

Optimization of frying process in food safety

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SUMMARY

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The mechanics of frying are fairly simple. Hot oil serves as a heat exchange medium in which heat is transferred to the food being fried. As a result, the heat converts water within the food to steam and melts the fat within the food. The steam and fat then migrate from the interior of the food through the exterior and into the oil. Conversely, some of the frying oil is absorbed into the food being fried.

The chemistry occurring in the frying oil and in the food being fried includes a myriad of thermal and oxidative reactions involving lipids, proteins, carbohydrates and minor food constituents.

Decomposition products by autoxidation above 100°C, polymerization without oxygen between 200-300°C and thermal oxidation at 200°C, can be produced in frying oil and their amounts are related to different chemical and physical parameters such as temperature, heating time, type of oil used and food being fried, oil turnover rate, management of the oil and finally type of equipment used.

Different studies have remarked as the toxicity of these by-products, is due to their chemistry and concentration.

Since the prime requirement in food quality is the safety of the products, attainable through preventive analysis of the risks and total control through all frying processes, in this work the critical points of particular importance are identified and showed:

- Oil composition, and in particular its antioxidant capacity.
- Proper fryer design.
- Food/oil ratio.
- Good manufactured practice.

Beside the quality screening has to be directed towards the chemical quality evaluation by easy and rapid analysis of oil (colour, polar compounds, free fatty acids and antioxidant capacity) and food fried (panel test and/or consumer test).

Conclusion, to maintain high quality in the frying medium, choose efficient equipment, select a fat with desirable flavour and good antioxidant capacity, eliminate crackling as soon and often as possible, choose better components with minimal but desirable browning tendencies, and monitor the quality of the fat being used.

KEY-WORDS: By-products – Critical points – Frying – Safety.

1. INTRODUCTION

Frying represents a particular way of cooking food using oil or fat as a fluid heat vector. This process is used to give a particular organoleptic characteristics (colour, aroma, consistency), to various food products either of vegetable origin or animal origin.

Besides frying has a preserving effect on food as a consequence of both the thermic destruction of microorganisms and the inactivation of the enzymes

and of the reduction in the water activity on the product surface (Brooks, 1991).

During the deep fat frying process of food in oil, besides the occurrence of chemical and physical modifications which affect the nutritional and organoleptic characteristics of food and the fluid heat vector, reactions forming products of decomposition having a potential risk of toxication can also occur.

The most important requirement regarding the quality of food is the product safety which is obtainable by a preventive analysis of risks and by total control of the whole process. The main points of particular importance are identified and illustrated in this report.

2. DESCRIPTION OF THE PROCESS

Deep fat frying is a cooking method in which two fundamental process parameters intervene such as the temperature of the fluid and the activity of the product's water.

When a product is immersed in boiling oil there is a quick rise in the surface temperature and the water present on the interface (oil/product) quickly evaporates (Figure 1).

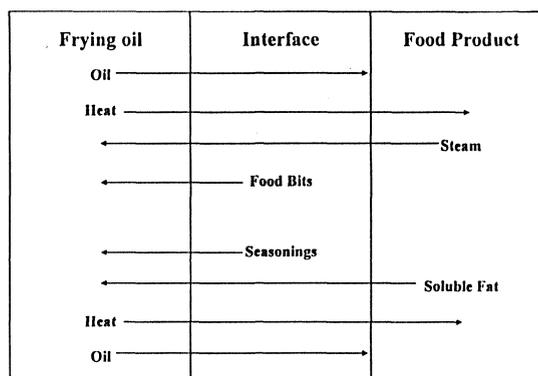


Figure 1
Frying mechanics

The surface relative to the evaporation of the water moves progressively towards the centre of the food and the most external side of the product progressively starts drying, similar to what happens during other cooking methods, with the formation of a superficial crust. Consequently, the temperature of the product surface increases, tending towards the value of the oil's temperature, meanwhile the inside of the product slowly reaches the value of the temperature of boiling water.

The speed of the heat transfer is controlled by the gradient of temperature between oil and product and by the thermic conductivity typical of the material under examination.

The thickness of the oil-product interface will have an effect on the speed of the heat transfer and the material. This will depend on the viscosity and therefore on the speed of the oil's movement.

The gradient of the steam between the inside of the product and the oil represents the motive power for losing humidity which occurs during the drying process in a hot airsteam.

given off by the food, can undergo noticeable changes in their chemical composition and with formations of new very complex substances of the polar type.

The set of reactions (Figure 2) such as oxidation, polymerization, hydrolisis, isomerization, pyrolysis and cyclization brings about the formation of a wide range of compounds which are classifiable, generally according to the persistency in the mass reactions as volatile and non volatile (Figure 3).

3. POTENTIAL FACTORS OF CONTAMINATION

It has been previously stated that in general by contamination one must understand any organism, object or substance foreign to the nourishment that may cause a risk for the consumers health. Possible contaminaters during the frying process can be identified as being only those of the chemical type.

In fact the oils and fats exposed to heat treatment with the presence of oxygen and humidity which is

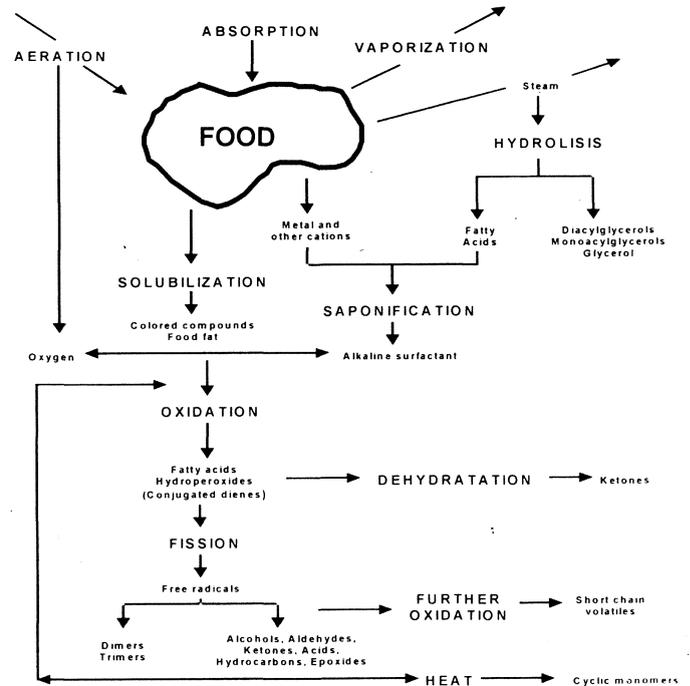


Figure 2
Degradative reactions of fats (Fritsch C.W. 1981)

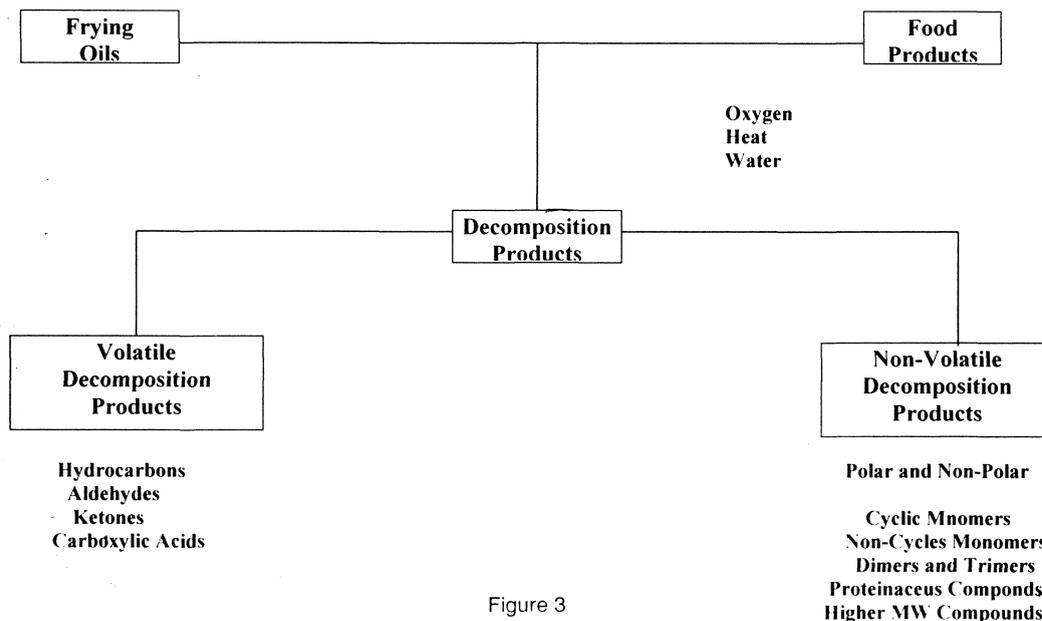


Figure 3
Decomposition of products in fats frying

Reactions which occur during the oil heating process and the potential health risks (Clark *et al.*, 1991):

- Autoxidation above 100°C
- Polymerization in the absence of oxygen between 200 and 300°C
- Thermic oxidation at 200°C

Autoxidation

The type of mono-carboxyl found (aldehydes, peroxides and hydroperoxides) indicate that autoxidation is the main reaction that occurs during the frying process. Wishner and Keeney (1965) concluded that frying in a corn oil bath does not produce any degradation of the oil which could be harmful to human health. They did not find any significant changes in the composition of fatty acids during the frying process.

Thermic Oxidation and Polymerization

Oxidation involves double bonds of fatty acids producing hydroperoxides (linolenic acid 9-hydroperoxides, linolenic acid 13-hydroperoxides and 9-hydroperoxy-10, 12 epoxy-13 trans, 15-cis octadienoic acid), and cholesterol with the production of hydroxycholesterol and epoxycholesterol. Different polymeric compounds derive from triglycerides. Crampton E.W. (1953) reports studies of toxicity of the compounds polymerized by oil. These show that oils with a high content of unsaturated fatty acids (cotton seed oil, soya oil, corn oil, peanut oil and rape seed oil) heated at 250-300°C for 6-12 hours contain polymerized material: cyclic monomeric, dimeric, trimeric and a higher polymers. The growth-depressing effects of these overheated oils on animals subjected to examination, was caused by the polymeric substances. Also non-volatile compounds deriving from triglycerides have been found during the frying process. Perkins *et al.* (1973) working 1-lynoyl-2,3 diesterin oxidized thermically were able to identify cycling and non-cycling dimers. By heating and cooling the cotton seed oil at intervals during 62 hours they obtained much more polar compounds than with the same oil heated continuously for 166 hours. Apparently this seems to be caused by an increase in the acyl-peroxides.

Also the presence of water in the form of steam sharply increases the deterioration of the oil. It has been shown that polymers with a high molecular weight were responsible for the formation of foam. Melnick (1957) suggested that as these polymeric compounds are not absorbed, they cannot produce long-term toxic effects.

Not all scientific studies agree with the assertion that oxidized lipids are so toxic at least no more than you can normally find in coronary heart diseases.

Harmful effects have been reported as being: the onset of cancer, effects on the membrane, effects on the enzymes, mutagenicity, and cytotoxicity. In many cases, the effects are interconnected: atherogenicity can be based on cytotoxicity, which can be caused by the combination and alterations of the membrane and of the enzymes.

Scientific papers (Addis *et al.* 1991, Alexander J.C. 1983, Alexander J.C. *et al.* 1987, Poling C.E. *et al.* 1969, Park S.W. and Addis P.B. 1986a, b.) report a lot of work that has been carried out on the toxicity of heated oils, but much of the data obtained (especially after the first studies made) lead us to two false conclusions:

- 1) The toxicological results are often imprecise and do not include the possibility of the onset of arterosclerosis phenomena. The correlation of coronary heart disease illnesses and the consumption of heated oil has still to be explored.
- 2) In the first tests carried out, oils were heated too drastically, conditions which do not exist in restaurants or in the home.

When an oil is heated oxidizing products form, followed by a formation of polymers, but these are not absorbed by the organism and so they result as not being very toxic for the intestinal mucous. What is not clear, however, is what concerns aldehydes, hydroperoxides, peroxide lipids, dimers, cyclic compounds, and in particular the malonaldehyde, which are formed before the polymers. Oxidized cholesterol has also been shown to be toxic in many pieces of research.

The effect of elevated temperatures on oil's chemical and nutritional composition has been studied by simulating commercial and domestic frying, but frequently in exaggerated conditions.

This point of view has been reported in numerous publications and there is a certain number of authors who believe that the noticed harmful effects do not reflect the real phenomenon that may occur in a restaurant or in the home for three main reasons:

1. The temperature of the oil was unrealistically too high.
2. The oils were heated for longer periods, superior to those normally used in restaurants or in the home.
3. Very often the conclusion were taken from results of experiments carried out on laboratory animals.

However, excessive frying produces toxic compounds only after they become unacceptable for the sensorial analysis and therefore rejected by the consumer.

4. CRITICAL POINTS

The following paragraph identifies and illustrates the critical points which are of particular importance and can be shown in:

- The composition of the oil and in particular its antioxidant activity
- Appropriate planning of the frying apparatus
- Good working knowledge

4.1 The composition of the oil and in particular its antioxidant activity

The influence of the unsaturation degree on fatty acids on modifications in the composition of oils submitted to heat treatments is well known; the higher the content of polyunsaturated fatty acids of an oil, the quicker the transformation reactions in the same are with a consequent decrement of the essential fatty acids, and the browning and ulterior reactions of polymerization.

It is necessary to choose an oil with a correct ratio of saturated, monounsaturated and polyunsaturated fatty acids, preferably choosing one with a low level of polyunsaturated fatty acids (olive, peanuts, etc.), hence reducing the potential risk due to the peroxides or the hydroperoxides which form while frying.

The oxidation reactions due to the fatty acids can be slackened by the presence of antioxidant substances which are naturally present in the oils.

Research (Gordon *et al.*, 1983, Quaglia *et al.*, 1985, Endo *et al.*, 1985) has highlighted the antioxidant activity and the consequent protection concerning the oils of sterols like the Δ^5 avenasterol and the fucosterol, of the chlorophyll and of the pheophytin, of the E vitamin and of the polyphenols.

As far as the sterols are concerned, it has been highlighted that while the Δ^5 avenasterol and the fucosterol are effective as antioxidants, other sterols including cholesterol and stigmaterol are ineffective (Gordon *et al.*, 1983).

The iodine index (protective index = PI) taken as a reference to the antioxidant activity, it is agreed that values above 1, show an antioxidant activity; table I shows the values of some sterols which are naturally present in olive oil compared with antioxidants used as additives.

It can be seen how the Δ^5 avenasterol and the fucosterol represent the sterols with the higher antioxidant activity while this property is lower in the case of other sterols and in BHA.

The importance of the antioxidant property of Δ^5 avenasterol can be highlighted by the proven effect on the composition in essential fatty acids in the oils to which this substance was added. Without its addition, with a heating-up to 180°C, it has been

noticed a reduction equal to 50% of the linoleic acid after 28 hours. The presence of Δ^5 avenasterol allows the oxidation reaction of the linoleic acid to slow down with a reduction of only 50% after 59 hours.

Table I
Protective indices (PI) of sterol during heating of technical trioleylglycerol at 180°C

Additive	Concentration PI after heating for:			
	%	24 h	48 h	72 h
α -Tocopherol	0.02	0.97	1.01	1.01
BHA	0.02	0.96	1.04	1.00
Cholesterol	0.1	0.96	1.12	1.12
Stigmaterol	0.1	0.95	1.11	1.09
Fucosterol	0.1	1.52	1.71	1.66
Δ^5 -Avenasterol	0.1	1.78	1.69	1.59
Δ^5 -Avenasterol	0.05	1.16	1.19	1.09
Δ^5 -Avenasterol	0.01	1.10	1.09	1.07

These observations can be explained from the hypothesis that the structure allows the sterols to react quickly with the free radicals to create free radicals which are relatively stable and react as antioxidants.

Chlorophyll and pheophytins also react as antioxidants, but their power is influenced by the preservation temperature and by the type of oil. (Endo *et al.*, 1985).

The natural antioxidants contained in food, are considered to be the major protective factors for human health (Ames *et al.*, 1993; Diplock, 1991; Block, 1992; Gey *et al.* 1991). Because of this the importance of determining the antioxidant capacity of a food type following a reaction of all the antioxidant compounds.

For example virgin olive oil has, besides the α -tocopherol, a series of polyphenolic compounds which help increasing its antioxidant activity (Clark *et al.*, 1991; Papadopulos *et al.*, 1991).

Recently, a new analytic method (Tubaro *et al.*, 1996) gives us informations about the quantity of α -tocopherol needed to have a determined antioxidant activity. This capacity is calculated by measuring the contents of an antioxidant substance needed to protect the *crucin* in the presence of an oxidant agent and using the antioxidant activity of α -tocopherol as a molecule of reference.

The total antioxidant activity of seven types of virgin olive oil, analysed by this method, is given in tab. II. These data show that their antioxidant activity is variable and corresponds to that found in one gram of α -tocopherol contained in a quantity of oil equivalent to 680-3700 grammes.

Table II
Kinetics of crocin bleaching inhibition by virgin olive oils

OIL	Competition Kinetics Equation	R	Oil/ α -Tocopherol ^a
1	$y=1.654 \times 10^{-4}x+1.039$	0.98	1818
2	$y=1.874 \times 10^{-4}x+1.149$	0.92	1628
3	$y=4.526 \times 10^{-4}x+0.935$	0.95	664
4	$y=1.667 \times 10^{-4}x+1.119$	0.91	1804
5	$y=0.810 \times 10^{-4}x+1.078$	0.97	3713
6	$y=2.131 \times 10^{-4}x+1.076$	0.99	1411
7	$y=1.766 \times 10^{-4}x+1.107$	0.93	1606

^a: The ratio indicates the relative amount of oil exhibiting the antioxidant effect of α -Tocopherol (Tubaro 1996).

In tab. III is showed the amount of α -tocopherol accounting for by the overall antioxidant capacity of the oil, by comparison with the real α -tocopherol content. Sample 3 shows a high content of α -tocopherol as well as a good antioxidant activity. Samples 5 and 7, also contain the same quantity of α -tocopherol (172 mg/Kg) differing enormously in their antioxidant activity. This information highlights the effect of minor components of virgin olive oil as possible antioxidants and could be relevant for assessing the oxidative stability and the quality of the oil during frying processes.

Table III
Vitamin E content and percentage of the overall antioxidant effect in different virgin olive oils

Oil	α -Tocopherol (mg/Kg)	% of Overall antioxidant effect
1	236	12.9
2	130	21.1
3	297	79.0
4	138	24.9
5	172	63.9
6	182	25.7
7	172	27.6

4.2 Appropriate planning of the frying apparatus

A facilitating element for the obtaining of a fried food with full health guaranties is the use of a well planned deep-fryer. Both the heating-up temperature (not greater than 180°C) and the heating-up of the oil limited to the time help it to keep stable.

The temperature must be kept as constant as possible during the working cycle. Every fluctuation in temperature may have a negative effect on the product quality. The second element which is indispensable for an optimum deep-fryer is the filtering system of the deposits which has to be quick, functional and continuous. If the filtering is not optimum the product may emerge from the deep-fryer with sediments attached which contribute to the alteration reactions of the oils. Consequently a good fryer has to be projected to have a maximum level of production with the minimum quantity of oil possible.

On this subject, deep-fryers have been designed to have an inclined container (that is to say not parallel to the base of the apparatus) which, is associated with a moving cilinder, to allow a lower oil consumption (Miller, 1990).

Besides, some have been given a «cold at the bottom» system to keep the oil clean: the last layer of oil at the bottom remains cold and the sediment that is deposited do not burn.

4.3 Good working knowledge

This section illustrates how the operator can prevent any risks of forming possible contaminants. The following gives some advices on how to carry out the process correctly:

a) right size of deep-fryer and appropriate source of heat according to the amount of food that is to be fried. A deep fryer that is over-sized requires a quantity of oil which has to be maintained hot whereas an under sized deep-fryer leads to an over-load and may result in the product not being completely cooked, or in need of an excessive cooking time and a much longer heat recovery in the deep-fryer;

b) use oil not more than two or three times and, in any case, filter it;

c) immerse the food in the oil after it has reached a temperature of about 180°C;

d) avoid overheating the oil, by using thermostated deep fryer;

e) break-up the food to be fried into small pieces in order to obtain a quick formation of the surface crust and hence preventing an excessive penetration of the oil itself in the food;

f) do not «renew» the used oil by adding fresh oil;

g) eliminate the excess oil from the food by straining it immediately after frying.

5. MONITORING

In general monitoring systems should give an indication, the more immediate the better, rapid and simple methods have therefore to be used.

In the frying process monitoring has to be conducted on the oil and on the product.

The quality of the oil

There are many different ways of controlling the quality of oil. Standard tests include the calculation of free fatty acids the ratio 18:2/16:0, the conjugated dienes and the total polar substances.

As far as the total polar substances are concerned, a value of around 25% has been shown as the limited value and above this, oil should be eliminated.

There are also numerous quick tests available commercially in order to evaluate the quality of an oil (White, 1991). The measurement of dielectric constant has been used by the Northern States Instrument Corp. to set up an instrument, Food Oil Sensor (FOS) which measures dielectric constant of an oil subject to frying in comparison to a fresh oil. A reading value with FOS of 4.0 should be the limit for an oil to be used.

The Merck has set up a colorimetric method under the name of Oxifri-test, which contains a redox indicator that reacts with the total quantity of oxidized compounds in a sample of oil.

The colour that evolves from the contact between the sample and the reagent is compared to a colour scale with four qualitative indicators: 1 - good, 2 - still good, 3 - intermediate quality, 4 - poor.

Another test which is also from Merck, provides a colorimetric measurement of the carbonyl compounds with a scale of 3 colours: 1 corresponds to a good quality; 2 intermediate and 3 poor.

Another test (Spot test) determines the content of free fatty acids with an indicator of hydrolytic rancidity. The colours shown are blue, green and yellow.

Finally, there is a quick colorimetric test which determines the presence and the semi quantitative content of the contaminating alkaline substances like the soaps that accumulate in the fried oil used during the interaction of the food residue with the degradation products of the oils. The method measures a concentration of ACM from 0 to 200 ppm.

Table IV shows data comparing the rapid methods. It can be seen that the FOS shows the best correlation with standard methods whereas that of free fatty acids (FFA) is not indicative of the change in fats (Wishner L. and Keeney 1965).

Table IV
Coefficient of Correlation (n=100) between methods for testing frying-oil degradation

	Polar components	Food-oil Sensor	RAU-Test	Fri-Test	Spot-Test	Free fatty acids
Polar components	1.00					
Food-oil Sensor	0.94	1.00				
RAU-Test	0.74	0.72	1.00			
Fri-Test	0.75	0.71	0.95	1.00		
Spot-Test	0.59	0.59	0.77	0.81	1.00	
Free fatty acids	0.33	0.24	0.53	0.54	0.61	1.00

Product quality

Generally, it can be stated that the quality of fried food, other characteristics being equal, comes mainly from its low content in oil after frying. By way of example, in one potato stick you can have oil content values in the product weight which fluctuate from 12 to 20% approximately, using the working conditions adopted, while for potato chips the oil content is close to the values of around 40-50%.

One important element that reduces the excessive use of oil during the frying process and which gives the product the desired organoleptic characteristics (colour, browning, aroma, crispness) is the presence of a surface crust.

The formation of a surface crust is helped by the presence of starch, which, if it is a constituent of the food product itself (for example in potatoes), or is added to the food in the form of bread-crumbs and/or

batter, dehydrates and therefore allows a quick formation of the crust. It is well known that a bread-crust topping consists of egg and breadcrumbs, while batter normally consists of flour and egg.

The surface layer normally produces a porous structure, with capillaries, pores and canals of different sizes and diameters. During the frying process the water in the form of steam is removed from the centre of the product, by means of very large capillaries while in the opposite direction the oil partially enters.

The formation of the crust transfers a barrier effect on the water discharge from the inside of the product, on the entrance of the oil into the product and the movement of heat from the oil to the internal parts of the product.

The effects of the frying process on the nutritional value of the products depend on the type of method adopted. The crust formation superficially prevents

the release and the leaching of the nutritional substances inside the product on the oil, and besides, for those fried products consumed immediately after cooking, there is not a great loss in the nutritional value owing to, on the other hand, long periods of time of warm storage (see collective restoration).

In general terms therefore, the transfer of heat towards the interior of the product may have noticeable thermic effects which can be positive (improvement of the nutritional and organoleptic characteristics) or negative (excessive dehydration, pyrolysis reactions).

In general the quality of a fried product is valued by appearance, taste and the olfaction.

The appearance of a fried product can be controlled by using chromatic card, the panel test or the consumer test.

The chromatic card is used for example to measure the browning of fried chicken. The typical scale of colour goes from 4 to 6 with a decreasing order of preference from 6 to 4.

6. CONCLUSIONS

The risk analyses, the control of critical points and an adequate system of monitoring the quality of oil and the product give frying an image of safety for the consumer.

The risk analyses in particular highlight how, usually during the frying process you never reach those drastic conditions corresponding to those conditions which may form products of decomposition from oils at a level of concentration that has shown to have different types of toxic effects during tests carried out on experimental animals.

The choice of oil has to be an oil with a low level of insaturation and a high level of antioxidant activity. The choice of deep-fryer has to be based on the load, the size ratio of food to be fried/oil on the system of temperature control and on an adequate filtering system.

The use of a good procedure of the frying process and a good maintenance of the deep-fryer are aspects to be tested and also critical points to be controlled, following a whole series of advice.

Finally an adequate system of monitoring at an industrial level of the oil and the frying product, by using quick and simple methods, enable the process to be kept under control and the ability to intervene immediately should the index values show any sign of danger.

An approach of this type followed either by someone in the home or above all by restaurants or fast food restaurants enables the frying process to be seen in a new safe light, regarding hygiene and health and in particular nutrition. Apart from supplying particular organoleptic characteristics to the product, it also allows a new connotation for the different lipidic contributions - particularly of fatty acids in respect to the original product caused by the migration of fats in two directions: from the oil to the product and viceversa.

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