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review

Effect of Food Components on Changes in Frying Oil

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Summary

Frying oil is oxidized by air oxygen and degradation takes place due to high temperature, but its changes are influenced by fried food, too. The most important reaction is the formation of steam by contact of hot oil with water present in fried food. Steam hydrolyses triacylglycerols of frying oil. Fried food absorbs a part of frying oil, but the absorption may be inhibited by batter, especially covered by a layer of polysaccharides. In case of fatty foods, fat is released from fried food into frying oil. Proteins inhibit oxidation reactions, with formation of lipid-protein complexes, but excessive temperatures may cause formation of heterocyclic mutagens, mainly isoquinolines and isoquinoxalines. The oxidation of frying oil is inhibited by various other components of fried food, such as tocopherols, carotenoids, phenolics or certain sterols, mainly avenasterols. On the contrary, heavy metals, chlorophylls and other prooxidants are released into oil, enhancing its oxidation. Fried food contributes to the formation of flavour substances, such as pyrazines, pyrroles or sulphides, which modify the typical fried flavour.

Key words: deep fat frying, flavour formation, fried food influence, frying oil quality, oxidation

Introduction

The food processing by deep fat frying has become among the most widely used methods of meal preparation. The main reason is the highly acceptable flavour of fried products, but another factor is also very important, namely, that fried foods are easily and rapidly prepared. Much attention is paid to changes of frying oil during the process *(1,2)*, which is natural as it is necessary to replace oil if it becomes too deteriorated. The effect of fried food on changes of frying oil is often undervaluated *(3)*. Fried food affects the composition of frying oil, its flavour, and its stability against deterioration. On the contrary, interactions between frying oil and fried food influence the flavour and the nutritional value of fried products.

Conditions of Deep Frying

They differ from the conditions of shallow frying, mainly in the excess of frying oil. Therefore, the oxidation and other changes during deep frying are much slower. Typical frying temperatures vary between 130–180 °C, sometimes even above 200 °C. They decrease after introduction of food material, but increase again during the frying process. The frying time varies between 3–10 min, depending on the temperature and on the composition of the fried substance. In case of deep fat frying, the frying may be continued 6–60 times, before used oil has to be rejected *(4)*. As frying oil is absorbed by fried food, its amount gradually decreases, especially in case of potatoes, so that it has to be replenished with fresh oil from time to time *(5)*; essentially, only a small part of total oil is really heated for the whole time of frying *(6)*.

The processes characteristic for deep frying are determined by limited access of air, and by steam produced in contact of fried food with preheated frying oil.

The composition of frying oil has great effect on changes during frying. A traditional frying fat in Central Europe is pork lard, which imparts a typical agreeable flavour to the product. Its disadvantage is high content

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of nutritionally objectionable palmitic acid, the presence of cholesterol, and the absence of natural antioxidants. Refined edible oils, possessing medium to high content of linoleic acid, are the optimum medium, as linoleic acid oxidation products are precursors of typical fried flavour compounds *(7)*. Their disadvantage is their low resistance against oxidation and polymerization.

The content of oxylabile polyunsaturated fatty acids can be decreased by hydrogenation, catalyzed with nickel catalysts. The oil thus becomes much more resistant against autoxidation during frying, but solid hydrogenated oils are manipulated with difficulties when they solidify, and contain higher amounts of saturated and trans-unsaturated fatty acids, which are objectionable from the standpoint of correct nutrition. A compromise is mild hydrogenation, followed by removal of the solid fraction.

Another type of raw materials has become available, *i. e.* genetically modified high-oleic/low-linoleic vegetable oils *(8)*, particularly, high-oleic sunflower, safflower and peanut oils, resembling olive oil in their fatty acid composition, low rate of oxidation and polymerization. Palm olein, a fraction of palm oil, has similar properties.

All types of frying oils may be stabilized by addition of trace amounts of silicone oils, which form a thin layer on the interphase between oil and air, thus limiting the access of oxygen into oil by diffusion.

Processes in Frying Oil During Deep Frying

Frying oil is not much changed by heating under nitrogen, but it is easily attacked by air oxygen and by fried food (Fig. 1), which usually contains a high percentage of water. In contact with overheated oil, water is converted into steam, hydrolyzing frying oil triacylglycerols into diacylglycerols, monoacylglycerols and free fatty acids *(9)*, which are distilled off with excess steam into atmosphere (Fig. 1). Glycerol is liberated, which is pyrolyzed into acrolein, a gas irritating eyes and mucosa of frying operators. Many other reactions proceed in

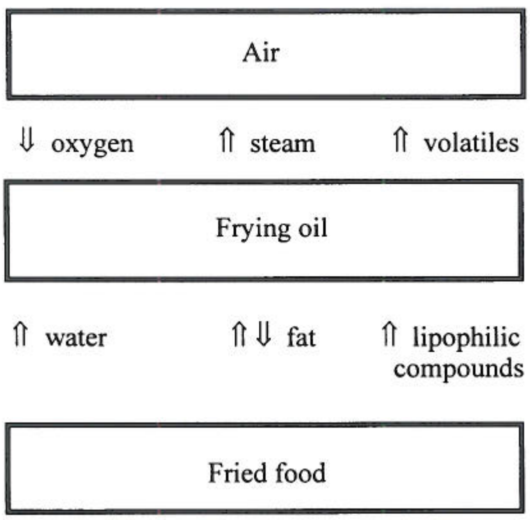

Fig. 1. Reactions in frying oil during deep frying

Table 1. Main processes in fried food during deep frying

Type of reactions	Examples of reactions
Reactions due to heating on the surface of fried food	Dehydration and pyrolysis Polymerization and condensation Hydrolysis
Interchange between frying oil and fried food	Transfer of water into frying oil Transfer of fat in both directions Formation of flavour compounds by interactions between oxidation products of frying oil with aldehydes and heterocyclic compounds of fried food

fried food (Table 1). Various natural components and reaction products can enter into frying oil from fried food. Transfer of fat between frying oil and fried food belongs to the most important processes.

Transfer of Fat between Frying Oil and Fried Food

The exchange of fat depends on the fried material. Products of plant origin, such as potatoes or doughnuts, contain only low amount of lipids, which are mainly bound in membranes or lipoproteins. Therefore, they are released only modestly during frying, and the absorption of frying oil prevails.

In animal products, the process depends on the fat content. Pork, beef, lamb, and even sometimes poultry, may contain high percentages of fat, which is released into frying oil. On the contrary, lean muscle tissues, such as chicken breasts or thighs, can absorb frying oil.

In case of fish, the transfer of oil depends on the oil content in fish. Lean products, such as cod fillet, will absorb frying oil, but fatty fish may release oil. Therefore, in frying herring or sardines, frying oil contains higher polyunsaturated fatty acids, such as eicosapentaenoic or docosahexaenoic acids *(10–12)*. They may impart fishy off-flavour to frying oil, and decrease its stability against rancidification.

Inhibition of Fat Transfer into Frying Food

If fried products are rich in fat, they bring much available energy to the consumer. People in developed countries need to reduce their energy intake, and therefore, they prefer low-fat fried products. The reduction of fat thus became a very important consumers´ requirement. The description of kinetics of fat transfer is very important from this standpoint *(13)* in order to optimize fat content.

A very simple procedure is pre-drying the material to be fried. It is used particularly in frying potatoes, which are easily dried on the surface after cutting before the frying.

In case of meat, it is preferable to preheat slices in very hot oil, so that proteins are rapidly precipitated, forming an impermeable crust, able to prevent access of fat. Preheating oil to 220–300 °C was found suitable in our laboratory.

Another procedure is to use batter and breading. They form a barrier reducing the access of fat into meat, mushrooms, vegetables or in other foods. The disadvantage is low firmness of the batter layer so that small particles get loose, and dark loose burnt particles of batter discolour frying oil, enhancing its degradation *(14)*.

Recently, dietary fibre was used as a substitute of clasical batter, such as cellulose and various hydrocolloids *(15,16)*. They form a solid, impermeable crust, reducing substantially the oil uptake. The use of such additives may be subject to approval by authorities.

Oxidation of Frying Oil

Frying oil contains dissolved oxygen, which reacts only extremely slowly at room temperature. At frying temperatures, oxygen is consumed in several minutes by reaction with unsaturated fatty acids bound in frying oil. Other molecules of oxygen enter the oil by diffusion from air. The rate of oxygen diffusion is rather slow in comparison with the rate of oxidation. The rate is increased by foaming; on the contrary, it is decreased by the presence of saturated hydrocarbons or silicone oil.

Oxidation products are more polar than original triacylglycerols of frying oil. The fried material is also relatively polar. Therefore, polar oxidation products from frying oil are absorbed more readily on the surface, and even in inner layers of fried substances than unchanged oil (Table 2). The oxidized fraction is thus continually removed from frying oil, which prevents their accumulation *(17)*.

Table 2. Distribution of oxidized products between fried food and frying oil

Fried product	Oxidized lipids in frying oil/%	Oxidized lipids in fried food lipids/%
Potatoes	4.2 – 6.6	5.7 – 8.8
Bread	6.1 – 8.2	7.5 – 10.1
Meat, fish	2.5 – 7.9	3.4 – 9.5

Oxidation products deteriorate the nutritional value of fried material, therefore, the oxidation should be suppressed.

Inhibition of Frying Oil Oxidation

Free radicals are the most important intermediates in lipid oxidation. For this reason, the process of lipid oxidation in frying oil is inhibited by substances reacting with free radicals. Such substances are called antioxidants. Several antioxidants are natural components of frying oils, such as tocopherols, some sterols or phospholipids. Tyrosol derivatives are natural antioxidants of olive oil.

Other antioxidants are transferred from fried food into frying oil: again tocopherols, but also carotenes and related carotenoids. Other active substances are not soluble in frying oils, therefore, they remain in the fried material, but still, they may react with free radicals, at least at the interphase. Phenolic derivatives, such as chlorogenic acids, tannins, flavonoids and anthocyanins, but also ascorbic acid (vitamin C) belong to this group.

The antioxidant activity of tocopherols has been known since more than fifty years. The activity of γ- and δ-tocopherols is much higher in frying oil than that of α-tocopherol. The antioxidant activity of some sterols was discovered only recently. Avenasterols belong to the group of active antioxidants (Fig. 2) because they form a stable vinyl radical by reaction with lipid free radicals *(18)*. They were discovered in olive oil, where they contribute to the excellent stability, however, avenasterols are present in other common edible oils as well (Table 3).

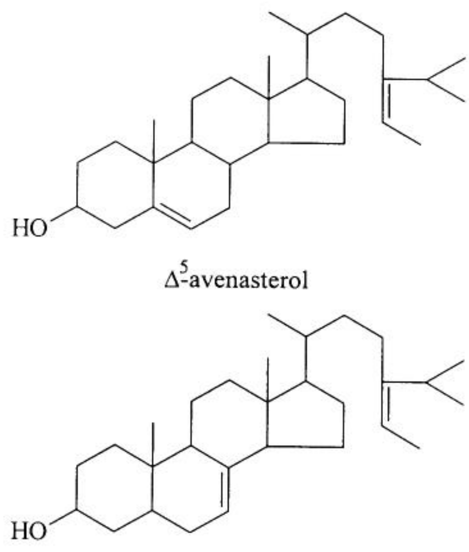

Fig. 2. Chemical structures of avenasterols (after IUPAC)

Table 3. Content of avenasterols in vegetable oils

Oil	Total sterols*	Δ^5-avenasterol**	Δ^7-avenasterol**
Rapeseed	4.5 – 7.8	3.1 – 6.6	0.0 – 0.8
Soybean	2.4 – 4.5	1.9 – 3.7	1.0 – 4.6
Sunflower	1.8 – 4.1	1.5 – 7.0	3.0 – 6.5
Palm	0.4 – 0.6	0.0 – 2.8	0.0 – 5.1
Olive	1.0 – 2.0	3.9 – 8.9	traces

* expressed in g per kg of oil;
** expressed in % of total sterols

Another group of natural antioxidants, which my be transferred from fried material into oil, are active substances from spices. Their activity is high at storage temperatures, becoming lower at higher temperatures, but still, they increase the stability even during frying (Table 4). Antioxidants from rosemary and sage, discovered more than 40 years ago *(19)*, were found as the most active antioxidants in spices, and the extracts are produced even commercially. They are active during frying of animal products *(20)*. In our experiments, rosemary extracts were active not only in reducing the rate of oxi-

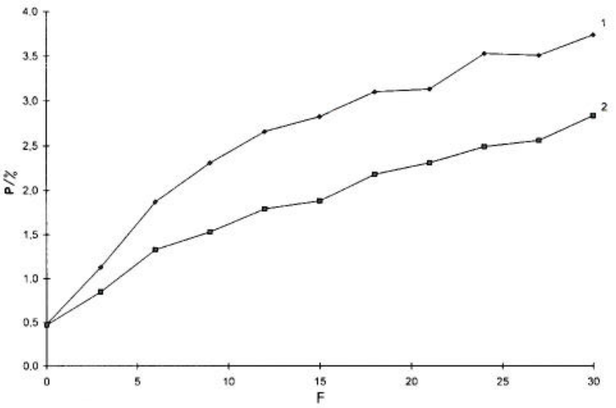

Fig. 3. Effect of rosemary extract on the polymerization of frying oil
Frying potato stripes in rapeseed oil; P = concentration of polymers in %; F = number of fryings; 1 = oil without addition of antioxidants; 2 = oil containing acetone extract of rosemary leaves

dation of polyunsaturated frying oil, but particularly, the rate of subsequent polymerization of oxidation products (Fig. 3). This effect is very important as polymers are more dangerous to human health than monomeric oxidation products.

On the contrary, some substances present in fried material may increase the rate of oxidation. Heavy metal ions and some complexes belong to this group. Heavy metals, such as copper or iron, are present in the fried substance at concentrations 10–100 times higher than in frying oil. At high frying temperatures, they are released from their complexes, and pass into frying oil. Iron bound in myoglobin or haemoglobin is easily set free under conditions of frying meat or fish.

Influence of Protein, Peptides and Amino Acids

The fried substance always contains protein, at least in moderate amounts, which is very reactive, particularly the present sulphur and amino groups. Sulphur groups are derived from sulphur-containing amino acids, such as cysteine, cystine or methionine. Free amino groups are those of basic amino acids, especially lysine. These two types of amino acids are bound in proteins and peptides. In meat or fish, creatine and creatinine – a basic amino acid and its cyclic amide – are present, which are particularly reactive at frying temperatures.

Table 4. Effect of spices on the stability of rapeseed oil under frying conditions

Spice added to potato puree	Stability after Schaal test*	Protection factor**
	d	%
Control	5.01	100
Rosemary	11.48	207
Sage	9.21	170
Marjoram	6.54	130
Oregano	5.85	116

* the Schal test at 40 °C, gravimetric method
** induction period expressed in % of the control experiment

Table 5. Effect of fried food on the stability of frying oil against oxidation

Fried food	Stability after Schaal test*	Protection factor**
	d	%
Control (cellulose)	1.5 – 1.7	100
Potatoes	2.5 – 3.1	150 – 190
Bread, doughnuts	2.0 – 2.6	150 – 170
Chicken, fish	2.2 – 2.6	130 – 150

* the Schaal test at 40 °C, gravimetric method
** expressed as % of the induction period of control experiment

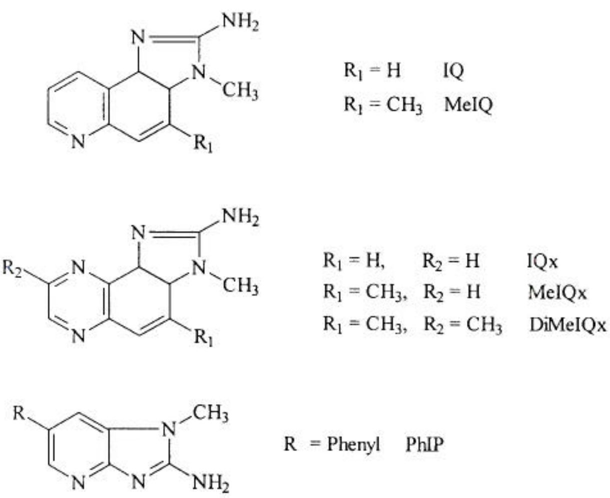

Fig. 4. Chemical structures of mutagenic polycyclic heterocycles produced by frying meat at excessive temperatures (from various sources)
IQ = imidazoquinoline; MeIQ = methylimidazoquinoline; IQx = imidazoquinoxaline; MeIQx = methylimidazoquinoxaline; DiMeIQx = dimethylimidazoquinoxaline; PhIP = phenylimidazopyridine

Proteins react with lipid free radicals or with lipid oxidation products, such as hydroperoxides or aldehydes, thus inhibiting their oxidation (Table 5).

The disadvantage of the protein reactivity is the formation of polycyclic aromatic heterocycles under frying conditions *(21)*. Creatine and creatinine are the most important precursors of these compounds. These substances, mainly imidazoquinolines and imidazoquinoxalines (Fig. 4), but also various nitroxyl derivatives *(22)*, are very active carcinogens, especially in mammals. Fortunately, they are formed mostly at temperatures substantially higher than common frying temperatures, which are, however, easily exceeded in shallow frying or on borders of a pan. The frying temperature of 180 °C should not be exceeded for this reason.

Effect of the Fried Substrate and Frying Oil on the Flavour

For the explanation of attractive fried flavours, it is necessary to review reactions proceeding in the fried substrate (Table 1). The most important reactions from the standpoint of flavour are pyrolytical and condensation reactions as they produce precursors of flavour compounds. Some flavour substances are absorbed from frying oil (Table 5), others are formed by reactions near the surface inside the fried substance, but many flavour substances are produced on the interphase between the fried food and frying oil. The fried flavour is very complicated, being the result of more than 100 contributing substances *(23)*. Various nitrogen, oxygen and sulphur low-molecular weight substances are derived from the fried product, which react with volatile lipid oxidation products, mainly aldehydes *(24)*.

Conclusion

In conclusion, we should like to summarize that the most important reactions occurring during deep frying are very complex, including reactions in frying oil, in fried food, and interactions between oil and fried food. The optimum frying conditions should be based on profound knowledge of complex processes during deep fat frying.

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Utjecaj sastojaka hrane na promjene ulja za prženje

Sažetak

Kisik iz zraka oksidira ulje za prženje. Do degradacije ulja dolazi zbog visoke temperature, a na te promjene utječe i pržena hrana. Najvažnija reakcija je stvaranje pare prilikom dodira vrućeg ulja s vodom prisutnom u hrani. Para hidrolizira triacilglicerole u ulju za prženje. Pržena hrana apsorbira dio ulja, a kad se prži namirnica prekrivena slojem tijesta, apsorpcija je inhibirana osobito ako tijesto sadrži sloj polisaharida. Ako je hrana masna, tada masti prelaze iz pržene hrane u ulje za prženje. Proteini inhibiraju reakcije oksidacije stvarajući komplekse lipid-protein, a jako visoke temperature mogu uzrokovati stvaranje heterocikličkih mutagena, uglavnom izokinoline i izokinoksaline. Oksidaciju ulja za prženje inhibiraju i razni sastojci hrane kao što su tokoferoli, karotenoidi, fenolni spojevi i određeni steroli, ponajviše avenasteroli. Nasuprot tome, teški metali, klorofili i drugi spojevi koji omogućuju oksidaciju ulaze u ulje, pojačavajući time oksidaciju. Pržena hrana pridonosi stvaranju sastojaka arome, kao što su pirazini, piroli ili sulfidi koji modificiraju tipičan okus po prženju.