Comparison of a Low-Linolenic and a Partially Hydrogenated Soybean Oil Using Pan-Fried Hash Browns

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ABSTRACT: Hash browns (HB) were fried (Teflon-coated pan, ~180°C) with low-linolenic acid (LL-SBO) and creamy partially hydrogenated soybean oils (PH-SBO). High-performance size-exclusion chromatography of the oil extracted before heating indicated a relatively low polymer content (LL-SBO, 3.8%; PH-SBO, 1.6%), although the oil remaining in the pan after frying had a much greater polymer content (38.8%, LL-SBO; 17.5%, PH-SBO). The percentage of altered TAG in the LL-SBO sample (extracted from HB) was 34.4% after frying, whereas the PH-SBO had 33.2% altered TAG (as determined by supercritical fluid chromatography). In the LL-SBO pan-fried HB samples (not the extracted oil), 2-pentanone, hexanal, 2-hexenal, *trans*-2-heptenal, 2-pentylfuran, and *trans*-2-octenal were found, whereas the major volatile compounds in the HB fried with PH-SBO included hexanal, *trans*-2-hexenal, and *trans*-2-heptenal. Hexanal was the most abundant volatile compound in both HB samples (LL-SBO, 2.7 ppm; PH-SBO, 0.3 ppm). There were significant differences in the polymer content, hexanal content, *p*-anisidine values, and Foodoil Sensor readings between LL-SBO and PH-SBO ($P < 0.05$). The PH-SBO sample was more stable than the LL-SBO sample. Moreover, the LL-SBO oil sample in the pan after frying had the greater increase in polymer content.

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KEY WORDS: Hash browns, low-linolenic acid soybean oil, pan-frying.

Deep-fat frying requires a substantial amount of oil, whereas pan-frying is generally done with either a thin layer or a thin film of oil applied as a spray. There are numerous types of oil-based products for pan and grill frying on the market today, which are used in both the food service industry and in the home (1,2).

Frying oils are relatively heat stable. Nevertheless, the combination of high temperature and the large surface-to-volume ratio encountered with pan frying is expected to induce rapid oxidation and an accumulation of highly oxidized material (2,3).

Usuki *et al.* (4) studied the deterioration of oils during pan-frying. The chemical changes in the oil samples after 5 min of heating were similar to the changes that occur in oil samples after 10 h of deep-fat frying. Dagerskog and Sorenfors (5) compared four different cooking methods and concluded that by selecting optimal conditions for each procedure, the frying time and the product color could be approximately the same with any of the four methods.

Pan-frying has raised some health concerns. A study by Johansson *et al.* (6) showed that heterocyclic amines, which are carcinogenic, can be found in meat patties after pan-frying. The compounds were found in the pan residue in greater amounts than in the patties. They recommended not to exceed a frying temperature of 175°C and to discard the residue (6).

In 1999 (7), researchers heated 0.5-cm layers of rapeseed, soybean, and sunflower oil samples at 180°C for 15 min. Upon heating, there was a slight increase in the polymer content and no changes were found in the FA compositions. Heated oil samples were fed to rats to study oil absorption in the lymphatic system. The transport of FA was significantly lower for the heated oils as compared to the unheated oil samples (7). Although investigators have used meat, eggs, cabbage, and rice as model food systems to investigate heat transfer using pan-frying (6,8), previous studies have not included the combination of oil and pan-fried hash browns (HB).

The purpose of this study was to determine the extent of oil degradation during pan frying of HB. Two oil samples, low-linolenic acid soybean oil (LL-SBO) and partially hydrogenated soybean oil (PH-SBO), were used. Samples of the oil extracted from the HB and samples of the oil remaining in the pan at the end of frying were analyzed.

EXPERIMENTAL PROCEDURES

Materials and methods. Ore-Ida frozen HB (Ore-Ida, Boise, ID) were used. Immediately prior to frying, the thawed patties had an average internal temperature and weight of ~5°C and ~84 g, respectively. The package cooking directions recommended frying the frozen patties at 350°F (177°C), which is similar to methods recommended by the United States Department of Agriculture (9). The frozen HB did not contain any significant amount of oil or any significant amount of volatile compounds. Samples of LL-SBO and creamy PH-SBO were obtained from Kraft Food Ingredients (Memphis, TN). The unheated oil samples did not contain any polymer or significant amounts of volatile compounds. The unheated LL-SBO and PH-SBO oil samples had a *p*-anisidine value (*p*-AV) of 2.8 and 5.5, respectively. The characteristics of the unheated oil samples, including the FAME composition, have been published previously (10). The iodine value

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was 94.8 for the PH-SBO sample and 120.7 for the LL-SBO oil sample. The pan-frying protocol and chromatographic analyses used for the oil analysis have been published (10). Briefly, a Teflon-coated pan (26 × 26 cm, T-Fal Ultrabase, Rumilly, France) was used for frying. A 10-mL sprayer (Kontes brand, Fisher Scientific, Pittsburgh, PA) was used to apply approximately 5 mL of oil to the pan surface, although a substantial portion of the oil was lost during the spraying process. The amount of oil recovered from the pan surface after application averaged approximately 2.5 g. Single HB patties were fried for 30 min at approximately 180°C. The pan surface temperature was measured with an IR reflectance thermometer (Cole-Parmer, Vernon Hills, IL) at five locations on the pan surface (four corners and the center). The surface and internal temperatures of the HB were recorded at 5-min intervals. Patties were turned every 5 min to ensure uniform cooking. The end point was determined based on a combination of internal temperature (~100°C) and visual doneness. After frying, the pan-fried HB weighed an average of ~60 g. Samples were fried and analyzed in triplicate for each oil (LL-SBO and PH-SBO).

For the analyses of the oil in the HB, the fried HB were collected and dried under vacuum at 50°C for 10 h. A Soxhlet extraction system (Kontes Soxhlet apparatus, glass thimble, 500 mL flask receiver; Fisher Scientific) with 150 mL petroleum ether and a 2-h extraction for each thimble was used for extraction of oil from each dried HB patty. Approximately 1 g of oil was extracted from each patty.

Chromatographic analysis. Extracted oils were analyzed by high-performance size-exclusion chromatography (HPSEC) for the TAG polymer content (10). The oil remaining in the pan at the end of frying also was collected and analyzed by HPSEC. A mobile phase of THF and four Phenogel columns (Phenomenex, Torrance, CA) with 5 µm particles were used. The particle pore sizes in the four columns were 500, 100, 100 (500 mm in length × 8.0 mm in diameter), and 50 Å (300 mm × 7.8 mm). The columns were connected to an ELSD (Varex Corp., Burtonsville, MD).

For analysis of volatiles, fried HB were immediately blended after heating at "Power Burst, No. 14" for 5 min (PowerX Plus 239; Krups, Closter, NJ) and ~2-g samples were placed in each vial. An internal standard of methyl hexanoate was added to each vial using a 1-µL syringe for the quantification of volatile compounds with headspace GC–FID. Headspace GC–MS was used for identification of volatile components. A Tekmar 7000 static headspace sampler with a heated 3 m × 0.32 mm transfer line was used to transfer the volatile compounds to a GC capillary column (Durabond, DB-5, 50 m × 0.32 mm i.d. × 1.0 µm film; J&W Scientific, Folsom, CA). Helium was the carrier gas. The GC initial temperature was 40°C, followed by a temperature ramp of 5°C/min to 85°C and then 25°C/min to 250°C. The GC cycle time was 60 min. The FID temperature was 300°C. The supercritical fluid chromatography (SFC) system included SFC-grade CO_2 (MG Industries, Malvern, PA) as the mobile phase and a 14-m SB-cyano-25 (50 µm i.d., d_f = 0.25 µm) capillary column (10).

Physicochemical analysis. The *p*-AV were determined in triplicate according to AOCS Official Method Cd 18-90 (11). The dielectric constant was measured in triplicate with a Foodoil Sensor (FOS) (Northern Instruments Corp., Lino Lakes, MN). The iodine value, AOCS Official Method Cd 1b-87, was determined in triplicate (11).

Statistical analysis. The values in the tables represent the average of three replicate analyses, each analyzed in triplicate ± SD. The statistical analysis included a *t*-test and the ANOVA to determine if significant differences existed between samples with respect to polymer content and the concentrations of the major volatile compounds after frying. The software used for the statistical analysis was the Statistical Analysis System Version 8.0 (SAS Institute, Cary, NC).

RESULTS AND DISCUSSION

The two oil samples differed in their iodine values (LL-SBO, 120.7; 94.8, PH-SBO) and in their FA composition. The LL-SBO oil sample contained 10.2% palmitic acid, 4.8% stearic, 28.0% oleic, 53.3% linoleic, and 3.0% linolenic acid, whereas the PH-SBO oil sample had 10.7% palmitic acid, 11.7% stearic, 43.5% oleic, 30.3% linoleic acid, and 2.7% linolenic acid (10). The PH-SBO contained much more stearic and oleic acid and less linoleic acid than did the LL-SBO, which likely explains much of the difference in stability between the two oils upon pan-frying. The HB contributed only negligible amounts of oil.

HB were fried for 30 min at ~180°C in either LL-SBO or PH-SBO oil samples. The oil extracted from the HB and the oil remaining in the pan at the end of the frying were analyzed with HPSEC (Table 1). The polymer content of the oil sam-

TABLE 1
Polymer Content of Oil Extracted from Hash Browns, and the Oil in the Pan at the End of Frying[a]

	HB LL-SBO[b]	HB PH-SBO[b]	Pan LL-SBO	Pan PH-SBO
% Total polymer	3.8[d]	1.6[e]	38.9[f]	17.5[g]
Higher M.W.[c]				
t_r (min)	ND	ND	32.1 ± 0.0	32.4 ± 0.1
% Component			19.8 ± 0.6	1.9 ± 0.1
Trimers[c]				
t_r (min)	36.6 ± 0.1	36.7 ± 0.1	36.8 ± 0.0	36.9 ± 0.1
% Component	1.1 ± 0.2	0.3 ± 0.0	9.2 ± 0.8	6.4 ± 0.3
Dimers[c]				
t_r (min)	38.1 ± 0.1	38.2 ± 0.1	38.0 ± 0.0	38.4 ± 0.1
% Component	2.7 ± 0.2	1.3 ± 0.1	9.9 ± 0.4	9.2 ± 0.3
Monomers[c]				
t_r (min)	41.4 ± 0.1	41.8 ± 0.1	41.3 ± 0.0	41.3 ± 0.1
% Component	96.2 ± 0.4	98.5 ± 0.1	61.2 ± 1.2	82.6 ± 0.4

[a]As determined by high-performance size-exclusion chromatography. The total polymer content includes dimers, trimers, and higher-M.W. polymers of TAG.
[b]Abbreviations: HB, hash browns; LL-SBO, low-linolenic acid soybean oil; PH-SBO, partially hydrogenated soybean oil; ND, not detected; t_r, retention time.
[c]Values represent the average of three replicate analyses, each analyzed in triplicate ± SD.
[d,e]These two values are significantly different at $P < 0.05$.
[f,g]These two values are significantly different at $P < 0.05$.

ples extracted from the HB increased slightly to 3.8 and 1.5% for LL-SBO and PH-SBO, respectively. A slight, rather than substantial, increase was expected since the oil absorbed by the HB was exposed to lower temperatures than the rest of the oil in the pan, as indicated by the maximal internal temperature of the HB (100°C) during heating. The reduced amount of oxidation probably resulted from a combination of reduced temperature caused by the high moisture content of the HB patties, and the physical inhibition to oxygen absorption by the position of the HB patty directly on the oil/pan surface.

The polymer content of the oil in the pan after frying was much greater than the polymer content of the oil extracted from the HB samples. The total polymer content increased from 0 to 38.8 and 17.4% for the LL-SBO and PH-SBO samples, respectively. The polymer content of the heated PH-SBO sample was less than 20%, which was selected as the discard point for this experiment. The recommended discard point for used frying oil for many European countries is 25 to 27% polar compounds (12), which corresponds to a polymer content of 20% (13). However, the LL-SBO sample had a polymer content nearly twice that of the acceptable discard concentration of 20%. This factor is important, because oil left in the pan is often consumed with the food or used for preparation of sauces or gravies (6).

The major volatile flavor compounds and their concentrations in the HB fried in LL-SBO are listed in Table 2 and include 2-pentanone, hexanal, 2-hexanal, *trans*-2-heptenal, 2-pentylfuran, and *trans*-2-octenal. The major volatile compounds from HB fried with PH-SBO included hexanal, *trans*-2-hexenal, and *trans*-2-heptenal (Table 3). The volatile compounds were present at much lower concentrations in the HB fried in both oil samples in the current study than in the oil from the previous experiments (10), where the oil was heated in the absence of any food product. The extent of oxidation of the heated oil samples, as well as the amount and identity of the volatile lipid oxidation products in the heated oil, was determined.

Statistical analyses of the HPSEC results indicated that the PH-SBO sample had a lower polymer content at the end of frying than did the LL-SBO sample. HB fried with either LL-SBO or PH-SBO contained both hexanal and *trans*-2-heptenal. There was no significant difference in the concentration of *trans*-2-heptenal for the two samples, but there was a significant difference in the concentration of hexanal for both samples ($P < 0.05$). Hexanal, the most abundant volatile compound found in both samples, was found at greater concentrations in patties fried with LL-SBO (2.7 ppm) than in the samples fried with PH-SBO (0.3 ppm). Hexanal is one of the major volatiles produced during the thermal oxidation of linoleic acid (14,15), unlike oleic acid (16). Linoleic acid was present in much greater concentration in the LL-SBO oil sample (53.3%) than in the PH-SBO oil sample (30.3%), so more hexanal was expected in the oil sample containing the most linoleic acid. Hexanal has been found in greater concentrations in chips fried in high-linoleic acid oils than in regular frying oils (17). Hexanal can be a good index of oxidation (18) of unsaturated FA because of its characteristic odor and production in relatively large amounts in frying oils.

TABLE 2
Concentrations of Flavor-Significant Volatile Compounds in Pan-Fried Hash Browns

Compound	LL-SBO[a] (ppm)	PH-SBO[a] (ppm)
2-Pentanone	0.4 ± 0.3	ND
Hexanal	2.7 ± 2.5[c]	0.3 ± 0.1[d]
2-Hexanal	0.2 ± 0.2	ND
trans-2-Hexenal	ND	0.1 ± 0.1
trans-2-Heptenal	0.3 ± 0.2[e]	0.3 ± 0.1[e]
2 Pentylfuran	0.2 ± 0.1	ND
trans-2-Octenal	0.3 ± 0.2	ND

[a]Values represent the average of three replicate analyses, each analyzed in triplicate ± SD. Values with different superscript letters in the same row indicate significant differences at $P < 0.05$. For abbreviations see Table 1.

TABLE 3
Physicochemical and Supercritical Fluid Chromatographic Analysis of Extracted Oil from Pan-Fried Hash Browns[a,b]

Oil sample	TAG loss[b] (%)	*p*-AV[b] (Abs/g oil)	FOS[b]
LL-SBO	34.4 ± 4.5[c]	199.1 ± 1.4[d]	6.96 ± 0.03[d]
PH-SBO	33.2 ± 4.3[c]	53.0 ± 0.9[e]	1.62 ± 0.03[e]

[a]Values represent the average of three replicate analyses, each analyzed in triplicate ± SD.
[b]Abbreviations: SFC, supercritical fluid chromatography; *p*-AV, *p*-anisidine value; FOS, Foodoil Sensor (values are dimensionless); for other abbreviations see Table 1. Values with different superscripts in the same column indicate significant differences at $P < 0.05$.

The oil samples extracted from the HB were slightly oxidized, as indicated by the loss of TAG and high values for *p*-AV and FOS (Table 3). The unheated frying oil samples had *p*-AV values of 2.8 (LL-SBO) and 5.5 (PH-SBO), and FOS readings of zero (10). No significant amount of oil was found in the uncooked HB, so no analysis of the oil was completed. The reduction in the unaltered TAG concentration in the extracted LL-SBO samples from the HB was 34.4% after 30 min of frying. The oil extracted from the HB fried in PH-SBO had a reduction in TAG of 33.2%, whereas the polymer content of the two oils was only 3.8% for the LL-SBO sample and 1.6% for the PH-SBO sample. In samples of vegetable oil (transesterified soybean oil) heated in a deep-fat fryer, a polymer content of ~22% corresponded to an unaltered TAG% of ~55% (19).

Even though the percentage of altered TAG (chemically altered due to oxidative reactions) in the extracted oil from HB was not significantly different between the LL-SBO and PH-SBO samples (Table 3), there were significant differences in the *p*-AV and, more importantly, the polymer content, the volatile content, and the FOS readings ($P < 0.05$). The FOS reading of the oil extracted from the HB fried in LL-SBO also was greater than that of the oil from the HB fried in PH-SBO.

The difference in LL-SBO and PH-SBO stability, as reflected in the volatile concentrations, the polymer contents, and the FOS and *p*-AV values, was not unexpected. The

LL-SBO sample was less saturated (IV = 120.7) than the PH-SBO oil sample (IV = 94.8), which was primarily a result of the greater linoleic acid content in the LL-SBO (53.3%) oil sample than in the PH-SBO oil sample (30.3%).

Overall, the LL-SBO samples had a greater polymer content and hexanal concentration at the end of the pan-frying than did the PH-SBO samples. HB frying indicated that PH-SBO is slightly more stable than LL-SBO with regard to both volatile and nonvolatile compound formation. Moreover, the LL-SBO remaining in the pan at the end of frying had a greater increase in polymer content than did the PH-SBO sample.

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