

Frying Performance of No-*trans*, Low-Linolenic Acid Soybean Oils

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Received: 8 December 2006 / Revised: 1 February 2007 / Accepted: 21 March 2007 / Published online: 8 May 2007
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Abstract Two extruded-expelled physically refined soybean oils with reduced contents of linolenic acid, ultra-low-linolenic acid (ULL, 1.5%) and low-linolenic acid (LL, 2.6%), and a extruded-expelled physically refined control oil (control, 5.3% linolenic acid) were evaluated by frying French fries in a commercial-like setting for 6 h day⁻¹ during 23 days. The oils became darker, increased in yellow color at the beginning, and became redder and less green throughout the process. Free fatty acids levels were not different among the oils until day 14, after which, ULL was different from the control for the remainder of frying. The conjugated dienoic acid values were greatest in the control. Generally, ULL and LL oils had lower percentages of polar compounds than did the control, providing a frying life 2 days longer than the control and ~30% increase in frying time. A trained sensory panel evaluated the French fries on days 2, 5, and 6. Buttery and potato flavors decreased, and rancid and painty flavors increased over frying time for all products. Rancid flavor was highest in the fries from the control oil. Overall, the ULL and LL oils

performed better than did the control oil and ULL tended to perform better than the LL.

Keywords French fries · Frying · Oil stability · Sensory evaluation · Soybean oil · Ultra-low-linolenic acid · Extruded-expelled oil · Physical refining

Introduction

Frying is one of the most common practices used to cook food in both home and industrial operations. The essence of the fast-food industry is the frying process that provides tasty, ready-to-eat food in a relatively short period of time. In addition to saving time, frying reduces the amount of waste because it allows cooking of small batches of food to order. The stability of the oil is a crucial factor when choosing a frying medium because of the highly aggressive process involving high temperature in the presence of oxygen, water, and the formation of pro-oxidants. Partially hydrogenated oils have been commonly used as the frying media because of their stabilities. In 2003, the Food and Drug Administration passed a ruling requiring labels of all food products containing 0.5 g or more of *trans* fat per serving to list the *trans* content on the nutrient label by 1 January 2006 [1]. Other countries, such as Denmark [2] and Canada [3], have passed legislation regulating *trans* fat content labeling in food products. Companies are increasingly marketing products that do not contain *trans* fats. *Trans* fatty acid consumption has been linked to health, including increased serum levels of low-density lipoprotein cholesterol and decreased high-density lipoprotein cholesterol [4]. Because of these health issues and the accompanying *trans* fats labeling requirements, the food industry has been trying to find alternatives to partially hydrogenated oils.

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Typical soybean oil with about 7–8% linolenic acid (18:3) is known to be oxidatively unstable, especially during frying. A recent study showed that soybean oil with only 1.9–2.9% of the very unstable 18:3 had better flavor scores and increased stability during frying than commodity and even partially hydrogenated soybean oils [5]. Frying stability of soybean and other oils also is impacted by the extraction method. Warner and Dunlap [6] reported that French fries, fried in screw-pressed soybean oil, had better sensory characteristics than fries fried in hexane-extracted soybean oil with TBHQ added and fries fried in partially hydrogenated soybean oil. Screw pressing is thought to create Maillard browning reaction products that contribute natural antioxidants to the pressed oils [6].

The combination of low 18:3 composition along with extrusion expelling has not been tested for performance during frying. In this study, the extended frying performance of three extruded-expelled physically refined soybean oils was evaluated: two oils from soybean varieties with reduced amounts of 18:3 and one oil from commodity soybeans with a typical amount of 18:3. A main goal of the study was to determine whether substantial differences occurred among these three oil types to help buyers decide the value of selecting one of the low 18:3 acid oils over typical commodity oil.

Materials and Methods

Soybean Oils

Extruded-expelled physically refined soybean (*Glycine max* (L.) Merr.) oils with three different fatty acid compositions were obtained from American Natural Soy, Inc, Cherokee, IA. An ultra-low-linolenic acid oil (ULL), having 1.5% 18:3 after processing, was obtained from the soybean cultivar IA2064 produced by Taylor Seeds, Inc, near Hartley, IA in 2003. Low-linolenic acid oil (LL), having 2.6% 18:3 after processing, was obtained from the soybean cultivar IA3018 produced by Pleasant Valley Farms near Iowa City, IA in 2004. Oil with 5.3% 18:3 (control) after processing came from a mixture of conventional soybean cultivars produced by American Natural Soy in 2004. Both ULL and LL oils originated from soybean cultivars developed by Iowa State University (ISU) [7] through traditional breeding practices to reduce the 18:3 content of the oil.

Frying of French Fries

The frying process was performed simultaneously for two replicates of the three oils in a total of six twin-frying wells of Star Twin Pot deep-fat fryers, model 530TA with

automated thermostat control (Star Manufacturing International Inc, St Louis, MO). Fryer wells were filled up to their maximum capacity (7.2 l) with fresh oil. Three 0.225-kg batches of commercial extra-long (XL) fancy 0.635 cm (0.25 in.) shoestring par-fried frozen French fries obtained commercially were fried per hour, for 6 h per day for 23 days. The fries were provided by a single supplier from a single lot and were par-fried using partially hydrogenated vegetable shortening (canola and/or soybean oil) and/or palm oil and/or beef fat. The fatty acid composition of the fat extracted from the par-fried fries was 19.4% 16:0 (palmitic acid), 16.3% 18:0 (stearic acid), 61.9% 18:1 (all isomers), and 2.4% 18:2 (all isomers). The available column did not allow geometric isomer separation. A 100-m column is needed to obtain a complete profile of fatty acids. The manufacturer also claimed the addition of dihydrogen pyrophosphate (to promote color retention), dextrose and natural flavoring. The initial frying temperature was 190 °C and each batch was fried for 165 s. With the addition of each batch of frozen par-fried fries, the oil temperature decreased to 165 °C, with the temperature recovering to 175 °C by the end of the frying time. The oil temperature was recorded at 30 s intervals and the temperature monitored to ensure consistent frying temperatures for all batches. At the end of each frying day, the oils were filtered through fast flute shortening filters (DF1600FF Disco, McDonough, GA) to remove food particles. Aliquots of the oils were removed for further evaluation and stored at –22 °C in glass jars under nitrogen in the dark to prevent further oxidation. The bulk of the oils was left overnight in the fryers at room temperature loosely covered with aluminum foil. The following day, fresh oil was added to bring the level back to normal before heating.

Fry Chef Evaluations

Fry chefs (9 chefs × 2 frying replicates = 18 total observations per evaluation day) from the ISU dining service served as an expert panel to evaluate the frying oils during the operation. They were familiarized with the frying set-up and trained to use the scoring sheet provided for them. They visited the frying operation on days 2, 5, 9, 11, 14, 16, 19, 21, and 23 and at each visit were asked to independently judge the unidentified oils for their need to be changed, based on their expert judgment as to when they would typically change the oil during normal use. Frying continued until all the chefs agreed that the oils (both replicates) needed to be changed (day 23).

Composition of Fatty Acid Methyl Esters (FAME)

The FAME composition of each oil was determined by gas-liquid chromatography and was reported in relative

area percentage. The FAME were obtained by using the method described by Hammond [8] and analyzed with an HP5890GC chromatograph. The chromatography conditions were similar to those described by Onal-Ulusoy et al. [9]. Based on FAME composition, oxidizability was calculated [10]. The oils were analyzed fresh and periodically throughout the frying operation.

Free Fatty Acids (FFA)

The FFA concentration expressed as oleic acid was determined on the fresh oils and on days 2, 5, 6, 9, 11, 14, 16, 19, 21, and 23 by titration following AOCS official method Ca 5a-40 [11] as modified by Rukunudin et al. [12].

Conjugated Dienoic Acid (CDA)

The CDA content expressed as percentage was spectrophotometrically determined on the fresh oils and on the same days as for FFA according to AOCS official method Ti 1a-64 [11].

Total Polar Compounds (TPC)

TPC were determined on the fresh oils and on the same days as for FFA according to AOCS official method Cd 20-91 [11].

Peroxide Value (PV)

PV of each oil was determined before frying according to AOCS official method Cd 8-53 [11].

Oil Stability Index (OSI)

The oil resistance to oxidation was evaluated according to AOCS official method Cd 12b-92 [11] using an oxidative stability instrument (Omnion Inc, Rockland, MA). OSI was run at 100 °C.

Tocopherol Content

The α -, γ -, and δ -tocopherol contents of the fresh oils were determined by HPLC following the AOCS official method Ce 8-89 [11].

Color

Oil color was analyzed on the fresh oils and on the same days as for FFA by using a Hunter Lab LabScan XE colorimeter (Hunter Lab, Reston, VA). The illuminant used was D65 and the standard observer was set at 10°. The oil aliquots were placed in 60 × 15 mm Petri dishes with the

edge previously covered with two layers of white, 1.27-cm width tape (Fisherbrand, Fisher Sc. 11–880A) to avoid light dispersion caused by sample translucence. The Petri dish was placed on a standard white tile for oil color measurement. The color results were expressed in Hunter Lab units.

Sensory Evaluation

Sensory evaluations were performed on French fries fried in the oils on days 2, 5 and 6 to correspond with the typical timing of fast food operations, in which frying oil is changed on a weekly basis. Rancid, painty, potato, and buttery flavors were assessed by a sensory panel of 12 individuals, previously trained during three separate sessions to recognize and quantify these attributes. The attributes were rated on a 15-cm line, with the perceived flavor increasing in intensity from 0 to 15. French fries were randomly coded and served to all panelists in a monadic sequential order (randomized among sessions).

Statistical Analysis

All data were analyzed by using analysis of variance (ANOVA) with the SAS mixed models procedure [13]. For tests performed over time, repeated measures were used. Multiple comparisons between means were assessed by F-protected contrasts. The level of significance was set at $\alpha = 0.05$.

Results and Discussion

The 18:3 concentration in the fresh oils was different among the treatments (Table 2), but was greater in ULL and less in control oils than expected. The 18:3 of ULL was measured at 1.0% in the 2003 seed before the oil was extracted and refined (Unpublished data). Also, the control oil, at 5.3%, was lower than is typical for commodity soybean oil [5]. During processing, there likely was some carryover of previously processed commodity oil into the ULL oil, and of ULL and/or LL oil into the control oil, thus contributing to some of the differences in the final 18:3 concentrations of the processed oils. Also, growing conditions may have slightly altered fatty acid composition in the beans. The reduction of 18:3 in LL and ULL, compared to the control, was accompanied by increased linoleic (18:2) and oleic (18:1) acid levels, but the 18:2 acid concentrations were not different between ULL and LL. The amount of stearic acid (18:0) was greater in the ULL than in the control and LL. These changes were reflected in the calculated oxidizability (Table 1). ULL had the lowest value (highest theoretical stability), LL had an intermediate value, and the control had the highest value.

Table 1 Initial oil quality values of ultra low-linolenic acid (ULL), low-linolenic acid (LL), and control soybean oils

Oils	Oxidizability	Tocopherol ($\mu\text{g/g}$)				OSI (h at 100 °C)	PV (meq \times kg ⁻¹)
		α	γ	δ	Total		
ULL	6.4 ^c	67 ^c	759 ^a	245 ^c	1071 ^b	19.40 ^a	0.72 ^a
LL	6.6 ^b	117 ^b	803 ^a	261 ^b	1181 ^a	19.34 ^a	0.18 ^c
Control	6.9 ^a	136 ^a	676 ^b	272 ^a	1084 ^b	14.65 ^b	0.24 ^b

Values in the same column with the same superscript letters are not significantly different ($P < 0.05$)

ULL ultra-low-linolenic soybean oil, LL low-linolenic soybean oil, Control = commodity soybean oil, OSI oxidative stability index, PV peroxide value

Oxidizability = (oleic acid % + 10.3(linoleic acid %) + 21.6(linolenic acid %)) [10]

Throughout the frying study, the percentages of the unstable 18:3 and 18:2 decreased at the beginning and the percentages of the more stable 18:1, 18:0 and palmitic (16:0) acids increased. This same tendency was reported by Onal-Ulusoy [9] for soybean oil heated at frying temperatures. After approximately day 9, the changes in the percentages of each fatty acid reached a plateau, probably because of an equilibrium between the degradation and the turnover rates of the oils (Table 2).

The α -, γ -, and δ -tocopherol concentrations of the fresh oils were different for each of the oils (Table 1). The total tocopherol concentration was greater for LL than for both ULL and the control, which were not different from each other (Table 1). Warner suggested that although fatty acid composition is crucial in determining oxidative stability in oils, tocopherol content also plays an important role in oil stability [14]. The greater tocopherol content may have given LL a slight stability advantage over ULL and the

Table 2 FAME Composition (%) and Hunter Lab values of ultra-low-linolenic acid (ULL), low-linolenic acid (LL), and control soybean oils throughout frying

	Oil	16:0	18:0	18:1	18:2	18:3	Hunter Lab		
							a	b	L
Fresh	ULL	9.9 ^b	6.0 ^a	26.0 ^b	56.6 ^a	1.5 ^c	-2.2 ^a	4.7 ^b	23.5 ^a
	LL	10.0 ^b	4.5 ^c	26.5 ^a	56.4 ^a	2.6 ^b	-1.8 ^a	3.2 ^b	51.5 ^a
	Control	10.9 ^a	4.7 ^b	25.5 ^c	53.7 ^b	5.3 ^a	-2.2 ^a	6.0 ^a	53.4 ^a
2 days	ULL	10.8 ^b	6.9 ^a	28.8 ^b	52.3 ^a	1.2 ^c	-1.0 ^a	18.6 ^a	43.0 ^a
	LL	10.9 ^b	5.5 ^c	29.6 ^a	51.9 ^a	2.2 ^b	-0.7 ^a	19.4 ^a	42.0 ^a
	Control	12.1 ^a	5.8 ^b	28.5 ^b	49.0 ^b	4.7 ^a	-0.5 ^a	18.8 ^a	40.8 ^a
5 days	ULL	11.5 ^b	7.9 ^a	31.0 ^b	48.6 ^a	1.0 ^c	3.4 ^b	17.6 ^a	34.2 ^a
	LL	11.6 ^b	6.3 ^c	31.5 ^a	48.7 ^a	1.9 ^b	3.3 ^b	18.1 ^a	34.2 ^a
	Control	12.7 ^a	6.7 ^b	30.7 ^b	46.1 ^b	3.9 ^a	4.5 ^a	17.6 ^a	32.9 ^a
9 days	ULL	12.2 ^b	8.6 ^a	32.9 ^a	45.5 ^a	0.9 ^c	5.1 ^a	13.4 ^a	27.5 ^a
	LL	12.1 ^b	7.1 ^c	33.2 ^a	45.9 ^a	1.8 ^b	5.7 ^a	13.9 ^a	27.5 ^a
	Control	13.0 ^a	7.3 ^b	32.2 ^b	43.8 ^b	3.7 ^a	5.9 ^a	13.4 ^a	26.6 ^a
14 days	ULL	12.2 ^b	8.9 ^a	33.6 ^b	44.4 ^a	0.9 ^c	6.5 ^a	13.2 ^a	25.9 ^a
	LL	12.1 ^b	7.5 ^c	34.1 ^a	44.6 ^a	1.7 ^b	7.3 ^a	13.2 ^a	25.1 ^{ab}
	Control	13.1 ^a	7.7 ^b	33.2 ^b	42.5 ^b	3.6 ^a	6.7 ^a	11.9 ^b	23.4 ^b
19 days	ULL	12.2 ^b	9.1 ^a	33.6 ^b	43.9 ^a	0.9 ^c	6.5 ^{ab}	11.7 ^a	23.5 ^a
	LL	12.3 ^b	7.8 ^c	34.1 ^a	43.4 ^a	1.7 ^b	6.2 ^b	11.2 ^a	22.7 ^{ab}
	Control	13.2 ^a	8.1 ^b	33.2 ^b	41.9 ^b	3.5 ^a	7.1 ^a	10.7 ^a	21.2 ^b
23 days	ULL	12.2 ^b	9.1 ^a	34.3 ^a	43.5 ^a	0.9 ^c	5.8 ^a	11.1 ^a	22.8 ^a
	LL	12.2 ^b	7.6 ^c	34.3 ^a	44.2 ^a	1.7 ^b	5.8 ^a	10.8 ^a	22.2 ^{ab}
	Control	13.4 ^a	8.2 ^b	34.4 ^a	40.6 ^b	3.4 ^a	4.5 ^b	9.5 ^b	20.3 ^b

Values in the same column within the same day with the same superscript letters are not significantly different ($P < 0.05$)

FAME = fatty acid methyl esters of 16:0 (palmitic acid); 18:0 (stearic acid); 18:1(oleic acid); 18:2 (linoleic acid); 18:3 (linolenic acid)

+ a = red, -a = green; + b = yellow, -b = blue; L, 0 = black, 100 = white

control. Previously, the tocopherol content affected the TPC content in oils heated at frying temperatures [15].

The PV of the three fresh oil treatments were all less than $1 \text{ meq} \times \text{kg}^{-1}$, indicating that all oils were unoxidized and of high quality, although statistical differences occurred among the oil types (Table 1). The OSI of the fresh oils was greater (more stable) for ULL and LL than for the control, which was likely a direct result of the lower level of 18:3 in ULL and LL (Table 2). These values were consistent with the calculated oxidizability (Table 1), which showed that the lower the 18:3 the greater the theoretical stability. OSI predicts the oxidative stability of the oils under the severe conditions employed by this method, but does not necessarily indicate stability during deep-fat frying of food, because of the differences in the systems (unpublished data).

Figure 1 shows the FFA evolution over frying time for each of the oil treatments. There was no evidence of differences in FFA among the oils until 14 days of frying. At that point, and generally during the rest of the frying period, the control had a greater FFA level than did LL and ULL. The control tended to have a higher FFA level throughout frying. Oils with high FFA are known to have a lower smoke point [16] and the surfactant effect of FFA contributes to the foaming which leads to further oxidation of the oil.

The concentrations of polar compounds were not significantly different among the oils throughout frying. However, the control tended to have the greatest values, probably a result of its higher level of 18:3 and overall greater oxidizability (Fig. 2). In many countries, the level of 25% polar compounds is considered to be the discard point for a frying oil [17]. With that criterion and by interpolating the polar compound levels presented in Fig. 2, both ULL and LL had a frying life 2 days longer than the control (~30% increase in frying time).

Throughout frying, the control had the greatest levels of CDA (Fig. 3), which may be directly related to its higher

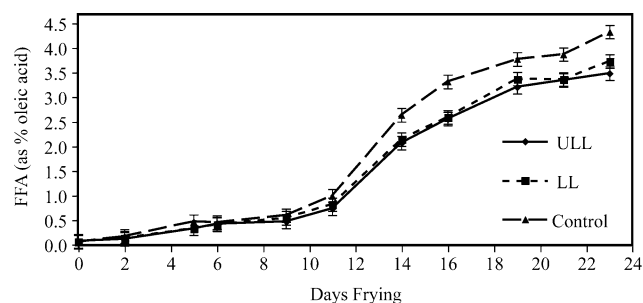


Fig. 1 FFA evolution in ultra-low-linolenic acid (ULL), low-linolenic acid (LL) and control soybean oils throughout frying. Each value represents the mean of two replications. Bars around each data point indicate standard error of the mean for all data points

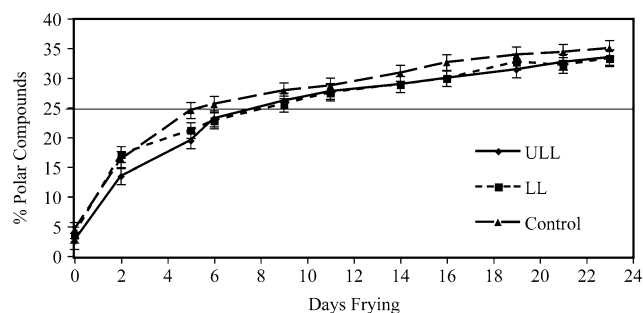


Fig. 2 Total polar compounds in ultra-low-linolenic acid (ULL), low-linolenic acid (LL) and control soybean oils throughout frying. Each value represents the mean of two replications. Bars around each data point indicate standard error of the mean for all data points. The value of 25% polar compounds is used in some countries as the maximum allowed, i.e. the discard value for frying oils [17]

18:3 content. ULL and LL were not different from each other. Even though the LL had a greater 18:3%, its higher tocopherol content may have helped reduce the CDA formation. The greatest changes in CDA content occurred at the beginning of the frying period: after day 5 the evolution in the CDA content was much slower. A previous study showed the same trend in CDA development during the initial stages of frying [18]. All the oils had reached their maximum levels of CDA by day 6. At that point, the CDA of the control and LL started to decrease in value but ULL remained at the maximum level until day 9. The further decrease might be explained by the degradation of the CDA to form other secondary breakdown products. FFA, formed mostly through hydrolysis, began to increase more quickly at about day 9 for all treatments.

There was no clear tendency with respect to Hunter *a* value changes among the oils (Table 2, values not shown for all frying days). The control was more red (higher *a*) than were ULL and LL on days 5 and 6. On day 16, LL was redder than ULL, the only point at which ULL and LL were significantly different from each other. The control

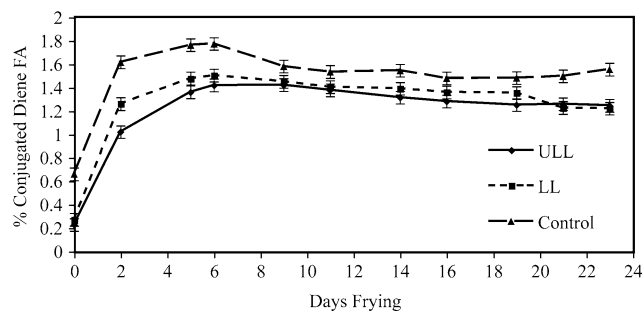


Fig. 3 Conjugated diene acid content in ultra-low-linolenic acid (ULL), low-linolenic acid (LL) and control soybean oils throughout frying. Each value represents the mean of two replications. Bars around each data point indicate standard error of the mean for all data points

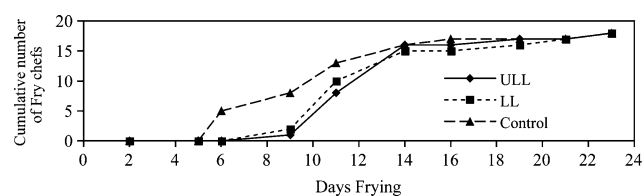


Fig. 4 Cumulative number of fry chefs who judged at least one of the replicates of ultra-low-linolenic acid (ULL), low-linolenic acid (LL) and control soybean oils ready for changing during frying (9 chefs \times 2 replicates = 18 total observations)

was redder than LL on day 19. After 21 days and until the end of frying, LL became redder than the control as did ULL on day 23. In the fresh oils, the Hunter **b** value was greatest in the control (most yellow), followed by ULL and LL (fresh oils). On days 14, 21, and 23, LL and ULL were more yellow than the control. Hunter **L** values decreased (oils became darker) throughout frying. On day 9, the rate of darkening decreased and, starting on day 14 and until the end, ULL was significantly lighter (higher Hunter **L** value) than the control. The darkening of the oils during frying has been previously associated with the formation of polymers [16]. It is probable that Maillard browning products formed in the fries leached into the oil also contributing to its darkening.

Overall, Hunter **a** values for all oils tended to increase (became more red) during frying, with a subsequent decrease during the last 4 days. In general, Hunter **b** values increased during the first 2 days of frying and then decreased (became less yellow). The initial rapid increase in darkness, redness and yellowness in the first phase of the process was likely related to the accumulation of the Maillard browning reaction products from the fries. Color formation gradually changed as the oil degradation products formed. These findings agree with the study of Su and White in which bread cubes were fried in various soybean oils [19]. In the current study, CDA and color evolved at faster paces during the first phase of the process. After day 9, the changes in these two parameters were less pronounced. At this point, the changes in FFA accelerated. Generally, CDA and color changes were reflective of the early changes in the oil during frying, whereas changes in FFA were more pronounced later in frying.

There were strong linear correlations among all the treatments between TPC content and Hunter **L** value. The regression equations obtained for the oils and their respective correlation coefficients (r) are: ULL, $L = -0.960 \text{ TPC} + 54.119$ ($r = 0.98$); LL, $L = -1.045 \text{ TPC} + 56.324$ ($r = 0.97$); control, $L = -1.087 \text{ TPC} + 58.094$ ($r = 0.98$). All the correlations were significant at $P < 0.001$. This decrease in the lightness of the oils with the increase of

TPC content in the measured range agrees with the results obtained by Paul and Mittal [20], who noted a third-degree correlation between TPC and lightness in canola oil shortening during frying.

Figure 4 shows the mean cumulative number of fry chef observations indicating that at least one replicate of the frying oils was ready for changing by the day noted. By day 9, 8 out of 18 possible observations noted that the control needed to be changed, whereas only one indicated ULL and two indicated LL needed replacement. After day 9, the control continued to be recommended for changing at a greater rate than the other two oils. Thus, a longer fry life, and potential monetary savings could arise from use of the ULL or LL.

There were no differences in buttery, potato, and painty flavors among the different oils (data not shown) throughout the first 6 days of frying. For rancid flavor, ULL and LL were not different from each other, but both were significantly lower (better) than the control throughout frying. All values, except for potato, were relatively low in intensity throughout testing with values ranging from 0.7 to 4.7 cm on a 15-cm scale, indicating there were few rancid and painty off flavors and a low amount of buttery flavor. Potato flavor predominated in all treatments, with overall values of 7.6 to 9.0. There was a tendency, however, for both ULL and LL to score lower (better) than the control with respect to painty flavor. For example, on days 5 and 6, the control oil had values of 3.6 and 4.7 respectively, whereas the ULL was 2.5 and 3.6 and the LL was 2.1 and 2.9 (data not shown).

In general, both ULL and LL oils performed better than the control. ULL tended to be more stable than LL. Both LL and ULL may be good alternatives to partially hydrogenated oils in frying operations. The extruded-expelled extraction and physical refining of the soybean oils evaluated in the current paper may have had an impact on the overall results, thus, it would be good to evaluate these oils treated by the more traditional hexane-extraction and chemical refining procedures.

Acknowledgments We thank the Michigan Soybean Promotion Committee and the Center for Crops Utilization Research (CCUR) at Iowa State University for funding, CCUR for facility use, Drs. Lester Wilson and Tong Wang for use of their laboratory equipment, the Center for Designing Foods to Improve Nutrition for assistance with sensory evaluations, and Dr. Philip Dixon for help with the statistical design and analyses.

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