Polar Content vs. TAG Oligomer Content in the Frying-Life Assessment of Monounsaturated and Polyunsaturated Oils Used in Deep-Frying

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ABSTRACT: The frying-lives of olive oil (OO), sunflower oil (SO), and a blend of these oils (BO) were assessed and compared by measuring the polar content (PC) and the TAG oligomer content (TOC) in the oils. Oil was replenished with fresh oil every 10 uses in all three oils. Changes in the PC and TOC in relation to the number of frying uses were fitted to different curvilinear models. The power model yields the highest R^2 value in the three oils. The 25% PC was surpassed after 32.2 fryings [95% confidence interval (95% CI) 29.1–36.8] in the OO, 22.5 (95% CI, 21.0–24.6) fryings in the SO, and 27.5 (95% CI, 25.5–30.1) fryings for BO. However, according to the 10% TOC cutoff point, OO should be discarded after 25.0 (95% CI, 22.8–28.7) fryings, SO after 15.0 (95% CI, 14.8–15.4) fryings, and BO after 17.7 (95% CI, 17.0–19.1) fryings. Nevertheless, changes in PC and TOC were different only between OO and SO ($P < 0.05$ and $P < 0.02$, respectively), indicating that OO performs better than SO, and that BO can be used as an alternative when both frying-life and price are under consideration. Present findings suggest the need to unify criteria in different countries for oil disposal because the 25% PC corresponds to a TOC higher than 10%.

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KEY WORDS: Blend oil, deep-frying, frozen prefried foods, frying-life, HPSEC, olive oil, polar content, sunflower oil, triacylglycerol oligomers.

Frying of food is a very popular way of cooking at home and in fast-food restaurants. However, factors such as price, stability, and nutritive value must be considered (1). In the last decades, the use of olive oil (OO) for frying purposes in Spain and other Mediterranean countries has significantly decreased in the home and in small restaurants in favor of other oils, mostly sunflower oil (SO) (2,3). Furthermore, the use of a blend of OO and SO (BO) for frying has become popular in homes, small restaurants, and institutions (3). Such usage must be understood in terms of making frying cheaper while retaining some nutritional properties and taste of OO.

The debate on deep-fat frying in commercial establishments is primarily focused on the point at which any oil used for frying should be discarded (4). Many countries have passed specific laws and regulations concerning culinary oil used in frying. Most countries assess used frying oil according to its polar content (PC). Belgium, the Czech Republic, France, Hungary, Italy, the Scandinavian countries, and Spain have set a maximal PC level of 25%, whereas other countries, including Austria and Germany, have established a PC cutoff point between 20 and 27%. Moreover, among European countries the TAG oligomer (TAG dimers plus polymers of low M.W.) content (TOC) is another criterion used for evaluating used frying oil. Belgium and the Czech Republic have legislated a 10% maximal TOC, whereas the Netherlands permits up to 16% of these compounds in oil used for frying (4).

The goals of this study were (i) to evaluate the frying-life of OO, SO, and BO used in discontinuous deep-fat frying of different foods (mostly frozen prefried foods), with low replenishment with fresh oil, by measuring their PC and TOC and (ii) to compare results obtained using both PC and TOC.

MATERIALS AND METHODS

Materials. All foods and oils were provided by EDOCUSA S.A. (Madrid, Spain). The selection of foods and oils and the frying frequency employed in the present study were those used most frequently in deep-fat frying among a representative sample of housewives in Spain (EDOCUSA S.A.'s survey, unpublished data). We used OO of 0.4° acidity value (Carbonell™; Andújar, Jaén, Spain), refined SO of 0.4º acidity value (Koipesol™, Andújar) and frozen prefried potatoes and battered squid (Pryca hypermarkets, Spain), frozen croquettes (La Cocinera™; Torrejón de Ardoz, Madrid, Spain), frozen tuna pastries (Findus-Nestlé España S.A., Esplugues de Llobregat, Barcelona, Spain), frozen spring rolls and frozen breaded veal filets (Sánchez Romero, Jabugo, Huelva, Spain), frozen fish fingers (breaded hake) (Frudesa, l'Alcudia, Valencia, Spain), sausages (Gran Prix, Getafe, Madrid, Spain), and fresh potatoes (Kennebec variety; Xinzo de Limia, Galicia, Spain). Battered anchovies, battered green peppers, battered sliced eggplant, and meatballs (beef plus wheat flour) were prepared in the laboratory using standard culinary recipes. Oil blends were olive oil 0.4°/sunflower oil 0.4° (50:50).

Frying performance. Domestic stainless steel deep-fat fryers (Solac, Vitoria, Spain) with a frying capacity of 2.5 L were used for frying. One fryer was used per oil. Frying sequence and the amount of food used in the successive fryings are shown in Table 1. The food amount selected to be fried corresponded to the quantity suggested by the food companies

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TABLE 1
Frying Sequence, Type and Amount of Food, and Frying Time

Frying number	Food	Commercial name or variety name	Average amount of raw foodstuffs (g)	Frying time[a] (min)
1, 10, 11,	Fresh potatoes	Kennebeck	415	6
2, 15, 21, 24, 32, 34, 35	Frozen prefried potatoes	Pryca	415	6
3, 7, 12, 18, 22, 29, 33	Frozen croquettes	La Cocinera	295	4
4, 14, 23, 31	Tuna pastries	Findus	322	4
5, 28	Spring rolls	Sánchez Romero	305	6
6, 16, 26, 36, 38	Breaded hake (fish fingers)	Frudesa	317	4
8	Sausages	Gran Prix	182	2
9, 25	Frozen breaded veal filets	Sánchez Romero	230	4
13, 30	Battered anchovies	*[b]	187	4
17	Battered green peppers	*	375	4
19, 27, 39	Battered squid	Pryca	337	4
20, 37	Battered eggplant	*	345	4
40	Meatballs	*	330	4

[a]In accordance with recommendations of manufacturers or domestic recipes.
[b]Prepared in laboratory following standard recipes.

(e.g., one piece/person), when available, or the average amount to serve four persons.

Forty frying operations were performed while maintaining the oil volume constant by adding fresh oil after every 10 fryings. Two frying operations were carried out every day, one in the morning and another in the afternoon, letting the oil reach room temperature between fryings. The study was performed over 4 wk with no fryings carried out during weekends. Oil was replenished every 10 frying operations. Replenishment of oil throughout the 40 frying operations implied the addition of a total of 1.52 L of fresh OO, 1.40 L of BO, and 1.55 L of SO. The following frying conditions were used: oil temperature (180°C), heating time 9–12 min/frying (total: 412 min), frying time 2–6 min/frying (total: 198 min), and cooling time ~4 h/frying (total: ~9600 min). The frying numbers when oil was taken for analyses were 0, 5, 10, 20, 30, and 40.

This design was selected by taking into account data from a survey of fryer users (5), which showed that most people discarded the oil they use for frying after 2–4 wk or 15–20 uses. However, in some cases the number of frying uses was very high. The addition of fresh oil after a given number of fryings was a common practice in small restaurants or in homes with a large number of family members.

PC. Total PC of the oil was determined by silica column chromatography (6) as described previously (7). Samples of fresh OO, SO, and BO and from the 5th, 10th, 20th, 30th, and 40th uses of each respective oil were analyzed. The use of two fryers per type of oil was considered unnecessary, taking into account the low average SD found for PC (between 0.5 and 2%) in previous studies (8,9). Separation of nonpolar and polar fractions was checked by TLC as previously described (7).

High-performance size-exclusion chromatography (HPSEC). To obtain further information about polymerization changes that occur during frying, polar fractions previously obtained by column chromatography were analyzed by HPSEC (10). 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 × 7.5 mm i.d. (5 μm particle size) PLgel (polystyrene-divinylbenzene) columns (Hewlett-Packard) with 0.01 and 0.05 μm pore size were connected in series and operated at 40ºC. Details of the method have already been published (7). Determinations of TOC in fresh OO, SO, and BO and from the 5th, 10th, 20th, 30th, and 40th frying uses of each corresponding oil were performed. TOC was calculated as the sum of polymers of low M.W., and dimers of TAG as has been described previously (1).

Statistical methods. Changes in PC and TOC were correlated with the number of frying operations by using several curvilinear models (linear, power, squared root, reciprocal, double reciprocal, logarithmic, multiplicative, s-curve, logistic, log probit).
The power model,

$$Y = k{*}X^b \quad [1]$$

where Y = PC or TOC, k = constant, and X = number of fryings, was selected because it yields the highest R^2 value. Equation 1 was linearly transformed to

$$\ln Y = a + b{*}\ln X \quad [2]$$

where Y = PC or TOC, a = intercept, b = slope, and X = number of fryings. Furthermore, Equation 2 was modified to

$$\ln Y = a + b{*}\ln (X + 1) \quad [3]$$

as a consequence of the inclusion of the unused oils (frying number = 0).

The maximum number of frying operations before discarding the oil was obtained by using Equation 3 and subtracting one frying from this number. The PC and TOC regression equations obtained for the three oils were compared by an analysis of covariance (ANCOVA) test. A significant F ratio ($P < 0.05$) indicates that the slopes and/or intercepts differ beyond chance between oils. Pearson product–moment correlations were applied to identify the relationship between PC and TOC.

RESULTS AND DISCUSSION

The changes in the PC and TOC content and the different critical levels established for discarding frying oils are shown in Figures 1 and 2. The three fresh oils showed a very similar PC (3.4–3.6 mg/100 mg oil) and TOC (0.1–0.4 mg/100 mg oil).

Changes in PC and TOC were very significantly fitted ($P < 0.001$) to a power adjustment (Table 2). This model explains more than 98.3 and 96.2% of the data variability for the PC and TOC changes, respectively in any of the studied oils (Table 2). For each separate oil, PC and TOC were highly correlated ($P < 0.001$). However, the regression equation was different for each oil. The ANCOVA test showed that, according to the PC and TOC changes, OO performed differently ($P < 0.05$ and $P < 0.02$, respectively) from SO (Table 2).

Considering the different cutoff points for PC and TOC, Figure 3 shows the maximal amount of food that should have been fried in the three oils before discarding the oil. This was lower when the 10% TOC cutoff point was selected in spite of the 25% PC.

Both the PC and the TOC methods have been employed for years as a criterion to evaluate oil alteration and to indicate when to dispose of an oil. The former has been recommended owing to its simplicity and accuracy (11). However, some compounds defined as polar components are not necessarily altered (e.g., DAG, FFA) (12). TOC measurement probably gives more precise information about the alteration of an oil and therefore of the potential toxicity of the oil when it is consumed.

PC of the fresh oils used in the current study reflects the good quality of the oils, as PC of unused oils normally ranges between 0.4 and 6.4 mg/100 mg oil (13). Data are similar to other findings reported by our group in SO (14–16) and in other oils (1). In the present paper, discontinuous frying increased the PC and TOC more intensively, mainly in SO, during the initial 20 frying operations than in fryings 20–40. Cuesta *et al.* (15) found that changes in PC were highly adjusted to a cubic equation. However, Romero *et al.* (17,18) found that a second-degree equation accurately and significantly reflected ($r > 0.99$; $P < 0.001$) the adjustment of the PC levels, which varied according to the number of frying operations.

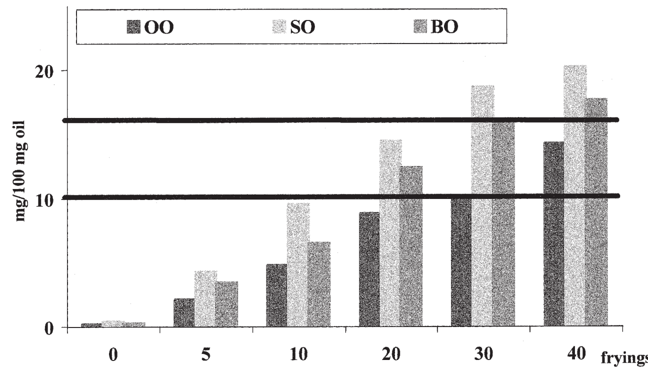

FIG. 2. Changes in TAG oligomer content (TOC) (mg/100 mg oil) of OO, SO, and BO. Lines at the 10 and 16 mg/100 mg oil levels reflect cutoff points for oil disposal in some countries. For abbreviations see Figure 1.

After 25 frying operations with SO, PC reached the 25% level. This occurred later with BO or OO. The critical level of 10% in TOC was surpassed about 10 fryings earlier in SO than in OO. Thus, results suggest that SO, and to a lesser degree BO, is rather susceptible to polymerization during frying, an aspect that has also been found in previous studies (7,9).

One interesting finding of the present paper is the rather different number of uses needed to reach the critical level of 25% PC and 10% TOC. The 25% PC corresponds to 11.3% TOC in OO, and to 15.8 and 14.5% TOC in SO and BO, respectively. A 16% TOC would correspond to 26.5% PC in SO, 33.8% in OO, and 27.2% in BO.

Before the oils reached the 10% TOC critical level, 83 and 48% more food could be fried in OO than in SO and BO, respectively. However, differences were lower considering the 25% PC, because 41 and 12% more food could be fried in OO than in SO and BO, respectively.

OO performed better and with less TOC production in 40 discontinuous fryings of foods than SO did. These findings suggest that, although the price of OO is much higher than that of SO (or BO), the longer frying-life of OO permits its use a few more times, decreasing both the TOC and the actual price of OO. Taking into account the potential toxicity of TAG oligomers (12,19,20) and the increased use of SO, BO,

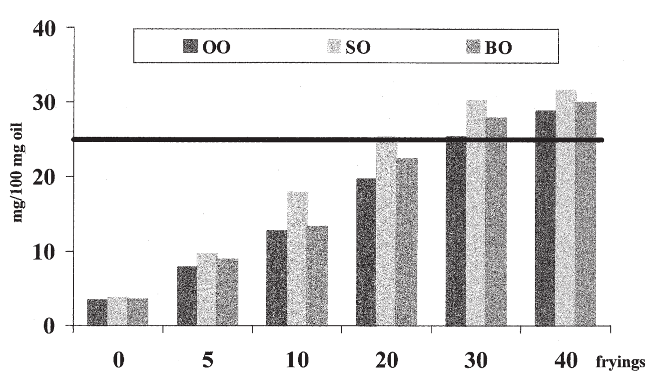

FIG. 1. Changes in polar content (mg/100 mg oil) of olive oil (OO), sunflower oil (SO), and the blend of both oils (BO). Line at 25 mg/100 mg oil reflects the cutoff point selected for oil disposal in many countries.

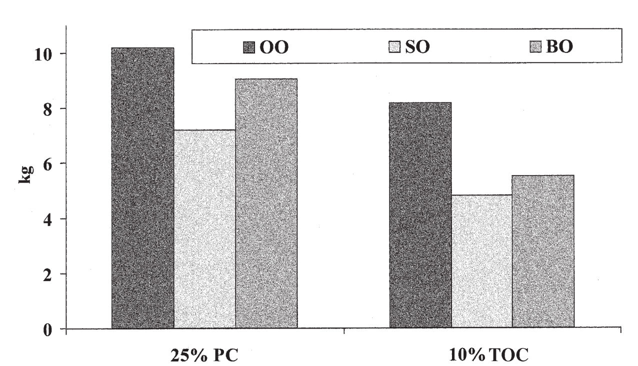

FIG. 3. Amount of food fried in OO, SO, and BO before the oils should be discarded according to the 25% polar content (PC) and the 10% TOC. For abbreviations see Figures 1 and 2.

TABLE 2
Power Adjustment of Polar Content and TAG Oligomer Content Change (both in mg/100 mg oil) in Olive Oil, Sunflower Oil, and a Blend of Both Oils and the Number of Frying Operations[a]

	Polar content			TAG oligomer content		
	Olive oil	Sunflower oil	Blend oil	Olive oil	Sunflower oil	Blend oil
Intercept	1.142	1.280	1.196	–1.566	–0.697	–1.077
(95% CI)	(0.918 to 1.367)	(1.012 to 1.549)	(0.999 to 1.393)	(–2.189 to –0.943)	(–1.417 to 0.023)	(–1.782 to –0.372)
Slope	0.593	0.614	0.604	1.188	1.082	1.153
(95% CI)	(0.510 to 0.676)	(0.515 to 0.714)	(0.531 to 0.677)	(0.957 to 1.418)	(0.815 to 1.348)	(0.892 to 1.414)
Correlation coefficient	0.995	0.993	0.996	0.990	0.985	0.987
R^2 (%)	98.7	98.3	99.1	97.6	96.2	96.8
Standard error of estimate	0.092	0.109	0.080	0.254	0.293	0.287
ANOVA *F* value	392.5	294.7	527.5	207.7	126.9	150.6
P-value of model	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
ANCOVA test	a	b*	a,b	a	b**	a,b***
Maximum number of fryings[b]	32.2	22.5	27.5	25.0	15.0	17.7
(95% CI)	(29.1 to 36.8)	(21.0 to 24.6)	(25.5 to 30.1)	(22.8 to 28.7)	(14.8 to 15.4)	(17.0 to 19.1)

[a]Linear transformation of $Y = k{*}X^b \rightarrow \ln Y = a + b{*}\ln X$; for more details see text. In parentheses, 95% confidence interval (95% CI).
[b]To reach 25% polar content or 10% TAG oligomer content. Different letters for the same parameter mean significant differences (*$P < 0.05$; **$P < 0.02$, ANCOVA test; ***$P < 0.1$).

and other unsaturated oils for frying purposes, we suggest that the cutoff point for oil disposition should be set at 10% for TOC instead of at 25% for PC. The need to unify the criteria for the disposal of a frying oil in different countries can be easily understood.

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