

Chemistry of Deep-Fat Frying Oils

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ABSTRACT: Deep-fat frying produces desirable or undesirable flavor compounds and changes the flavor stability and quality of the oil by hydrolysis, oxidation, and polymerization. Tocopherols, essential amino acids, and fatty acids in foods are degraded during deep-fat frying. The reactions in deep-fat frying depend on 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 fryings, the contents of free fatty acids, polyvalent metals, and unsaturated fatty acids of oil decrease the oxidative stability and flavor quality of oil. Antioxidant decreases the frying oil oxidation, but the effectiveness of antioxidant decreases with high frying temperature. Lignan compounds in sesame oil are effective antioxidants in deep-fat frying.

Keywords: deep-fat frying, frying oil quality, hydrolysis, oxidation, polymerization

Introduction

Deep-fat frying is one of the oldest and popular food preparations. The economy of commercial deep-fat frying has been estimated to be \$83 billion in the United States and at least twice the amount for the rest of the world (Pedreschi and others 2005). Fried foods have desirable flavor, color, and crispy texture, which make deep-fat fried foods very popular to consumers (Boskou and others 2006). Frying is a process of immersing food in hot oil with a contact among oil, air, and food at a high temperature of 150 °C to 190 °C. The simultaneous heat and mass transfer of oil, food, and air during deep-fat frying produces the desirable and unique quality of fried foods. Frying oil acts as a heat transfer medium and contributes to the texture and flavor of fried food.

Frying time, food surface area, moisture content of food, types of breading or battering materials, and frying oil influence the amount of absorbed oil to foods (Moreira and others 1997). The oil contents of potato chips, corn chips, tortilla chips, doughnuts, French fries, and fried noodle (*ramyon*) are 33% to 38%, 30% to 38%, 23% to 30%, 20% to 25%, 10% to 15% (Moreira and others 1999a), and 14% (Choe and others 1993), respectively. The absorbed oil tends to accumulate on the surface of fried food during frying in most cases (Moreira and others 1999b) and moves into the interior of foods during cooling (Moreira and others 1997).

Foods fried at the optimum temperature and time have golden brown color, are properly cooked, and crispy, and have optimal oil absorption (Blumenthal 1991). However, underfried foods at lower temperature or shorter frying time than the optimum have white or slightly brown color at the edge, and have ungelatinized or partially cooked starch at the center. The underfried foods do not have desirable deep-fat fried flavor, good color, and crispy texture. Overfried foods at higher temperature and longer frying time than the optimum frying have darkened and hardened surfaces and a greasy texture due to the excessive oil absorption.

Deep-fat frying produces desirable or undesirable flavor compounds, changes the flavor stability and quality, color, and texture

of fried foods, and nutritional quality of foods. The hydrolysis, oxidation, and polymerization of oil are common chemical reactions in frying oil and produce volatile or nonvolatile compounds. Most of volatile compounds evaporate in the atmosphere with steam and the remaining volatile compounds in oil undergo further chemical reactions or are absorbed in fried foods. The nonvolatile compounds in the oil change the physical and chemical properties of oil and fried foods. Nonvolatile compounds affect flavor stability and quality and texture of fried foods during storage. Deep-fat frying decreases the unsaturated fatty acids of oil and increases foaming, color, viscosity, density, specific heat, and contents of free fatty acids, polar materials, and polymeric compounds (Figure 1).

Frying temperature and time, frying oil, antioxidants, and the type of fryer affect the hydrolysis, oxidation, and polymerization of the oil during frying. This review focuses on the chemical reactions of frying oil and improvement of the oxidative stability and flavor quality of frying oil during deep-fat frying.

Chemical Reactions of Oil during Deep-Fat Frying

Hydrolysis of oil

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 acids contents in frying oil increase with the number of fryings (Chung and others 2004) as shown in Figure 2. Free fatty acid value is used to monitor the quality of frying oil. Thermal hydrolysis takes place mainly within the oil phase rather than water–oil interface (Lascaray 1949). Hydrolysis is more preferable in oil with short and unsaturated fatty acids than oil with long and saturated fatty acids because short and unsaturated fatty acids are more soluble in water than long and saturated fatty acids. Water from foods is easily accessible to short-chain fats and oils for hydrolysis (Nawar 1969).

Large amounts of water hydrolyze the oil rapidly (Dana and others 2003). Water hydrolyzes the oil faster than steam (Pokorny 1989). Large contact between the oil and the aqueous phase of food increases hydrolysis of oil. Mono- and diacylglycerols in cottonseed oil during frying of potato chips at 155 °C to 195 °C increased initially

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and then reached a plateau (Houhoula and others 2003). Frequent replacement of frying oil with fresh oil slows down the hydrolysis of frying oil (Romero and others 1998). Sodium hydroxide and other alkalis used for cleaning a fryer increase the oil hydrolysis. The duration of frying did not affect the hydrolysis of oil (Naz and others 2005).

Free fatty acids and their oxidized compounds produce off-flavor and make the oil less acceptable for deep-fat frying. Di- and monoacylglycerols, glycerol, and free fatty acids accelerate the further hydrolysis reaction of oil (Frega and others 1999). Glycerol evaporates at 150 °C and the remaining glycerol in oil promotes the production of free fatty acids by hydrolysis (Naz and others 2005). Stevenson and others (1984) suggested that the maximum free fatty acid content for frying oil is 0.05% to 0.08%.

Oxidation of oil

The oxygen in deep-fat frying reacts with oil (Peers and Swoboda 1982; Cuesta and others 1993; Sanchez-Muniz and others 1993a; Houhoula and others 2003). The chemical mechanism of thermal

oxidation is principally the same as the autoxidation mechanism. The thermal oxidation rate is faster than the autoxidation, but specific and detailed scientific information and comparisons of oxidation rates between thermal oxidation and autoxidation are not available. The mechanism of thermal oxidation involves the initiation, propagation, and termination of the reaction as shown in Figure 3.

Nonradical singlet state oil does not react with triplet state diradical oxygen due to the spin barrier. Ordinary oxygen in air is a diradical compound. Radical oxygen requires radical oil for the oxidation of oil. Oil should be in a radical state to react with radical oxygen for oil oxidation reaction. The hydrogen with the weakest bond on the carbon of oil will be removed first to become radical. The energy required to break carbon-hydrogen bond on the carbon 11 of linoleic acid is 50 kcal/mole (Min and Boff 2002). The double bonds at carbon 9 and carbon 12 decrease the carbon-hydrogen bond at carbon 11 by withdrawing electrons. The carbon-hydrogen bond on carbon 8 or 11, which is α to the double bond of oleic acid, is about 75 kcal/mole. The carbon-hydrogen bond on the saturated carbon without any double bond next to it is approximately 100 kcal/mol (Min and Boff 2002). The various strengths of hydrogen-carbon bond of fatty acids explain the differences of oxidation rates of stearic, oleic, linoleic, and linoleic acids during thermal oxidation or autoxidation. The weakest carbon-hydrogen bond of linoleic acid is the one on carbon 11 and the hydrogen on carbon 11 will be removed first to form a radical at carbon 11 (Figure 3). The radical at carbon 11 will be rearranged to form conjugated pentadienyl radical at carbon 9 or carbon 13 with *trans* double bond as shown in Figure 3. Heat, light, metals, and reactive oxygen species facilitate the radical formation of oil. The polyvalent metals such

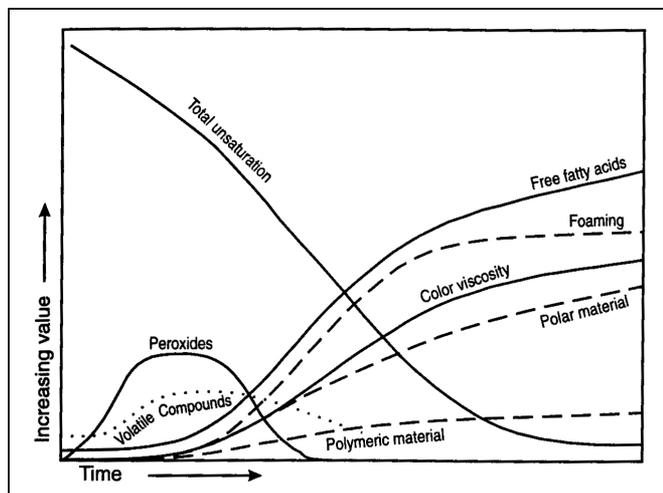


Figure 1—Physical and chemical changes of oil during deep-fat frying

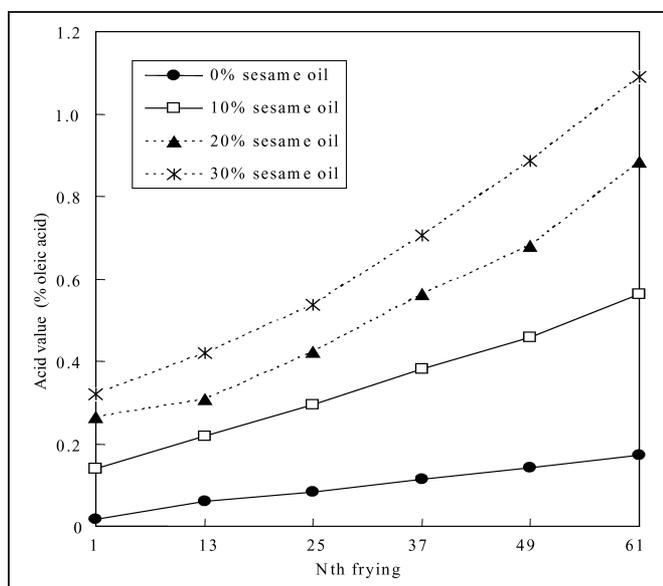


Figure 2—Free fatty acid formation in soybean and sesame oil mixture during consecutive frying of flour dough at 160 °C (Chung and others 2004)

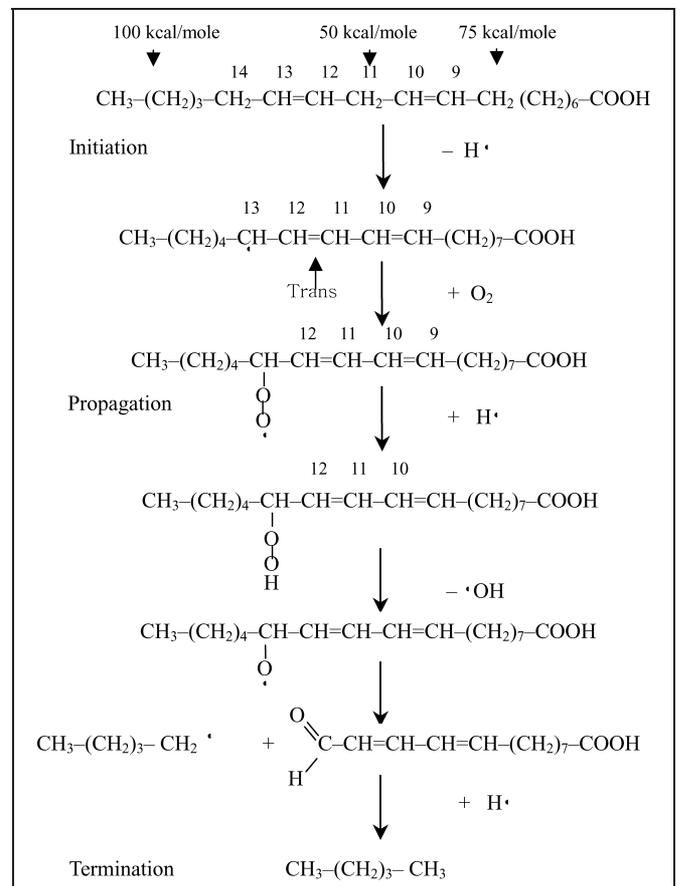


Figure 3—The initiation, propagation, and termination of thermal oxidation of oil

as Fe^{3+} and Cu^{2+} remove hydrogen protons from oil to form alkyl radicals by oxidation-reduction mechanism of metals even at low temperatures. The site of radical formation in saturated fatty acids is different from those of unsaturated oleic or linoleic acids. The alkyl radical of saturated fatty acids is formed at α position of the carboxyl group having electron-withdrawing property. The formation of the alkyl radical from an oil molecule by removing hydrogen is called the initiation step in the oxidation reaction of oil. The alkyl radical can also react with alkyl radicals, alkoxy radicals, and peroxy radicals to form dimers and polymers.

Alkyl radicals with a reduction potential of 600 mV react rapidly with diradical triplet oxygen and produce peroxy radicals at the rate of $10^9/\text{M/s}$. The peroxy radical with a reduction potential of 1000 mV abstracts hydrogen from oleic acid and linoleic acid and produces hydroperoxide at a rate of approximately $1 \times 10^0/\text{M/s}$ and $1 \times 10/\text{M/s}$, respectively. The peroxy radical abstracts a hydrogen atom from another oil molecule and forms new hydroperoxide and another alkyl radical. This chain reaction is called free radical chain reaction in foods and propagation step. Peroxy radicals also react with other radicals at the rate of about $1.1 \times 10^6/\text{M/s}$ to form dimers or polymers (Choe and Min 2005). The chain reactions of free alkyl radicals and peroxy radicals accelerate the thermal oxidation of oil.

The oxygen-oxygen bond strength of R-O-O-H is about 44 kcal/mole, which is a relatively weak covalent bond (Hiatt and others 1968). The hydroperoxides are not generally stable during the deep-fat frying as shown in Table 1 (Nawar 1984). Hydroperoxides are decomposed to alkoxy radicals and hydroxy radicals by homolysis of the peroxide bond. The hydroperoxide is decomposed to produce oxy- and hydroxy radicals. Toschi and others (1997) identified mono-oxygenated products such as 9-keto-10, 12-, and 13-keto-9-, 11-octadecadienoate and hydroxyl derivatives such as 9-hydroxy-10, 12-, and 13-hydroxy-9-, and 11-octadecadienoate from hydroperoxides of thermally oxidized methyl linoleate at 150°C . The alkoxy radical reacts with other alkoxy radicals or is decomposed to form nonradical products. The formation of nonradical volatile and nonvolatile compounds at the end of oxidation is called the termination step as shown in Figure 3.

Most volatiles are removed from frying oil by steam during deep-fat frying (May and others 1983). The addition of water to a frying system decreases the volatile compounds in oil (Wu and Chen 1992). The amount of volatile compounds present in the oil varies widely depending on the kind of oil, food, and frying conditions. The disappearance or loss of volatile compounds in frying oil is due to the combination of evaporation and decomposition, and the reaction of volatile compounds with other food components (Nawar 1985). The volatile compounds in frying oil undergo further reactions such as oxidation, dimerization, and polymerization. Volatile compounds significantly contribute to the flavor quality of the frying oil and the fried foods. The rate of oxidative degradation reactions increases as the concentration of oxygen and free radicals increases (Paul and

Mittal 1997). The amount of mono- and diacylglycerols is small at the beginning of frying. The high interfacial tension in the frying system breaks steam bubbles and forms a steam blanket over the oil surface. The steam blanket reduces the contact between the oil and oxygen, and lowers the oil oxidation (Blumenthal 1991). Refined oil usually contains less than 1 ppm of alkaline materials such as sodium or potassium salt of fatty acids. Fresh frying oil should have less than 10 ppm alkaline materials (Moreira and others 1999c).

Polymerization of oil

Volatile compounds are extremely important to the flavor qualities of frying oil and fried foods, but volatile contents in total decomposition products of frying oil are present at the concentration of part per million levels (Nawar 1985). The major decomposition products of frying oil are nonvolatile polar compounds and triacylglycerol dimers and polymers. The amounts of cyclic compounds are relatively small compared to the nonvolatile polar compounds, dimers, and polymers (Frankel and others 1984; Sanchez-Muniz and others 1993b; Takeoka and others 1997; Dobarganes and others 2000). 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 (Stevenson and others 1984; Kim and others 1999). Dehydroxydimer, ketodehydrodimer, monohydrodimer, dehydrodimer of linoleate, and dehydrodimer of oleate are dimers found in soybean oil during frying at 195°C (Christopoulou and Perkins 1989). Dimers and polymers have hydroperoxy, epoxy, hydroxy, and carbonyl groups, and -C-O-C- and -C-O-O-C- linkages.

Dimers or polymers are either acyclic or cyclic depending on the reaction process and kinds of fatty acids consisting of the oil (Cuesta and others 1993; Sanchez-Muniz and others 1993b; Takeoka and others 1997; Tompkins and Perkins 2000). Dimerization and polymerization in deep-fat frying are radical reactions. Allyl radicals are formed preferably at methylene carbons α to the double bonds. Dimers are formed from the reactions of allyl radicals by C-C linkage. The formation of acyclic polymers from oleic acid during heating is shown in Figure 4. Triacylglycerols react with oxygen and produce alkyl hydroperoxides (ROOH) or dialkyl peroxides

Table 1—Peroxide values (POV; meq/kg oil) for ethyl linolenate during heating at different temperature^a

Heating time (h)	70 °C		180 °C		250 °C	
	POV	Heating time (h)	POV	Heating time (h)	POV	Heating time (h)
6	1777	5	237	3	44	
24	1058	10	251	5	77	
45	505	20	119	10	198	
69	283	30	80	20	67	
		60	44	30	0	

^aNawar 1984.

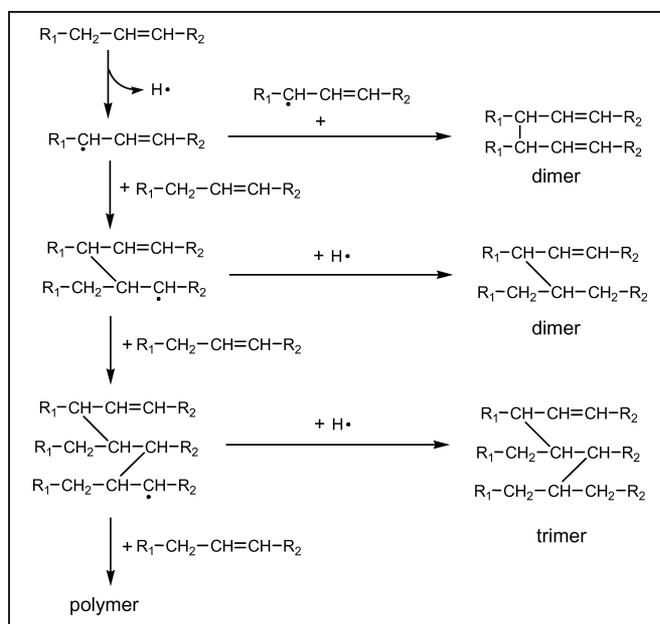


Figure 4—Acyclic polymer formation from oleic acid during deep-fat frying

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(ROOR). They are readily decomposed to alkoxy and peroxy radicals by RO-OH and ROO-R scission, respectively. Alkoxy radicals can abstract hydrogen from oil molecule to produce hydroxy compounds, or combine with other alkyl radicals to produce oxydimers. Peroxy radicals can combine with alkyl radicals and produce peroxy dimers (Figure 5). Formation of dimers and polymers depends on the oil type, frying temperature, and number of fryings. As the number of fryings and the frying temperature increase, the amounts of polymers increased as shown in Table 2 (Cuesta and others 1993) and Figure 6 (Sanchez-Muniz and others 1993b; Takeoka and others 1997). The oil rich in linoleic acid is more easily polymerized during deep-fat frying than the oil rich in oleic acid (Takeoka and others 1997; Tompkins and Perkins 2000; Bastida and Sanchez-Muniz 2001).

Cyclic polymers are produced within or between triacylglycerols by radical reactions (Figure 7) and the Diels-Alder reaction (Figure 8). The formation of cyclic compounds in frying oil depends on the degree of unsaturation and the frying temperature (Meltzer and others 1981). The formation of cyclic monomers and polymers increased as the amount of linolenic acid increased (Rojo and Perkins 1987; Tompkins and Perkins 2000). The formation of cyclic monomers was negligible until the linolenic acid content exceeds about 20%. Cyclic compounds are not formed to a significant extent until the oil tem-

Table 2 – Formation of triacylglycerol polymers (mg/100 mg oil) in sunflower oil during repeated frying of potatoes^a

	Number of fryings				
	0	20	30	50	75
Triacylglycerol polymers	0.10	1.65	2.50	3.15	3.44
Triacylglycerol dimers	0.75	6.25	7.09	7.37	7.51

^aCuesta and others 1993.

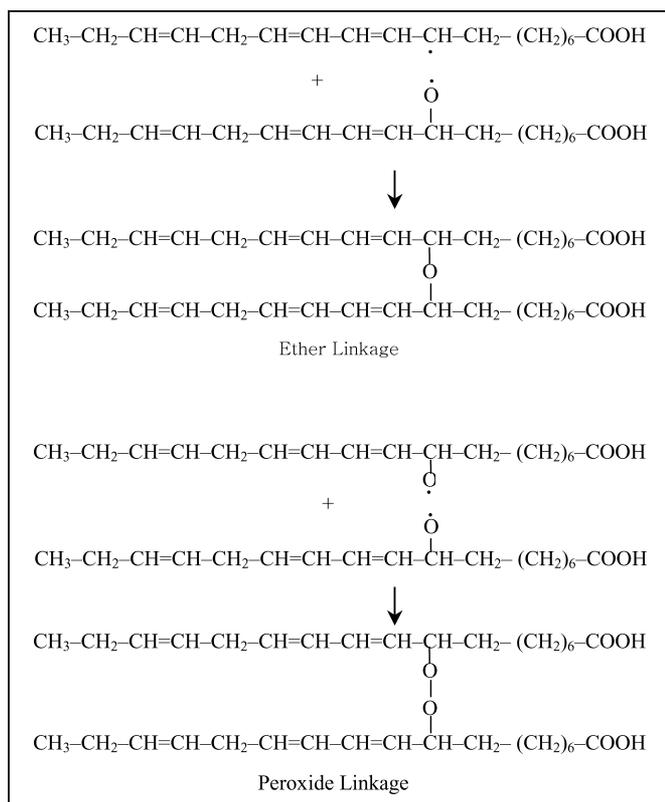


Figure 5 – Formation of ether or peroxide linkage polymers in oil during deep-fat frying

perature reaches 200 °C to 300 °C. Soybean oil produced tricyclic dimers and bicyclic dimers of linoleate (Christopoulou and Perkins 1989) as well as cyclic monomers (Frankel and others 1984) during deep-fat frying.

Polymers formed in deep-fat frying are rich in oxygen. Yoon and others (1988) reported that oxidized polymer compounds accelerated the oxidation of oil. Polymers accelerate further degradation of the oil, increase the oil viscosity (Tseng and others 1996), reduce the heat transfer, produce foam during deep-fat frying, and develop undesirable color in the food. Polymers also cause the high oil absorption to foods.

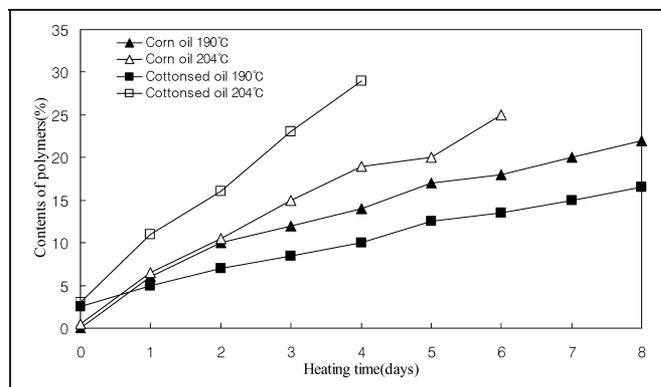


Figure 6 – Polymer contents of cottonseed and corn oils heated at 190 °C and 204 °C (Takeoka and others 1997)

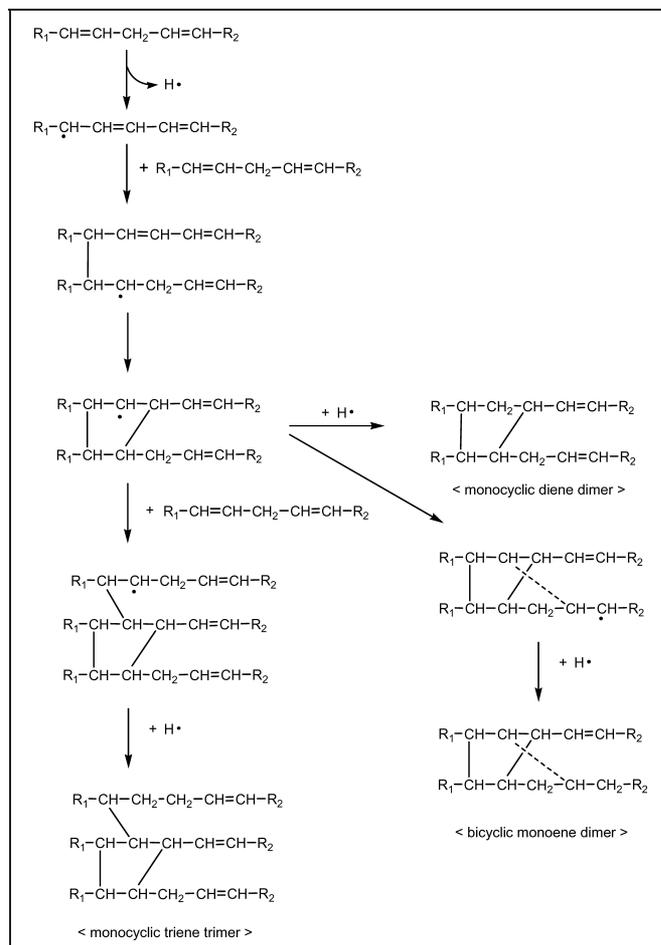


Figure 7 – Formation of cyclic dimers and polymers from linoleic acids during deep-fat frying

Polymers are highly conjugated dienes and produce a brown, resin-like residue along the sides of the fryer, where the oil and metals come in contact with oxygen from the air. Resin-like residue is often produced when the oil does not release the moisture but keeps it trapped while also incorporating air (Lawson 1995; Moreira and others 1999c).

Flavor Quality of Frying Oil and Fried Foods during Deep-Fat Frying

The flavor of oil formed during deep-fat frying is described as fruity, grassy, buttery, burnt, nutty, and fishy. It depends on the oil and number of fryings, but the frying temperature is not significant on the flavor of oil (Prevot and others 1988). The oxidation of linolenic acid during deep-fat frying increases fishy odor and decreases fruity and nutty odor. Sensory quality generally decreases with the number of fryings. The flavor quality of peanut oil was better than that of soybean oil or rapeseed oil in frying potatoes at 160 °C, 180 °C, and 200 °C (Prevot and others 1988). Wu and Chen (1992) reported 2-heptenal, 2-octenal, 1-octen-3-ol, 2, 4-heptadienal, and 2, 4-decadienal as major volatile compounds in soybean oil at 200 °C. The formation of 2, 4-decadienal from linoleic acid in soybean oil is shown in Figure 9.

Typical desirable fried flavor is produced at the optimal concentration of oxygen. Low amounts of oxygen produce poor and weak flavor, and high levels of oxygen produce off-flavor (Pokorny 1989). Fried flavor compounds in fried foods are mainly volatile compounds from linoleic acid and are dienal, alkenals, lactones, hydrocarbons, and various cyclic compounds (Pokorny 1989). 4-Hydroxy-2-nonenic acid and its lactone, 4-hydroxy-3-nonenic

acid and its lactone, *trans, trans*-2, 4-decadienal, *trans, trans*-2, 4-nonadienal, *trans, trans*-2, 4-octadienal, *trans*-2-heptenal, *trans*-2-octenal, *trans*-7-octenal, nonenolactone, and trienals are desirable flavor compounds found in frying oil and are produced from the oxidation of linolenic or linoleic acid (Buttery 1989). Linoleic acid is mainly responsible for desirable deep-fat fried flavor. Different oils produce different flavor during deep-fat frying due to the differences in quality and quantity of fatty acids of frying oil (Prevot and others 1988). Butanal, pentanal, hexanal, heptane, pentanol, 2-hexenal, heptanal, 1-octen-5-ol, 2-pentylfuran, and 2-decenal provide

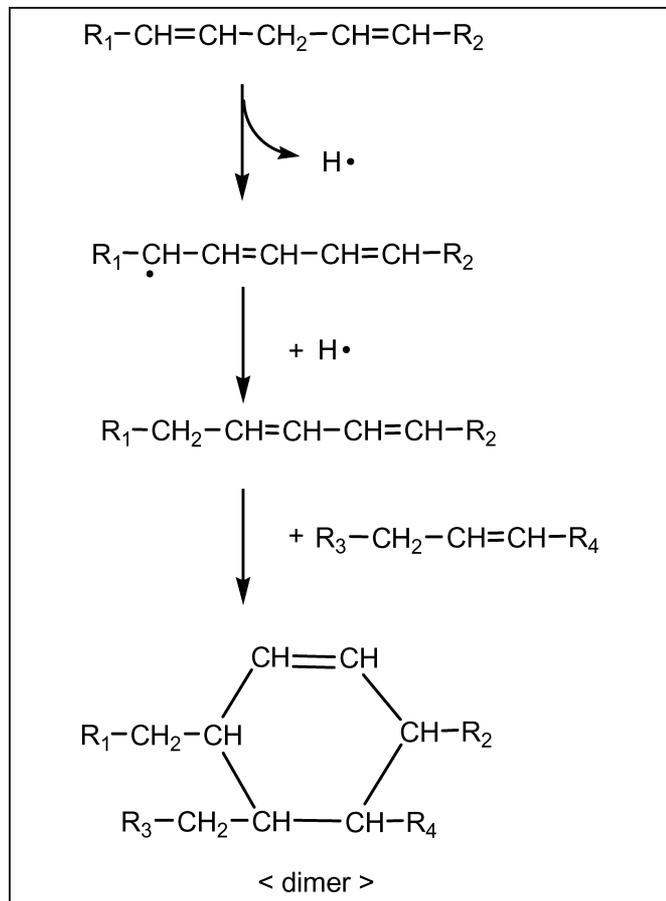


Figure 8—Cyclic compound formation from linoleic acid by Diels-Alder reaction during deep-fat frying

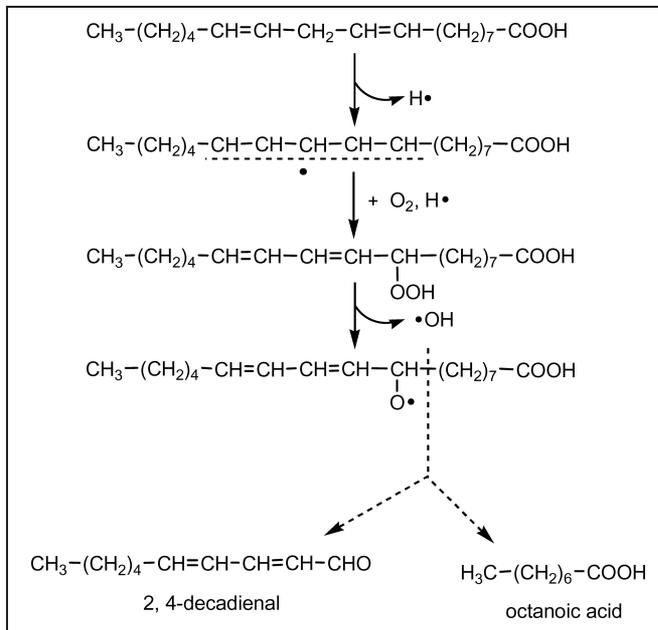


Figure 9—Formation of 2, 4-decadienal from oxidation of linoleic acid

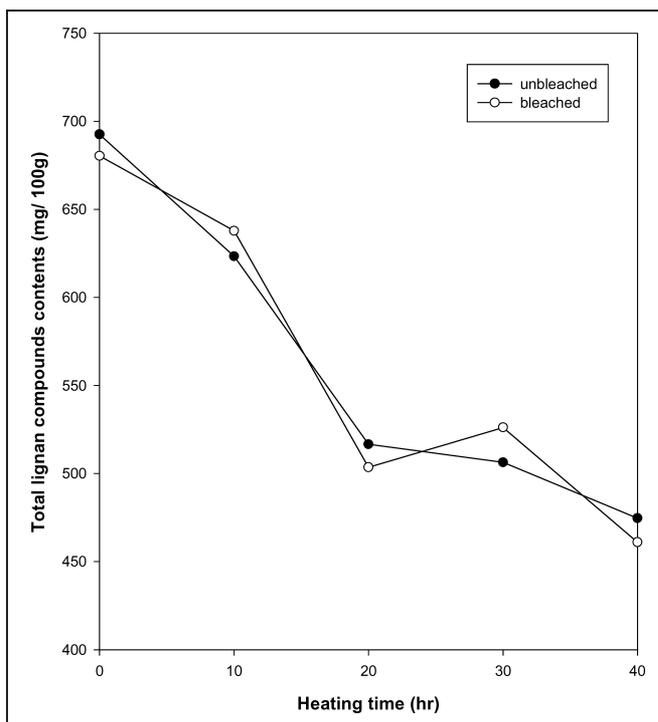


Figure 10—Changes in lignan compounds in roasted sesame oil during heating at 170 °C

off-odors in deep-fat frying (Prevot and others 1988). Carbonyl compounds formed during deep-fat frying can react with amino acids, amines, and proteins and produce desirable and nutty pyrazines (Negrone and others 2001).

Some of volatile compounds formed in deep-fat frying, 1, 4-dioxane, benzene, toluene, and hexylbenzene, do not contribute to desirable flavor and are toxic compounds.

Factors Affecting the Quality of Oil during Deep-Fat Frying

The turnover rate of oil, frying time and temperature, type of heating, frying oil composition, initial oil quality, composition of food to be fried, type of fryer, antioxidants, and oxygen content affect the deterioration of oil during deep-fat frying. The effects of frying factors on the quality of frying oil are sometimes reported differently or oppositely, due to the use of different analytical methods for quality determination and different experimental conditions.

Replenishment of fresh oil

A high ratio of fresh oil to total oil provides better frying oil quality (Paul and Mittal 1997). Frequent replenishment of fresh oil decreases the formation of polar compounds, diacylglycerols, and free fatty acids and increases the frying life and quality of oils (Romero and others 1998). Sanchez-Muniz and others (1993a) reported that replenishment with fresh oil improved the quality of frying oil only after the 30th frying. Cuesta and others (1993) reported that frequent turnover of oil caused more oxidative reaction than hydrolytic reaction during deep-fat frying of potatoes. A recommended daily turnover is 15% to 25% of the capacity of the fryer, and the high turnover can decrease the use of antifoaming agent such as silicones (Stevenson and others 1984).

Frying time and temperature

Frying time increases the contents of free fatty acids (Mazza and Qi 1992), polar compounds such as triacylglycerol dimers and oxidized triacylglycerols (Romero and others 1998; Xu and others 1999), dimers (Gordon and Kourimski 1995), and polymers (Tompkins and Perkins 2000). The 1st 20 fryings increase the formation of polar compounds rapidly. There was no significant increase of polar compounds after the 30th frying at $P > 0.05$ (Cuesta and others 1993).

High frying temperature accelerates thermal oxidation and polymerization of oils (Fedeli 1988; Blumenthal 1991; Tyagi and Vasishtha 1996). Soybean oil showed 3.09% and 1.68% of conjugated dienes and *trans* acids, respectively, after 70-h frying of potato chips at 170°C. However, soybean oil that performed the same frying at 190°C showed 4.39% and 2.60% of the respective values (Tyagi and Vasishtha 1996). High frying temperature decreased polymers with peroxide linkage and increased the polymers with ether linkage or carbon to carbon linkage (Kim and others 1999).

The intermittent heating and cooling of oils causes higher deterioration of oils than continuous heating due to the oxygen solubility increase in the oil when the oil cools down from the frying temperature (Clark and Serbia 1991). The 25% of linoleic acid of the sunflower oil was destroyed in the intermittent frying, whereas only the 5% was destroyed in continuous frying (Peers and Swoboda 1982).

Quality of frying oil

Free fatty acids increase the thermal oxidation of oils, and their unsaturation rather than chain length led to significant effects on thermooxidative degeneration; the addition of 0.53 mmol of tridecanoic, palmitic, and oleic acids to virgin olive oil showed 15.0, 14.3, and 10.1 h of induction period with a Rancimat (Metrohm) (Frega and others 1999). Stevenson and others (1984) and Warner and others (1994) reported that the oxidation rate of oil increased as the

content of unsaturated fatty acids of frying oil increased. This explains why corn oil with less unsaturated fatty acid is a better frying oil than soybean or canola oils with more unsaturated fatty acids (Warner and Nelsen 1996). The content of linolenic acid is critical to the frying performance, the stability of oil, and the flavor quality of fried food (Liu and White 1992; Xu and others 1999). Total polar compounds contents of sunflower oil (C16:0, 5.3%; C18:0, 4.8%; C18:1, 55.4%; C18:2, 32.4%) and high linolenic canola oil (C16:0, 4.1%; C18:0, 2.2%; C18:1, 69.3%; C18:2, 13.8%; C18:3, 6.8%) after 80-h frying at 190 °C were 44.6% and 47.5%, respectively (Xu and others 1999). The oil containing linolenic acid at 8.5% produced extremely undesirable acrid and fishy odors when heated above 190 °C (Frankel and others 1985). Low linolenic acid (2.5%) canola oil produced less free fatty acids and less polar compounds during deep-fat frying of potato chips at 190 °C (Xu and others 1999). Warner and others (1997) reported that polar compounds formation in cottonseed oil during deep-fat frying of potato chips increased proportionally with the linoleic acid content in the oil.

Hydrogenation and genetic modification are two of the processes to decrease the unsaturated fatty acids of frying oil. Hydrogenation increases the frying stability of oil (Morrison and others 1973; Warner and Knowlton 1997). However, hydrogenation produces *trans* fatty acid or metallic flavor, and it does not additionally improve the quality of oil with low linolenic acid (Warner and Mounts 1993). Hydrogenated soybean oil with 0.1% linolenic acid had more hydrolytic degradation, but lower *p*-anisidine values and polymer formation, than the soybean oil with 2.3% linolenic acid (Tompkins and Perkins 2000). Genetically modified high oleic corn oil improved frying stability over normal corn oil (Warner and Knowlton 1997). Therefore, low linolenic acid oil by genetic modification was suggested to be a potential alternative to hydrogenated frying oil (Mounts and others 1994). Blending of several oils can change the fatty acid compositions of oils (Shiota and others 1999; Mamat and others 2005) and can decrease the oxidation of oils during deep-fat frying.

The esterified acylglycerol does not show any prooxidant activity in the oil oxidation during deep-fat frying. Free fatty acids in frying oil accelerated thermal oxidation of the oil (Miyashita and Takagi 1986; Mistry and Min 1987; Frega and others 1999). The filtering of oil with adsorbents lowered free fatty acids and improved the frying quality of oil. Used frying oil was filtered with a mixture of 2% pekmez earth, 3% bentonite, and 3% magnesium silicate, and the filtering process decreased the contents of free fatty acids and conjugated dienoic acids of sunflower oil during deep-fat frying of potato samples at 170 °C and increased the formation of aldehyde compounds (Maskan and Bagci 2003). Daily filtering treatments of canola oil with a mixture of calcium silicate-based Hubesorb 600, magnesium silicate-based magnesol, and rhyolite and citric acid-based fry powder decreased free fatty acids and polar compounds formation and improved the frying quality of oil (Bheemreddy and others 2002). The treatment of shortening with bleaching clay, charcoal, celite, or MgO improved the oil quality for French fries (Mancini-Filho and others 1986). Daily addition of ascorbyl palmitate to fresh oil decreased free fatty acid formation, but increased dielectric constant and color changes (Mancini-Filho and others 1986). Stevenson and others (1984) reported that oils with less than 0.05% free fatty acids and 1.0 meq peroxides in 1 kg of oil are desirable for deep-fat frying (Table 3).

Compositions of foods

Moisture in foods creates a steam blanket over the fryer and reduces contact with air (Landers and Rathmann 1981; Peers and Swoboda 1982; Dana and others 2003; Kochhar and Gertz 2004). A

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large amount of moisture in foods increases the oil hydrolysis during deep-fat frying. The more the moisture content of food, the higher the hydrolysis of oils. Lecithin from frying foods caused foam formation at the initial stage of deep-fat frying (Stevenson and others 1984). Phosphatidylcholine decreased the oxidation of salmon oil at 180 °C for 3 h (King and others 1992). Starch increases the degradation of oil and amino acids protect the oil from degradation during deep-fat frying (Fedeli 1988).

Transition metals such as iron, which is present in meat, were accumulated in the oil during frying (Artz and others 2005a) and this increased the rates of oxidation and thermal degradation of oil (Artz and others 2005b).

Spinach powder at 5%, 15%, or 25% in flour dough decreased the formation of polar compounds in soybean oil (Lee and others 2002). Addition of red ginseng extract to the flour dough at 1% and 3% decreased the formations of free fatty acids, conjugated dienoic acids, and aldehydes in palm oil during deep-fat frying of the dough at 160 °C (Kim and Choe 2003). Beef nuggets battered with glandless cottonseed flour decreased free fatty acids, conjugated diene compounds, and thiobarbituric acid-reactive substances (Rhee and others 1992). Addition of carrot powder to the dough at 10%, 20%, or 30% decreased the oxidative stability of soybean oil at $P < 0.05$ during frying (Lee and others 2003).

Sodium pyrophosphate inhibited after-cooking darkening in French fries and decreased free fatty acid formation in the hydrogenated canola oil during 12 to 72 h frying. Calcium acetate shows little effects on the formation of free fatty acids in the oil during deep-fat frying (Mazza and Qi 1992).

The application of edible film to foods before frying decreases the degradation of frying oil during deep-fat frying. Holownia and others (2000) reported that a coating of hydroxypropylmethylcellulose films on fried chicken strips decreased free fatty acid formation in peanut oil during deep-fat frying.

Types of fryer

The types of fryer affect the frying oil deterioration. Even and fast heat transfer to the oil can prevent hot spots and the scorch of oil. Polymerized fat deposited on the fryer causes gum formation, the formation of foam, color darkening, and further deterioration of frying oil. A small surface-to-volume ratio of fryer for minimum contact of oil with air is recommended for deep-fat frying. Negishi and others (2003) reported that oil oxidation was slowed down by modifying a fryer to have a ratio of oil depth (D) to oil area (A) with $D/A^{1/2} = 0.93$. Copper or iron fryer accelerates the oxidation of frying oil.

Antioxidants

The naturally present or added antioxidants in oils and foods influence oil quality during deep-fat frying. Tocopherols, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG), and *tert*-butylhydroquinone (TBHQ) slow down the oxidation of oil at room temperature. However, they become less effective at

frying temperature due to losses through volatilization or decomposition (Boskou 1988; Choe and Lee 1998). Tyagi and Vasishtha (1996) reported the ineffectiveness of 0.01% BHA and TBHQ during deep-fat frying of potato chips in soybean oil. The decompositions of tocopherols in soybean oil, beef tallow, and palm oil after 8-h frying of steamed noodles at 150 °C were 12.5%, 100%, and 100%, respectively (Choe and Lee 1998). The retention of tocopherols in soybean oil decreased the oxidation of soybean oil than beef tallow or palm oil without any retention of tocopherols. Palm oil contained tocotrienols in addition to tocopherols at 169 ppm, all of which was decomposed during 8-h frying of steamed noodles (Choe and Lee 1998). Soybean oil contained more unsaturated fatty acids than beef tallow or palm oil.

Carotenes do not protect the oil from thermal oxidation in the absence of other antioxidants. Carotenes are major compounds that react with oil radicals in red palm olein (Schroeder and others 2006). Tocotrienols regenerate carotenes from carotene radicals. The combination of tocotrienols and carotenes decreased the oxidation of oil synergistically during frying of potato slices at 163 °C (Schroeder and others 2006).

Lignan compounds in sesame oil, sesamol, sesamin, and sesamol, are stable during heating and contribute to high oxidative stability of roasted sesame oil during heating at 170 °C as shown in Figure 10 (Kim and Choe 2004a). The blended soybean oil with roasted sesame oil lowered the formation of conjugated dienoic acids than soybean oil during frying at 160 °C in spite of the higher unsaturated fatty acids of the blended oil than soybean oil (Chung and Choe 2001). As the sesame oil contents in the blended oil increased, the formation of conjugated diene decreased, possibly due to the antioxidants in sesame oil. The addition of sesame oil and rice bran oil enhanced the oxidative and flavor stability of high oleic sunflower oil, possibly due to the avenasterol, which is stable at high temperature (Kochhar 2000).

Ascorbyl palmitate lowered dimers in oil during deep-fat frying (Gordon and Kourimska 1995). Sterols and their fatty acid esters improved the oxidative stability of oil during deep-fat frying (Boskou and Morton 1976; Gordon and Magos 1984; Blekas and Boskou 1986). Silicone protected the oil from oxidation during deep-fat frying (Freeman and others 1973, 1985; Rhee 1978; Sakata and others 1985) by the formation of a protective layer at the air-oil interface and the low convection currents of frying oil (Freeman and others 1973; Kusaka and others 1985). The combination of silicone and antioxidants (Sherwin and others 1974; Frankel and others 1985) synergistically decreased the oxidation of oil during deep-fat frying.

Rosemary and sage extracts reduce oil deterioration during a 30-h intermittent deep-fat frying of potato chips (Che Man and Tan 1999; Che Man and Jaswir 2000) as shown in Table 4. Jaswir and others (2000) reported the synergistic antioxidant effects of rosemary, sage, and citric acid on palm olein during deep-fat frying of potato chips. Kim and Choe (2004b) reported that the hexane-extracts of burdock decreased the formation of conjugated dienoic acids and aldehydes in lard significantly ($P < 0.05$) at 160 °C. The hexane-extract of burdock is a potential antioxidant of oil for deep-fat frying.

Dissolved oxygen contents in oil

Nitrogen or carbon dioxide flushing decreased the dissolved oxygen in oil and reduced the oxidation of oil during deep-fat frying (Przybylski and Eskin 1988). Carbon dioxide gives better protection from oxidation due to its higher solubility and density than nitrogen. Przybylski and Eskin (1988) suggested that a minimum of 15 min of nitrogen or 5 min of carbon dioxide flushing prior to heating decreases the oxidation of oil during deep-fat frying.

Table 3—Common specifications for deep-fat frying fats and oils^a

Parameter	Levels in unused fat and oil
Free fatty acids	0.05–0.08%
Peroxide value	1.0 meq/kg oil
Smoke point	200 °C
Moisture	0.10%
Flavor and odor	Bland

^aStevenson and others 1984.

Changes in Nutrients in Foods during Deep-Fat Frying

The rate of tocopherol decomposition during deep-fat frying depends on the frying time and oil. The decomposition rate of γ -tocopherol in deep-fat frying of potato in the mixture of soybean and rapeseed oil at 180 °C was the fastest, followed by δ - and α -tocopherol as shown in Table 5 (Miyagawa and others 1991).

The aldehydes, epoxides, hydroxyketones, and dicarboxylic compounds formed from the lipid oxidation react with amines, amino acids, and proteins in fried foods (Pokorny 1981; Gardner and others 1992). The Maillard reaction causes nutrient loss and browning. The intensity of browning is primarily correlated with the losses of lysine, histidine, and methionine. The reaction between epoxyalkenals and proteins produces polypyrrolic polymers as well as volatile heterocyclic compounds (Hidalgo and Zamora 2000).

Carbonyl compounds formed in lipid oxidation would react with amino acids, especially asparagines, and produce acrylamide and decrease the nutritional value and safety of foods. The acrolein formed from oil reacted with asparagines and produced acrylamide in deep-fat frying (Yasahura and others 2003). Acrylamide formation required the heating temperature of above 100 °C (Becalski and others 2003) and increased as the temperature increased (Kim and others 2004; Pedreschi and others 2005). The types of oil and addition of silicone had no influence on the acrylamide concentration in foods at $P > 0.05$ (Matthaus and others 2004). Acrolein and carbonyls formed during deep-fat frying are not the main precursors of acrylamide (Tareke and others 2002; Zhang and others 2005).

Table 4 – Effects of rosemary and sage extracts on the quality of refined, bleached, and deodorized palm olein during frying of potato chips^a

Characteristics	Heating time (d)	Antioxidant		
		Control	Rosemary (0.4%)	Sage (0.4%)
Anisidine value	0	0.96	0.95	0.96
	2	36.0	30.6	29.3
	4	51.4	42.1	42.0
	6	62.0	50.2	50.8
Free fatty acid (%)	0	0.05	0.05	0.05
	2	0.19	0.15	0.16
	4	0.42	0.26	0.25
	6	0.59	0.42	0.44
Polymer content (%)	0	0.01	0.01	0.01
	2	1.00	0.73	0.70
	4	1.55	1.30	1.35
	6	2.65	1.82	1.90
C18:2/C16:0 ratio	0	0.29	0.29	0.29
	2	0.26	0.27	0.28
	4	0.21	0.25	0.24
	6	0.17	0.20	0.21

^aChe Man and Jaswir 2000.

Table 5 – Retention of tocopherol in a mixture of soybean and rapeseed oils during frying of potatoes at 180 °C^a

Number of fryings	Tocopherol retention (%)		
	α	γ	δ
0	100	100	100
4	86.2	82.1	91.0
8	85.9	74.0	87.1
12	83.1	67.6	80.3
16	75.9	59.3	74.3
20	71.9	49.6	67.8
24	64.5	41.6	63.7
28	60.9	33.5	51.5

^aMiyagawa and others 1991.

Conclusion

Deep-fat frying causes the hydrolysis, oxidation, and polymerization of the oil. 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. Intermittent frying with a lower turnover rate and higher temperature accelerates the oxidation and polymerization of oil during deep-fat frying. The frying quality of oil with high unsaturated fatty acids and free fatty acids is not as good as oil with low unsaturated fatty acids and free fatty acids. Addition of spinach and ginseng extract to the dough increases the oxidative stability of oil. Frying in a fryer with a small surface-to-volume ratio is desirable to slow down the oxidation of frying oil. Tocopherols, BHA, BHT, PG, and TBHQ decrease oil oxidation, but they become less effective at frying temperature. Lignan compounds in sesame oil are more stable than tocopherols, BHA, BHT, PG, and TBHQ at frying temperature and are effective antioxidants during deep-fat frying. Desirable fried flavor compounds such as hydroxynonenic acid, 2, 4-decadienal, and nonenlactone are produced during deep-fat frying at an optimal concentration of oxygen.

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