



Chemical Reactions Taken Place During Deep-Fat Frying and Their Products: A Review

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Article history: Received: 12.11.2014

Accepted: 18.12.2014

ABSTRACT

Deep-fat frying at 180 °C or above is one of the fastest, oldest and simplest methods used for food cooking. It involves heating an edible oil or fat, and uses the hot oil to cook food. During deep-fat frying, the oil is exposed to elevated temperatures in the presence of air and moisture. Under these conditions a series of complex reactions such as oxidation, composition are taken place. The influence of these reactions results from a number of their products including volatile compounds, hydrolysis products, oxidized triacylglycerol monomers, cyclic compounds, trans configuration compounds, polymers, sterol derivatives, etc. which are present in both frying oil and the fried food. In addition, these reactions are interacted and influenced by various impact factors such as replenishment of fresh oil, frying conditions, original quality of frying oil, food materials, type of fryer, antioxidants, and oxygen concentration. High frying temperature, the number of frying, the contents of free fatty acids, polyvalent metals, and unsaturated fatty acids of oil decrease the oxidative stability and flavor quality of oil. However, repeated use of frying oils produces undesirable constituents that may cause health hazards.

المستخلص

القلي العميق في درجة 180° مئوية أو أعلى هي واحدة من أسرع وأقدم وأبسط الطرق المستخدمة لطهي الطعام. أنه ينطوي على تسخين زيت الطعام أو الدهون ويستخدم الزيت الساخن لطهي الطعام. أثناء القلي العميق الدسم، يتعرض الزيت لدرجات حرارة مرتفعة في وجود الهواء والرطوبة، في ظل هذه الظروف تحدث سلسلة من التفاعلات المعقدة مثل الأكسدة، والجلد الحرة، والتحلل المائي، المماكية، والبلمرة، وهذا التفاعلات تؤثر سلبا على جودة المنتج النهائي مثل النكهة، والملمس، والعمر الافتراضي وتكوين المادة الغذائية. وذلك يحدث نتيجة لعدد من نواتج هذه التفاعلات بما في ذلك مركبات طيارة، ومنتجات التحلل، مونومرات الدهون الثلاثية المؤكسدة، المركبات الحلقية، المركبات المتحولة، والبوليمرات، والمشتقات ستيرول وغيرها والتي هي موجودة في كل من زيت القلي والاطعمة المقلية. إن درجة حرارة القلي العالية، وعدد مرات القلي، وتركيز الاكسجين، و محتويات الأحماض الدهنية الحرة، والمعادن متعددة التكافؤ،

والأحماض الدهنية غير المشبعة في الزيوت تقلل من استقرار الأكسدة ونوعية نكهة الزيوت. ومع ذلك، الاستخدام المتكرر لزيوت القلي ينتج مكونات غير مرغوب فيها قد تشكل مخاطر صحية.

KEYWORDS: Deep-fat frying, Free radicals, Hydrolysis, Oxidation, Polymerization.

INTRODUCTION

It is well known that deep-fat frying is a prevalent and old food cooking method which can go back to 1600 BC. Although 180°C is usually recommended for frying foods, it is always higher than 180° C in the practical deep-fat frying⁽¹⁾. Fast food processing, palatable taste of fried food and considerable economic benefit make the deep-fat frying one of the most popular food cooking methods used. The fried food is endowed with attractive flavor, golden pellicle and crisp texture or mouth feel when it is fired under the appropriate conditions^(2,3). Under the established conditions of fried material's natural properties corresponding sample handling, frying can involve all of the components to participate in a series of physical and chemical alterations. These changes not only include the decomposition reactions of the constituents such as the nutrients of raw material and triacylglycerols (TAGs) of frying oil oxidized TAGs with keto, epoxy, hydroxyl, aldehyde and epoxy groups saturated or unsaturated, but also include the inter-actions among these constituents⁽³⁻⁵⁾.

Moreover, deep-fat frying is a complicated physicochemical processes which simultaneously influenced by many factors such as the nature of fried material and frying oil, time, temperature, intermittent or continuous heating, fresh oil complement, fryer model and use of filters. Therefore, many products are formed due to these complex substrates and chemical conditions⁽⁶⁾.

The major reaction products and their characteristics are shown in Table 1 for

direct and systematic understanding of the whole deep-fat frying course. The specific product types and their possible formation mechanisms are elucidated blow. Frying is one of the fastest, oldest and simplest methods of food cooking, since it involves heating on edible oil or fat and simply using the hot oil to cook food during deep – frying.

Oil is exposed to elevated temperatures in the presence of air and moisture. Under these conditions a number of chemical reactions occur, including oxidation, hydrolysis, cyclization, and polymerization of unsaturated FA(fatty acid)^(7,8). Deep- fat frying enhances the sensory properties of food (color, texture and flavors); however, repeated use of frying oils produces undesirable constituents that may pose health hazards⁽⁹⁾. During frying, a number of complex reactions take place in the oil, which depend not only on the biological composition of the raw material, but also on the choice of ingredients and processing conditions (frying method, heating time and temperature used during frying, type of fats and oils used etc.).

Oxidation of food lipids is one of the main causes of deterioration of food quality in terms of sensory and nutritional values. It is well known that autoxidation is an important degradation reaction which is attributed to the rancidity of oil and fat. Rancid oils are a major source of destructive free radicals in our diet. Exposure to air, heat, and light causes oils to oxidize, becomes rancid, and forms free radicals^(10,11).

There are numerous studies that report changes in fats and oils after heating or frying procedures^(12,13).

Most of them conclude that such changes depend on the temperature, the heating cycles, the surface/ volume and food/oil ratios, the fatty acid and the antioxidant composition of the oils. In general, deep-fat frying increases foaming, color, viscosity, density, the

amount of polymeric and polar compounds and the free fatty acid content of frying oils⁽¹²⁾.

During deep-fat frying various deteriorative chemical processes (e.g., hydrolysis, oxidation, and polymerization) take place, and oils decompose to form volatile products and nonvolatile monomeric and polymeric compounds (Figure 1)^(16,17).

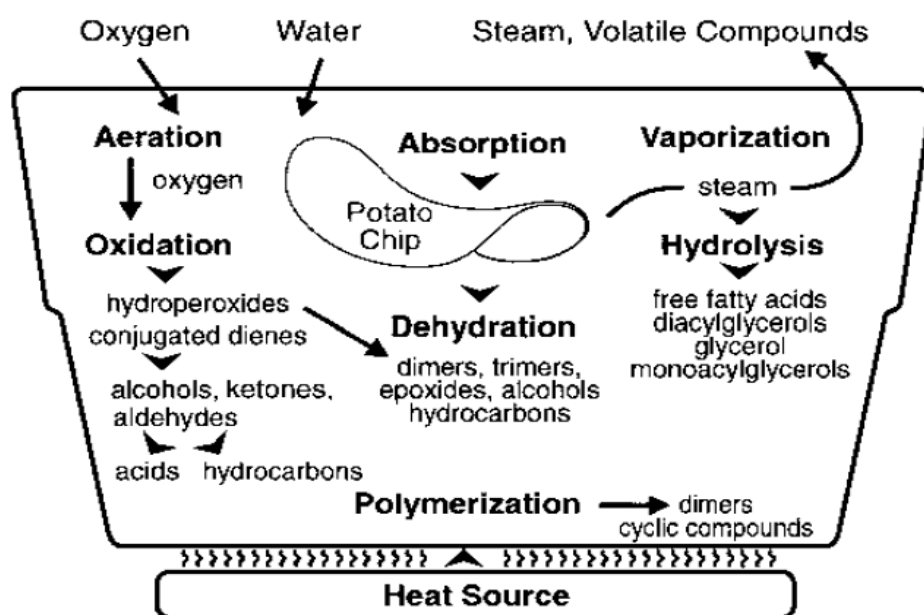


Figure1: Physical and chemical reactions that occur during frying

Chemical reactions and their products taken place during deep-fat frying

Hydrolysis

When food is fried in heated oil, the moisture forms steam, which evaporates with a bubbling action and gradually subsides as the foods are fried. Water, steam, and oxygen initiate the chemical reactions in the frying oil and food. Water, a weak nucleophile, attacks the ester linkage of triacylglycerols and produces di- and monoacylglycerols, glycerol, and free fatty acids. Free fatty acid contents in frying oil increase with the number of frying as shown in (Figure 2)^(16,18). Free fatty acid value is used to

monitor the quality of frying oil. The extent of hydrolysis is a function of various factors, such as oil temperature, interface area between the oil and the aqueous phases, and amount of water and steam because water hydrolyzes oil more quickly than steam⁽⁸⁾.

Free fatty acids and low molecular weight acidic products arising from fat oxidation enhance the hydrolysis in the presence of steam during frying⁽¹⁶⁾. Hydrolysis products, like all oil degradation products, decrease the stability of frying oils and can be used to measure oil fry life, e.g., free fatty acids.

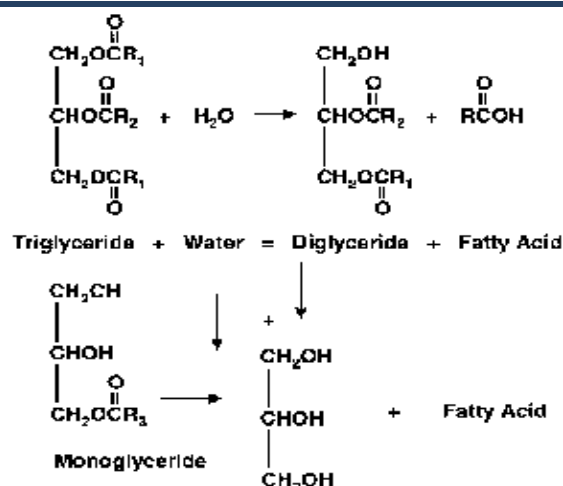


Figure 2: Hydrolysis reactions in frying oils

Oil and fat is a mixture of triacylglycerides (TAGs) which are composed of one glycerol and three groups of saturated or unsaturated fatty acids with different carbon numbers. Not only the natures of fatty acid, but also the various combination positions of fatty acids to glycerol molecule would impact the reaction activity of TAG.

Therefore, the TAG degradation products mainly result from the breakages occurred in the carbon-carbon double bond (C=C) of aliphatic chains and ester bond. These compounds have a smaller molecular weight compared with to of the parent TAG and almost possess of volatility such as the decomposition compounds of lipid oxidation and TAG hydrolysis (3).

Oxidation

Edible fats containing unsaturated molecules are susceptible to attack by molecular oxygen. This process is referred to as lipid oxidation and can give rise to undesirable volatile flavour compounds, potentially toxic oxidation products and a general deterioration in the quality of the fat. Fat oxidation is influenced by a range of parameters, including light exposure, temperature, presence of prooxidant metals (Cu, Ni, Co), presence of antioxidant compounds, and the degree of unsaturation of the fat⁽²¹⁾. Oxidation of

edible oils is influenced by an energy input such as light or heat, composition of fatty acids, types of oxygen, and minor compounds such as metals, pigments, phospholipids, free fatty acids, mono- and diacylglycerols, thermally oxidized compounds, and antioxidants. On the other hand oxygen, which is present in fresh oil and is introduced into the frying oil at the oil surface and by addition of food, activates a series of reactions involving formation of free radicals, hydroperoxides, and conjugated dienoic acids. The chemical reactions that occur during the oxidation process contribute to the formation of both volatile and nonvolatile decomposition products. For example, ethyl linoleate oxidation leads to the formation of conjugated hydroperoxides that can form noncyclic long chain products, or they can cyclize and form peroxide polymers.

The volatile degradation products are usually saturated and monounsaturated hydroxyl, aldehydic, keto, and dicarboxylic acids; hydrocarbons; alcohols; aldehydes; ketones; and aromatic compounds are primarily responsible for undesirable oxidized (rancid) flavors⁽¹⁶⁾. Oxidation of oil is very important in terms of palatability, nutritional quality, and toxicity of edible oils^(16,22).

Oxidation Mechanisms of Fats and Oils

The oxidation mechanism in frying oils is similar to autoxidation at 250°C; however, the unstable primary oxidation products, hydroperoxides, decompose rapidly at 190°C into secondary oxidation products such as aldehydes and ketones (Figure 1). Secondary

oxidation products that are volatile significantly contribute to the odor of the oil and flavor of the fried food^(24,25). If the secondary oxidation products are unsaturated aldehydes, such as 2,4-decadienal, 2,4-nonadienal, 2,4-octadienal, 2-heptenal, or 2-octenal, they contribute to the characteristic fried flavor in oils that are not deteriorated and can be considered desirable⁽²⁵⁾. Different chemical mechanisms are responsible for the oxidation of edible oils during process, storage, and cooking, depending upon the types of oxygen. Two types of oxygen can react with edible oils. One is called atmospheric triplet oxygen, $^3\text{O}_2$, and the other is singlet oxygen, $^1\text{O}_2$ ^(22,23). Triplet oxygen, $^3\text{O}_2$ reacts with lipid radicals and causes autoxidation, which is a free radical chain reaction. The nonradical electrophilic singlet

oxygen does not require radicals to react with; it directly reacts with the double bonds of unsaturated fats and oils with high electron densities, which is called photosensitized oxidation^(26,23). Fats and oils should be in radical forms to react with triplet oxygen in autoxidation. Lipids are normally in nonradical singlet state and heat, metals, or light accelerates their radical formation. Allylic hydrogen, especially hydrogen attached to the carbon between 2 double bonds, is easily removed due to low bond dissociation energy^(21,22,26). The carbon and hydrogen dissociation energies are the lowest at the bis-allylic methylene position^(8,21). Bis-allylic hydrogen at C11 of linoleic acid is removed at 75 to 80 kcal/mol. The energy required to remove allylic hydrogen in C8 or C14 of linoleic acid is 88 kcal/mol, and 101 kcal/mol is necessary to remove alkyl hydrogen from C17 or C18 show (Figure 3)^(8,21,26). Upon formation of lipid radicals by hydrogen removal, the double bond adjacent to the carbon radical in linoleic and linolenic acids shifts to the more stable next carbon, resulting in conjugated diene structures. The shifted double bond mostly takes the more thermodynamically stable *trans* form.

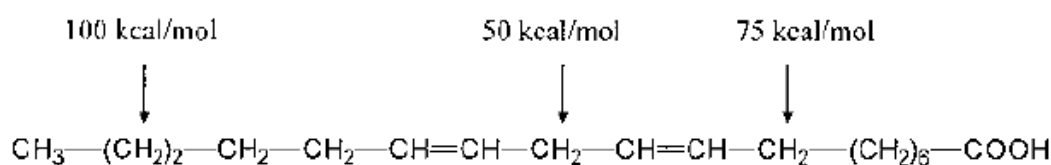


Figure 3: Energy required for hydrogen removal from linoleic acid

The lipid radical reacts with triplet oxygen very quickly at normal oxygen pressure ($2 \text{ to } 8 \times 10^9 \text{ M/s}$) and forms lipid peroxy radical. The lipid peroxy radical abstracts hydrogen from other lipid molecules to form lipid hydroperoxide and another lipid radical^(8,21). Rate of oxidation is dependent on several factors, including

temperature, presence of inhibitors or catalysts, and nature of the substrates. Unsaturated fatty acids are more susceptible to oxidation than saturated fatty acids. A property that is primarily due to the lowered activation energy in the initiation of free radical formation for triplet oxyautoxidation. Hydroperoxides formed by singlet oxygen

oxidation are at positions that formerly contained double bonds. Singlet oxygen produced conjugated and nonconjugated hydroperoxides from linoleic and linolenic acids, but the triplet oxygen produced only conjugated hydroperoxides from linoleic and linolenic acids. The reaction rates of singlet oxygen and triplet oxygen with linoleic acid are $1.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and $8.9 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$, respectively^(8, 16,21,26).

Free radical autoxidation

Autoxidation is an important degradation reaction which is attributed to the rancidity of oil and fat. Autoxidation depends on free-radical chain reactions, which involve the interaction of oxygen with free radicals generated at methylene groups adjacent to double bonds, especially at methylene groups between two double bonds⁽²⁷⁾. Autoxidation access of atmospheric oxygen to unsaturated fatty acids or glycerides leads to deterioration through oxidation. Saturated and monounsaturated fatty chains oxidize very slowly and do not as a rule cause problems. Di-unsaturated chains, as in 18:2 n-6, oxidize more rapidly and polyunsaturated chains very rapidly⁽²⁷⁾. The reaction of oxygen with unsaturated lipids (RH) involves free radical initiation, propagation and termination processes⁽³⁾. Initiation takes place by loss of a hydrogen radical in the presence of trace metals, light or heat. The resulting lipid free radicals (R \cdot) react with oxygen to form peroxy radicals (ROO \cdot). In this propagation process, ROO \cdot react with more RH to form lipid hydroperoxides (ROOH), which are the fundamental primary products of autoxidation⁽²⁸⁾. The primary products of lipid peroxidation are hydroperoxides (ROOH), which can dissociate into free radicals. Lipid hydroperoxides are stable at physiological temperatures,

and a major role of transition metals is to catalyze their decomposition. Transition metal ions catalyze homolysis lipid hydroperoxides that are cleaved to alkylperoxyl radicals (ROO \cdot) by metal ions in the oxidized state such as ferric ion, whereas reduced metal ions, such as ferrous ion, lead to alkoxy radicals (RO \cdot)^(29, 30). The free radicals produced in these processes are believed to stimulate the chain reaction of lipid peroxidation by abstracting further hydrogen from unoxidized lipids.

Thermal oxidation and their products

Thermal oxidation, which is accelerated at the high temperature used in deep frying, creates rancid flavors and reduces the organoleptic characteristics of fried food. During frying, oils are degraded from thermal oxidation to form volatile and non-volatile decomposition products. The chemical changes in frying oil also result in changes in the quality of fried food⁽³¹⁾. The fatty acid composition of the frying oil is an important factor affecting fried food flavor and its stability; therefore, it should be low level of polyunsaturated fatty acid such as linoleic or linolenic acids and high level of oleic acid with moderate amounts of saturated fatty acid^(32, 33). As a result, the quality of frying oil is important because of absorbed oil of fried products during deep frying. Soybean oil has a good nutritional profile due to high level of unsaturated fatty acid but less oxidative stability. The chemistry of lipid oxidation at the high temperatures of food processes like baking and frying is highly complex since both oxidative and thermal reactions are involved simultaneously. As the temperature increases, the solubility of oxygen decreases drastically, although oxidation reactions are accelerated⁽³³⁾. (Figure 4) shows the well-known scheme of the oxidation process. It

proceeds via a free radical mechanism of chain reactions, where RH represents here the triacylglycerol

molecule undergoing oxidation in one of its unsaturated fatty acyl groups^(17,34).

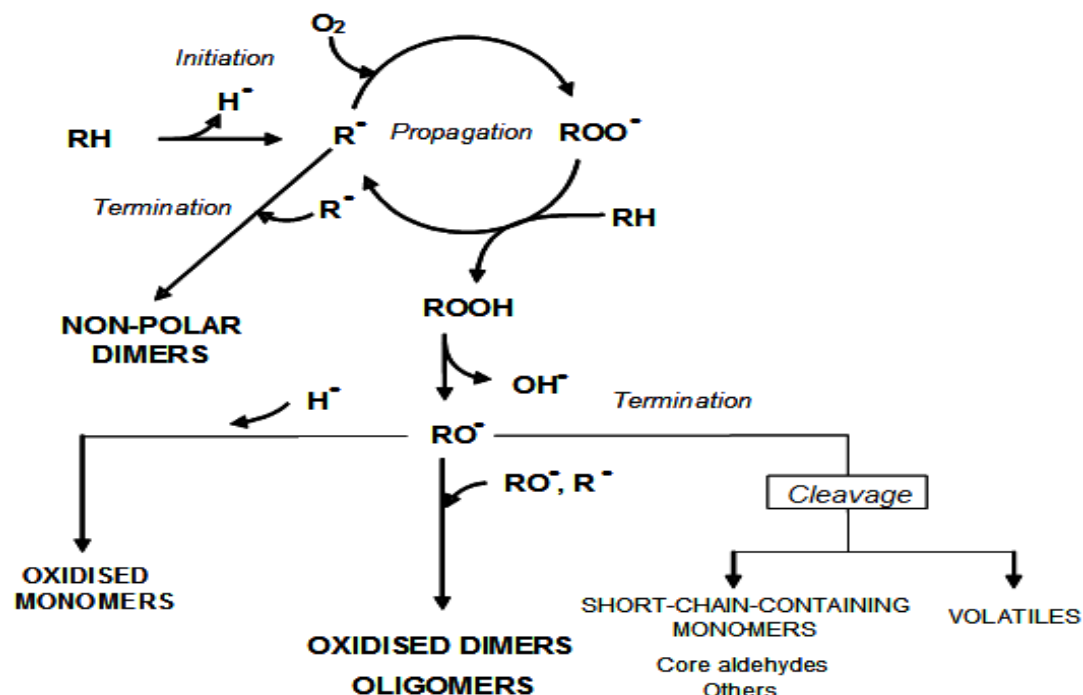


Figure4: Simplified scheme of thermal oxidation

Heating in the presence of air causes partial conversion of fats and oils to volatile chain-scission products, non-volatile oxidized derivatives, and dimeric, polymeric, or cyclic substances. There is some evidence that high oxidized and heated fats may have carcinogenic properties because of potentially toxic substances⁽⁹⁾.

Formation of Volatiles and Short-Chain Bound Compounds during Thermal Oxidation

An important route for formation of new compounds is breakdown of hydroperoxides giving rise to volatiles and short-chain compounds attached to the glyceridic backbone forming part of non-volatile molecules. Whereas the volatiles are largely removed from the oil during frying and have implications in the flavour of both the frying oil and the fried food. The non-volatile compounds remain in the frying oil

and are absorbed by the food modifying the oil nutritional and physiological properties^(32,33). There is a general acceptance on the mechanism of formation of short-chain compounds from the hydroperoxides formed through autoxidation reactions. They are originated by homolytic β -scission of the alkoxy radicals coming from allylic hydroperoxides. Homolytic β -scission takes place on both sides of the alkoxy carbon through route A or B (Figure 5).

Through this mechanism two types of aldehydes (volatile aldehyde and esterified aldehydes) and an alkyl or alkenyl radical are produced. Further interaction of alkyl and alkenyl radicals with other low molecular weight radicals present in the oil (H^\cdot and OH^\cdot) contributes to their stabilisation to form alcohols, and hydrocarbons^(12,21).

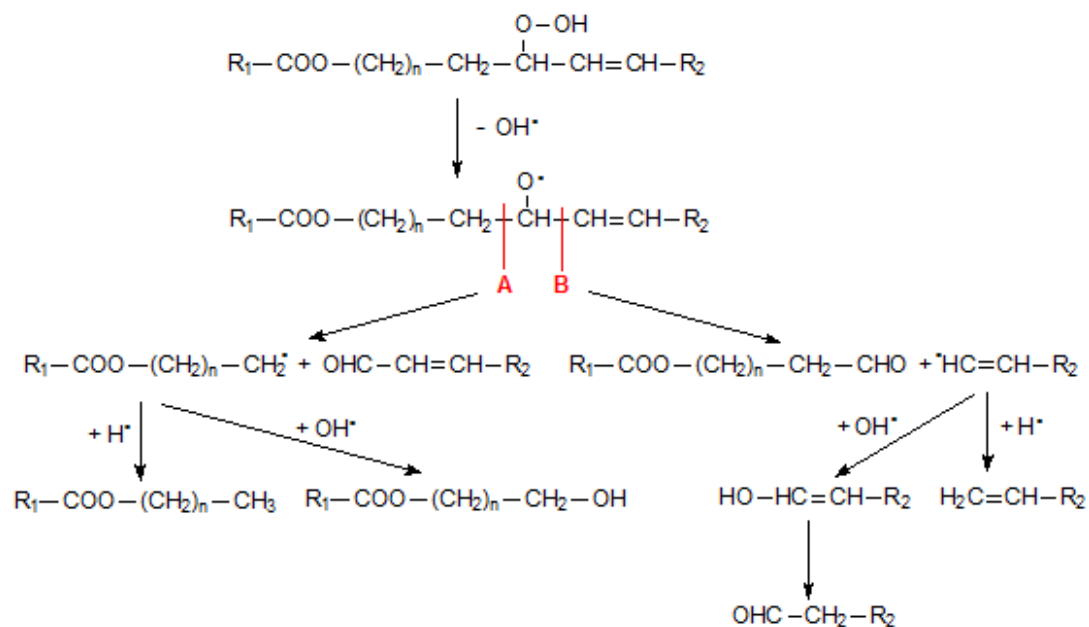


Figure 5: Formation of short-chain compounds from allylichydroperoxides^(35, 21).

Polymerization

The most likely decomposition pathway of hydroperoxide is the cleavage. Many nonvolatile polar compounds and triacylglycerol dimers and polymers are produced in thermally oxidized oil by radical reactions. Dimerization and polymerization are major reactions in the thermal oxidation in oil. Dimers and polymers are large molecules with a molecular weight range of 692 to 1600 Daltons and formed by a combination of -C-C- , -C-O-C- , and -C-O-O-C- bonds⁽⁸⁾. Polymerization occurs more easily in oil with high linoleic acid than in high oleic acid oil contents. C-C bonds are formed between 2 acyl groups to produce acyclic dimers in heated oil under low oxygen. The Diels-Alder reaction produces cyclic dimers of tetrasubstituted cyclohexene, and radical reactions within or between triacylglycerols also produce cyclic polymers. Polymers are rich in oxygen and highly conjugated dienes and produce a brown, resin-like residue

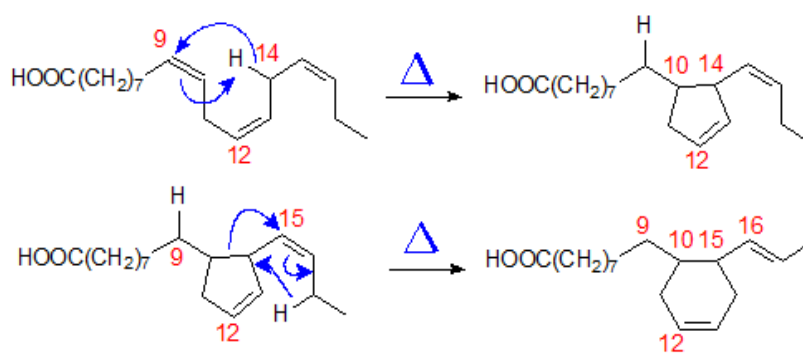
⁽²³⁾. As polymerized products increase in the frying oil, viscosity of the oil also increases. Peroxide value (mg/kg) analysis of primary oxidation products, such as hydroperoxides, at any point in the frying process provides little information because their formation and decomposition fluctuate quickly and are not easily predicted^(22,23). During frying, oils with polyunsaturated fatty acids, such as linoleic acid, have a distinct induction period of hydroperoxides followed by a rapid increase in peroxide values, then a rapid destruction of peroxides. Measuring levels of polyunsaturated fatty acids, such as linoleic acid, can help to determine extent of thermal oxidation⁽¹⁶⁾ reported that oxidative degradation produced oxidized triglycerides containing hydroperoxide, epoxy, hydroxy, and keto groups and dimeric fatty acids or dimeric triglycerides.

Formation of cyclic fatty acids during Thermal oxidation

Cyclization can occur in both the fatty acyl chains in TAG and the

decomposed fatty acids, as long as the occurrence of C-C. Then epoxy-TAGs, Cyclic fatty acid monomers (CFAM) ring with only carbon atom also present in the deep-fat frying system. In spite of the low concentration of these cyclic monomers present in the frying products⁽³⁵⁾. The suspicious latent biological hazard to the health of consumer is a topic of worth exploring⁽³⁶⁾. Several vegetable oils have been used to investigate the influence thereof on the formation amount of CFAMs and the results indicated that frying oil with high oleic acid had well frying effect and lower CFAMs yield^(37,38). It is well known that C-C is essential for cyclization; however, the degree of cyclization, content and composition of the formed CFAMs during the deep-fat frying course could be varied according to the unsaturation degree, position and configuration of C-C in different unsaturated aliphatic chains of frying oil^(40,41). The mechanism proposed for

the formation of cyclic fatty acids in heated oils involved a free radical reaction. However, if this were indeed to operate, it would probably produce more isomers than were in fact found. A recent publication by Destailats and Angers⁽⁴²⁾, suggested an explanation that is more likely, i.e. thermally induced and prototropic migrations. As an illustration, the mechanisms for formation of two of the isomers from α -linolenate are shown in (Figure 6). Thus, reaction of carbon C-10 with C-14 results in the formation of a five-membered ring by a pericyclic rearrangement. The resulting cyclopentenyl compound may then in turn undergo a sigmatropic rearrangement with double bond migration and structural reorganization to form a six-member ring with a double bond between carbons 12 and 13. The mechanism correctly predicts the stereochemistry of the new double bonds in each case^(41,43).



Figur 6: Proposed mechanism for the formation of cyclic fatty acids from α -linolenate

Trans Isomers

In fact, some of the aforementioned cyclic monomers referred to cis/trans isomerization belonged to the trans isomers category. Except for the trans cyclic compounds, there were several other kinds of trans isomers. It is well known that trans isomers of fatty acid have many adverse effects on human health such as coronary heart disease, sudden cardiac death⁽⁴⁴⁾, and systemic

inflammation. However, the source of trans isomers is very extensive in terms of both raw food materials and food products^(45,46). During the deep-fat frying, all the breakage, shift and formation of C-C involve the presence of trans configuration.

Therefore, it is inevitable that the formation of trans fatty acid during vegetable oil heating or frying. Trans, trans-2,4-decadienal which related to

the induction of low density lipoprotein oxidation was by-produced in fried potatoes^(47,48). Fortunately, an ordinary frying process in suitable time using un-hydrogenated edible oils has little impact on intake of trans fatty acid from edible oils. With the increase of frying time, the amount of trans fatty acid increased but decreased when butylated hydroxyanisole (BHA) or phenolic extracts of dry rosemary was added to the frying system^(49,50).

Oxysterol Formation during Thermal Oxidation

Sterol derivatives as minor components existing in the oils and fats, sterols, mainly the phytosterols, have many benefits to human health⁽⁵¹⁾. The known kinds of sterols are cholesterol (animal sterol), stigmasterol, sitosterol, campesterol, brassicasterol, avenasterol, etc., which broadly exist in various kinds of food. As a kind of triterpenoid, 28 or 29 carbons and one or two C-C (the first one in sterol nucleus and the second one in the alkyl side chain) are present in the most phytosterols⁽⁵²⁾. Autoxidation of cholesterol and phytosterols is facilitated by many factors, for example, temperature, light, oxygen, free radical initiators, metal ions, pro-oxidizing agents, and a shortage of antioxidants.

Oxidation mechanisms of phytosterols are believed to follow the same pathways as cholesterol oxidation. Formation of different oxysterols by autoxidation, as documented by experiments, proceeds through a free radical chain reaction⁽⁴³⁾. The process is initiated by abstraction of hydrogen from allylic C7 in the ring structure of cholesterol and tertiary carbons at the C20 and C25 positions. The radicals thus formed react with oxygen to produce corresponding peroxy radicals, which in turn are stabilized by yielding different cholesterol hydroperoxides. The thermal decomposition of these hydroperoxides produces 7 α -hydroxy-, 7 β -hydroxy-, 7-keto-, 20-hydroxy-, and 25-hydroxycholesterol. Epimeric 7-hydroperoxides of cholesterol can also attack the Δ^5 double bond of cholesterol, forming secondary oxidation products of cholesterol, such as epimeric epoxycholestanol. Both epoxides, in turn are converted to 5 α -cholesta-3 β ,5,6 β -triol, through epoxy ring opening by hydration⁽⁵³⁾. Concerning oxysterols in fat and oil used for frying and cooking, only six to eight components are generally reported. Formation of the main ring structure oxidation products are shown in (Figure 7) with the example of sitosterol⁽⁴³⁾.

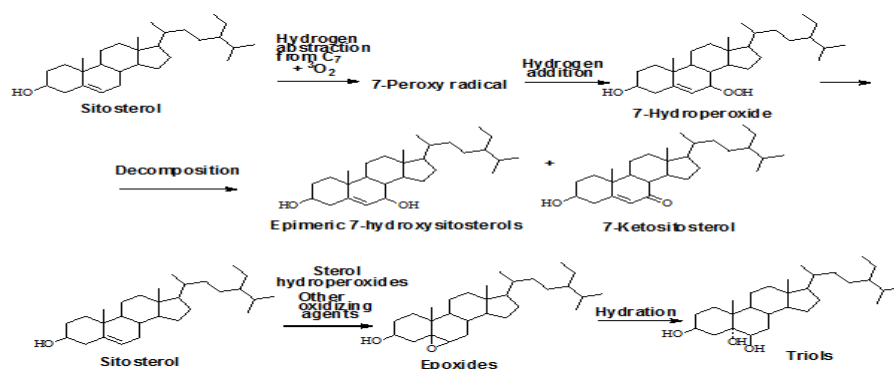


Figure 7: Formation of the main ring structure oxidation products from sitosterol following the autoxidation pathway

Table 1: The major reaction products formed during deep-fat frying, their characteristics and proposed formation mechanism and identifying methods according to the previously reported studies

| Main products and Characteristics | Proposed formation mechanism | Identifying methods |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|
| Oxidized decomposition compounds (Degradation product; volatility; alcohol, aldehyde, ketone, acid, lactone and hydrocarbon etc.; short-chain compounds) | Oxidation Homolytic reaction (Free radical reaction). | NMR ⁽⁵⁴⁾ , TD-GC-MS ⁽⁵⁵⁾ |
| Hydrolysis products (Degradation product; polar; diacylglycerol (DAG), monoacylglycerol (MAG), glycerol and free fatty acids). | Hydrolysis Oxidation Epoxidation Free radical reaction. | GC (Gas chromatography) ⁽⁵⁶⁾ . GC-MS ⁽⁵⁷⁾ , NMR ^(58,59) . |
| Oxidized TAG monomers Oxidized TAGs with keto, epoxy, hydroxyl, aldehyde and epoxy groups (saturate or unsaturate). | Cyclization Intramolecular rearrangement catalyzed by free radicals Concerted reaction. | Ag-HPLC , GC-MS ⁽⁶⁰⁾ , GC-EI-MS ⁽⁶¹⁾ . |
| Cyclic fatty acid monomers Nonpolar; low concentration and latent biological hazard; five- or six-membered ring structures (saturate or unsaturate); monocyclic and bicyclic rings; cis and trans configurations. | Free radical reaction (Addition-elimination mechanism) Heat-induced isomerization Concerted reaction Oxidized. | GC-MS ⁽⁶²⁾ . HPSEC ^(63,64) , LC-EI-MS ⁽⁶⁵⁾ . |
| Trans isomers Nonpolar; trans fatty acids, conjugated linoleic acids; adverse effects on human health. | polymerization and thermal polymerization Free radical reaction Concerted reaction (Diels-Alder reaction). | GC-MS ⁽⁶⁶⁾ , LC-APCI-MS ⁽⁶⁷⁾ . |
| TAG polymerized products Dimers, trimers and oligomers, etc. | Oxidation (Free radical reaction) Polymerization. | GC-MS ⁽⁶⁶⁾ , HPLC ⁽⁶⁸⁾ . |
| Sterol derivatives Formed mainly result in special molecule structure; Hydroxy, keto and epoxy group-contained compounds; sterol dimers, trimers and oligomers also present; homologous. | | |

CONCLUSIONS

During deep-fat frying various deteriorative chemical processes (e.g., hydrolysis, oxidation, cyclization and polymerization) take place, and oils decompose to form volatile products and nonvolatile monomeric and polymeric compounds. With continued heating and frying, these compounds decompose further until breakdown products accumulate to levels that produce off-flavors and potentially toxic effects, rendering the oil unsuitable for frying. The amounts of these compounds that are formed and their chemical structures depend on many factors, including oil and food types, frying conditions, and oxygen availability. Also these processes may reduce the amount of antioxidants in the oil, decrease its stability and produce new products which are responsible for loss of the nutritional value and quality of the oil (odour, flavour, absorption, etc). The oxidized products of fatty acids give off-flavours and odors (hydrolytic rancidity) to the medium and fried foods. Hydrolysis increases the amount of free fatty acids, mono- and diacylglycerols, and glycerols in oils. Oxidation occurs at a greater rate than hydrolysis during deep-fat frying. Oxidation produces hydroperoxides and then low molecular volatile compounds such as aldehydes, ketones, carboxylic acids, and short chain alkanes and alkenes. Dimers and polymers are also formed in oil by radical and Diels-Alder reactions during deep-fat frying. Replenishment of fresh oil, frying conditions, quality of frying oil, food materials, fryer, antioxidants, and oxygen concentration affect the quality and flavor of oil during deep-fat frying. High frying temperature accelerates thermal oxidation and polymerization of oils. Free radicals are now known to play an important role in many areas of

biology and are therefore being actively investigated in connection with various human health problems. Free radicals are in general reactive species that can be of benefit to an organism, e.g.; the radicals produced during phagocytosis, as well as a liability, e.g.; in producing DNA damage, or lipid peroxidation. The initiation step of thermally oxidation is the main source for the presence of free radicals. As a kind of reactive intermediate, free radicals easily attack other chemicals and capture their electron to form a more stable substance. In the light of this point of view, the interpreting to the formation of some volatile products, short-chain compounds, oxidized TAG monomers, CFAMs, trans isomers polymers, heterocyclic compounds, etc. is reasonable and acceptable. The chemical changes in frying oil also result in changes in the quality of fried food. The fatty acid composition of the frying oil is an important factor affecting fried food flavor and its stability; therefore, it should be low level of polyunsaturated fatty acid such as linoleic or linolenic acids and high level of oleic acid with moderate amounts of saturated fatty acid. As a result, the quality of frying oil is important because of absorbed oil of fried products during deep frying.

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