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Quality control during repeated fryings

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SUMMARY

Quality control during repeated fryings.

Most of the debate is about how the slow or frequent turnover of fresh fat affects the deterioration of fat used in frying. Then, the modification of different oils used in repeated fryings of potatoes without or with turnover of fresh oil, under similar frying conditions, was evaluated by two criteria: by measuring the total polar component isolated by column chromatography and by the evaluation of the specific compounds related to thermoxidative and hydrolytic alteration by High Performance Size Exclusion Chromatography (HPSEC). The results indicate that with frequent turnover of fresh oil, the critical level of 25% of polar material is rarely reached, and there are fewer problems with fat deterioration because the frying tended to increase the level of polar material and thermoxidative compounds (polymers and dimers of triglycerides and oxidized triglycerides) in the fryer oil during the first fryings, followed by minor changes and a tendency to reach a near-steady state in successive fryings. However, in repeated frying of potatoes using a null turnover the alteration rate was higher being linear the relationship found between polar material or the different thermoxidative compounds and the number of fryings. On the other hand chemical reactions produced during deep-fat frying can be minimized by using proper oils. In addition the increased level of consumers awareness toward fat composition and its impact on human health could had an impact on the selection of fats for snacks and for industry. In this way monoenic fats are the most adequate from a nutritional point of view and for its oxidative stability during frying.

KEY-WORDS: Column chromatography – Deep-fat frying – HPSEC – Oil Turnover – Polar compounds.

1. INTRODUCTION

Deep fat frying can be defined as a process of controlled dehydratation and browning with hot oil as the heat transfer medium (Gupta, 1993). On the other hand, deep fat frying is a complex process because many factors are present in the technological operation of frying. Some factors are dependent on the process itself and others on the food and the type of fats used. As described by Varela (1988) the factors that could be affecting the frying process of foods are as follows: Depending on the process: temperature, time, frying method, vessel material. Depending on the type of fat: properties of the fat alone (chemical, physical). Additives, contaminants. Depending on the food: commodity preparation (size and form of the food, battered), direct action (on termolabile nutrients improving nutrient interactions, nutrient interchange between the foodstuff and the frying fat). The combination of these parameters determines the rate at which the individual reactions take place.

There are studies on fat deterioration in frying process carried out without an adequate turnover of fresh oil in which more changes may occur in frying fats and foods, than under the regulated conditions prevailing in industrial cooking (Arroyo *et al.*, 1992, 1995).

The conditions under which frying is done therefore need to be clearly established to avoid obtaining apparently contradictory findings. Our research workers have been employed «model systems» to simplify and control the various parameters affecting the frying process.

In this lecture the design of the experiences have been projected taking into account the most salient factors that could be implicated in the deterioration of the fat during the technological operations of frying, taking in mind that is rather difficult to set up experimental desing because the complexity of the frying process.

In addition, because matters become complicated when a food with a high fat content is tested, we began by testing potatoes because the fact that potatoes contain no fat and then we avoided the complex interactions between the frying fat and the fat of the food.

The drawbacks to frying are also particularly relevant in repeated fryings. In this procedure the proportions of food weight/frying fat is one of the factors that has to be kept constant, because so much oil is removed along with the fried product. As described by Morton (1988), the amount of oil taken up during frying will be an important factor in the rate of oil turnover in the fryer and the achievement of equilibrium conditions. This is not easily done unless the right precautions are taken. Then deep-fat frying without or with an adequate turnover of fresh oil should be considered.

Quality assessment of a frying oil before use or assessment of changes taking place during frying or after being used, at the end of its frying life can be carried out by routine chemical and physical test such as colour, free fatty acids, iodine value or fatty acid composition (Gutierrez-González-Quijano *et al.*, 1988, Cuesta *et al.*, 199l, López-Varela *et al.*, 1995).

However the alteration of the frying oil can be evaluated by measuring the percentage of total polar content by the column chromatographic method of Waltking and Wessels (1981). Azpilicueta *et al.*

(1991) and Syis (1991) have stated that the polar fraction is the parameter that best represents the overall changes in the oil used for deep-fat frying. In this fraction they included most of the entities that are formed whilst the oil is submitted to continuous heating. Moreover total polar content determination is used now as the official method for quality control of frying fats in many countries.

On the other hand during deep fat frying a wide variety of chemical reactions takes place. The steam from a moist food will cause hydrolysis of triglycerides, resulting in the formation of free fatty acids, glycerol and mono and diglycerides, while the air released into the frying system will iniciate a cycle of oxidation reactions involving the formation of free radicals. These oxidation processes will involve fatty acids in intact triglycerides as well as the products of triglycerides hydrolysis. The fatty acid residues of triglycerides formed can react to form polymers and other complex reaction products. Intact or thermally modified triglycerides may be involved in polymerization via Diel-Alders reactions. In addition, many of the aforementioned reactions are interrelated and a complex mixture of products is formed (Nawar 1984, Gutierrez-Quijano *et al.*, 1988, Sebedio, 1990, Cuesta *et al.*, 1993, Sánchez-Muniz *et al.*, 1993).

Althought not requiered in routine control the use of high performance size-exclusion chromatography (HPSEC) should be of interest in providing more detailed information on changes other than the development of free fatty acids, foam, colour or peroxide formation. This is of a great interest to nutritionist because potentially specific toxic compounds might be present in an oil used in fryings or in edible frying products.

The technique of HPSEC permits to investigate the specific polar compounds related to thermoxidative alteration and those of the polar compounds related to hydrolytic alteration. Although many analytical methods have been used for determination of the monomers, dimers and higher polymers of oxidized fats and oils, the technique of HPSEC may be considered as one of the most promising because it increase the possibility of quantitation of all classes of alteration compounds: polymers and dimers of triglycerides, oxidized triglycerides, diglycerides, monoglycerides and free fatty acids (Dobarganes *et al.*, 1988; Christopoulou, 1989).

In short in this lecture we reported the modification of different oils used in repeated fryings of potatoes without or with turnover of fresh oil, under similar frying conditions. The alteration of the oils employed was evaluated by two criteria: by measuring the percentage of total polar component by the column chromatographic method of Waltking and Wessels (1981), because it is claimed that a fat or oil must be discarded when its polar fraction is more than 25% (Castang, 1981; Dobarganes *et al.*, 1989; Friedman, 1991; Blumenthal, 1991) and the evaluation of the specific compounds related to thermoxidative alteration and hydrolytic modification by HPSEC.

2. THERMOXIDATIVE AND HYDROLYTIC CHANGES IN SUNFLOWER OIL USED IN REPEATED FRYINGS OF POTATOES WITHOUT OR WITH FAST TURNOVER OF FRESH OIL

Experimental procedures

Performance of Fryings.— Refined sunflower oil and potatoes were purchased at a local store. The oil was stored below 15°C in the dark and used as purchased. In both systems of deep-fat fryings null turnover (NT) or fast turnover (FT) domestic fryers with a 3-L aluminum vessel were used for frying. The potatoes were chopped into slices ca. 2 mm thick. Potatoes were fried for 8 min at an initial temperature of 180°C. Time required to reach and keep the oil at 180°C, before introduction of potatoes, was 20 min. After the end of each frying operation, the oil was again heated at 180°C to start a new frying, and the time required was 10 min. This cycle was repeated until five fryings of potatoes were completed. After 5 h, another set of five fryings was performed before letting the oil cool to room temperature until the following day. The overall time the oil was heated throughout the whole experiment in the case of NT can be estimated as 18 h and 30 min, whereas in FT it was 18 h, 40 min. Aliquots of 50 mL from the unused oil and from the 10th, 20th, 30th, 50th, 60th and 75th fryings were taken for analysis.

NT and FT systems were performed at different times (one 30 days later than the other) demanding large volumes of sunflower oil. This explains why the fresh sunflower oil comes from different lots. Table I shows the fatty acid composition (percentage of chromatographed methyl esters) of unused sunflower oils.

Table I
Major fatty acid composition (percentage of chromatographed methyl esters) of unused sunflower oils

	Sunflower oil used in fryings with null turnover[a]	Sunflower oil used in fryings with a frequent turnover of fresh oil[b]
Palmitic	7.1±0.01	6.8±0.25
Stearic	4.0±0.05	3.8±0.15
Oleic	31.3±0.28	32.4±0.15
Linoleic	55.6±0.15	55.5±0.09

[a] Values are means of two analysis ± standard deviation.
[b] Values are means of three analysis ± standard deviation.

Figures 1 and 2 show the scheme of the frying method used in NT and FT fryings respectively. In the NT, the ratio of food to frying oil in the fryers was kept at 500 g/3 L without addition of fresh oil, by eliminating one fryer after ten fryings and emptying its contents to make up the volume of the other fryers to 3L. In the FT throughout the first 20 fryings, the frying bath volume was replenished with fresh oil every four fryings. After the 20th frying, the fryer volume was made up with unused oil every five fryings in order to carry out ten fryings per day. The addition of fresh oil each five fryings instead of four fryings did not change the aim of this study. Because after five fryings the oil loss (mainly oil absorbed by potatoes) was about l0%, the turnover of unused oil throughout the seventy-fyfth fryings in the FT can be estimated as 4.5 L per fryer.

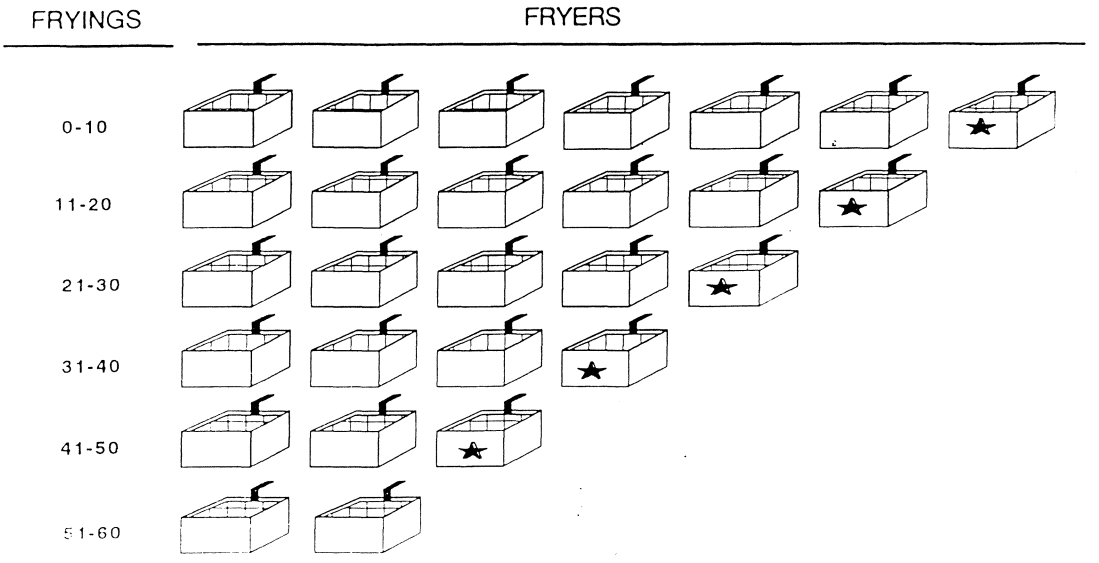

Figure 1
Performance of fryings with a null turnover of fresh sunflower oil. Star signifies fryer eliminated after each ten fryings and emptying its contents to make up the volume of the other fryers to 3 L in order to keep the proportion of food to frying oil at 500 g/3L

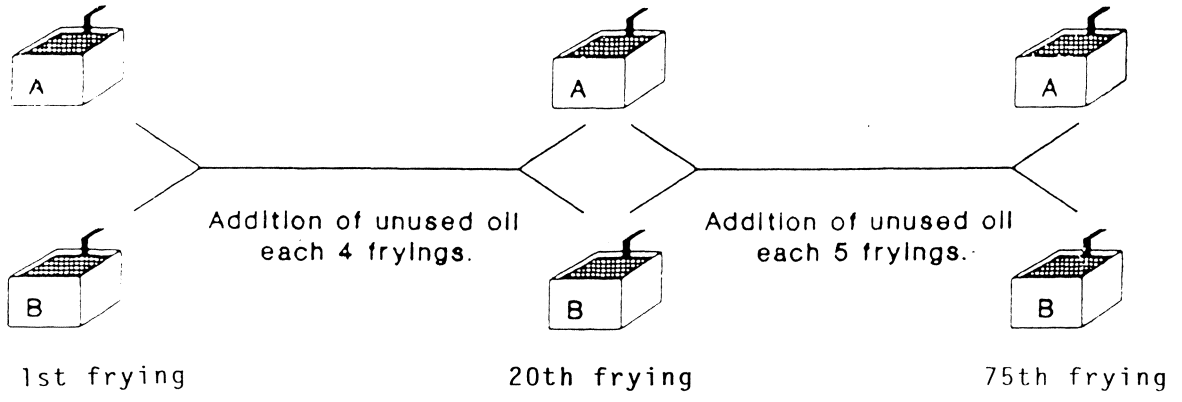

Figure 2
Performance of fryings with a frequent turnover of fresh sunflower oil in order to keep the proportion of food to frying oil at 500 g/3L

Determination of the Polar Fraction.— Polar fractions were evaluated by a modified column chromatographic method of Waltking and Wessels (1981). The modification was the proportion of light petroleum/diethyl ether used to fill the column and to elute the nonpolar fraction. The control of the separation of the nonpolar and polar fractions was accomplished by thin-layer chromatography (TLC) on 0.5 mm thick 60 F250 silica gel plates (20 x 20 cm glass) (Merck) as was indicated in previous works (Arroyo *et al.*, 1992, Cuesta *et al.*, 1993).

Two samples, of each oil (unused, and from the tenth, twentieth, thirteth, fiftieth, sixtieth and seventy-fyfth fryings), were homogeneously mixed and analyzed. An accurately weighed sample of 1 ± 0.01 g of sunflower oil was dissolved in 20 mL light petroleum/diethyl ether (87:13 v/v) when unused oil was analyzed. The solution was transferred to a silica gel chromatographic column following the method of Dobarganes *et al.* (1984). A final elution of the column with chloroform-methanol (1:1 v/v) was performed to improve the recovery of the sample.

High-Performance-Size Exclusion Chromatography (HPSEC).— Polar fractions previously obtained by column chromatography were analyzed by HPSEC following the Dobarganes *et al.* method (1988) to obtain further information about hydrolytic and/or thermal oxidative alteration that occurred in the oil during the fryings. The polar fractions isolated were analyzed in a Konik 500 A chromatograph with a 10 μL sample loop. A Hewlett-Packard 1037A refractive index detector and two 25 cm x 0,7 cm i.d. (5<μm particle size), 0.01 μm and 0.05 μm Ultrastyragel columns (Waters Associates) connected in series were operated at 45°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 precleaned by passing them through a filter (2 μm). Alteration products belonging to polar fractions were as follows: triacylglycerol polymers, triacylglycerol dimers, oxidized triacylglycerols, diacylglycerols and free fatty acids. Samples of each oil, unused and used in the different fryings were taken for analysis. Pure free fatty acids, diacylglycerols and triacylglycerols, (Sigma Química) and total polar fractions at different concentrations were studied. Correlations obtained between detector response and μg of different compound groups injected were quite high (r>0.99) indicating a good linear relationship. Response factors for fatty acids, diacylglycerols, triacylglycerols and total polar components were similar. Due to the nonexistence of triacylclycerol polymer and triacylglycerol dimer standards and because each peak corresponds to a complex group of compounds, the same response factors for all the altered compounds measured must be assumed.

2.1. Changes in these oils during frying

Total polar content (% w/w on oil) for NT system of frying as a representative measurement of the total alteration of the oil and absolute (% w/w on oil) contents for different groups of alteration products are given in Table II. After the tenth, thirtieth, fiftieth and sixtieth fryings, the percentage of the polar fraction of the oil showed an increase from 3.75% (when unused) to 11.05%, 17.29%, 24.13% and 27.28% respectively.

Table II
Distribution of polar components in different groups of alteration compounds in unused sunflower oil and after being used in successive fryings of potatoes[a] without turnover of fresh oil (Arroyo *et al.*, 1992).

Number of fryings	0	10	30	50	60
Total polar content % (w/w) on oil	3.75	11.05	17.29	24.13	27.28
Triglyceride polymers % (w/w) on oil	0.06	0.52	2.05	4.15	5.39
Triglyceride dimers % (w/w) on oil	0.50	3.27	7.03	9.75	10.91
Oxidized triglycerides % (w/w) on oil	1.79	5.52	6.53	8.26	8.78
Diglycerides % (w/w) on oil	0.92	1.26	1.25	1.53	1.67
Free fatty acids % (w/w) on oil	0.47	0.46	0.42	0.43	0.53

[a] Data from a single determination of a homogeneous mixture of two oils from their respective fryings.

Nevertheless in the FT system of frying (Table III) the results indicate a dramatic leap of total polar content in the oil from 5.09 ± 0.21 (mean ± SD) mg/100 mg unused oil to 15.99 ± 0.40 mg/100 mg oil when used in twenty repeated and discontinuous fryings followed by a tendency to reach a near-steady state.

The polar fraction was further examined by HPSEC to investigate the thermoxidative and hydrolytic alterations in the frying oil. Table II and Table III and Figure 3 show that for NT system of fryings, both triglyceride polymers and triglyceride dimers increased continuously throughout the successive fryings, although there was a higher tendency for formation of triglyceride polymers than of triglyceride dimers because triglyceride polymers content (% w/w on oil) increased by factors of 8.7 and 89.8 after ten and syxty fryings with respect to the basal values, while triglyceride dimers content only increased 6.3 and 21.8 times, respectively.

Table III
Distribution of polar components into different groups of alteration compounds in unused sunflower oil and after being used in repeated fryings of potatoes[a] with turnover of fresh oil (Cuesta *et al.*, 1993)

	ANOVA	Number of fryings				
		0	20	30	50	75
Total polar content	«0.001	$5.09^{a}\pm0.21$	$15.99^{b}\pm0.40$	$17.99^{c}\pm0.41$	$18.92^{c}\pm0.49$	$19.11^{c}\pm0.40$
Triglyceride polymers	«0.001	$0.10^{a}\pm0.01$	$1.65^{b}\pm0.13$	$2.50^{c}\pm0.20$	$3.15^{d}\pm0.20$	$3.44^{d}\pm0.17$
Triglyceride dimers	«0.001	$0.75^{a}\pm0.12$	$6.25^{b}\pm0.28$	$7.09^{bc}\pm0.31$	$7.37^{bc}\pm0.45$	$7.51^{c}\pm0.34$
Oxidized triglycerides	<0.001	$2.70^{a}\pm0.27$	$6.26^{b}\pm0.30$	$6.49^{b}\pm0.29$	$6.58^{b}\pm0.39$	$6.26^{d}\pm0.30$
Diglycerides	NS	$1.11^{a}\pm0.17$	$1.33^{a}\pm0.06$	$1.32^{a}\pm0.09$	$1.39^{a}\pm0.10$	$1.41^{a}\pm0.02$
Free fatty acids	NS	$0.43^{a}\pm0.10$	$0.50^{a}\pm0.10$	$0.59^{b}\pm0.10$	$0.43^{a}\pm0.06$	$0.48^{a}\pm0.05$

[a] Mean of two samples ± SD expressed in mg/100 mg oil. Values in the same row bearing a common letter are not significantly different. NS, not significant; ANOVA, analysis of variance.

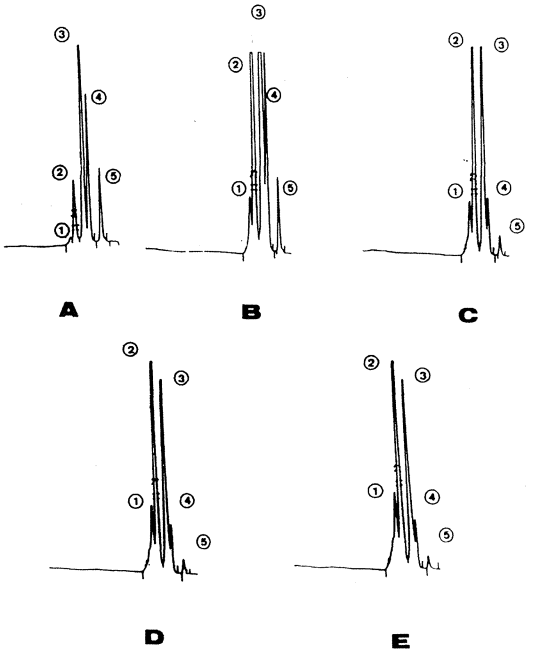

Figure 3
HPSE chromatograms of unused (A) and used sunflower (NT) oil samples; B (tenth), C (thirtieth), D (fiftieth) and F (sixtieth fryings). Peaks 1, 2, 3, 4 and 5 are triglyceride polymers, triglyceride dimers, oxidized triglycerides, diglycerides and free fatty acids, respectively. Relation times: 1-11.7 min; 2-12.2 min; 3-13.2 min; 4-13.7 min; 5-15.0 min. Conditions: Column: series-connected Ultrastyragel, 25 cm x 0.7 cm i.d., <5 μm particle size; eluent: tetrahydrofurane at 1 mL/min, 20 μL injection volume, refractive index detection.

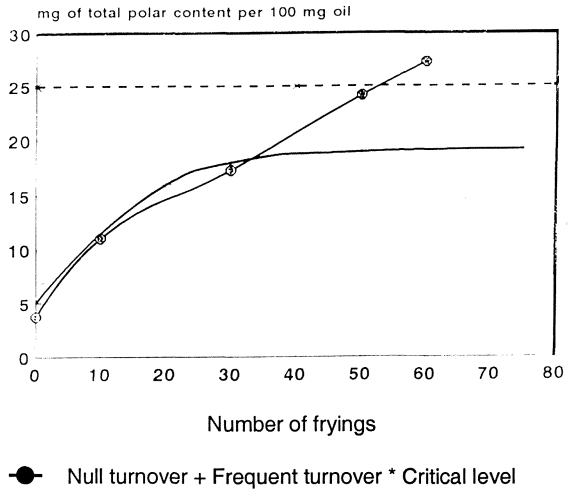

Figure 4
Total polar content evolution as a function of the number of fryings performed with a null or a frequent turnover of fresh sunflower oil in order to keep the proportion of food to frying oil at 500 g/3L.

However for FT system of frying the amount of triglyceride dimers increased continuously throughout 30 fryings, whereas oxidized triglycerides did not change after the twentieth frying, and the triglyceride polymers increased rapidly during the first fifty fryings and also did not increase further with continued fryings. The total polar content evolution as a function of the number of frying performed with NT or FT system is also presented in Figure 4.

Data of these experiments suggest that when a reduced number of fryings was performed no relevant differences were found between the use of NT or FT systems. However, after twenty or thirty fryings the use of an FT system appears to be more beneficial than the NT one because the level of polar material is substantially below the critical level of 25%.

A turnover of approximately 300 mL (l0% of the fryer volume when 500 g of potatoes are frying) each 4-5 fryings looks adequate to keep the alterations products at a reasonably low level. According to present data, 50% of the initial oil has been removed and/or renewed after 20 fryings following the FT system, and 100% has been at the 50th fryings.

3. THERMOXIDATIVE AND HYDROLYTIC CHANGES IN A HIGH OLEIC ACID SUNFLOWER OIL OR IN A EXTRA VIRGIN OLIVE OIL USED IN REPEATED FRYINGS OF POTATOES WITH FAST TURNOVER OF FRESH OIL.

To investigate the utility of a frequent turnover of fresh oil during the performance of fryings with oils that exhibite high thermoxidative stability, we realized experiments where monoenic oils were employed to frying potatoes. In this way investigations were undertaken to determine the amount of oil degradation based on two variables a high quality of the starting oil for frying purposes (high oleic sunflower oil or a virgin olive oil) and a high turnover of fresh oil throughout the frying process.

Performance of Fryings.— Both of these experiments were realized under the same conditions. Table IV, shows the fatty acid composition of unused high oleic acid sunflower oil and extra virgin olive oil, respectively. Table V shows the variables of frying operations.

3.1. Changes in these oil during frying

The total polar content in the starting high oleic acid sunflower oil (Table VI) was 3.6 ± 0.1 (mean ± SD) mg/100 mg oil and it increased to 7.6 ± 0.4 mg/100 mg oil after 20 repeated fryings and tended to reach a near-steady state of approximately 9.2 ± 0.0 mg/100 mg oil throughout the succesive fryings.

Results also indicate that the amount of triglyceride dimers increased continously throughout the first 40 fryings and did not change further with succesive fryings. However the amount of triglyceride polymers and the amount of oxidized triglycerides also increased continously throughout approximately 60 and 50 fryings, followed by a tendency to reach a near-steady state in later succesive fryings.

Quantitative results for total polar content and for the distribution of polar compounds throughout the frying process, when an extra virgin olive oil was employed are given in Table VII.

Table IV

Fatty acid composition (percentage of chromatographed methyl esters) of unused high oleic acid sunflower oil and olive virgin oil[a]

	Extra virgin olive oil	High oleic acid sunflower oil
Palmitic (C16:0)	9.8±0.1	4.4±0.8
Palmitolecic (C16:1)	0.8±0.3	–
Stearic (C18:0)	3.7±0.1	4.2±0.0
Oleic (C18:1)	80.0±0.7	78.3±0.3
Linoleic (C18:2)	4.5±0.1	10.9±0.0
Linolenic (C18:3)	0.6±0.1	0.3±0.0
Arachidic (C20:0)	0.3±0.0	0.2±0.0
Eicosenoic (C20:1)	0.2±0.0	–
Behenic (C22:0)	–	1.0±0.0
Lignoceric (C24:0)	–	0.4±0.0

[a] Values are mean ± SD of two determinations for virgin olive oil or four determinations for high oleic acid sunflower oil.

Table V

Variables of frying operations

Oil types	Commercial high oleic sunflower[a] and extra virgin olive oils[b]
Frying vessel	Domestic electrical fryer with aluminum vessel
Oil quantity (litres per batch)	3
Proportion of food to frying oil (g/L per batch)	500/3
Food type	Potatoes[c]
Number of fryings	75
Total oil turnover rate (per entire frying time)	4.25 L for high oleic sunflower oil or 4 L for extra virgin oil
Initial temperature	180°C
Batch time (min)	8
Total frying time (h)	16.5
Frying frequency	Intermittent, 10 fryings/day
Total amount of food fried (Kg)	37.5

[a] High oleic sunflower oil (Andújar, Jaén, Spain).
[b] Virgin olive oil (Mora, Toledo, Spain)
[c] Kennebec variety, Galicia (Spain)

Table VI

Total polar content and different polar compounds in unused high oleic sunflower oil and after being used in repeated fryings of potatoes[a] (Romero *et al.*, 1995)

	Number of frying								
	0	8	20	30	40	50	60	70	75
Total polar content	3.6±0.1[a]	6.0±0.4[b]	7.6±0.4[c]	7.9±0.6[c]	8.6±0.4[c]	9.1±0.4[c]	9.5±0.3[c]	9.2±0.0[c]	9.2±0.0[c]
Triglyceride polymers	0.03±0.0[a]	0.18±0.06[b]	0.40±0.05[c]	0.44±0.4[d]	0.54±0.03[c]	0.62±0.03[d]	0.70±0.01[a]	0.74±0.02[g]	0.72±0.01[a]
Triglyceride dimers	0.18±0.01[a]	1.26±0.29[b]	2.00±0.21[c]	2.15±0.23[c]	2.42±0.12[d]	2.61±0.12[d]	2.75±0.07[d]	2.48±0.11[d]	2.64±0.05[d]
Oxidized triglycerides	1.13±0.06[a]	2.26±0.13[b]	2.88±0.12[c]	3.02±0.17[c]	3.31±0.13[d]	3.58±0.09[c]	3.70±0.10[c]	3.58±0.05[c]	3.60±0.05[c]
Diglycerides	1.89±0.05[a]	1.91±0.10[a]	1.91±0.02[a]	1.87±0.05[a]	1.90±0.03[a]	1.92±0.05[a]	1.96±0.03[a]	1.98±0.03[a]	1.87±0.03[a]
Monoglycerides	0.00±0.00[a]	0.00±0.00[a]	0.01±0.00[a]	0.01±0.00[a]	0.01±0.00[a]	0.01±0.00[a]	0.01±0.00[a]	0.01±0.00[a]	0.01±0.00[a]
Free fatty acids	0.37±90.06[a]	0.41±0.01[a]	0.41±0.01[a]	0.40±0.02[a]	0.39±0.03[a]	0.39±0.05[a]	0.38±0.07[a]	0.42±0.01[a]	0.40±0.01[a]

[a] Mean of two samples ± SD for total polar content, or mean of four samples for the different polar compounds, expressed as mg/100 mg oil.
Values in the same row bearing a different letter are significantly different ($p<0.05$), Newman-Keuls multiple comparison test).

Table VII

Total polar content[1] and distribution of polar compounds[2] in unused extra virgin olive oil and after being used in repeated frying of potatoes (Romero *et al.*, 1995)

		Number of frying								
	ANOVA	0	8	20	30	40	50	60	70	75
Total polar content	«0.001	2.76± 0.1^{a}	4.29± 0.33^{b}	5.59± 0.50^{c}	6.60± 0.00^{d}	7.08± 0.35^{d}	7.47± 0.28^{e}	7.81± 0.25^{d}	7.74± 0.25^{d}	8.01± 0.00^{d}
Triglyceride polymers	«0.001	ND	0.07± 0.01^{a}	0.19± 0.04^{b}	0.25± 0.03^{c}	0.28± 0.00^{d}	0.30± 0.02^{d}	0.38± 0.01^{c}	0.41± 0.01^{c}	0.42± 0.01^{c}
Triglyceride dimers	«0.001	0.03± 0.01^{a}	0.81± 0.15^{b}	1.27± 0.18^{c}	1.65± 0.05^{d}	1.77± 0.09^{d}	1.88± 0.04^{d}	2.02± 0.91^{d}	1.97± 0.06^{d}	2.13± 0.04^{d}
Oxidized triglycerides	«0.001	0.56± 0.03^{a}	1.22± 0.12^{b}	1.85± 0.16^{c}	2.33± 0.04^{d}	2.56± 0.14^{e}	2.81± 0.19^{f}	2.95± 0.15^{g}	2.93± 0.17^{g}	3.00± 0.4^{g}
Diglycerides	NS	1.66± 0.05^{a}	1.67± 0.03^{a}	1.77± 0.03^{a}	1.86± 0.03^{a}	1.91± 0.07^{a}	1.92± 0.04^{a}	1.90± 0.05^{a}	1.87± 0.02^{a}	1.88± 0.06^{a}
Monoglycerides	NS	ND	ND	ND	ND	0.01± 0.01^{a}	0.01± 0.00^{a}	0.01± 0.00^{a}	0.01± 0.00^{a}	0.01± 0.00^{a}
Free fatty acids	NS	0.50± 0.06^{a}	0.51± 0.01^{a}	0.56± 0.02^{a}	0.56± 0.02^{a}	0.55± 0.04^{a}	0.54± 0.05^{a}	0.56± 0.01^{a}	0.55± 0.01^{a}	0.56± 0.01^{a}

[1] Mean of two samples ± SD expressed in mg/100 mg oil.
[2] Mean of four samples ± SD expressed in mg/100 mg oil.
Values in the same row bearing a different letter were significantly different.
NS: Not significant. ND: Non detected.
ANOVA: Analysis of variance. Newman-Keuls multiple comparison test.

Data show that the polar content in the starting extra virgin olive oil 2.76 ± 0.01 (mean ± SD) mg/100 mg oil increased up significantly in the fryer's oil to 5.59 ± 0.50 mg/100 mg oil when used in thirty repeated and discontinuous fryings followed by a tendency to reach a near-steady state of 8 mg/100 mg oil in later succesive fryings. Table VII also shows that the amount of triglyceride dimers increased up until the thirtieth frying, while triglyceride polymers did not change after the sixtieth frying and oxidized triglycerides increased to the sixtieth frying. All of these compunds did not increase further with continued fryings.

The total polar content evolution as a function of the number of fryings performed with high oleic sunflower oil or an extra virgin olive oil with a fast turnover of fresh oil is presented in Figure 5.

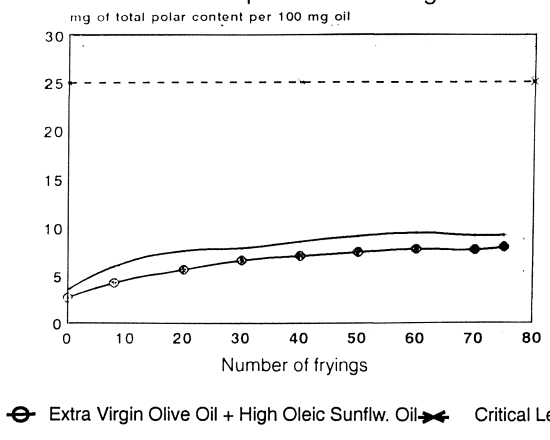

Figure 5
Total polar content evolution as a function of the number of fryings performed with a high oleic acid sunflower oil or olive virgin oil respectively and with a frequent turnover of fresh oil

Thermoxidative and hydrolytic modifications in a high oleic sunflower oil and an extra virgin olive oil used for frying are presented in Figure 6. Compounds related to thermoxidative alteration in a high oleic sunflower oil (H.0.S.0) or an extra virgin olive oil (E.V.O.O) used for frying are also presented (Figure 7).

The results obtained from all of the above described experiences are in agreement with those found by different authors which reported an increase of the polar content with the number of fryings (Fedelli, 1988; Sánchez-Muniz *et al.*, 1989; Cuesta *et al.*, 199l; Cuesta *et al.*, 1993; Sánchez-Muniz, 1993).

Data from the present experiments and those found in previous works (Gere, 1984, Perrin *et al.*, 1985, Kupranycz *et al.*, 1986) indicate that triglycerides initially react to produce triglyceride dimers. Then the rates of dimers accumulation during the first fryings exceeded the rates of oligomeric triglycerides formation. Further the amount of oligomeric triglycerides continued to increase throughout the successive fryings to reach (when an adequate turnover of oil is used) a near-steady state after a large number of fryings (Figure 7).

The higher contribution of oxidized triglycerides with respect to the other compounds altered by frying also should be noted (Figure 7). Also, during the deep fat frying of potatoes, more thermoxidative than hydrolytic processes took place (Figure 6). Hence, the measurement of the amount of free fatty acids or diglycerides related to hydrolytic alteration may not be the best criterion to test the state of degradation of the oils. As has been described (Friedman, 199l), a high level of free fatty acids can exist with low levels of polar material, and the oil should be acceptable for further

frying operations. In addition Dobarganes *et al.* (1988) described that hydrolytic modification may be investigated by quantifying diacylglycerides, but not free fatty acids because the latter are partially lost during frying.

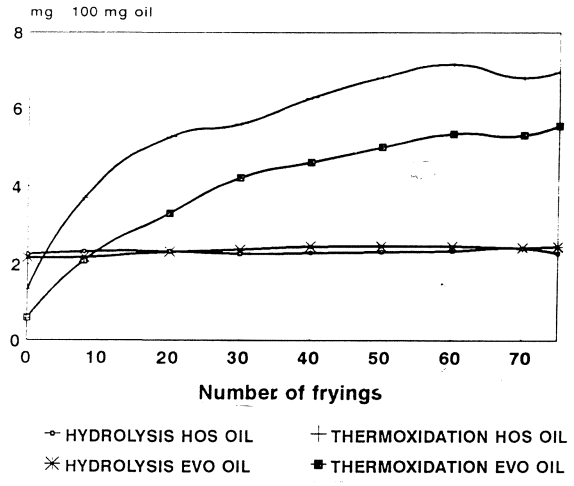

Figure 6
Thermoxidative and hydrolytic modifications in a high oleic sunflower (HOS) oil and an extra virgin olive (EVO) oil used for frying.

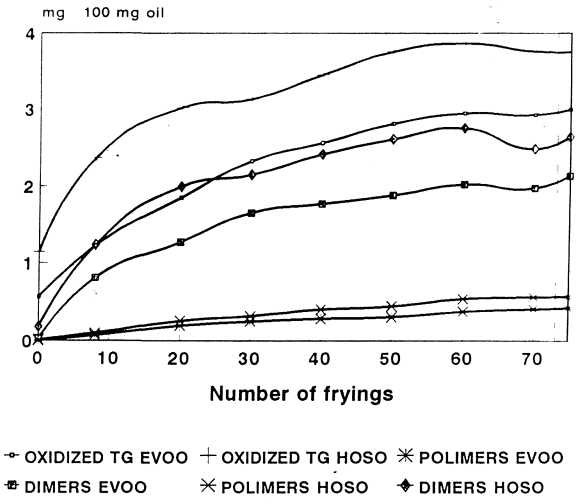

Figure 7
Thermoxidative alteration in a high oleic sunflower oil (HOSO) or an extra virgin olive oil (EVOO) used for frying

In conclusion the reactions produced during deep-fat fryings can be minimized by using proper oils, frying equipment and frying conditions. The present studies suggest the necessity of controlling two variables - amount of fried food and replenishment of oil in the fryer in order to maintain quality of oils. Data suggest that. with frequent turnover of fresh oil, the critical level of 25% of polar material is rarely reached, and there are fewer problems with fat deterioration. On the other hand oxidative stability of the frying oil can be improved using fats with low insaturation, but the high saturated fatty acid content makes it less desirable from a nutritional stand point. In this way the monoenic fats are the most adequate for its oxidative stability during frying. In the present lecture it has pointed out that extra virgin olive oil performs very satisfactorily in frying.

The advantages of oleic acid from a nutritional point of view have been also recognized in recent years (Nestel, 1994). The increased level of consumers awareness toward fat composition and its impact on human health could have an impact on the selection of fats for the snacks and for industry. In addition it is obvious that the frying oil selection should be also made upon its performance in the frying process.

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