one of the major compounds characteristic of potato flavor (15,16). Heterocyclic compounds, including methylpyrazine, 2- and 3-methylbutanal, 3-ethyl-2,5-dimethylpyrazine, 2,5-dimethylpyrazine, and 2-ethyl-6-methylpyrazine, have been identified previously in the flavor profiles of baked potatoes (17).

Since there was a wide range in the relative concentrations of volatile compounds detected, volatile compounds with relative concentrations greater than 10 ng/g in at least one or more fried samples were used for comparisons of volatiles between the two fried hash browns samples. Only nonanal and 2,4-heptadienal concentrations were statistically different by oil type (Table 3). With respect to nonanal, the large SD in hash browns fried in mid-oleic acid sunflower oil indicated that the data for nonanal might not be reliable or that nonanal might have been degrading. With respect to 2,4-heptadienal, most of the difference observed can be explained by the large difference in linolenic acid content between the two oil samples. The canola oil sample contained almost 30 times as much linolenic acid as the mid-oleic acid sunflower oil sample; 2,4-heptadienal is considered to be an oxidation product formed primarily from linolenic rather than linoleic acid.

Volatile analysis results agreed with the triangle test results from the sensory evaluation in that the hash browns fried in mid-oleic acid sunflower oil and canola oil did not differ significantly. Similar volatile compounds in similar concentrations were detected in both fried samples, and generally there were no significant differences in the major flavor compound concentrations between the potato samples fried in the two oils.

The two most easily oxidized FA present in appreciable amounts in the two oil samples were linoleic and linolenic acids. Linolenic acid oxidizes at approximately twice the rate of linoleic acid. Since the difference in the linoleic acid concentration (10.7%) between NuSun oil and canola oil is approximately twice the difference in the linolenic acid concentration (6.3%) between the two oils, little if any difference in the rate of oxidation of the two oil samples was expected. The small difference in IV suggests this as well, and the data presented (acid values, FOS, % polymer, and the degradation rates) confirm it.

NuSun or mid-oleic acid sunflower and canola oil have similar pan-fry stabilities as there were few significant differences in the physicochemical properties of the two oils during heating. In addition, both sensory evaluation and volatile analyses suggested that the fried hash browns obtained in each sample did not differ. Therefore, these oils differed little in either oxidative stability or fried food flavor.

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