Effect of Oil Replenishment During Deep-Fat Frying of Frozen Foods in Sunflower Oil and High-Oleic Acid Sunflower Oil

Antonio Romero[a], Carmen Cuesta[a,]*, and Francisco J. Sánchez-Muniz[b]

[a]Instituto de Nutrición y Bromatología (CSIC-UCM), and [b]Departamento de Nutrición y Bromatología I (Nutrición), Sección Lípidos, Facultad de Farmacia, Universidad Complutense, E-28040 Madrid, Spain

ABSTRACT: Frying stability of sunflower oil (SO) with 23% oleic acid and 61% linoleic acid, and of high-oleic acid sunflower oil (HOSO) with 74% oleic acid and 13% linoleic acid was studied during 20 discontinuous deep-fat fryings of various frozen foods, with or without frequent replenishment of the used oil with fresh oil. Alterations of both oils were measured by column, gas–liquid and high-performance size-exclusion chromatography. Total polar content and compounds, related to thermoxidative changes, and diacylglycerides, related to hydrolytic changes, increased in all oils during frying but reached higher levels in SO than in HOSO. Nevertheless, the increased levels of diacylglycerides observed may result from the frozen potatoes prefried in palm oil. Oleic acid in HOSO and linoleic acid in SO significantly decreased, but the fatty acid modifications that occurred during the repeated fryings were not only related to thermoxidative alteration but also to interactions between the bath oil and the fat in the fried products. Data from this study also indicated that HOSO performed more satisfactorily than SO in repeated fryings of frozen foods. Moreover, frequent addition of fresh oil throughout the deep-frying process minimized thermoxidative and hydrolytic changes in the frying oils and extended the frying life of the oils.
JAOCS 75, 161–167 (1998).

KEY WORDS: Deep-fat frying, fatty acids, frozen foods, high-oleic acid sunflower oil, high-performance size-exclusion chromatography, oil replenishment, polar compounds, sunflower oil.

Consumption of frozen foods has greatly increased during the last decades. This development has promoted the growth of new industries, and frozen foods are now commonly used by fast-food restaurants, catering services, and consumers. Frying is a process of heat and material transfer, where oil is both a heating medium and an enhancer of flavor. Unfortunately, physical properties and flavor characteristics of oil can change quite rapidly (1). Previous studies have suggested the necessity of controlling two variables—the amount of fried food and the replenishment of oil in the fryer—to maintain oil quality (2–4). However, the debate on deep-fat frying is still primarily focused on how the frequent replenishment of used oil with fresh oil affects deterioration of the frying oil (5).

Oxidative stability of frying oil can be improved by using fats with low unsaturation (6,7), but their high saturated fatty acid content makes them less desirable from a nutritional standpoint (8,9). For this reason, consumption of monoenoic fats has increased throughout the world (10). Nutritional advantages of oleic acid have been recognized in recent years (11). The increased level of consumer awareness toward fat composition and its impact on human health could have an effect on selection of fats in the snack food industry. In addition, the choice of frying oil should also be made according to its performance in the frying process. Although the traditional source of dietary monounsaturated fatty acids (MUFA) in Mediterranean countries has been olive oil, other sources are now becoming available, such as low-erucic acid rapeseed oil (canola oil) and oleic acid-rich variants of sunflower (SO) or safflower oils. Economic reasons are involved in this important change in these countries' dietary habits (12).

The objective of this study was to evaluate frying stability differences of SO and a high-oleic acid SO in 20 discontinuous deep-fat fryings of frozen foods with either frequent or null replenishment with fresh oil, by measuring the total polar material. Furthermore, the polar fraction was examined by high-performance size-exclusion chromatography (HPSEC) to investigate the thermoxidative and hydrolytic changes.

MATERIALS AND METHODS

Samples. Refined SO (trademark Coosol, Vilches, Andalucía, Spain) and refined high-oleic acid SO (HOSO) (trademark VIPA, Andújar, Andalucía, Spain), and frozen prefried potatoes (McCain Alimentaire S.A., Harnes, France), croquettes, tuna pastries, fish fingers, battered squid and breaded fish (Pescanova, Redondela, Galicia, Spain), spring rolls (Oetker, Bielefeld, Germany), fritters (La Cocinera, Torrejón de Ardoz, Madrid, Spain), and breaded ham and cheese (Findus-

---

*To whom correspondence should be addressed at Departamento de Nutrición y Bromatología I (Nutrición), Facultad de Farmacia, Universidad Complutense, 28040-Madrid, Spain. E-mail: frasan@eucmax.sim.ucm.es.

Nestlé España S.A., Esplugues de LLobregat, Barcelona, Spain) were purchased at a local store. These frozen foods were selected to be fried in both oils because they are the most frequently used in deep-fat frying by a representative sample of university students in the Madrid Autonomy Community (13). The sample frying sequence is listed in column 1 in Table 1. For example, the first sample fried was prefried potatoes, the second was fish fingers, while the ninth sample fried was battered squid, and so on.

Frying procedure. Domestic deep-fat fryers with 3-L vessels were used for frying. The amounts of frozen foods in the successive fryings were 305 to 460 g (Table 1). In total, 20 fryings were carried out by employing two methods: null replenishment (NR) and frequent replenishment (FR). The NR method was performed by avoiding replenishment of the bath oil, whereas the FR method was carried out with replenishment of the bath oil with fresh oil after each frying. Two fryings were carried out per day, one in the morning and the other in the afternoon. The 20 fryings took place over 10 consecutive days. The frying sequence of frozen food is shown in Table 1. Time required to bring the bath oil to 180°C before introduction of frozen foods was ~12 min. Frozen foods were then fried for 3 to 8 min (Table 1). The overall time that the oil was heated throughout the whole experiment can be estimated as ~100 min. Oil loss throughout the frying process required the addition of ~1.1 L throughout the 20 fryings and was carried out in the frequent replenishment modality. Samples of frying oils were packaged under nitrogen and stored at −20°C.

Lipid extractions. Lipids from the prefried frozen potatoes were extracted four times with hexane at a 1:50 (wt/vol) ratio in each extraction operation.

Fatty acid determination. Analysis of fatty acids was carried out by gas–liquid chromatography. Samples of the oil were saponified for 30 min at 60°C with 40 mL/g 0.5 N NaOH in methanol and then methylated with boron trifluoride–methanol complex to achieve complete conversion to methyl esters (14). The esters were extracted into hexane, freed of moisture over anhydrous sodium sulfate, and dried under nitrogen gas. The fatty acid content of the oils was analyzed in a Hewlett-Packard 5890 Series II gas chromatograph (Palo Alto, CA), equipped with a 50-m, i.d. 0.22 mm, capillary column (BPX70) with 0.25 µm film thickness (SGE, Austin, TX). Three samples each of unused HOSO and SO oils and three samples of the same oils after being used in eight and 20 fryings were analyzed.

TABLE 1
Frying Sequence of Frozen Foods

Frying order	Type of frozen food	Batch time (min)	Food weight (g wet matter)
1,5,8,12,16,20	Frozen prefried potatoes	8	495
2	Fish fingers	4	415
3	Fritters	6	305
4,11	Tuna pastries	5	440
6,14,19	Croquettes	3	365
7,13	Breaded ham and cheese	4	335
9,17	Battered squid	3	400
10,18	Breaded hake	3	400
15	Spring rolls	5	460

Polar content. Total polar fraction of the oils was determined by silica column chromatography (15), with the following modification: an accurately weighed sample of 1 ± 0.01 g of each oil was dissolved in 20 mL hexane/diethyl ether (87:13, vol/vol) when unused oil was analyzed, and (90:10, vol/vol) when used oil was analyzed. The same proportion of hexane/diethyl ether was used to fill the column and to elute the nonpolar fraction, to obtain a sharper separation (16,17). Two samples each of unused SO and HOSO oils and of used oils from the eighth and twentieth fryings were analyzed.

Separation of nonpolar and polar fractions was checked by thin-layer chromatography on 0.5-mm thick 60 F 250 silica gel plates (20 × 20 cm glass). Polar and nonpolar fractions were diluted 50 times (wt/vol) in hexane/diethyl ether 80:20 (vol/vol). Samples were applied as 20-µL spots with a 705 Hamilton microsyringe. Plates were developed with hexane/diethyl ether/acetic acid (80:20:1, vol/vol/vol) in a lined tank for *ca.* 25 min (*ca.* 17 cm) and then removed to let the solvent evaporate. The spots were visualized by exposure to iodine vapors.

HPSEC. To obtain further information about hydrolytic and/or thermoxidative changes occurring during frying, polar fractions of both oils, previously obtained by column chromatography, were analyzed by HPSEC by following the method of Dobarganes *et al.* (18) while taking also into account later HPSEC studies (19). Isolated polar fractions were analyzed in a Waters 501 chromatograph (Milford, MA) with a 20-µL sample loop. A Waters 410 refractive index detector and two 300 mm × 7.5 mm i.d. (5 µm particle size) pL gel (polystyrene-divinylbenzene) columns (Hewlett-Packard) with 0.01 and 0.05 µm pore size were connected in series and operated at 40°C. High-performance liquid chromatography (HPLC)-grade tetrahydrofuran served as the mobile phase with a flow rate of 1 mL/min. Sample concentration was 15 to 20 mg/mL in tetrahydrofuran. All eluents, as well as samples, were filtered through a 2-µm filter. Two determinations of each polar fraction of both fresh and used HOSO and SO were performed. The quantity of each polar compound was calculated as has been described previously (2).

RESULTS AND DISCUSSION

Amounts of total polar content, oligomeric triacylglycerides and oxidized triacylglycerides, related to thermoxidative alteration, and diacylglycerides (DAG), monoacylglycerides and free fatty acids (FFA), related to hydrolytic alteration, were monitored. Quantitative results for total polar content and for the distribution of polar compounds during the frying process are given in Tables 2 and 3. The coefficient of variation was less than 1.5% for total polar content. The polar compound distribution, determined by HPSEC, allowed differentiation of the main groups of compounds present and the establishment of the relative influence of the three degradation pathways predominant in frying: hydrolysis, polymerization, and oxidation (20,21).

Table 2 shows that the total polar content in the starting oils was similar at 3.06 ± 0.08 (mean ± SD) and 3.70 ± 0.12 mg/100 mg oil for HOSO and SO, respectively. Discontinuous frying increased the polar content in all used oils [NR high-oleic acid SO (NR-HOSO), FR high-oleic SO (FR-HOSO), NR SO (NR-SO), and FR SO (FR-SO)]. Nevertheless, HOSO appeared to be more stable in both frying methods, particularly in the NR modality. This comparison is relevant because, under the same frying conditions, the behavior of HOSO is better than that of SO. Moreover, the FR modality increased the frying life and thereby the quality of both oils.

Sánchez-Muniz *et al.* (5) observed no differences in total polar content due to the frying method (NR or FR), up to the 30th frying of potatoes in SO. However, the total polar content was higher in the NR modality at the 50th frying (24.1%) than in the FR modality (18.9%).

Pérez-Camino *et al.* (22) found an increase of the total polar content in olive oil and SO used six times to fry frozen prefried potatoes and battered hake. However, comparisons between both oils suggest a lower alteration for the oleic acid. After 21 fryings of frozen prefried potatoes in peanut oil and in soybean oil, Sébédio *et al.* (23) found levels of 27.5 and 26.8 (wt%) of polar components, respectively. According to these authors, soybean oil and peanut oil behave similarly at 180°C, despite differences in the linolenic, linoleic, and oleic acid contents.

Hence, the frying process improves when an oil with a high MUFA content is used. Nevertheless, in the current study, the total polar content was not higher than 25%, which some countries suggest as a criterion for discarding the oil (24,25).

Despite the similar levels of polar compounds in the initial fresh oils, the polar compound distribution was different in these oils. Table 3 shows that DAG were the major compounds in the initial HOSO and that triacylglyceride polymer content was practically null in this oil, whereas the main compounds for unused SO were oxidized triacylglycerides, and triacylglyceride polymers were already present. Pérez-Camino *et al.* (22) indicated that DAG were the major compounds in olive oil, while oxidized triglyceride monomers predominated in SO, in spite of similar concentrations of polar compounds in initial oils. Romero *et al.* (26) found DAG as the major compounds in unused HOSO.

TABLE 2
Total Polar Content[a], Hydrolytic Alteration[b], Thermoxidative Alteration[b], and Thermoxidative-to-Hydrolytic Alteration Ratio in Frozen Prefried Potatoes and in Unused Oils and After Being Used in Frying of Frozen Foods

Method of frying	Frozen prefried potatoes[c]	Fresh oil	NR-HOSO		FR-HOSO	
Number of fryings		0	8	20	8	20
Total alteration (polar compounds) % (w/w) on oil	13.0 ± 0.07	3.1 ± 0.09	8.0 ± 0.13	15.4 ± 0.06	7.8 ± 0.01	13.3 ± 0.03
Thermoxidative alteration (PTG + DTG + OTG) % of polar fraction	38.6 ± 0.85	36.5 ± 0.36	72.4 ± 0.36	82.3 ± 0.10	71.7 ± 0.21	80.2 ± 0.22
% (w/w) on oil	5.0 ± 0.09	1.1 ± 0.04	5.8 ± 0.06	12.7 ± 0.05	5.6 ± 0.02	10.7 ± 0.02
Hydrolytic alteration (DAG + FFA) % of polar fraction	61.5 ± 0.85	63.5 ± 0.36	27.6 ± 0.36	17.7 ± 0.10	28.3 ± 0.21	19.8 ± 0.22
% (w/w) on oil	8.0 ± 0.16	1.9 ± 0.04	2.2 ± 0.05	2.7 ± 0.01	2.2 ± 0.02	2.6 ± 0.03
Thermoxidative alteration/hydrolytic alteration	0.6	0.6	2.6	4.7	2.5	4.1
Method of frying	Frozen prefried potatoes[d]	Fresh oil	NR-SO		FR-SO	
Number of fryings		0	8	20	8	20
Total alteration (polar compounds) % (w/w) on oil	13.7 ± 0.28	3.7 ± 0.14	12.3 ± 0.25	20.5 ± 0.14	11.2 ± 0.29	15.9 ± 0.09
Thermoxidative alteration (PTG + DTG + OTG) % of polar fraction	43.2 ± 0.77	60.9 ± 0.40	87.3 ± 0.34	91.4 ± 0.05	85.9 ± 0.16	89.2 ± 0.05
% (w/w) on oil	5.9 ± 0.23	2.3 ± 0.08	10.7 ± 0.11	18.7 ± 0.10	9.6 ± 0.24	14.2 ± 0.07
Hydrolytic alteration (DAG + FFA) % of polar fraction	56.8 ± 0.77	39.1 ± 0.40	12.7 ± 0.34	8.6 ± 0.05	14.1 ± 0.16	10.8 ± 0.05
% (w/w) on oil	7.8 ± 0.09	1.4 ± 0.04	1.6 ± 0.05	1.8 ± 0.02	1.6 ± 0.05	1.7 ± 0.00
Thermoxidative alteration/hydrolytic alteration	0.8	1.6	6.9	10.6	6.1	8.2

[a] Mean ± SD of two samples.
[b] Mean ± SD of four samples.
[c] Frozen prefried potatoes used for frying in HOSO.
[d] Frozen prefried potatoes used for frying in SO. Abbreviations: NR, null replenishment; FR, frequent replenishment; HOSO, high-oleic acid sunflower oil; SO, sunflower oil; PTG, triacylglyceride polymers; DTG, triacylglyceride dimers; OTG, oxidized triacylglycerides; DAG, diacylglycerides; FFA, free fatty acids.

TABLE 3
Distribution of Polar Compounds[a] in Frozen Prefried Potatoes and in Unused Oils and After Being Used in Frying of Frozen Foods[b]

Method of frying	Frozen prefried potatoes[c]	Fresh oil	NR-HOSO		FR-HOSO	
Number of fryings		0	8	20	8	20
PTG% of polar fraction	0.0 ± 0.00	0.0 ± 0.02	5.8 ± 0.14	11.2 ± 0.28	5.7 ± 0.09	10.0 ± 0.27
PTG% (w/w) on oil	0.0 ± 0.00	0.0 ± 0.00	0.5 ± 0.01	1.7 ± 0.04	0.4 ± 0.01	1.3 ± 0.04
DTG% of polar fraction	20.8 ± 0.77	8.7 ± 0.47	30.9 ± 0.22	35.2 ± 0.21	30.9 ± 0.21	34.3 ± 0.13
DTG% (w/w) on oil	2.7 ± 0.12	0.3 ± 0.02	2.5 ± 0.04	5.4 ± 0.04	2.4 ± 0.02	4.6 ± 0.01
OTG% of polar fraction	17.8 ± 1.66	27.8 ± 0.41	35.7 ± 0.37	36.0 ± 0.13	35.1 ± 0.08	35.9 ± 0.34
OTG% (w/w) on oil	2.3 ± 0.20	0.9 ± 0.03	2.9 ± 0.02	5.5 ± 0.03	2.7 ± 0.01	4.8 ± 0.04
DAG% of polar fraction	60.3 ± 0.98	50.4 ± 0.85	22.5 ± 0.21	15.3 ± 0.11	23.1 ± 0.08	17.0 ± 0.15
DAG% (w/w) on oil	7.8 ± 0.17	1.5 ± 0.04	1.8 ± 0.04	2.4 ± 0.01	1.8 ± 0.01	2.3 ± 0.02
FFA% of polar fraction	1.1 ± 0.03	13.1 ± 0.56	4.9 ± 0.33	2.3 ± 0.09	5.0 ± 0.25	2.7 ± 0.19
FFA% (w/w) on oil	0.1 ± 0.00	0.4 ± 0.02	0.4 ± 0.03	0.4 ± 0.01	0.4 ± 0.02	0.4 ± 0.03

Method of frying	Frozen prefried potatoes[c]	Fresh oil	NR-SO		FR-SO	
Number of fryings		0	8	20	8	20
PTG% of polar fraction	0.0 ± 0.00	1.7 ± 0.04	7.9 ± 0.45	15.1 ± 0.18	7.1 ± 0.42	11.3 ± 0.22
PTG% (w/w) on oil	0.0 ± 0.00	0.1 ± 0.00	1.0 ± 0.05	3.1 ± 0.04	0.8 ± 0.05	1.8 ± 0.03
DTG% of polar fraction	23.8 ± 0.37	16.7 ± 0.06	40.1 ± 0.29	41.2 ± 0.12	38.8 ± 0.76	43.7 ± 0.13
DTG% (w/w) on oil	3.3 ± 0.12	0.6 ± 0.02	4.9 ± 0.08	8.4 ± 0.06	4.3 ± 0.20	7.0 ± 0.01
OTG% of polar fraction	19.5 ± 0.41	42.5 ± 0.33	39.3 ± 0.18	35.1 ± 0.11	40.0 ± 0.68	34.1 ± 0.40
OTG% (w/w) on oil	2.7 ± 0.11	1.6 ± 0.06	4.8 ± 0.03	7.2 ± 0.04	4.5 ± 0.04	5.4 ± 0.09
DAG% of polar fraction	55.5 ± 0.20	27.0 ± 0.34	9.4 ± 0.08	6.7 ± 0.03	10.3 ± 0.13	8.4 ± 0.05
DAG% (w/w) on oil	7.6 ± 0.13	1.0 ± 0.04	1.1 ± 0.02	1.4 ± 0.00	1.2 ± 0.05	1.3 ± 0.00
FFA% of polar fraction	1.3 ± 0.31	12.1 ± 0.53	3.3 ± 0.29	1.8 ± 0.08	3.8 ± 0.18	2.4 ± 0.05
FFA% (w/w) on oil	0.2 ± 0.04	0.4 ± 0.02	0.4 ± 0.04	0.4 ± 0.02	0.4 ± 0.02	0.04 ± 0.01

[a] Mean ± SD of four samples.
[b] See Table 2 for abbreviations.
[c] Frozen prefried potatoes used for frying in HOSO.
[d] Frozen prefried potatoes used for frying in SO.

However, during frying, dimers, polymers and oxidized triacylglycerides were the major compounds formed in all used oils, although FR-HOSO had the best stability in frozen-food frying. In a previous paper (5), we also found that polymers and dimers of acylglycerides, oxidized triacylglycerides, and DAG were higher in the NR-treatment after 50 fryings. After the 21st repeated use of peanut and soybean oils in frying frozen prefried potatoes, Sebedio *et al.* (23) found that polymers increase to 13.6–13.7%, respectively. The higher amount of oligomers (dimers plus polymers) in our study was found in NR-SO and accounted for about 11.5 g/100 g oil.

Total thermoxidative alteration levels changed in a similar way to the total polar alteration for all used oils (Table 2). After 20 frozen-food fryings, the thermoxidation product content was 18.72 (NR-SO) and 14.18 (FT-SO) mg/100 mg oil. These amounts were higher than those produced with HOSO, even in the NR-HOSO frying modality.

During the first eight fryings, oxidized triacylglycerides were the major compounds in all used oils, except in NR-SO. After 20 fryings, triacylglyceride dimers predominated in SO, although not in HOSO, in which oxidized triacylglycerides remained the major compounds (Table 3). These results are in accordance with those of Cuesta *et al.* (2) and Kupranycz *et al.* (27) in SO, and with those of Romero *et al.* (26) in HOSO.

Total hydrolytic alteration values increased throughout fryings (Table 2), but only DAG increased, while FFA remained unaltered (Table 3). Nevertheless, in previous works, we found that DAG remained quite stable during potato fryings (2,26). In this study, we observed higher DAG amounts in frozen prefried potatoes than in both fresh oils (Table 2). Thus, the increased levels of DAG observed in oils may come from the frozen prefried french fries.

In this study, FR-SO frying displayed similar results at the 20th frying to those of a previous study in which fresh sliced potatoes were fried in SO with the FR modality (2). This seems to be relevant because different foods, with different moisture contents, were fried. Furthermore, the initial polar content of that unused SO was different from that of the unused SO of the current study (5.1 *vs* 3.7%, respectively). Thus, the alteration rate was higher in frying frozen foods than in fresh sliced potatoes, just as occurs in FR-HOSO (26) and NR-SO (21). The temperature of the oil (data not shown) during these frozen-food fryings was higher (about 10°C during almost the whole process) than when fresh potatoes were fried in other studies (3,26), suggesting a more damaging temperature.

In addition, Table 3 shows that the thermoxidative-to-hydrolytic compounds ratio in both used oils increased during frying. FR-HOSO presented the best frying behavior because this ratio increased the least (from 0.58 to 4.06). Nevertheless, in a previous study (26), the same ratio increased from 0.6 to 3.1 after 75 FR-fryings of potatoes in HOSO. Thus, results clearly suggest that frying frozen foods has a greater deteriorative effect than frying fresh sliced potatoes.

The rate of oxidation and formation of the decomposition products is reported to be roughly proportional to the degree of unsaturation of the fatty acids present in the frying medium (15,28,29). SO, which contains almost 62% linoleic acid (Table 4), would be more susceptible to oxidation when used for frying than HOSO (13.5% linoleic acid). This is of great interest to the deep-fat frying industry because of the necessity of maintaining a good-quality frying medium as long as possible because of the fat absorption by foodstuffs during frying.

Measurements of fatty acid methyl esters (FAME) are given in Table 4. Linoleic acid decreased significantly after 20 fryings, from 61.9 to 53.1% (NR-SO) and 55.6% (FR-SO), respectively. However, after 20 fryings in HOSO, this fatty acid increased slightly in NR or FR methods. On the contrary, oleic acid after 20 fryings decreased from 74.9 to 70.1% (NR-HOSO) and 71.5% (FR-HOSO), but this fatty acid increased from 23.6 to 28.7% (NR-SO) and 27.4% (FR-SO). In addition, stearic acid levels were stable in both frying oils in NR and FR methods. Despite the stability of stearic acid, the level of palmitic acid increased during the fryings in both oils in both NR and FR methods.

Sebedio *et al.* (23) observed an increase of palmitic, stearic, and oleic acids in soybean oil (23.4% oleic acid; 51.9% linoleic acid; 7.2% linolenic acid) because of the degradation of linoleic and linolenic acids when frying prefried frozen potatoes. In the same study (23), however, they also found an increase of palmitic, stearic, and oleic acid in peanut oil (48.5% oleic acid, 29.4% linoleic acid, traces of linolenic acid) because of linoleic acid degradation.

Pozo-Díez *et al.* (30) observed, during 15 NR-HOSO fryings of frozen prefried potatoes, a marked decrease in unsaturated fatty acids (oleic and linoleic acids), while saturated fatty acids increased. Although the composition of this unused HOSO (80.9% oleic acid and 10.9% linoleic acid) was similar to that used in our study, Pozo-Díez *et al.* observed a decrease in linoleic acid.

In this study, the percentage of unsaturated fatty acid tended to decrease, whereas the percentage of saturated fatty acids, such as palmitic acid, increased, probably due to linoleic and oleic acid degradation. The results are in agreement with those found by Rodríguez *et al.* (31). However, the fatty acid modifications that occur during repeated fryings are not only related to thermoxidative alteration but also to interaction between the bath oil and the fat of the food product to be fried (32). Thus, the increase in the linoleic acid concentration observed after 20 fryings performed with HOSO is not easy to explain, but it could be due to the migration of this fatty acid from the food products into the bath oil. In this sense, batters of the frozen foods of this study, which included soybean oil or SO, could have accounted for additional amounts of linoleic acid in the bath oil.

The fat extracted from frozen prefried potatoes revealed that this food product was prefried with palm oil, because the fatty acid profile resembled the fatty acid pattern of this oil (Table 4). Thus, the increased levels of palmitic acid throughout the fryings in both oils may come from the palm oil used to par-fry these potatoes. These results are in agreement with those found by different authors. Pozo *et al.* (30), frying frozen prefried potatoes in HOSO, described that about 80% of the fat from the prefried potatoes was found in the bath oil. Previously, Pérez-Camino *et al.* (22) observed similar results after frying frozen prefried potatoes and battered hake.

After 20 fryings, the higher level of alteration of SO, compared to HOSO, with respect to fatty acids, corresponded with the data of several authors (29,32,33) who indicated that alterations of used frying fats are related to their unsaturated fatty acid content as well as to the heat treatment itself and the number of fryings.

Differences in the distribution of polar compounds could

TABLE 4
Fatty Acid Composition in Frozen Prefried Potatoes and in Unused Oils and After Being Used in Frying of Frozen Foods[a]

Method of frying	Frozen prefried potatoes[b]	Fresh oil	NR-HOSO		FR-HOSO	
Number of fryings		0	8	20	8	20
Palmitic acid: C$_{16:0}$	44.5 ± 0.05	4.3 ± 0.04	5.4 ± 0.06	6.8 ± 0.04	5.3 ± 0.04	6.2 ± 0.02
Stearic acid: C$_{18:0}$	4.5 ± 0.01	4.1 ± 0.03	4.1 ± 0.07	4.4 ± 0.02	4.1 ± 0.03	4.3 ± 0.01
Oleic acid: C$_{18:1}$ (ω9)	38.3 ± 0.03	74.9 ± 0.03	73.4 ± 0.10	70.1 ± 0.04	73.6 ± 0.10	71.5 ± 0.03
Linoleic acid: C$_{18:2}$ (ω6)	9.1 ± 0.01	13.6 ± 0.02	13.6 ± 0.20	14.7 ± 0.02	13.6 ± 0.02	14.4 ± 0.06
Method of frying	Frozen prefried potatoes[c]	Fresh oil	NR-SO		FR-SO	
Number of fryings		0	8	20	8	20
Palmitic acid: C$_{16:0}$	46.0 ± 0.14	6.8 ± 0.03	8.0 ± 0.04	9.4 ± 0.05	7.8 ± 0.02	8.6 ± 0.03
Stearic acid: C$_{18:0}$	4.9 ± 0.02	4.9 ± 0.05	5.1 ± 0.04	5.3 ± 0.06	5.0 ± 0.10	5.2 ± 0.01
Oleic acid: C$_{18:1}$ (ω9)	35.6 ± 0.11	23.6 ± 0.04	25.6 ± 0.03	28.7 ± 0.04	25.2 ± 0.03	27.4 ± 0.02
Linoleic acid: C$_{18:2}$ (ω6)	9.6 ± 0.01	61.9 ± 0.05	58.1 ± 0.04	53.1 ± 0.17	58.9 ± 0.08	55.6 ± 0.02

[a] Mean of three samples ± SD, expressed as percentage of total fatty acid methyl esters.
[b] Frozen prefried potatoes used during frying in HOSO.
[c] Frozen prefried potatoes used during frying in SO.

be associated with differences in the nutritional significance of the fats (34). DAG and fatty acids are usual compounds formed during fat metabolism, but polymers and oxidized triacylglycerides contain modified acyl groups, which impair the nutritional value of the fats. FR-HOSO displayed the lowest content of polymers and oxidized triacylglycerides during frying.

ACKNOWLEDGMENTS

This work was supported by the Spanish Comisión Interministerial de Ciencia y Tecnología (CICYT) Project ALI-92-0289-C02-01. Thanks are due to the fellowship application to Antonio Romero by the Consejería de Educación y Cultura of the Comunidad de Madrid.

REFERENCES

1. Friedman, B., New Control of Frying Process Provides Major Reduction of Oil in Food, in *Fat and Cholesterol Reduced Foods: Technologies and Strategies*, edited by C. Haberstroh, and C.E. Morris, Gulf Publishing Co., Houston, Texas, 1988, pp. 141–152.
2. Cuesta, C., F.J. Sánchez-Muniz, C. Garrido-Polonio, S. López-Varela, and R. Arroyo, Thermoxidative and Hydrolytic Changes in Sunflower Oil Used in Fryings with a Fast Turnover of Fresh Oil, *J. Am. Oil Chem. Soc. 70*:1069–1073 (1993).
3. Sánchez-Muniz, F.J., C. Cuesta, and C. Garrido-Polonio, Sunflower Oil Used for Frying: Combination of Column, Gas and High-Performance Size-Exclusion Chromatography for Its Evaluation, *Ibid. 70*:235–240 (1993).
4. Thompson, L.U., and R. Aust, Lipid Changes in French Fries Heated Oils During Commercial Deep Frying and Their Nutritional and Toxicological Implications, *Can. Inst. Food Sci. Technol. 16*:246–253 (1983).
5. Sánchez-Muniz, F.J., C. Cuesta, S. López-Varela, M.C. Garrido-Polonio, and R. Arroyo, Evaluation of the Thermal Oxidation Rate of Sunflower Oil Using Various Frying Methods, in *Proceedings of World Conference on Oilseed and Technology and Utilization*, edited by T.H. Applewhite, American Oil Chemists' Society, Champaign, 1993, pp. 448–452.
6. Arroyo, R., C. Cuesta, J.M. Sánchez-Montero, and F.J. Sánchez-Muniz, High-Performance Size Exclusion Chromatography of Palm Olein Used for Frying, *Fat Sci. Technol. 97*:292–296 (1995).
7. Keijbets, M.J.H., G. Ebbenhorst-Seller, and J. Ruisch, Suitability of Hydrogenated Soybean Oils for Prefrying of Deep-Frozen French Fries, *J. Am. Oil Chem. Soc. 62*:720–724 (1985).
8. Cuesta, C., F.J. Sánchez-Muniz, A. Rodríguez, and G. Varela, Alteraciones Fisicoquímicas de un Aceite de Oliva Empleado en Frituras Repetidas y Su Incidencia Sobre la Lipoproteinemia de Ratas, *Rev. Esp. Fisiol. 43*:51–56 (1987).
9. Billek, G., Heated Oils—Chemistry and Nutritional Aspects, *Nut. Metab. 24*:200–210 (1980).
10. Gupta, M.K., Designing Frying Fat, in *Proceedings of World Conference on Oilseed and Technology and Utilization*, edited by T.H. Applewhite, American Oil Chemists' Society, Champaign, 1993, pp. 204–208.
11. Nestel, P., P. Clifton, and M. Noakes, Effects of Increasing Dietary Palmitoleic Acid Compared with Palmitic and Oleic Acids on Plasma Lipids of Hypercholesterolemic Men, *J. Lipid Res. 35*:656–662 (1994).
12. Berger, K.G., Problems and Opportunities in Market Development of Oils, in *Fats for the Future*, edited by R.C. Cambie, Ellis Horwood Ltd., Chichester, England, 1989, pp. 217–232.
13. Cuesta, C., F.J. Sánchez-Muniz, and A. Romero, Use of Domestic Fryer Among University Students Families. Preliminary Data, in *2nd International Symposium on Frying of Foods*, January 25–26, 1996, Madrid, Spain.
14. International Union of Pure and Applied Chemistry, in *Standard of Methods for the Analysis of Oils, Fats and Derivatives*, edited by C. Paquot and A. Hautfenne, Blackwell Scientific Publications, Oxford, 1987, Method 2.301.
15. Waltking, A.E., and H. Wessels, Chromatographic Separation of Polar and Nonpolar Components of Frying Fats, *J. Assoc. Off. Anal. Chem. 64*:1329–1330 (1981).
16. Dobarganes, M.C., M.C. Pérez-Camino, and R. Gutiérrez González-Quijano, Métodos Analíticos de Aplicación en Grasas Calentadas. I. Determinación de Esteres Metílicos No Alterados, *Grasas y Aceites, 35*:172–177 (1984).
17. Perrin, J.L., F. Rodero, and A. Prevost, Dosage Rapide des Polymers de Triglycerides par Chromatographie d'Exclusion. I. Aspects Qualitatif, *Rev. Franç. Corps Gras. 31*:131–133 (1984).
18. Dobarganes M.C., M.C. Pérez-Camino, and G. Márquez-Ruíz, High-Performance Size-Exclusion Chromatography of Polar Compounds in Heated and Nonheated Fats, *Fat. Sci. Technol. 90*:308–311 (1988).
19. Christopoulou, C., and E.G. Perkins, High-Performance Size-Exclusion Chromatography of Monomer, Dimer and Trimer Mixtures, *J. Am. Oil Chem. Soc. 66*:1338–1343 (1989).
20. Arroyo, R., C. Cuesta, C. Garrido-Polonio, S. López-Varela, and F.J. Sánchez-Muniz, High-Performance Size-Exclusion Chromatographic Studies on Polar Components Formed in Sunflower Oil Used For Frying, *Ibid. 69*:557–563 (1992).
21. Frankel, E., Review. Recent Advances in Lipid Oxidation, *J. Sci. Food Agric. 54*:495–511 (1991).
22. Pérez-Camino, M.C., G. Márquez-Ruiz, M.V. Ruiz-Méndez, and M.C. Dobarganes, Lipid Changes During Frying of Frozen Prefried Foods, *J. Food Sci. 56*:1644–1650 (1991).
23. Sebedio, J.L., A. Bonpunt, A. Grandgirard, and J. Prevost, Deep Fat Frying of Frozen Prefried French Fries: Influence of the Amount of Linolenic Acid in the Frying Medium, *J. Agric. Food Chem. 38*:1862–1867 (1990).
24. Castang, J., Etude sur les Huiles de Friture. Caractères Analytiques et Projet de Règlementation, *Ann. Falsif. Expert. Chim. 74*:701–708 (1981).
25. Meyer, V.H., Eine Neve Und Einfache Schellmethode zur Erfassung des Oxidativien Zersetzungsgrades Thermisch Belasteter Fette, *Fette Seifen. Anstrichm. 81*:524–533 (1979).
26. Romero, A., F.J. Sánchez-Muniz, and C. Cuesta, High-Performance Size-Exclusion Chromatographic Studies on a High-Oleic Sunflower Oil During Potato Frying, *J. Am. Chem. Soc. 72*:1513–1517 (1995).
27. Kupranycz, D.B., M.A. Amer, and B.E. Baker, Effects of Thermal Oxidation on the Constitution of Butterfat, Butterfat Fractions and Certain Vegetable Oils, *Ibid. 63*:332–337 (1986).
28. Billek, G., Heated Fats in Diet, in *The Role of Fats in Human Nutrition*, edited by F.B. Padley, and J. Podmore (in collaboration with J.P. Brun, R. Burt, and B.W. Nicols), Ellis Horwood Ltd., Chichester, England, 1985, pp. 163–172.
29. Gutiérrez-González Quijano, R., and M.C. Dobarganes, Analytical Procedures for the Evaluation of Used Frying Fats, in *Frying of Food, Principles, Changes, New Approaches*, edited by G. Varela, A.E. Bender, and I.D. Morton, Ellis Horwood Ltd., Chichester, England, 1988, pp. 141–154.
30. Pozo-Díez, R.M., T.A. Masoud-Musa, M.C. Pérez-Camino, and M.C. Dobarganes, Intercambio Lipídico durante la Fritura de Patatas Prefritas Congeladas en Aceite de Girasol Alto Oleico, *Grasas y Aceites 46*:85–91 (1995).
31. Rodríguez, A., C. Cuesta, F.J. Sánchez-Muniz, and G. Varela. Estudio de las Alteraciones en Grasas Producidas por Frituras e Incidencia de su Administración sobre el Peso e Ingesta, *Ibid. 35:*22–28 (1984).

32. Guillaumin, R., Kinetics of Fat Penetration in Food, in *Frying of Food, Principles, Changes, New Approaches*, edited by G. Varela, A.E. Bender, and I.D. Morton, Ellis Horwood Ltd., Chichester, 1988, pp. 544–549.
33. Nawar, W.W., Chemical Changes in Lipids Produced by Thermal Processing, *J. Chem. Educ. 61*:299–302 (1984).
34. González-Muñoz, M.J., C. Tulasne, R. Arroyo, and F.J. Sánchez-Muniz, Digestibility and Absorption Coefficients of Palm Olein. Relationships with Thermal Oxidation Induced by Potato Frying, *Fett/Lipid, 98*:104–108 (1996).

[Received November 14, 1996; accepted November 11, 1997]