

Substrate influence on the frying process

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SUMMARY

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The substrate affects frying oil in different ways during the frying. Water is released from the substrate, which is converted into steam and participates in hydrolytical processes of frying fats. The transfer of fat into the substrate and from the substrate into frying fat depends on the fat content in the substrate and on the frying conditions. Other, more polar substances than triacylglycerols, including pigments and their precursors, pass in frying oil. Oxidation processes in frying oil are inhibited by the substrate, especially by proteins, starch or phenolic substances. Mutagenic polycyclic aromatic heterocycles are produced during the interaction of frying fat and protein. Oxidation products are bound to proteins and other components of the substrate. Flavour substances are produced by reactions of oxidized frying oil with proteins and other sulphur and nitrogen substances in the substrate.

KEY-WORDS: Fat transport – Frying process – Hydrolysis – Oxidation – Substrate.

INTRODUCTION

Five types of main processes take place during deep fat frying of food products: (a) Hydrolytical processes, affected by water present in the substrate and penetrating into oil in the pan; (b) fat migration (either from the pan into the substrate or from the substrate into the frying fat; (c) oxidation reactions, both in frying oil and in the substrate; (d) pyrolytic reactions, mainly consisting of dehydration, often preceded by condensation reactions; (e) polymerization reactions, again both in frying oil and in the substrate.

Much attention has been paid to changes occurring in the frying oil even when it is not consumed after frying. Changes in the fried substrate, which is consumed after frying, were much less studied. I reviewed the topic 18 years ago at a congress on the effect of heating on food in Italy (Pokorný, 1980). Therefore, I find interesting to discuss the progress since then.

EFFECT OF SUBSTRATES ON HYDROLYTIC PROCESSES IN FRYING FATS

Hydrolysis of frying oil triacylglycerols is the most important reaction during the deep fat frying. It is effected by water present in the substrate. The fried

material, usually at room temperature or even refrigerated, comes into contact with frying oil preheated to 130 - 200 °C. Water present in the substrate is almost immediately heated to the boiling point, and steam produced enters the hot oil. Under these conditions, triacylglycerols are partially hydrolyzed into free fatty acids and partial glycerol esters (diacylglycerols, monoacylglycerols and even glycerol) in relatively short time (about 5-10 min) of deep frying.

Water is preferentially eliminated from outer layers of the substrate. The surface part of substrate where the temperature exceeds 100 °C is almost completely dehydrated, becomes crispy, and it is called the crust (Skjöldebrand *et al.*, 1982). Addition of water to coconut or niger seed oils before the frying increased the transient formation of epoxy acids and stimulated the formation of free fatty acids during the subsequent heating (Ramanna, Sen, 1983). Water evaporated during the frying was proportional to the square root of frying time, and was direct proportional to the difference between the temperatures of oil and of boiling water (Ashkenazi *et al.*, 1984). Water present in the substrate affects the frying oil more than other components (Barbanti *et al.*, 1994).

Drying of the outer layers in frying french fries or potato chips is of great importance for the fat content in the final product. The absorption of frying fat is related to the initial water content of potato strips or slices, and to the interfacial tension between frying oil and fried substrate (Pinthuis, Saguy, 1994). Therefore, frying of prefried potato strips reduces the hydrolysis of frying oil during the finish frying (Kouřimská *et al.*, 1992). It will be discussed in the next chapter. Pre-drying or preliminary frying suppress the fat content in the fried product. Potatoes coated with an aqueous starch slurry yielded more crispy and crusty product.

The evaporation of water from the substrate during the frying operation means a substantial loss of weight, which is particularly important in case of fried meat products as meat is much more expensive than potatoes. If meat becomes too dry during the frying, the texture is unfavourably affected as well. Therefore, meat is usually coated with batter before frying, which suppresses the weight loss and keeps the fried product softer and more chewy. The breaded batter is sometimes replaced by other

materials. Coating of carrageenan, carboxymethyl cellulose and xanthan gum suppressed weight losses of fried minced fish products, and improved the texture (Da Ponte *et al.*, 1987). Protein-rich dispersions replaced common batter in frying fish or meat, producing a crispy and chewy crust (Bhardwaj, 1990).

FAT AND OIL TRANSFER DURING THE FRYING

Some substrates, mainly of plant origin, absorb frying oil during frying, which makes them more palatable, but also increases their energy content, which is undesirable. High water content and low fat content stimulates the oil absorption (Makinson *et al.*, 1987). It is useful to dry potato strips or slices a little on the surface during frying. Rapid pre-frying of meat in oil preheated to 220 - 250 °C reduces the fat transfer during subsequent frying. The penetration of fat into the substrate is namely prevented by formation of a crusty outer layer (Varela, 1988). The crust formation is slower and the necessary frying time longer in high-water-content substrates, therefore, the fat absorption increases with increasing water content in the surface layer and the increasing frying time (Lamberg *et al.*, 1990). Pre-fry drying is preferable to post-fry fat removal to obtain low-fat crisp products (Gamble, Rice, 1987).

Cooking prior to frying denaturates proteins, decreasing thus the water content, which affects the fat transfer. Leaching of amino acids and soluble proteins during cooking has an influence on the nutrition value of fried products, particularly fish (Steiner *et al.*, 1991).

The protein matrix has great effect on fat transfer of fried products. Hamburgers have relatively unstable fat fraction and coarse protein matrix. A quadratic relationship was observed between the fat loss and the fat content. In sausage, on contrary, the fat fraction is relatively stable, and meat proteins dense; the fat loss is then correlated with the water loss (Tornberg *et al.*, 1989).

During the frying of prefried French fries, hydrogenated oil present in prefried products is partially transferred into frying oil and replaced with frying oil (Kouçimská *et al.*, 1992).

The batter facilitates the crust formation and decreases the content of absorbed fat. Different additives were proposed to improve the performance of batter against fat absorption. Small amounts (1-4 %) of powdered long-fibre cellulose were found efficient for frying cakes or doughnuts (Ang, Miller, 1991). Hydroxypropyl methylcellulose could be used as well. Wheat flour or corn starch had a similar activity. The crust could be produced by coating the product with gum arabic, tapioca dextrin or xanthan gum. Even synthetic materials were proposed, such

as polyvinylpyrrolidone. Coating with protein latex is suitable as it forms a hydrophobic protein layer on the surface of fried product, possessing very good barrier properties.

Lean fish absorbs fat during frying, too, which may be partially prevented by coating it with a layer of batter. Fatty fish release fat during frying so that the frying oil becomes contaminated with fish oil (Sánchez-Muñoz *et al.*, 1992). As fish oil is highly polyunsaturated, frying oil contaminated with fish oil turns rapidly deteriorated. Hamburgers contain high percentage of fat as well, which may penetrate into frying oil; weight losses are thus increased. Physical dispersion of the fat phase, especially emulsification with gelatin, are important to protect hamburgers from the weight loss (Olsson, Tornberg, 1991). During the frying of fish and meat products, cholesterol enters the frying fat and contaminates it with decomposition or oxidation products as well. Therefore, the frying oil used for frying animal products may contain cholesterol, even when the original frying oil was cholesterol-free (Kajimoto *et al.*, 1993).

TRANSFER OF POLAR SUBSTANCES AND THEIR DEGRADATION PRODUCTS FROM THE SUBSTRATE TO FRYING OIL

Various compounds are released from the substrate into frying oil, enhancing discolouration or off-flavours. During the frying of cabbage and other green *Brassicaceae* vegetables, glucosinolates are decomposed, and their decomposition products, such as nitriles, indolyl derivatives or vinyl oxazolidinethione contaminate the frying oil. Chlorophylls and their decomposition products (mainly pheophytins) pass into frying oil producing absorption peaks between 600 - 700 nm (Taha *et al.*, 1988). On the contrary, pigments present in frying oil may be adsorbed on the surface of fried substrate.

Maillard browning products and their precursors are major contributing substances to the discolouration of frying oil. They are produced from free amino acids and reducing sugars, either originally present or formed from sucrose under frying conditions. Lysine, γ -aminobutyric acid and glycine are the most potent precursors of brown pigments. Lysine may cause browning even when bound in proteins as the 6-amine group remains free. The decomposition of free or bound amino acids is enhanced by oxidized products in frying oil (Ribarova *et al.*, 1993); cysteine and proline are particularly affected. Biogenic amines enter the browning reactions as well as amino acids. Browning products are formed in fried potato products more than in fried meat. The discolouration is very pronounced in fish fried in used frying oil, as polyunsaturated fatty acids

of fish oil participate in the formation of brown pigments (Pokorný, 1981).

Vitamins, such as thiamin, pyridoxin, riboflavin, ascorbic acid, are decomposed on heating, and some oil-soluble decomposition products dissolve in frying oil, affecting the colour and the flavour. The decomposition is accelerated by contact with oxidation products of frying oil.

Mineral components are released from the substrate during frying. Heavy metal ions, such as iron or copper salts, accelerate the oxidation of frying oil. Sodium and potassium ions are transported to frying oil, forming alkaline soaps, which stimulate foaming. The foaming increases the interface between oil and air, which promotes the oxidation (Blumenthal *et al.*, 1985). Our experiments (Réblová *et al.*, 1996) show that the foaming activity of alkaline soaps depends on the chain length, unsaturation degree and the concentration.

Several N-nitroso derivatives are produced in fried bacon or other cured products, such as 2-(hydroxymethyl)-N-nitrosothiazolidine, N-nitrosothiazolidine, N-nitrosothiazolidine-4-carboxylic acid (Sen *et al.*, 1986) or N-nitrosopyrrolidine. Such nitros-amines, which are strong carcinogens, may contaminate frying oil and the subsequently fried products.

Transport of substances through the surface of fried substrate is inhibited by batter, however, particles separated from the batter in oil soon get deep coloured by pyrolytic reactions, and contribute to the degradation of frying oil. These dark particles are often removed by filtration during the process because they impart bitter taste to the fried product. The texture of batter may be improved by various operations to obtain more rigid barrier. Chitosan was applied with success to form solid crust on the surface of fish-in-flour during frying, improving not only the taste, but also preventing the coating to fall off and to contaminate thus frying oil (Bogdanov, Sur'kova, 1985).

EFFECT OF THE FRIED SUBSTRATE ON THE OXIDATION OF FRYING OIL

Oxidation by air oxygen is the most important deterioration reaction of frying oil, which is relatively rapid, especially in case of polyunsaturated oils, such as soybean or sunflower oils. Free peroxy radicals are unstable intermediates, and hydroperoxides—the primary oxidation products—are rather unstable under frying conditions as well. Both peroxy radicals and hydroperoxides react with the substrate, particularly with thiol, sulphide, disulphide, and primary amine groups of proteins. They are deactivated, and partially remain attached to the protein moiety (Pokorný *et al.*,

1988). Therefore, fat is not quantitatively extracted from fried material with use of conventional extraction methods.

Frying fat adsorbed on the surface of substrate is generally more oxidized than frying oil as oxidized products are selectively adsorbed on protein molecules (Table I). Denaturation of protein in fried material stimulates the interactions. The interaction products deteriorate the sensory value of the fried product, such as chicken muscle (Pokorný *et al.*, 1982). The sensory value of French fries is more resistant to the oxidation degree of frying oil than meat. The products formed by interaction of oxidized lipids with protein are partially liposoluble (Pokorný, Davídek, 1979), contaminating thus frying oil, but they are mostly insoluble, remain in the fried material, and are digestible only slowly and incompletely. Protein oligomers containing cross-linked polypeptide chains are produced in this way.

Table I
Absorption of oxidized products from frying oil on the surface of French fries

Products	Content in frying oil	Content in French fries
Polar compounds [mg.g ⁻¹]	34	48
Carbonyls [mg.g ⁻¹]	11	16
Polymers [mg.g ⁻¹]	10	24

Unpublished results by L. Kourimská, S. Pokorný, J. Pánek and J. Pokorný.

Starch present in substrates of plant origin reacts with oxidized frying oil as well as polypeptides or proteins, forming interaction products where triacylglycerols are bound to starch macromolecules in several ways, e. g. by ether bonds (Fedeli *et al.*, 1983). The digestible starch is partially converted into resistant (undigestible) starch, which could explain the increase of dietary fibre during frying (Heranz *et al.*, 1983).

In our model experiments, frying oil was oxidized more rapidly when frying starch than when frying protein substrates (Table II). This inhibition is due to reactions of lipid peroxides with amino acid residues in protein. Surprisingly, oils rarely contain high levels of oxidation products when frying potato strips or slices, which are a typical starch-rich and low-protein product. The reason may be the presence of chlorogenic acids and other phenolic substances in potatoes, but another reason is intensive sorption of oxidized products in the fried material. The absorbed oil has to be replenished by adding fresh oil in the pan, and the content of oxidized products is thus diminished.

Table II
Effect of carbohydrates and proteins
(ratio 1 : 3 m/m) on the induction period [min]
of frying oil (determined using the AL Oxipres
apparatus (Aarhus AL, Denmark))

Nonlipidic substrate	Induction period of frying oil	Prolongation of induction period compared to control
Cellulose	414	- 17
Wheat starch	585	+ 17
Egg albumin	842	+ 69
Casein after Hammarfels	2022	+ 306

Unpublished results by L. Trojáková, Z. Réblová and J. Pokorný.

The oxidation of frying oil may be inhibited by antioxidants from the fried substrate, such as tocopherols, sulphur compounds, ascorbic acid or phenolic substances, present in fried plant foods or added to animal foods with spices. Ginger oleoresins had antioxidant activity in frying in soybean oil (Kim, Ahn, 1993). Oleoresins from rosemary and sage are active under frying conditions and were not volatilized even at frying temperatures. Acetone and ethyl acetate extracts suppressed the formation of polymers in oil during frying french fries (Réblová *et al.*, 1997). Pinene was found active as well. Oil-soluble material from carrots, potato tubers or oat flakes inhibited the oxidation of frying oil and hydrogenated frying oil (Pokorný, 1980). Amino acids or phospholipids act as synergists of phenolic antioxidants or tocopherols. Phospholipids suppressed the formation of polymers in frying oils (Kourimská *et al.*, 1994), and they inhibited the decomposition of tocopherols (Kajimoto *et al.*, 1987).

FORMATION OF MUTAGENS DURING FRYING PROTEIN-RICH SUBSTRATES

Mutagens are formed during deep frying of protein-rich foods, such as meat. They belong to polycyclic aromatic heterocycles of the aminoimidazo-azarene and amine-carbolin series (Hatch *et al.*, 1991). Creatine and creatinine are the most important precursors of these aromatic heterocyclic compounds (Laser-Reuterswärd *et al.*, 1987).

Meat dispersions, suitable for making meatballs or sausages, were fried with addition of creatine, which is converted into creatinine under frying temperatures. The mutagen activity in the fried crust

was related to the amount of creatine added (Nes, 1986).

Lean pork fried in various fats showed mutagenic activities, which were higher at frying temperature of 250 °C and lower at 200 °C (Overvik *et al.*, 1987). Each 50 °C rise in frying temperature doubled the mutagen formation in beef and pork patties (Gry *et al.*, 1986). The mutagenic activity of fried and flame-broiled meats was approximately tenfold to fiftyfold higher than the mutagenicity of baked meals (Doolittle *et al.*, 1989). Low frying temperatures (about 130 - 150 °C) are thus preferable in the preparation of meat meals.

Other components of the substrate influence the formation of heterocycles as well. Maillard products react with creatinine producing various imidazoquinoline and imidazoquinoxaline mutagens (Dahlqvist, 1986). While mutagens are formed by reactions of creatinine with Maillard reaction products, on the contrary, Maillard precursors, such as glucose, lactose or powdered milk, inhibited the formation of mutagens in meat patties (Skog *et al.*, 1993).

The production of mutagens is much lower in absence of fat so that frying fat is important for their formation. Model mixtures containing Maillard precursors (glycine and glucose) and creatinine were heated with addition of iron salts and fats; substituted imidazoquinoxalines were identified among the mutagenic products (Johansson, Jägerstad, 1993). The reaction was enhanced by oxidized fats and iron salts, but it was not inhibited by tocopherol. Some mutagenic activity of frying fats is due to nitrogen-free lipid-hydroperoxide decomposition products as well, i. e. it is independent from the fried substrate. They are due only to oxidation products of oxidized and polymerized triacylglycerols or free fatty acids.

FORMATION OF FLAVOUR SUBSTANCES BY SUBSTRATE INTERACTION WITH OXIDIZED FRYING OIL

The typical flavour of fried products is mostly due to fat degradation products adsorbed on the surface of the fried material. Between 30-60 % total fried flavour-active volatiles are derived from frying oil (Pokorný, 1989). The substrate contributed by various pyrolytic products as well. The third group of flavour compounds are interaction products between amino acids or their decomposition products with aldehydes produced from frying oil. Sulphur-containing amino acids, free or bound in protein, are the most important group of substances in substrates. A typical frying product, *cis,trans*- and *trans*, *trans*-2,4-decadienals, reacted with either cysteine or glutathione forming 45 and 42 volatiles, respectively

(Zhang, Ho, 1989), such as thiazines. Meat flavour have similar structures. Sulphur substances from garlic and onion react with aliphatic aldehydes as well. Another precursor of interesting flavour is thiamin.

The formation of flavour components will be discussed in more detail by W. Nawar (these Proceedings).

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