Evolution of the quality of the oil and the product in semi-industrial frying

By **M. Beatriz, P. P. Oliveira** and **Margarida A. Ferreira***
Laboratory of Bromatology, Faculty of Pharmacy, University of Oporto, Oporto,
R. Anibal Cunha 4000 Porto, Portugal

RESUMEN

Evolución de la calidad del aceite y del producto en fritura semi-industrial.

La evolución de la calidad de dos marcas comerciales de aceite comestible fue estudiada según la forma tradicional de fritura usada en el mercado portugués, por el cual trescientas empanadillas rellenas fueron fritas a temperatura de 160-170°C durante un período de una hora. Se determinaron los indices de peróxido , p-anisidina, Totox, acidez y compuestos polares totales. Los ácidos grasos isoméricos cis y trans fueron cuantificados por cromatografía gaseosa en columna capilar rellena con CP-Sil 88.

PALABRAS-CLAVE: Aceite comestible - Calidad (evaluación) - Empanadilla rellena - Fritura semi-industrial.

SUMMARY

Changes in the quality of the oil and the food product in semi-industrial frying.

Changes in the quality of two commercial brands of cooking oil were studied under the frying conditions traditionally used in the Portuguese hospitality trade. Three hundred rissoles were fried at a temperature of 160-170°C for 1 hour. Values of peroxide, p-anisidine, Totox, acidity and total polar compounds were determined. Isomeric cis and trans fatty acids were quantified using CP-Sil 88-packed capillary column via gas chromatography.

KEY-WORDS: Edible oil - Quality (change) - Rissole - Semi-industrial frying.

1. INTRODUCTION

Frying is an ancient method of food preparation, originally developed by Mediterranean peoples "(Cuesta *et al.,* 1991)". It is an excellent method for transferring heat to food, one that usually takes less than ten minutes, develops flavour and gives long-lasting colour and texture to the food. Furthermore, its easy and rapid execution make this inexpensive and advantageous both to the producer and the consumer. Today it is one of the most successful and widespread forms of processing food "(Graziano, 1979)".

During frying, the cooking oil or fat, is submitted to the action of three variables that have a detrimental influence on quality: the humidity and electrolytes that the food gives off and that promote the hydrolyzation of the triglycerides; the atmospheric oxygen that affects the surface area and intervenes in oxidation; high temperatures that can cause thermal alterations "(Dobarganes *et al.,* 1989)". Innumerable chemical reactions may result from the intervention of these variables, such as oxidation, polymerization, hydrolysis, isomerization, and cyclization "(Sebedio et al., 1987)", to create new chemical entities such as volatile components, dimers and monomers of cyclical fatty acids, polymeric triglycerides, oxidized compounds, free fatty acids, mono and diglycerides and geometric isomers of fatty acids, or *trans* forms thereof.

"(Poumeyrol, 1987)", in his study of waste frying oil from restaurants, observed that it contained less than the maximum legal amount of altered glycerides and less than 0.09% cyclical monomers.

Other authors, "(Azpilicueta *et al., 1991)"* e "(Suys, 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.

Several other authors have referred to the presence of *cisltrans* isomers in heated vegetable oils. This is the case of the presence of *trans* isomers of linolenic acid, after rape and soya oils were heated to 200 and 240°C for 10 and 40 hours "(Grandgirard *et al.,* 1984)" and linseed oil heated to 275°C during 12 hours in atmospheric nitrogen "(Grandgirard *et al.,* 1987, 1989)"; and sunflower seed oil heated at 275°C during 12 hours in atmospheric nitrogen and at 200°C during 48 hours with daily 2-hour cycles "(Sebedio *et al.,* 1988)" for the case of the presence of *trans* isomers of linoleic acid . The same isomers have also been detected in deodorized and in frying oils, and in margarine and shortening "(Oliveira *et al.,* 1992)".

The publication of this information has led to nutritionists and consumers becoming concerned about the possible health risks of consuming these products, although the majority of the studies performed so far have used temperatures greater than those usually reached during frying, and as such do not truly express the reality of the situation.

The purpose of this study was to examine the evolution of the quality of two oils used for frying and of the product, under semi-industrial conditions.

2. EXPERIMENTAL

2.1 Samples

Two brands of edible oil, a blend of two or more edible vegetable oils excluding olive oil, widely available on the market, sample 1 and sample 2, were studied. Both were in shelflife period and had been stored at room temperature in opaque containers. Three hundred frozen rissoles from the same source were fried in each sample.

Two samples of each oil (oil sample 1 and oil sample 2) were taken before heating and after 1 hour's frying of the rissoles. Two samples of rissoles cooked at the beginning and two samples of rissoles cooked at the end were selected from each oil. The fat content of the uncooked rissole was also measured.

2.1.1. Heating

The oils were heated, in a continuous process, in the University of Oporto canteen under conditions similar to those practiced elsewhere in catering (restaurants, canteens, snack-bars, etc.). Each oil (5 liters) was heated, during 10 minutes, up to a temperature of 210°C and the product was then fried. The frying time was about 8 minutes. When the rissoles were added, the temperature dropped to 170°C and remained between 160-170°C whilst the 300 rissoles were fried (1 hour). Figure 1. A semi-industrial stainless steel, 55cm square, deep-fat fryer was used. The oil was about 5cm deep.

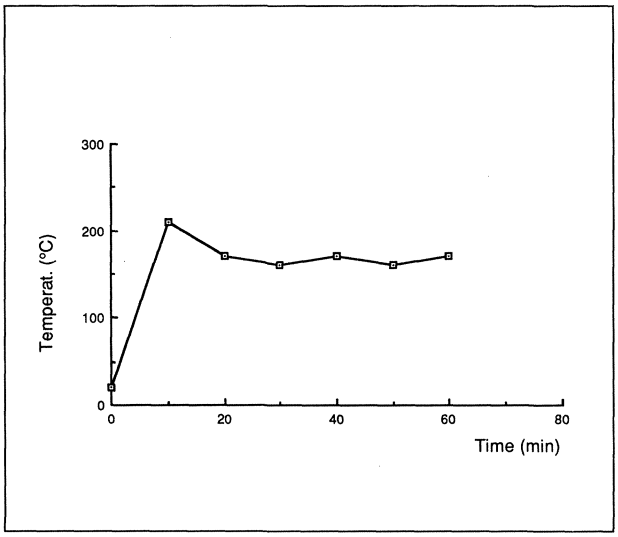

Figure 1
Evolution of the temperature of the frying medium

2.1.2. Preparation of the samples

The rissoles were pulped and the fat extracted in a Soxhlet apparatus by petroleum ether during 6 hours. The oil samples were dehydrated with sodium sulfate anhydrous and filtered through paper.

2.2 Reagents

All the reagents used were Merck p.a. grade. The standard methyl esters used were Sigma and Alltech Associates Inc.

2.3. Methods

The following procedure was used for quantifying the fatty acids: Chromatograph Pye Unicam, adapted to capillary column, fitted with a flame ionization detector (FID); a 0,25mm x 50m fused silica capillary column coated with CP-Sil 88 (Chrompack) was used for separation of fatty acids methyl esters; the column was maintained at 185°C; 1:50 was the split ratio and the injected volume was 1µl. Helium was the carrier gas. Peak areas were processed by using a Pye Unicam CDP4 computing integrator.

The methyl esters were prepared by transesterification with BF_3/MeOH "(Oliveira et al., 1992)". Before metilation the samples were hydrolysed with KOH/MeOH (11g/l) and the methyl esters were extracted with n-heptano.

The Portuguese official methodologies, NP-1819, NP-904 and NP-903, were used for quantifying p-anisidine value (AV), peroxide value (PV), and acidity (FFA). The Totox (TV) value was determined by the formula 2PV+AV "(Rossell, 1983)". Polar compounds were evaluated with the Food Oil Sensor (FOS) and by the Very-Fry (R) test (VF(R)).

3. RESULTS AND DISCUSSION

Table I presents the evolution of the peroxide (PV), p-anisidine (AV), Totox (TV) values, acidity (FFA) and polar compounds evaluated by FOS and VF(R) for oil samples 1 and 2, before and after frying.

Table I
Evolution of the peroxide (PV), p-anisidine (AV) and Totox (TV) values, acidity, and polar compounds (PC), in oil samples 1 and 2, before and after 1 hour's frying.

	OIL SAMPLE 1		OIL SAMPLE 2	
Parameter	**Initial**	**After 1hr**	**Initial**	**After 1hr**
PV	4±0	15±1.1	10±1.4	26±1.4
AV	6±0	31±1.4	5±0	54±1.4
TV	14±0	62±0	25±2.8	106±1.4
Acidity	0.1±0	0.1±0	0.1±0	0.2±0.07
PC FOS*	0	4	0	5
PC VF (R)**	0	5-11%	0	12-16%

* as determined by the Food Oil Sensor
** as determined by the Very-Fry (R) test

Table II

Fatty acids in oil sample 1, before and after 1 hour's frying, extracted from uncooked rissoles, and from rissoles at the beginning and end of frying (expressed as relative percentages).

FATTY ACIDS %	INITIAL OIL	OIL AFTER FRYING	RISSOLES AT BEGINNING OF FRYING	RISSOLES AT END OF FRYING	UNCOOKED RISSOLES
C14	0.13±0.009	0.13±0	0.23±0	0.23±0.007	0.60±0.037
C15	0.01±0.005	0.02±0	0.03±0.007	0.02±0.007	0.05±0.010
C16	9.35±0.039	9.52±0.065	11.49±0.085	11.52±0.127	19.93±0.448
C16:1t	0.01±0.004	0.01±0.004	0.02±0.014	0.02±0.007	0.02±0.033
C16:1c	0.10±0.014	0.09±0.017	0.15±0.007	0.14±0.007	0.33±0.030
C17	0.07±0.020	0.07±0.018	0.09±0	0.10±0.007	0.07±0.010
C17:1	0.03±0.009	0.03±0.004	0.04±0.014	0.03±0	0.03±0.006
C18	4.55±0.155	4.75±0.056	4.82±0.014	4.85±0.078	5.78±0.045
C18:1t	0.01±0.011	0.04±0.058	0.25±0.057	0.21±0.007	1.35±0.096
C18:1c	26.30±0.124	27.02±0.115	26.86±0.085	26.93±0.106	30.22±0.109
C18:2t	0.63±0.089	0.65±0.298	0.76±0.085	0.63±0.035	0.25±0.008
C18:2c	55.61±0.269	54.45±0.174	52.40±0.198	52.45±0.198	39.10±0.251
C20	0.27±0.022	0.29±0.050	0.34±0.028	0.30±0.014	0.37±0.010
C18:3t	0.31±0.059	0.33±0.065	0.33±0.148	0.19±0.049	–
C18:3c	1.60±0.037	1.52±0.048	1.26±0.113	1.14±0.078	0.58±0.015
C20:1	0.08±0.010	0.07±0.033	0.07±0	0.07±0	0.16±0.035
C22	0.63±0.018	0.69±0.039	0.58±0.021	0.60±0.007	0.55±0.050
C24	0.22±0.089	0.23±0.063	0.19±0.049	0.22±0	0.19±0.039

Table III

Fatty acids in oil sample 2, before and after 1 hour's frying, extracted from uncooked rissoles, and from rissoles at the beginning and end of frying (expressed as relative percentages).

FATTY ACIDS %	INITIAL OIL	OIL AFTER FRYING	RISSOLES AT BEGINNING OF FRYING	RISSOLES AT END OF FRYING	UNCOOKED RISSOLES
C14	0.07±0.005	0.08±0.005	0.23±0.006	0.24±0.010	0.60±0.037
C15	0.02±0.005	0.02±0	0.02±0.006	0.02±0.005	0.05±0.010
C16	6.86±0.065	7.16±0.064	9.57±0.057	9.44±0.059	19.93±0.448
C16:1t	0.02±0.006	0.01±0.005	0.01±0.006	0.02±0.006	0.02±0.033
C16:1c	0.15±0.005	0.16±0.032	0.16±0.006	0.17±0.005	0.33±0.030
C17	0.05±0.005	0.05±0.041	0.06±0.006	0.06±0	0.07±0.010
C17:1	0.03±0.006	0.03±0.010	0.02±0.006	0.03±0.005	0.03±0.006
C18	4.37±0.039	4.57±0.032	4.61±0.031	4.68±0.021	5.78±0.045
C18:1t	0.02±0.023	0.06±0.032	0.23±0.053	0.25±0.054	1.35±0.096
C18:1c	28.35±0.096	28.81±0.087	28.09±0.057	28.17±0.048	30.22±0.109
C18:2t	0.14±0.024	0.13±0.013	0.14±0.021	0.17±0.015	0.25±0.008
C18:2c	58.45±0.171	57.28±0.194	55.01±0.127	54.97±0.037	39.10±0.251
C20	0.29±0.010	0.29±0.017	0.29±0.010	0.31±0.008	0.37±0.010
C18:3t	-	-	-	-	-
C18:3c	0.20±0.045	0.20±0.025	0.35±0.006	0.36±0.013	0.58±0.015
C20:1	–	–	0.02±0.006	0.02±0.013	0.16±0.035
C22	0.76±0.024	0.85±0.126	0.72±0.012	0.72±0.008	0.55±0.050
C24	0.23±0.025	0.32±0.110	0.25±0.032	0.26±0.022	0.19±0.039

Tables II and III show the fatty acid content (x±sd) of oil samples 1 and 2, before and after heating during 1 hour's frying at an average temperature of 160-170°C, the description of the fatty acids in the fat extracted from the rissoles fried in the aforementioned samples, and the fat composition of the product before frying.

Table IV shows the evolution of the total *trans* isomers in oil samples 1 and 2 before and after heating, and the total values of these isomers in the rissoles fried in these oils and in the product before frying.

Table IV
Evolution of total content of trans isomers in oil samples 1 and 2 in the fat extracted from the rissoles before and after frying.

	TRANS ISOMERS %			
	OIL SAMPLE 1		OIL SAMPLE 2	
Samples	Initial	After 1hr	Initial	After 1hr
Oil	0.96±0.151 %	1.14±0.467 %	0.29±0.074 %	0.31±0.017%
Fried rissoles 1		1.36±0.304 %		0.61±0.110%
Fried rissoles 2		1.03±0.014 %		0.61±0.078%
Uncooked rissoles	1.62±0.101 %		1.62±0.101 %	

Oil sample 2 presented an initial PV value of 10, the maximum allowed by Portuguese law for vegetable oils. This increased 2.6 fold (PV=26) with heating. The value of oil sample 1 which was initially lower (PV=4), increased 3.8 fold (PV=15).

Although oil samples 1 and 2 presented similar initial AV values, 6 and 5 respectively, after heating sample 2 appeared to have suffered the greatest change as the increase of this parameter was almost two-fold that observed in sample 1 (AV_1 = 31 and AV_2=54).

Albeit TV values, according to "(Rossell, 1983)" should be less than 10, both samples initially presented higher values of this parameter. After heating, these values were respectively 6 and 11 times greater (TV_1=62 and TV_2=106).

Given that the PV, AV, and TV supply information regarding the oxidative state of the sample (PV is of interest only at the initial stage of oxidation as the peroxides decompose throughout the process; AV as a measure of the products of secondary oxidation informs us of the history of the oil "(Grompone, 1991)"; TV gives us the total oxidation of the product as it is the sum of AV and 2 PV "(Rossell,1983)", we can conclude than sample 2 suffered a greater change during frying. This behaviour could however be due to the initial state of auto-oxidation of this sample (PV=10, as compared to PV=4 for sample 1) or to the diverse nature of its triglycerides.

As regards FFA, we observed that there was no variation in its value in oil sample 1 after heating; in oil sample 2, this value doubled after 1 hour's heating although it was only of 0.2%. In the USA this held to be an important parameter, especially in industrial frying, as the law limits the content of free fatty acids to a maximum of 1% for frying fats "(Pérez-Camino *et al.,* 1988)".

Regarding the polar compounds, we note the difference in the values obtained with the two methods we used for their quantification. With the Very-Fry (R) test, the reading is done according to a colour scale and this, aside from being somewhat subjective, gives us values that are scaled within limits rather than absolute values. With the Food Oil Sensor, the determination results from the variation in the dielectric constant due to the appearance of compounds whose polarity is greater than that of the triglycerides. To convert the value into polar compounds we used the formule PC= (FOS + 0,642)/0,236.

Oil sample 2 presented a high content of polar compounds, as quantified by both tests, and as one would expect, is well above the legal maximum in most countries "(Suys, 1991)".

The initial analysis of fatty acids in both oils showed that sample 1 contained soya oil because of the percentage of linolenic acid present (1.91%) and that sample 2 appeared to consist predominantly of sunflower seed oil ($C_{18:3}$ = 0.20%).

With heating, both samples presented an increase in the relative percentages of fatty acids C_{16}, C_{18}, $C_{18:1}c$, C_{22} and C_{24}. On the other hand, there was a decrease in the percentage of linoleic acid in both samples. The values of linolenic acid remained unchanged in sample 2 and decreased in sample 1.

The increase in the percentage of saturated fatty acids and oleic acid is due to the decreased percentage of linoleic acid "(Arnau, 1988)" and probably to the percentage of linolenic acid, particularly noted in sample 1 where it dropped from 1.60% to 1.52%. According to "(Dobarganes *et al.,* 1988)", the percentage of oleic acid tends to increase in highly unsaturated vegetable oils, such as soya and sunflower seed oils, whereas it tends to remain unchanged or even decrease in less unsaturated oils such as olive and palm oils. These authors also state that it is possible to quantify all the acids present in a sample on the basis of the fatty acid content at the beginning and after usage. Hence, we noted that there was a more significant loss in the percentage of linoleic acid, 2.25% and 3.57% in samples 1 and 2 respectively.

The fatty acid composition of the fried product is strongly influenced by the fat that is used for frying "(Cuesta et al., 1991)". Given that the rissoles were of the same type and pertained to the same production lot, one presumes that they all had a similar composition. Furthermore, as we analyzed the fatty acids in the fat extracted from the rissoles before and after frying, we were able to evaluate the influence of the frying oil itself.

The fried product was richer in C_{14}, C_{16}, C_{18}, and C_{20} than the frying oil, and poorer than the uncooked product.

The fried product and the frying oil presented similar percentages of oleic acid yet these were slightly lower than those of the fat that was extracted from the product before frying. Fried rissoles presented a lower value of linoleic acid than the frying oil, but considerably higher than the value in the uncooked product (Tables II and III).

As regards linolenic acid, the rissoles fried in oil sample 1 presented a considerably greater percentage (1.34%) of this acid than that present in the uncooked product (0.58%) and an only slightly lower percentage than that in the frying oil (1.56%). The content of $C_{18:3}$ in the product fried in oil sample 2 (0.36%) was between that of the frying oil (0.20%) and that of the uncooked product (0.58%).

Regarding the *trans* isomer content of the unsaturated fatty acids in the frying oil, we noted that oil sample 1 presented a wealth of this type of isomer that was approximately three-fold that of oil sample 2 (Table IV).

The greatest contribution to this parameter comes from the linoleic acid, i.e., by the $C_{18:2}$ct and $C_{18:2}$tc isomers, as isomer $C_{18:2}$tt is usually present in very reduced amounts. As regards the *trans* isomers of $C_{18:2}$, oil sample 1 presented a value that was 4.5 times greater than that of oil sample 2.

Isomer $C_{18:1}$t was the most affected by heating as its percentage increased four and three-fold in oil samples 1 and 2, respectively.

Sample 1 initially presented a 19% isomerization of the linolenic acid *(transl* cis) that rose to 22% after heating. Given the minute amount of this acid in sample 2, we were unable to quantify its isomerization.

Regarding the evolution of the *trans* isomers content after heating, we noted that these increased over the initial values by 7% for sample 2 and 19% for sample 1.

We noted that the *trans* content in the fried product was greatly influenced by the values of these forms in the frying oil. Thus, the fat in the rissoles fried in oil sample 2 had twice as many *trans* forms than the frying oil. This was only slightly raised in those rissoles fried in oil sample 1. Given the greater amount of *trans* unsaturated fatty acids in oil sample 1, the rissoles fried in that oil presented fat that was 54% richer in *trans* isomers than those fried in oil sample 2.

The frying of the product led to a decrease in the content of *trans* isomers (Table IV) that is due to the fact that its fat content rose by 5% (from 3% before frying to 8% after). Obviously, the lesser the content of these isomers in the frying oil, the more significant is this decrease.

4. CONCLUSIONS

Considering the samples studied and the experimental conditions applied (frying during 1 hours at an average temperature of 160-170°C), regarded to be those usually practiced in the hospitality trade, we can conclude that:

- As regards the oxidative state of the samples, oil sample 2 suffered the greater change, created the greater amount of secondary oxidation products, and presented the greater degree of total oxidation. This could be due to the fact that oil sample 1 consisted also of soya oil and that oil sample 2 consisted predominantly of sunflower seed oil, and that both these oils presented a different degree of initial oxidation.
- As regards lipolytic hydrolysis, information obtained from the acidity (FFA), this was not significant although oil sample 2 suffered a greater change.
- Oil sample 2 presented the greater increase in the percentage of polar compounds.
- The total content of *trans* isomers of the unsaturated fatty acids was different in the two oils, oil sample 1 presented a value that was three-fold greater than that of oil sample 2. After frying, samples 2 and 1 presented a 7% and 19% over the initial values, respectively.
- The lipidic composition and, at the same time, the amount of *trans* isomers in the fried product are greatly influenced by the type of oil used for frying. Hence, rissoles fried in oil sample 1 were considerably richer in *trans* isomers than those fried in oil sample 2.
- Frying may, by increasing the fat content of the product, decrease the amount of *trans* isomers in the product. The lesser the content of *trans* isomers in the frying oil, the more significant is this decrease.

Finally, it would seem reasonable to advance that sunflower seed oil behaves in a more stable manner as regards the *cis/trans* isomerization. Nevertheless, the oil containing soya oil would appear to be better regarding auto-oxidation, acidity (hydrolysis), and the forming of polar compounds. Albeit the degeneration we noted is not particularly worrying, we recommend that maximum acceptable limits of p-anisidine and Totox values, polar compounds, and *trans* isomers of fatty acids, be set for those oils used for frying.

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