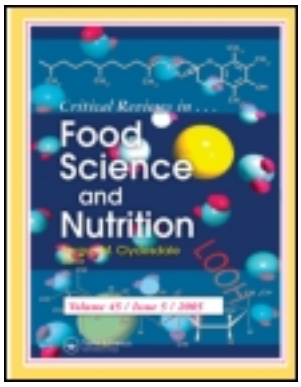

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Role of Physical Structures in Bulk Oils on Lipid Oxidation

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Lipid oxidation is important to food manufacturers especially when they increase unsaturated lipids in their products to improve nutritional profiles. Unfortunately, the number of antioxidants available to food manufacturers to control oxidative rancidity is limited and the approval of new antioxidants is unlikely due to economic barriers in obtaining government approval for new food additives. Therefore, new antioxidant technologies are needed for food oils. This paper reviews the current knowledge of lipid oxidation in foods with emphasis on how physical properties of food systems impact oxidation chemistry. In particular, the role of association colloids in bulk oils on lipid oxidation chemistry is discussed in an attempt to understand mechanisms of oxidation. Increasing the understanding of how physical properties impact lipid oxidation could lead to the development of novel antioxidant technologies that not only protect the oil against oxidation and increase shelf-life but also allow food manufacturers to include more nutritionally beneficial fatty acids in their products.

Keywords lipid oxidation, physical location, antioxidant, bulk oil, association colloids

INTRODUCTION

Lipid oxidation is one of the major causes of quality deterioration in natural and processed foods. Oxidative deterioration is a large economic concern in the food industry because it affects many quality characteristics such as flavor (rancidity), color, texture, and the nutritive value of foods. In addition, it produces potentially toxic compounds (Halliwell et al., 1995; Frankel, 1998; Liu and Huang, 1995; Kubow, 1992, 1993; Nawar, 1996). Thus lipid oxidation is one of the major processes that limit the shelf life of foods. In addition, the oxidative instability of polyunsaturated fatty acids often limits their use as nutritionally beneficial lipids in functional foods.

Traditionally, food manufacturers have increased the oxidative stability of their products by a variety of methods. Increased oxidative stability can be achieved by reducing polyunsaturated fatty acid concentrations. This can be accomplished by the replacement of polyunsaturated fatty acids with fats high in saturated fatty acids (e.g. tropical oils). However, this practice is contrary to current nutritional recommendations that advocate an increase in dietary unsaturated fatty acids for the purpose of decreasing the risk of coronary heart disease. Another method to decrease rancidity is to use partial hydrogenation of fats and oils to remove the most highly unsaturated fatty acids that are very susceptible to oxidation (e.g. linolenic acid). However, partial hydrogenation leads to the formation of *trans* fatty acids. Several studies have shown that *trans* fatty acids are more atherogenic than saturated fats because they both increase low density lipoprotein and decrease high density lipoprotein, which is often referred to as "good" cholesterol (Duxbury, 2005). These findings prompted the U.S. Food and Drug Administration (FDA) to require food manufacturers to list *trans* fat content on nutrition facts labels by January 1, 2006 (Duxbury, 2005). In order to have no *trans* fatty acids on the nutritional label of products such as fried foods, cookies, pastries, and crackers, food manufacturers will not be able to use partially hydrogenated fats in their product formulations.

Besides alteration in fatty acid content, there are only a limited number of approaches that can be used to control lipid oxidation in foods. Exclusion of oxygen from products, while effective, is often not practical during processing and storage. Addition of antioxidants that scavenge free radicals and control prooxidative metals are the most common methods used to retard lipid oxidation (Frankel, 1998; Decker, 2002) however, only a limited number of free radical scavengers and metal chelators are available for use in foods. Some of the most effective free radical scavengers and metal chelators are synthetic compounds which are often perceived negatively by consumers. Therefore, to overcome the challenge of developing consumer acceptable foods (e.g. no *trans* fatty acids or synthetic food additives)

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with nutritionally significant amounts of unsaturated fatty acids, the food industry will have to develop new antioxidant technologies.

Several antioxidant technologies have the potential to stabilize foods prone to oxidative rancidity. These technologies include control of prooxidants (e.g. reactive oxygen species and prooxidant metals) and reducing the damaging effects of free radicals (e.g. free radical scavengers) (Decker, 2002; Frankel, 1996, 1998). Unfortunately, very few new antioxidant ingredients have been introduced to the food industry over the past few decades. This means that the existing approved antioxidant ingredients available to solve oxidative rancidity problems in foods must be used more efficiently. One way to increase the efficiency of antioxidant ingredients is to deliver them to the site of the oxidative reactions or to use them in combination with other technologies that can reduce oxidation rates. However, in order to be able to develop technologies that utilize antioxidant ingredients to their full potential, the mechanisms of lipid oxidation reactions in the food must be thoroughly understood.

Lipid oxidation mechanisms have been studied extensively in bulk fats and oils and in oil-in-water emulsions (Abdalla and Roozen, 1999; Frankel et al., 1994; Fritsch, 1994; Halliwell et al., 1995; Naz et al., 2005; McClements and Decker, 2000; Hu et al., 2004a). Research into the factors that influence lipid oxidation in oil-in-water emulsions has provided important insights that show that the physical properties of foods have a dramatic effect on lipid oxidation chemistry (Frankel et al., 1994; McClements and Decker, 2000). The findings of numerous studies have shown that properties of the oil-water interface in oil-in-water emulsions play a critical role in lipid oxidation kinetics (Chaiyasit et al., 2000; Donnelly et al., 1998; Mancuso et al., 1999; Mei et al., 1998a, b, 1999; Silvestre et al., 2000). For example, producing lipid droplets in oil-in-water emulsions with a cationic interfacial membrane will cause transition metals (e.g. iron) to be electrostatically repelled from the oxidation substrate (lipid hydroperoxides at the emulsion droplet interface) thus decreasing oxidation rates. Such technologies not only increase oxidative stability of emulsified lipids but also increase the effectiveness of antioxidant ingredients (Djordjevic et al., 2004).

Oil-in-water emulsions can be more prone to oxidative deterioration due to factors such as high surface area that increases lipid interactions with aqueous phase prooxidants. However, oil-in-water emulsions can also present more opportunities for control of lipid oxidation since antioxidant technologies can be incorporated into the lipid, interfacial, and aqueous phases. Many of the recent studies on the mechanisms of oxidation in oil-in-water emulsions could provide important insights into oxidation reactions in bulk oils. The initial studies that established our understanding of the mechanisms of lipid oxidation were performed on bulk oils. Many of these studies assumed that lipid oxidation in bulk oil took place in a homogeneous medium. However, it is well known that edible oil contains polar lipids such as monoacylglycerols, diacylglycerols, free fatty acids, phospholipids, sterols, cholesterols, phenolic compounds, and polar amphiphilic products (e.g. aldehydes and ketones) that form during lipid oxidation reactions. Most of these compounds are amphiphilic, having non-polar region and polar region on the same molecule. These amphiphilic molecules can self-assemble due to hydrophobic interaction to form a variety of different types of association colloids, including lamellar structures and reverse micelles. Since commercial bulk oils contain small amounts of water that can alter the structure and characteristic of any association colloids formed. For example, Gulik-Krzywicki and Larsson (1984) reported that monoacylglycerols and water form reverse micelles in bulk oil. The existence of physical structures in bulk oil could be important in the chemistry of lipid oxidation since these nano- or micro-environments could alter the physical location of prooxidants, antioxidants, and oxidation substrates (e.g. hydroperoxides).

Understanding how the physical nature of bulk oils impacts lipid oxidation reactions could lead to the development of new antioxidant technologies and to the more efficient use of existing antioxidant ingredients. For example, if association colloids are found to be the major site of oxidation reactions in bulk oils, then altering these structures or more efficiently delivering antioxidants to the site of oxidation could significantly improve the oxidative stability of oils. Thus, increasing the understanding of oxidative mechanisms in oils could increase the use of nutritionally beneficial polyunsaturated lipids in foods.

LIPID OXIDATION

Lipid oxidation is a general term used to describe a complex sequence of chemical interactions between unsaturated fatty acyl groups in lipids with active oxygen species (Frankel, 1998; Nawar, 1996; McClements and Decker, 2000; Min and Boff, 2002). The unsaturated fatty acids on triacylglycerols and phospholipids have low volatility and do not directly contribute to the aroma of foods. However, these fatty acids will decompose during lipid oxidation to form small, volatile molecules that produce the off-aromas associated with oxidative rancidity. These volatile compounds are detrimental to food quality except in the case of food products such as fried foods, dried cereal, and cheeses, where small amounts of these volatile compounds are important in their flavor profile. The mechanisms of lipid oxidation in a particular food depend on the nature of the reactive species present and their physicochemical environment (Coupland and McClements, 1996a, b; Coupland et al., 1996; Erickson and Sista, 1997; McClements and Decker, 2000). Thus, a thorough understanding of lipid oxidation mechanisms is important in developing practical methods for controlling lipid oxidation in foods.

Mechanism of Lipid Oxidation

Theoretically, lipid oxidation is a free radical chain reaction between unsaturated fats and oxygen that can occur in

an autocatalytic manner. However, lipid oxidation in many food systems is accelerated by prooxidants such as transition metal ions, photosensitizers, UV light, and certain enzymes (Nawar, 1996; Kanner et al., 1987; Frankel, 1998; Kubow, 1992; Erickson, 2002). The overall mechanism of lipid oxidation involves three stages:

(1) initiation - the formation of free radicals;
(2) propagation - the free-radical chain reactions; and
(3) termination - the formation of nonradical products (Nawar, 1996; Kanner et al., 1987; Frankel, 1998; Kubow, 1992).

A simple scheme for the free radical mechanism can be summarized as follows (Erickson, 2002; Frankel, 1998).

$$\text{Initiation:} \quad In^{\bullet} + LH \rightarrow InH + L^{\bullet} \tag{1}$$

$$\text{Propagation:} \quad L^{\bullet} + O_2 \rightarrow LOO^{\bullet} \tag{2}$$

$$LOO^{\bullet} + LH \rightarrow LOOH + L^{\bullet} \tag{3}$$

$$\text{Termination:} \quad LOO^{\bullet} + LOO^{\bullet} \rightarrow LOOL + O_2 \tag{4}$$

$$L^{\bullet} + LOO^{\bullet} \rightarrow LOOL \tag{5}$$

$$L^{\bullet} + L^{\bullet} \rightarrow LL \tag{6}$$

In the initiation step, a fatty acid radical known as the alkyl radical ($L^{\bullet}$) is formed by abstraction of a hydrogen from a fatty acid in the presence of an initiator ($In^{\bullet}$) (Eq. (1)). Once the alkyl radical forms, the free radical can delocalize over the double bond system resulting in double bond shifting and in the case of polyunsaturated fatty acids, formation of conjugated double bonds. In bulk oils, the ease of formation of alkyl radicals in fatty acids increases with increasing unsaturation (Holman and Elmer, 1947). The first step of propagation involves the addition of oxygen to the alkyl radical resulting in the formation of peroxyl radical ($LOO^{\bullet}$), which has a higher energy than the alkyl radical (Eq. (2)). Thus, the peroxyl radical can abstract hydrogen from another unsaturated fatty acid and produce a lipid hydroperoxide (LOOH) and a new alkyl radical (Eq. (3)). The interaction of two free radicals to form non-radical species will terminate the process (Eq. (4)–(6)). This step is sometimes not very important in many foods as initiation and propagation since the food is already rancid before significant termination reactions take place. An exception is in the low oxygen environment of frying oils where the termination reaction can occur between alkyl radicals to form fatty acid dimers (Frankel, 1998).

Lipid Oxidation Decomposition Products

Rancidity in food occurs when unsaturated fatty acids decompose into volatile compounds. These volatile oxidation products

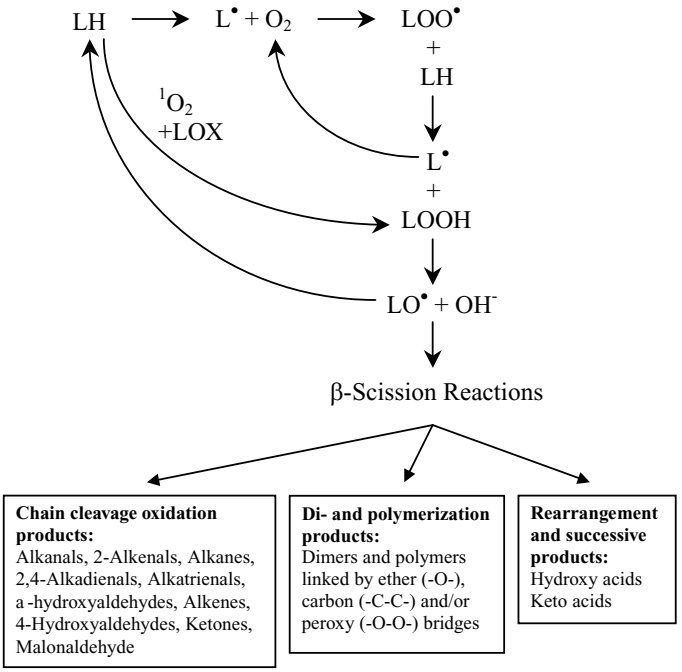


Figure 1 Schematic of lipid oxidation (Modified from Decker et al., 2002)

are produced from the decomposition of fatty acid hydroperoxides (Frankel, 1998). The homolytic cleavage of hydroperoxides (LOOH) between these two oxygen molecules is the most likely hydroperoxide decomposition pathway (Min and Boff, 2002). This reaction yields an alkoxyl ($LO^{\bullet}$) and a hydroxyl radical ($^{\bullet}OH$). The alkoxyl radical ($LO^{\bullet}$), which is more energetic than either the alkyl ($L^{\bullet}$) or peroxyl radical ($LOO^{\bullet}$), can enter into a number of different reaction pathways (Fig. 1). Alkoxyl radicals can attack another unsaturated fatty acid, a pentadiene group within the same fatty acid or the covalent bonds adjacent to the alkoxyl radical. This last reaction is known as β-scission reaction and is important to food quality as it can cause fatty acids to decompose into low molecular weight, volatile compounds that cause rancidity (Frankel, 1985).

In the β-scission reaction, the highly energetic alkoxyl radical ($LO^{\bullet}$) is able to abstract a hydrogen from the carbon-carbon bond on either side of the oxygen radical. The decomposition product on the carboxylic acid end of the fatty acid is usually esterified to the glycerol of a triacylglycerol or phospholipids, thus it would not be volatile and therefore would not contribute to rancidity unless it undergoes further decomposition reactions to form low molecular weight compounds. Cleavage of the hydrocarbon chain by alkoxyl radicals on the methyl end of the fatty acid will produce volatile compounds. Upon cleavage of the fatty acid chain, the resulting radicals will interact with a variety of compounds to produce secondary lipid oxidation products such as aldehydes, ketones, alcohols, furans, hydrocarbons and acids. A more detailed discussion of β-scission reaction can be found in Frankel (1998) and Min and Boff (2002).

Prooxidants

Lipid oxidation is often referred to as autooxidation. However, in most foods there are several prooxidative systems that produce free radicals and lipid hydroperoxides besides the classic initiation and propagation steps. Prooxidants, which are found in virtually all food systems, are compounds that initiate, facilitate or accelerate lipid oxidation. Many prooxidants are not true catalysts because they are altered during the reaction. For example, ferrous iron is converted to ferric iron during interactions with hydroperoxides, and singlet oxygen is converted to a hydroperoxide upon interaction with unsaturated fatty acids. Hydroperoxides are significant substrates for rancidity because their decomposition results in the scission of the fatty acid to produce the low molecular weight; volatile compounds that produce off-aromas (see discussion on β-scission reactions above). Prooxidants can accelerate lipid oxidation by directly interacting with unsaturated fatty acids to form lipid hydroperoxides (e.g. lipoxygenases and singlet oxygen) or by promoting formation of free radicals (e.g. transition metals or ultraviolet light promoted hydroperoxide decomposition).

The decomposition of hydroperoxides produces additional radicals that could be responsible for the exponential increase in oxidation rates that are seen in many foods. Elevated temperatures, light, and many prooxidants can promote the decomposition of hydroperoxides. At high temperatures, hydroperoxides rapidly breakdown after their formation, as is the case with frying oil; therefore, there is often no hydroperoxide accumulation during use and storage. Light causes hydroperoxide decomposition with decomposition rates increasing with decreasing wavelength. Transition metals, which are common contaminants in food, are often introduced via the water and ingredients used in food preparations (Taylor, 1987). These reactive metals decompose hydrogen peroxide and lipid hydroperoxides into free radicals through the following redox cycling pathway (Reische et al., 2002; Berger and Hamilton, 1995):

$$Mn^{n+} + LOOH \rightarrow Mn^{(n+1)+} + LO^{\bullet} + OH^{-} \quad (7)$$

$$Mn^{n+} + HOOH \rightarrow Mn^{(n+1)+} + HO^{\bullet} + OH^{-} \quad (8)$$

$$Mn^{(n+1)+} + LOOH \rightarrow Mn^{n+} + LOO^{\bullet} + H^{+} \quad (9)$$

Where Mn^{n+} and $Mn^{(n+1)+}$ are transition metals in their reduced and oxidized states, respectively. Hydroxyl radical ($HO^{\bullet}$) is produced from hydrogen peroxide (HOOH) while alkoxyl radicals ($LO^{\bullet}$) are produced from lipid hydroperoxides (LOOH). The oxidized state of the metal ion can be regenerated by lipid hydroperoxides (LOOH) in a slow consecutive reaction. The concentration, type, and chemical state of the metal influences the rate of hydroperoxide decomposition. Copper and iron are common transition metals in foods (Berger and Hamilton, 1995); however, iron is normally found at greater concentration than copper. The type of hydroperoxide species is also important, with the ferrous ion capable of decomposing lipid hydroperoxides about 10 times faster than hydrogen peroxide (Girotti, 1998).

Antioxidants

Incorporation of antioxidants into foods is one of the most effective methods of retarding lipid oxidation. However, many factors can impact the activity of antioxidants with some antioxidants retarding lipid oxidation under certain conditions but promoting lipid oxidation under other conditions (Huang et al., 1994). Antioxidants can be classified according to their mechanisms of action as either primary or secondary antioxidants (Reische et al., 2002). However, some substances have more than one mechanism of antioxidant activity and are referred to as multiple-function antioxidants.

Primary Antioxidants

Primary or chain-breaking antioxidants retard lipid oxidation by interfering with chain propagation, initiation, or β-scission reactions by accepting free radicals and forming stable free radicals that do not further promote initiation or propagation reactions (Frankel, 1998; Reische et al., 2002). An antioxidant (AH) reacts with lipid radicals as follows:

$$LOO^{\bullet} + AH \rightarrow LOOH + A^{\bullet} \quad (10)$$

$$LO^{\bullet} + AH \rightarrow LOH + A^{\bullet} \quad (11)$$

$$L^{\bullet} + AH \rightarrow LH + A^{\bullet} \quad (12)$$

For a primary antioxidant to be effective it must inactivate free radicals before they can attack unsaturated fatty acids. It is believed that free radical scavenging antioxidants interact mainly with peroxyl radicals ($LOO^{\bullet}$).

The effectiveness of free radical scavenging antioxidants depends on their ability to donate hydrogen to a free radical, which can be predicted by standard one-electron reduction potentials (Buettner, 1993). A compound with a lower reduction potential than a free radical (or oxidized species) is able to donate its hydrogen to that free radical except when the reaction is kinetically restricted (e.g. steric hindrance). For instance, hydrogens of the hydroxyl groups on catechol ($E^{0'} = 530\,\text{mV}$), α-tocopherol ($E^{0'} = 500\,\text{mV}$), and ascorbate ($E^{0'} = 282\,\text{mV}$) have reduction potentials below that of peroxyl radicals ($E^{0'} = 1000\,\text{mV}$) and thus are able to donate their hydrogen to the peroxyl radical to form a hydroperoxide.

The effectiveness of free radical scavenging antioxidants also depends on the energy of the resulting antioxidant radicals ($A^{\bullet}$). The most efficient antioxidant yields low energy radicals due to resonance delocalization (Shahidi et al., 1992; Nawar, 1996). Consequently, these antioxidant radicals do not react rapidly with unsaturated fatty acids to promote lipid oxidation. For instance, the α-tocopherol radical has lower reduction potential

($E^{0'} = 500$ mV) than the methylene-interrupted hydrogen of a polyunsaturated fatty acid ($E^{0'} = 600$ mV) (Buettner, 1993); therefore the α-tocopherol radical will not react rapidly with polyunsaturated fatty acids to promote oxidation. Effective free radical scavenging antioxidants will also not readily form hydroperoxides that can decompose and produce additional radicals which may cause oxidation of fatty acids. Antioxidant radicals are also able to participate in termination reactions with other antioxidant radicals or lipid radicals to form nonradical species as follows:

$$LOO^{\bullet} + A^{\bullet} \rightarrow LOOA \quad (13)$$

$$LO^{\bullet} + A^{\bullet} \rightarrow LOA \quad (14)$$

$$L^{\bullet} + A^{\bullet} \rightarrow LA \quad (15)$$

$$A^{\bullet} + A^{\bullet} \rightarrow AA \quad (16)$$

Although, there are many synthetic free radical scavenging antioxidants that are efficient and relatively cheap [e.g. butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG), and tertiary butylhydroquinone (TBHQ)], these synthetic compounds are "label unfriendly" additives. Special attention has been given to the use of natural free radical scavengers due to the worldwide trend to avoid or minimize the use of synthetic food additives. Many natural free radical scavengers such as catechins (catechin, epicatechin, epigallocatechin, epicatechin gallate, epigallocatechin gallate) also have health benefits as inhibitors of biologically harmful oxidation reactions in the body (Yang et al., 2000; Jankun et al., 1997; Leanderson et al., 1997; Lotito and Fraga, 1998; Vinson et al., 1995; Wang et al., 1994). Therefore a better understanding of the properties of natural free radical scavengers could lead to the development of food additives that could both prevent oxidative deterioration of foods while also providing health benefits. Taking advantage of rancidity prevention and health promoting properties of natural free radical scavengers could help overcome their limitation in effectiveness, price, associated flavors and colors.

Secondary Antioxidants

The secondary or preventive antioxidants decrease the rate of oxidation through numerous mechanisms but they do not convert free radicals to more stable products.

Chelators. As mentioned previously, transition metals are prooxidants capable of accelerating lipid oxidation reactions. Chelators are a group of secondary antioxidants that can bind and thus inactivate or reduce the activity of prooxidant metals. The most common food chelators are citric acid (and its lipophilic, monoglyceride ester), phosphoric acid (and its polyphosphate derivatives), and ethylenediaminetetraacetic acid (EDTA). It should be noted that some chelators can be ineffective when used alone but can greatly enhance the action of phenolic free radical scavengers when used in combination (Reische et al., 2002). In addition, some chelators may increase oxidative reaction under certain conditions by increasing metal solubility or altering the redox potential of the metal (Decker, 2002; Mahoney and Graf, 1986). For instance, the antioxidative properties of EDTA is determined by its concentration in relation to prooxidant metals, and can act as a prooxidant when the ratio of EDTA to iron is less than 1, and an antioxidant when the ratio is equal or greater than 1 (Mahoney and Graf, 1986).

Oxygen Scavengers and Reducing Agents. Oxygen is a substrate in lipid oxidation reactions. Ascorbic acid, ascorbyl palmitate, erythorbic acid, sodium erythorbate, and sulfites are able to scavenge oxygen and act as reductants. Ascorbic acid and sulfites retard lipid oxidation by reacting directly with oxygen to eliminate it from food. In recent years, oxygen scavengers have been directly incorporated into packaging materials, however these technologies are still too expensive for most food packaging applications.

Singlet Oxygen Quenchers. Singlet oxygen ($^1O_2$) is an excited state of oxygen that can be formed by enzymatic reactions in biological systems or in the presence of a photosensitizer, light, and triplet oxygen (Davies, 2003; Davies and Truscott, 2001; Decker, 2002). Singlet oxygen can be inactivated through both chemical and physical quenching pathways by compounds such as tocopherols, carotenoids (including β-carotene, lycopene, and lutein), polyphenols (including catechins, and flavonoids), amino acids, peptides, proteins, urate, and ascorbate (Decker, 2002; Mukai et al., 2005; Nagai et al., 2005; Shixian et al., 2005; Bradley and Min, 1999; Kanofsky, 1990).

Interactions between Antioxidants and Multiple Antioxidant Functions

It has been reported that when two antioxidants are used together, a synergistic or additive effect can be observed. Vitamin E and vitamin C are a well-known example of a synergistic system. Vitamin E acts as a lipid soluble chain-breaking antioxidant and vitamin C reduces the tocopherol radical back to its original state so that it can continue to inactivate free radicals in the lipid phase (Gordon and Roegid-Penman, 1999; Nawar, 1996). If a chain-breaking and a secondary antioxidant are mixed, both initiation and propagation are suppressed. Thus a combination of chelators and free radical scavenging antioxidants are often very effective. For instance, chelating antioxidants such as citric or other acids can enhance the activity of phenolic antioxidants. A synergistic relationship between ascorbic acid and phosphates in retarding lipid oxidation was also observed in meats (Tims and Watts, 1958; Sato and Hegarty, 1971).

Antioxidants can also have multiple functions such as free radical scavenging and metal chelation. Examples include propyl gallate (PG) (Paya et al., 1992), proteins (Faraji et al., 2004; Tong et al., 2000a, b; Rival et al., 2001; Hu et al., 2003a, b) and proanthocyanidins (Hu et al., 2004a; Yamaguchi et al., 1999; Shafiee et al., 2003). Ascorbic acid is also a multifunctional

antioxidant in food systems. It can quench singlet oxygen, reduce free radicals and antioxidant radicals, and remove molecular oxygen in the presence of metal ions (Schiler, 1990; Reische et al., 2002).

EDIBLE OILS

Lipids are important in foods due to their contribution to palatability, satiety, and nutrition. Consumption of lipids in the U.S. is high, with the annual per capita intake of 74.6 pounds in 2000 (O'Brien, 2004). Therefore, lipid quality is significant to consumers and may have a link to many health problems. Lipid oxidation is a major problem in many sectors of the food industry. Retarding lipid oxidation not only extends product shelf life but also reduces raw material waste, reduces nutritional loss, and widens the range of lipids that can be used in specific products. Thus, control of lipid oxidation could allow food processors to use more available, less costly and/or more nutritionally favorable oils for product formulation.

Lipid oxidation in bulk oil has often been considered a homogeneous liquid phase reaction. However, edible oils contain polar lipids, such as mono- and diacylglycerols, phospholipids, sterols, tocopherols, and free fatty acids that are not completely removed by the refining process. Oils can also contain polar oxidation products (e.g. lipid hydroperoxides, aldehydes, ketones, and alcohols) that have higher polarity than their original lipid substrates due to the addition of oxygen. Bulk oils also contain small amounts of water. Since polar lipids are surface active and thus have an affinity for both non-polar and polar environments, they tend to form associated colloid structures such as reverse micelles and lamellar structures. A good understanding of the impact of surface active compounds on lipid oxidation in bulk oils could lead to the development of new antioxidative techniques to control rancidity.

Composition of Edible Oils

Major Components of Edible Oils

The primary component in vegetable oils and food lipids is triacylglycerols (Frankel, 1998) which are comprised of three fatty acid molecules esterified to a glycerol backbone (Stockwell, 1988). The common fatty acids in foods contain an even number of carbon atoms in an unbranched chain (Coultate, 2002; Nawar, 1996). Fatty acids can generally be classified into three families: saturated fatty acids, monounsaturated fatty acids, and polyunsaturated fatty acids. Lately, long chain polyunsaturated fatty acids have received attention because of their health benefits and susceptibility to oxidation.

Minor Components of Oils

Most consumers and food manufacturers want bland-flavored, light-colored, and physically and oxidatively stable oils. Thus, numerous non-triacylglycerols compounds in crude oils need to be removed through an operation known as refining. Some oils, such as olive, tallow, and lard, are consumed with minimal refining. In general, excluding free fatty acids, crude vegetable oils contain 2% or more non-triglyceride compounds and animal fats contain even smaller quantities (O'Brien, 2004). Some of these non-triglyceride compounds are referred to as the unsaponifiable fraction and consist of compounds such as phenols (e.g. tocopherols), sterols, carbohydrates, pesticides, proteins, trace metals, and pigments such as gossypol, carotenoids, and chlorophyll. Some of the non-triacyglycerol compounds are deleterious to oil quality (e.g. free fatty acids and chlorophyll) however some are desirable, such as carotenoids for color, and phenolic antioxidant compounds (e.g. tocopherols) that both protect the oil against oxidation as well as providing beneficial nutrients to consumers. Table 1 shows composition of some crude and refined, bleached, deodorized (RBD) oils.

The edible oil refining processing intends to remove undesirable constituents from the oil with the least possible damage to the desirable constituents (Fig. 2). Unfortunately, these operations are not 100% selective and some of the beneficial compounds are removed along with the targeted undesirable compounds. In addition, the processes are not 100% efficient so not all of undesirable compounds are removed. This section will review minor components in oils with emphasis on those that could influence lipid oxidation by influencing the physical properties of the oil.

Mono- and Diacylglycerols. Mono- and diacylglycerols are mono- and diesters of fatty acids and glycerol. They occur naturally in small amounts in crude animal fats and vegetable oils. However, partial hydrolysis of triacylglycerols during oil extraction increases the concentrations of mono- and diacylglycerols. Most fats and oils obtained from low quality sources that have abnormally high free fatty acid concentrations will also have correspondingly high mono- or diacylglycerol concentrations. This is caused by the cellular decompartmentalization of lipases that can interact with water to hydrolyze free fatty acid from glycerol or sterols (O'Brien, 2004). Heat and pressure also accelerate fatty acid hydrolysis. Fatty acid hydrolysis, and thus mono- or diacylglycerol formation are especially prevalent in olives (Kitchcock and Nichols, 1971), palm fruits and safflower seeds (Hamrouni et al., 2004). The level of diacylglycerols in virgin olive oils ranges from 1–3% depending on the ripeness and variety of olive fruit (Perez-Camino et al., 2001; Vlahov, 1996; Fronimaki et al., 2002). The levels of diacylglycerols in fresh and commercial palm oils range from 1.7–3.8%, and 4.0–7.5%, respectively (Siew and Ng, 1995). In most other fats and oils the concentration of diacylglycerols ranges from 0.8–5.8% and monoacylglycerols are present in much smaller quantities than diacylglycerols (less than 0.2%) as shown in Table 2. Some mono- and diacylglycerols can be removed by the deodorization process (Johnson, 2002; Shahidi et al., 1997).

Mono- and diacylglycerols are amphiphilic and thus surface active. They are the most common emulsifiers in the food industry and account for about 70% of emulsifier usage (O'Brien,

Table 1 Average compositions for crude and refined, bleached, deodorized (RBD) oils

	Oils									
	Soybean[a]		Cottonseed[b]		Canola[c]		Palm[d]		Sunflower[e]	
Components	Crude oil	RBD	Crude oil	RBD	Crude oil	RBD	Crude oil	RBD	Crude oil	RBD
Triacylglycerols (%)	95–97	>99	NA	>99	NA	>99	NA	>99	NA	>99
Phosphatides (%)	1.5–2.5	0.003–0.045	0.7–0.9	NA	2.7–3.5	NA	0.006–0.013	0.012	0.5–1.0	NA
Unsaponifiable matter (%)	1.6	0.3	NA	NA	0.5–1.2	NA	NA	NA	<1.3	NA
Phytosterols	0.33	0.13	0.37	NA	NA	NA	0.036–0.062	0.011–0.016	NA	NA
Tocopherols	0.15–0.21	0.11–0.18	0.11	0.06	0.06	NA	0.06–0.10	0.04–0.06	0.05	NA
Hydrocarbons (Squalene)	0.014	0.01	NA	NA	NA	NA	0.02–0.05	NA	NA	NA
Free fatty acids (%)	0.3–0.7	<0.05	0.9–3.7	<0.05	0.4–1.0	<0.05	2.0–5.0	<0.10	0.8–2.4	<0.05
Trace metals										
Iron (ppm)	1–3	0.1–0.3	NA	NA	1.5	<0.1	5–10	0.12	NA	NA
Copper (ppm)	0.03–0.05	0.02–0.06	NA	NA	0.1	<0.01	0.05	0.05	NA	NA

NA: Data not available
[a]Adapted from (Pryde, 1980)
[b]Adapted from (Jones and King, 1990)
[c]Adapted from (Vaisey-Genser and Eskin, 1982; Mag, 1983)
[d]Adapted from (Basiron, 1995; Swoboda, 1985; Goh et al., 1985)
[e]Adapted from (Campbell, 1983)

2004). Monoacylglycerols with only one fatty acid attached to a glycerol molecule and two hydroxyl groups on the glycerol have a hydrophilic-lipophilic balance (HLB) of ≈3.4–3.8 (McClements, 2004). Diacylglycerols have two fatty acids attached to a glycerol molecule and only one hydroxyl group, therefore the HLB is lower at ≈ 1.8 (McClements, 2004). The low HLB numbers of mono- and diacylglycerols mean that they tend to stabilize water-in-oil emulsions (O'Brien, 2004).

Free Fatty Acids. Free fatty acids represent unesterified fatty acids produced from the hydrolysis of triacylglycerols or phospholipids. Free fatty acids cause problems because they cause foaming and reduce the smoke point of oils. As with mono- and diacylglycerols, crude oils from seeds or fruits that have been damaged or improperly stored may have high free fatty acids contents. Refined fats and oils normally have free fatty acid content less than 0.05%. However, tropical oils typically contain greater than 2% free fatty acids (Table 1 and 3).

Free fatty acids are removed during refining, especially in the neutralization and deodorization steps. In neutralization, free fatty acids react with caustic soda (generally sodium hydroxide) to form soaps (Johnson, 2002; Wang, 2002). The soap is then removed by settling or centrifugation (Johnson, 2002; Wang,

Refining Stage:	Compounds removed or reduced
Degumming:	Phospholipids, trace metals, pigments, carbohydrates, and proteins
↓	
Neutralization:	Free fatty acids, phospholipids, pigments, trace metals, sulfur, and insoluble matter
↓	
Washing :	Soap (form by free fatty acids or glycerols with sodium hydroxide)
↓	
Drying:	Water
↓	
Bleaching:	Pigments, oxidation products, trace metals, and traces of soap
↓	
Filtration:	Spent bleaching earth
↓	
Deodorization:	Free fatty acids, mono- and diacylglycerols, oxidation products, pigments, decomposition products, pesticides, sterols, sterol ester, tocopherols, and other antioxidants
↓	
Physical refining:	Free fatty acids, mono- and diacylglycerols, oxidation products, pigments, decomposition products, and pesticides
↓	
Polishing:	Any residual traces of oil insoluble

Figure 2 Refining stages of edible oils and the major impurities removed (Modified from Shahidi et al., 1997; Johnson, 2002)

Table 2 Monoacylglycerol, diacylglycerol, triacylglycerol composition of fats and oils (% w/w) (Adapted from D'Alonzo et al., 1982)

Oil	Monoacylglycerol (% w/w)	Diacylglycerol (% w/w)	Triacylglycerol (% w/w)
Soybean	–	1.0	97.9
Cottonseed	–	3.1	95.0
Palm	–	5.8	93.1
Corn	–	2.8	95.8
Sunflower	–	2.0	95.6
Safflower	–	2.1	96.0
Peanut	–	2.2	93.3
Sesame	–	2.6	95.0
Olive	0.2	5.5	93.3
Rapeseed	0.1	0.8	96.8
Cocoa butter	0.2	2.2	96.0
Tallow	–	3.8	89.6
Lard	–	1.3	97.9

– = Data not reported.

2002). Deodorization is another refining process that can reduce low molecular weight free fatty acids that can be volatilized under conditions of high temperature (180–270°C) and high vacuum (3–8 mm Hg) (Johnson, 2002). In some oils that have low phosphorus (less than 5 ppm) or phospholipid concentrations (e.g. palm, rice bran, coconut, and animal oils/fats), one operation combing neutralization and deodorization to remove of free fatty acids can be used. This process is known as physical refining or steam refining (Johnson, 2002).

Free fatty acids are surface active with an HLB number of $\approx$ 1.0 (McClements, 2004). Due to their low HLB number, free fatty acids tend to stabilize water-in-oil emulsions and form reverse micelles.

Phospholipids. Phospholipids, known as phosphatides to oil processors, originate from cell membranes and are the major source of polar lipids in crude oils. During oil extraction, plant cells are destroyed by crushing operations and cell membranes are solubilized into the released oil. Phospholipids negatively affect oil quality and yield because they readily form emulsions that can make oil extraction difficult and result in cloudy oils. Phospholipids in oils are categorized as hydratable or nonhydratable, depending on how they behave in the presence of water. Phosphatidylcholine and phosphotidylinositol are always hydratable and thus readily partition into water. Phosphatidylethanolamine and phosphatidic acid can form complexes with divalent metal ions (e.g. calcium and magnesium), rendering them nonhydratable. Degumming is a refining step used to remove hydratable phospholipids from oil by allowing phospholipids to become fully hydrated into a water phase. This is followed by removal of the water and hydrated phospholipids by centrifugation and/or filtration. Nonhydratable phospholipids, which are especially problematic in soybean oils, can be removed by superdegumming processes which make phospholipids more hydratable by adding a citric acid solution into warm oil to dissociate divalent metals from the phospholipids (see additional detail in Johnson, 2002). Enzymatic degumming can be used to convert nonhydratable phospholipids to hydratable phospholipids, especially in oils such as soybean and canola that have high concentrations of nonhydratable phospholipids (see additional detail in Johnson, 2002). The bleaching step of the refining operation also aids in the removal of phospholipids from oils. Table 4 is an example of the effect of refining on phospholipid levels in oil. After refining, most oils contain less than 0.1% phosphatides (Table 1).

Table 3 Free fatty acid concentrations in retail vegetable oils

Oil	Free fatty acids (% w/w)	Free fatty acids (mmol/kg)
Canola[a]	0.10	3.6
Coconut[a]	3.93	139.4
Corn[b]	0.12	4.3
Olive[b]	0.30	10.6
Extra virgin olive[a]	0.28	9.9
Peanut[a]	0.32	11.4
Palm kernel[b]	2.49	88.3
Palm olein[a]	0.15	5.3
Rapeseed[a]	0.04	1.4
Rice bran[a]	0.08	2.8
Safflower[a]	0.03	1.1
Sesame[b]	2.37	84.0
Soybean[b]	0.05	1.8
Sunflower[a]	0.09	3.2

[a]Adapted from (Gan et al., 2005).
[b]Adapted from (Tan et al., 2002).

Table 4 Effect of refining steps on phospholipid concentrations in soybean oil as followed by phosphorus levels (Adapted from Jung et al., 1989)

	Phosphorus (ppm)	Phosphorus (mmol/kg)
Crude	510	16.45
Degummed	120	3.87
Neutralized	5	0.16
Bleached	1	0.03
Deodorized	1	0.03

Due to the presence of fatty acids and charged phosphate groups, phospholipids are surface active with HLB values of around 8.0. Phospholipids can form structures such as reverse micelles. For instance, Gupta et al. (2001) found that phospholipids in a nonaqueous media of hexane and vegetable oil in the presence of small amounts of water (less than 0.3 wt%) formed spherical reverse micelles with a diameter in the range 50–92 Å. However, the intermediate HLB values of phospholipids mean that they can also form lamellar structures, especially in the presence of other surface active materials such as sterols. These lamellar structures are very difficult to characterize.

Tocopherols and Tocotrienols. Tocopherols and tocotrienols are important minor components in most vegetable oils because they are effective natural antioxidants and a source of vitamin E. There are four tocopherol and four tocotrienol homologs that

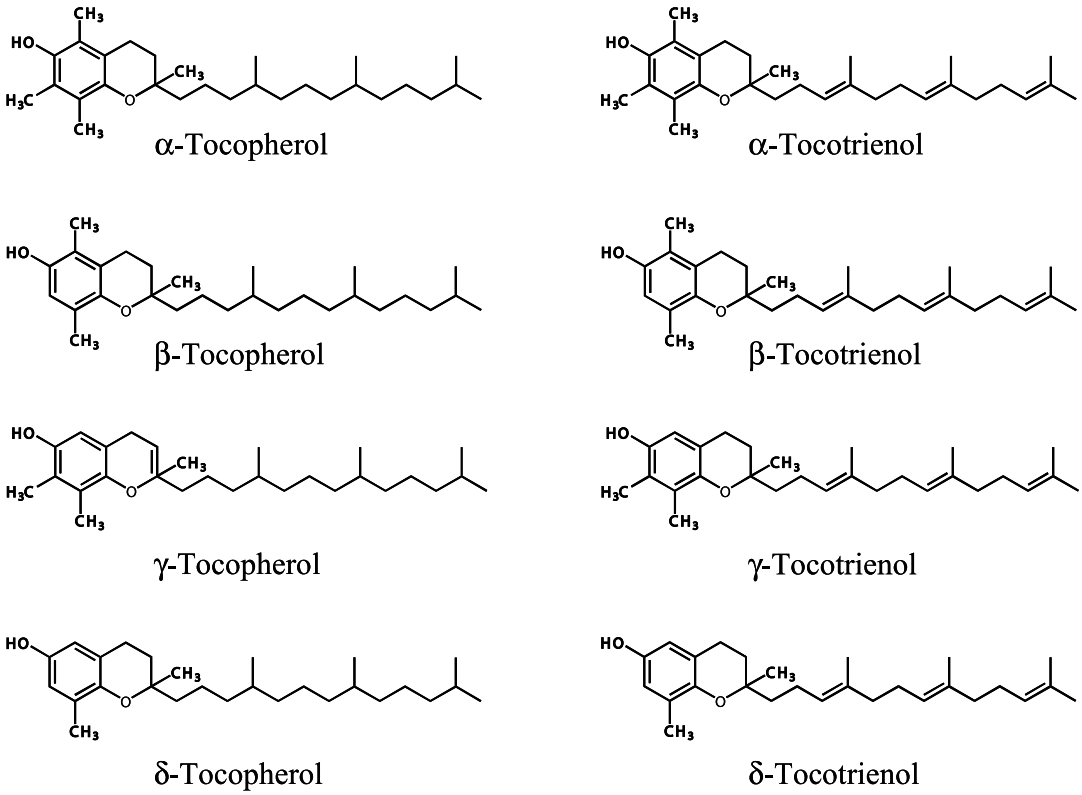


Figure 3 Structures of tocopherols and tocotrienols homologs alpha (α), beta (β), gamma (γ), and delta (δ)

occur in nature, designated as alpha (α), beta (β), gamma (γ), and delta (δ) on the basis of the degree of methylation of the chromanol ring (Fig. 3). The tocopherols have a saturated isoprenoid side chain and the tocotrienols have a tri-unsaturated isoprenoid side chain (double bonds at the 3′, 7′, 11′ position of the isoprenoid side chain). Tocopherols and tocotrienols are widely distributed in plants with vegetable oils providing the most concentrated sources (Table 5). In general, animal fats do not have high levels of tocopherols. The concentrations of various homologs vary in oils, as shown in Table 6. A portion of these desirable compounds are unintentionally removed during oil processing (Johnson, 2002; Reische et al., 2002) (Table 7). α-Tocopherol or mixtures of tocopherols/tocotrienols are sometimes added to fats and oils after processing to improve the oxidative stability of the finished product.

Table 5 Tocopherol and tocotrienol concentrations in crude oils) (Adapted from Firestone, 1999; White, 2000; Bagge, 1993; Harper, 2001)

Fat or oil	Tocopherols (% w/w)	Tocotrienols (% w/w)
Soybean	0.13 ± 0.03	0.009 ± 0.01
Canola	0.07 ± 0.01	NR
Corn	0.15 ± 0.02	0.04 ± 0.04
Cottonseed	0.09 ± 0.00	0.003 ± 0.003
Sunflower	0.07 ± 0.01	0.03 ± 0.03
Safflower	0.05 ± 0.02	0.002 ± 0.001
Peanut	0.05 ± 0.03	0.03 ± 0.02
Olive	0.01 ± 0.00	0.01 ± 0.01
Palm	0.02 ± 0.01	0.06 ± 0.01
Coconut	0.001 ± 0.001	0.0004 ± 0.001
Palm kernel	0.0003	0.003 ± 0.003

NR = Data not reported.

Table 6 Tocopherol homologs in selected vegetable oils (ppm) (Adapted from Zambiazi, 1997; Normand, 1998)

Oil	α	β	γ	δ
High-erucic acid rapeseed	268	–	426	–
Canola	272	–	423	–
Soybean	116	34	737	275
Sunflower	613	17	19	–
Corn	134	18	412	39
Flax oil with low content of linolenic acid	26	–	213	9

– = Data not reported.

Table 7 Effect of processing steps on tocopherol contents in soybean oil (Adapted from Ramamurthi et al., 1998)

	Tocopherols (ppm)
Crude	1132
Degummed	1116
Neutralized	997
Bleached	863
Deodorized	726

Table 8 Major sterols in selected oils (composition is expressed as percentage of total sterols) (Adapted from Ackman, 1990; Strocchi, 1987; Zambiazi, 1997; Gordon and Miller, 1997; USDA-ARS, 2005)

Sterol	Corn	Sunflower	Soybean	Canola	Coconut	Butter	Tallow	Lard	Chicken	Turkey	Cod liver	Menhaden	Salmon
Cholesterol (%)	0.1	0.1	0.3	0.1	1.8	98.2	100	100	100	100	100	100	100
Brassicasterol (%)	–	–	–	13.8	0.4	–	–	–	–	–	–	–	–
Campesterol (%)	17.2	7.5	18.1	27.6	8.8	0	–	–	–	–	–	–	–
Stimasterol (%)	6.3	7.5	15.2	0.5	12.7	0	–	–	–	–	–	–	–
β-Sitosterol (%)	60.3	58.2	54.1	52.3	46.1	1.8	–	–	–	–	–	–	–
Δ^5-Avenasterol (%)	10.5	4.0	2.5	1.9	27.4	–	–	–	–	–	–	–	–
Δ^7-Avenasterol (%)	1.1	4.0	2.0	1.1	1.6	–	–	–	–	–	–	–	–
Δ^7-Stimasterol (%)	1.8	7.1	1.4	2.3	0.3	–	–	–	–	–	–	–	–
% in oil	**0.97**	**0.41**	**0.46**	**0.69**	**0.08**	**0.22**	**0.11**	**0.10**	**0.08**	**0.10**	**0.57**	**0.52**	**0.48**
Esterified (% w/w)	0.57	0.21	0.06	0.42									

– = Data not reported.

Among the tocopherols, α-tocopherol has received the most attention because of its vitamin E activity; however, the other homologs are often superior in protecting fats and oils from rancidity. The antioxidant activity of the tocopherol homologs in fats and oils are often reported in the order of δ-tocopherol > γ-tocopherol > β-tocopherol > α-tocopherol (Mukai et al., 2005; Wagner et al., 2004; Isnardy et al., 2003; Kulas and Ackman, 2001; Wagner et al., 2001). However, the antioxidant effectiveness of tocopherol homologs is not consistent in all foods since their activity is dependent on experimental conditions, antioxidant concentrations, methods used to evaluate oxidation, and the physical nature of the food (Burton and Ingold, 1981; Kulas et al., 2003; Frankel, 1998). Recently, there is considerable interest in the biological activity of tocotienols, which are abundant in palm oil (Qureshi et al., 1991; Nesaretnam et al., 1995); however, it should be noted that their bioavailability is very low.

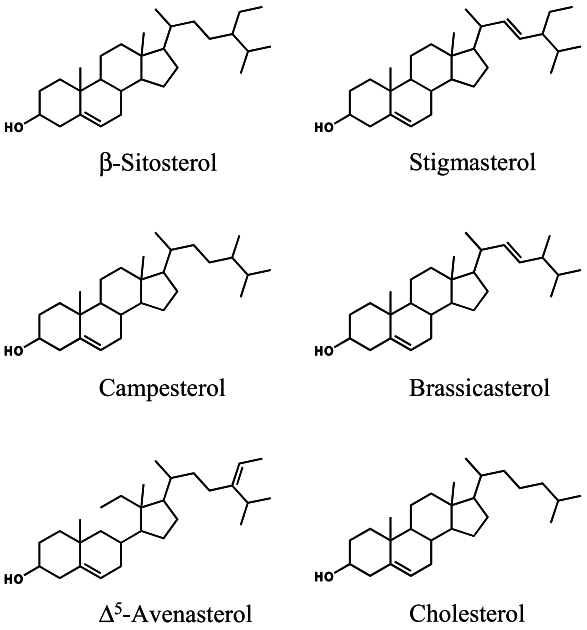


Figure 4 Structures of phytosterols and cholesterol

Sterols. Sterols are minor components found in all natural fats and oils. They are high melting, colorless, and heat stable (O'Brien, 2002). The plant sterols, known as phytosterols, are structural analogs of the cholesterol, the main sterol in animal tissue. The composition and concentration of major sterols in vegetable oils and animal fats is presented in Table 8 and their structures are presented in Fig. 4. High levels of low density lipoprotein cholesterol have been associated with an increased risk of cardiovascular disease. Unlike dietary cholesterol, dietary phytosterols and their derivatives can decrease human plasma cholesterol concentrations by inhibiting the absorption of dietary cholesterol and therefore may help reduce the risk of cardiovascular disease (Hendriks et al., 1999; Ling and Jones, 1995). Moreover, sterols can act as antioxidants. It is believed that sterols may act as hydrogen donors, resulting in inhibition of the propagation step of lipid oxidation (Reische et al., 2002). Sterols are affected by oil refining (Table 9), which causes the removal and isomerization of these compounds (Kochar, 1983; Marchio et al., 1987).

The oxidation of cholesterol can occur in processed foods such as dried eggs and cheeses (Obara et al., 2006; Al-Ismail and Humied, 2003). Cholesterol oxidation products present potential health risks, especially with regard to cardiovascular disease. Phytosterol oxidation products have been found in fried food products (Przybylski and Eskin, 1991), soybean oil, and wheat flour (Nourooz-Zadeh and Appelqvist, 1992). Recently, the biological effects of cholesterol and phytosterols oxidation products were compared and it was concluded that phytosterol oxidation products have qualitatively similar toxic effects to cholesterol oxidation products, but higher concentrations of

Table 9 Effect of processing steps on sterol content in soybean oil (Adapted from Ramamurthi et al., 1998)

	Sterols (ppm)
Crude	3870
Degummed	3730
Neutralized	3010
Bleached	3050
Deodorized	2620

phytosterols oxidation products are required to achieve comparable levels of toxicity (Ryan et al., 2005).

Trace Metals. Trace quantities of metals such as iron, copper, manganese, and nickel significantly reduce the oxidative stability of fats and oils while calcium, sodium, and magnesium reduce the efficiency of refining, bleaching, and hydrogenation systems. Trace amounts of metals are present naturally in oilseeds and fruits; however additional quantities can be introduced during handling and processing. Copper and iron are common transition metals in foods (Berger and Hamilton, 1995), however iron is normally found at higher concentrations than copper. To ensure stability, oils should have iron and copper concentrations less than 0.1 and 0.02 ppm, respectively. The effect of metals can be reduced by the use of chelating agents during refining and in the final oil or food product (Flider and Orthoefer, 1981).

Lipid Oxidation Products. Most fats and oils contain unsaturated fatty acids which are susceptible to oxidation. During the course of oxidation, the total unsaturated fatty acid content of lipids decreases with a concurrent increase in the amount of primary and secondary oxidation products such as lipid hydroperoxides, aldehydes, ketones, hydrocarbons, and alcohols. With the exception of hydrocarbons, these oxidation products are amphiphilic. Bleaching, deodorization, and physical refining can remove many oxidation products, but in reality most commercial fats and oils contain lipid oxidation products.

Lipid oxidation can occur during oil extraction and refining, resulting in the formation of lipid hydroperoxides. Lipid hydroperoxides have no flavor or odor but break down rapidly to form secondary products, many of which have a strong flavor and odor. The lipid hydroperoxide concentration in oils is generally expressed as peroxide value (PV), and can range from <1.0 to over 15.0 milliequivalents/kg in commercially available oils (Table 10).

Water. Water is used to wash oils during the refining process. After removing the majority of wash-water by centrifugation, the remaining water is usually removed by a vacuum dryer that controls the moisture content of the washed oil to below 0.1%, most often in the range of 0.05% (O'Brien, 2004). Table 11 presents the water content in freshly-opened, commercially available vegetable oils. These oils contained approximately 0.02% water with the exception of extra virgin olive oil (0.09%). Water concentrations in oil can change during prolonged storage after opening as water is absorbed from the environment or lost from the oil. Since water is essentially insoluble in oil, it is likely found in the form of association colloids stabilized by surface active compounds.

Table 10 Peroxide value in retail vegetable oils

	Peroxide Value	
Oil	(Meq/kg)	(mmol/kg)
Canola[a]	5.00	2.50
Coconut[a]	4.97	2.48
Corn[b]	3.93	1.96
Olive[b]	8.50	4.25
Extra virgin olive[a]	14.92	7.46
Peanut[a]	6.99	3.50
Palm kernel[b]	0.75	0.38
Palm olein[a]	7.99	4.00
Rapeseed[a]	3.97	1.98
Rice bran[a]	8.00	4.00
Safflower[a]	4.96	2.48
Sesame[b]	1.13	0.56
Soybean[b]	2.39	1.20
Sunflower[a]	3.99	2.00

[a]Adapted from (Gan et al., 2005).
[b]Adapted from (Tan et al., 2002).

Lipid Oxidation in Colloidal Dispersions

Many food lipids exist as association colloids, e.g. milk, mayonnaise, dressings, dips, sauces, beverages, margarine, butter, ice cream, etc. These dispersions consists of two immiscible liquids, usually oil and water, in which one is dispersed in the other in the form of small spherical droplets. These emulsions are thermodynamically unstable due to the positive free energy needed to increase the surface area between oil and water phases (Dickinson, 1992). Emulsifiers must be added prior to homogenization to form emulsions that are kinetically stable for a reasonable period of time. Emulsifiers are surface-active molecules that absorb to the surface of freshly formed droplets during homogenization, forming a protective membrane that prevents the droplets from coming close enough together to aggregate. An association colloid consisting of oil droplets dispersed in an aqueous phase is called an oil-in-water emulsion (e.g. milk, mayonnaise, and salad dressing) while water droplets dispersed in an oil phase is called a water-in-oil emulsion (e.g. butter and margarine).

Lipid oxidation reactions are dependent on the chemical reactivity of numerous components including reactive oxygen species, prooxidants, and antioxidants. However, research over the past few decades has shown that the physical properties of food systems are extremely important to the chemistry of lipid oxidation (Abdalla and Roozen, 1999; Frankel et al., 1994; Fritsch, 1994; Halliwell et al., 1995; McClements and Decker, 2000; Naz et al., 2005). The impact of physical properties on lipid oxidation chemistry has been best highlighted by research in oil-in-water emulsions (see below).

Table 11 Water content in freshly-opened, commercially available vegetable oils as determined by Karl Fischer Coulometer

	Water Content		
Oil	(ppm)	% w/w	mmol/kg
Sunflower	203 ± 1	0.02	11
Canola	236 ± 1	0.02	13
Peanut	221 ± 2	0.02	12
Sesame	197 ± 1	0.02	11
Extra Virgin Olive	865 ± 3	0.09	48

Impact of Physical Properties on Lipid Oxidation in Oil-in-Water Emulsions

The most extensive research on the impact of physical properties on lipid oxidation has been conducted in oil-in-water emulsions. This is because numerous methods are available to characterize the physical properties and location of compounds in oil-in-water emulsions. In general, an oil-in-water emulsion is thought to consist of three regions: the interior of the lipid droplet, the continuous/aqueous phase, and the interfacial layer. The interfacial layer is a narrow region surrounding each lipid droplet that consists of a mixture of oil, water, and emulsifier molecules, as well as any other surface active compounds that may be present in the systems. Normally, the interfacial layer has a thickness of a few nanometers, but often makes up a significant proportion of the total number of molecules present due to the large surface area of the droplets (Dickinson and McClements, 1995). The various molecules (e.g. prooxidants and antioxidants) in an emulsion partition themselves between the three different regions according to their solubility characteristics and surface activity (Hiemenz and Rajagopalan, 1997). Non-polar molecules are located predominantly in the oil droplet, polar molecules in the aqueous phase, and surface active molecules at the interface. The precise molecular environment of a molecule has a significant effect on its chemical reactivity (Wedzicha, 1988; Wang et al., 1999). The orientation of the lipid molecules at the interface region may also be another important factor, whether they are parallel or perpendicular to the interface (Hiemenz and Rajagopalan, 1997), since this will affect their accessibility to water soluble prooxidants or antioxidants. As oxidation proceeds the fatty acids become more polar because of addition of oxygen and thus the physical properties of the emulsion can change. Thus, the emulsion may become more or less susceptible to oxidation depending on the types and number of molecules present in their new environment.

Both lipid hydroperoxides and transition metals exist in foods. Transition metals can react with lipid hydroperoxides to produce high energy free radicals (e.g. alkoxyl radicals) that can promote the oxidation of unsaturated fatty acids. The oxidative stability of many food lipids is dependent on both hydroperoxide and metal concentrations. It has been observed that metals are not as strongly prooxidative in hydroperoxide-free lipids, and the hydroperoxides are relatively stable in the absence of metals and light (Decker and McClements, 2001). The importance of prooxidant metals on the oxidative stability of oil-in-water emulsions can be seen in Tween 20-stabilized salmon oil-in-water emulsions where lipid oxidation was strongly inhibited by both EDTA (50 μM) and transferrin (31 μM) even though no exogenous metals were added to the system (Decker and McClements, 2001). The ability of transferrin to decrease lipid oxidation rates indicates that iron was the major prooxidative metal since transferrin has a strong preference for the chelation of iron over other transition metals. In addition to chelating metals to decrease reactivity, the prooxidant activity of metals can also be reduced by changing their physical location. Both proteins and EDTA can bind and remove iron from the surface and lipid core of oil-in-water emulsions droplets. The ability of proteins and chelators to partition iron away from lipids decreases iron and lipid hydroperoxides interactions and thus lipid oxidation rates (Tong et al., 2000a, b; Cho et al., 2003; Hu et al., 2003a, b; 2004a, b).

The ability of iron to promote lipid oxidation in oil-in-water emulsions is also influenced by the net charge of the emulsion droplets interface. In the case of a corn oil-in-water emulsion stabilized with anionic (SDS), cationic (DTAB) or nonionic (Brij 35) surfactants, oxidation rates were highest for negatively charged droplets, intermediate for uncharged droplets and lowest for positively charged droplets (Mancusco et al., 1999). The observed alterations in oxidation rates are likely due to increased iron-lipid hydroperoxide interactions when positively charged iron ions were electrostatically attracted to the surface of the negatively charged emulsion droplets thus increasing metal-lipid interactions. Conversely, lipid oxidation was retarded when the iron ions were electrostatically repelled from the surface of the positively charged droplets. Similar results can also be observed in protein-stabilized emulsions where lipid oxidation rates were significantly lower when the lipid droplets were cationic at pH values below the pI of the emulsifying proteins (Donnelly et al., 1998; Hu, 2003b).

Another potential physical property that could decrease iron-lipid hydroperoxide interactions in association colloids is the presence of thick barrier at the lipid droplet interface. The ability of iron to promote cumene hydroperoxide decomposition as well as the oxidation of salmon oil was lower in emulsion droplets stabilized by Brij 700 than Brij 76 (Silvestre et al., 2000). These two surfactants have the same hydrophobic tail group length ($CH_3(CH_2)_{17}-$), but different length polar head groups with Brij 700 containing 100 compared to Brij 76's 10 oxyethylene groups. Increasing surfactant hydrophobic tail group size can also decrease lipid oxidation as can be seen in salmon oil-in-water emulsions stabilized by polyoxyethylene 10 lauryl ether (Brij-lauryl, C12 tail group) or polyoxyethylene 10 stearyl ether (Brij-stearyl, C18 tail group) (Chaiyasit et al., 2000). Similarly, the oxidative stability of oil-in-water emulsions stabilized by proteins also seems to be influenced by the thickness of the interfacial membrane. Casein-stabilized oil-in-water emulsion droplets should be less effective at electrostatically repelling iron at pH 3.0 (surface charge = +29.9 mV) than droplets stabilized with whey protein isolate (surface charge = +55.9 mV). However, casein forms a thick interfacial layer of up to 10 nm around dispersed oil droplets compared to 1–2 nm for whey proteins (Dickinson and McClements, 1995; Dalgleish et al., 1995). This thick emulsion droplet interfacial membrane may help explain why emulsions stabilized by casein are more oxidatively stable than emulsions stabilized by whey protein isolate (Hu et al., 2003a).

The impact of physical properties on lipid oxidation in oil-in-water emulsions can also be seen on the effectiveness of primary antioxidants (Frankel, 1998). For example, hydrophilic antioxidants have been shown to be less effective in oil-in-water emulsions than lipophilic antioxidants in numerous studies

(Porter, 1993; Frankel, 1998, 1999; Frankel et al., 1994; 1996a, b; 1997; Huang et al., 1996a, b; Huang and Frankel, 1997; Abdalla and Roozen, 1999; Hopia et al., 1996). The observed differences in the effectiveness of antioxidants of varying polarity in oil-in-water emulsions are thought to be due to the physical location of the antioxidants as described by "antioxidant polar paradox." Lipophilic antioxidants may be retained in the oil droplet where they can scavenge free radicals whereas hydrophilic antioxidants partition into the aqueous phase where they are ineffective (Porter, 1993; Frankel, 1998). However, more research is needed to fully elucidate how physical properties impact the chemical reactivity of antioxidants.

Table 12 Surface and interfacial tension of commercial vegetable oils as determined by Du Noüy Ring method at 30°C after 24 hours of equilibration

Oil	Surface Tension (mN/m)	Interfacial Tension (mN/m)
Sunflower	31.8 ± 0.1	24.6 ± 0.2
Canola	31.8 ± 0.1	18.6 ± 0.4
Peanut	31.6 ± 0.1	17.2 ± 0.1
Sesame	31.9 ± 0.0	24.4 ± 0.2
Extra Virgin Olive	31.6 ± 0.1	13.6 ± 0.2
Diacylglycerol	31.5 ± 0.1	14.8 ± 0.0
Corn Oil	31.8 ± 0.1	16.4 ± 0.0
Stripped Corn Oil	31.8 ± 0.1	29.6 ± 0.0
Oxidized Stripped Corn Oil	31.6 ± 0.1	19.5 ± 0.1

Lipid Oxidation in Bulk Oils

The recent requirement to label the *trans* fatty acids content of foods is pressuring food companies to abandon the use of hydrogenated fats. Therefore, many companies are attempting to use new lipid sources. Due to nutritional concerns, companies would like these new lipid sources to have similar levels of saturated fatty acids as the original hydrogenated fats. This generally results in an increase in unsaturated fatty acid levels in the food. Increasing levels of unsaturated fatty acids in foods increase lipid oxidation rates and thus decrease shelf-life unless antioxidant technologies are employed. Unfortunately, the number of antioxidants available to food manufacturers is limited and the approval of new antioxidants is unlikely due to economic barriers in obtaining government approval for new food additives. Thus, a major challenge for the food industry is to use existing antioxidants more efficiently. One way to use existing antioxidants more efficiently would be to manipulate their physical location to the sites where fatty acid oxidation is prevalent. In order to accomplish this goal, a better understanding of the physical location of oxidation chemistry in bulk oil is needed.

Does Lipid Oxidation Occur within Association Colloids in Bulk Oil?

Studies on lipid oxidation in bulk oils have been conducted for over 50 years. This research was instrumental in developing the basic knowledge of lipid oxidation chemistry. In many of these studies on lipid oxidation in bulk oil, the oil matrix was considered to be a homogeneous liquid phase. However, bulk oil contains numerous minor components that are amphiphilic, such as mono- and diacylglycerols, phospholipids, sterols, free fatty acids, and polar amphiphilic products arising from lipid oxidation, such as lipid hydroperoxides, aldehydes, ketones, and epoxides. The presence of amphiphilic compounds in commercial bulk oil are observed when the oils are stripped (e.g. alumina (Al_2O_3)) of their minor components, and the resulting stripped oil has a higher interfacial tension than the original refined oil (Table 12). The concentration and type of surface active compounds vary in different commercial bulk oil sources, as is evidenced by variations in interfacial tension from 14 to 25 mN/m (Table 12). These variations in interfacial tension among different oil sources are likely due to differences in minor components such as free fatty acids (Table 3). These surface active components in the presence of the small quantities of water in oil would tend to associate in the lipid media, forming association colloids such as reverse micelles and lamellar structures.

Reverse micelles are dynamic, nanoscopic, roughly spherical aggregates containing a hydrophilic core stabilized by a monolayer of surfactant molecules with the polar head groups of the surfactant extending into the water core and the aliphatic chains extending into the lipid medium (Fig. 5). Reverse micelles are efficient nano-reactors that allow increased interactions between lipid- and water-soluble components, and can greatly alter chemical reaction rates (Ghosh and Tiwary, 2001). Molecules such as phospholipids, especially in combination with sterols, can form bilayer or lamellar structures which vary greatly in shape and size. Reverse micelles and lamellar structures in bulk oils are typically formed by surfactants with low hydrophilic-lipophilic balances (HLB). Examples of surfactants with low HLB values in bulk oil include free fatty acids (HLB ≈1.0), diacylglyerols (≈1.8), and monacylglycerols (≈3.4–3.8) (McClements, 2004). Monoacylglycerols are known to form reverse micelles in triacylglycerol oils (Gulik-Krzywicki and Larsson, 1984). Phospholipids have intermediate HLB values (≈8, McClements, 2004), which may explain why they form lamellar structures as well as reverse micelles (Gupta et al., 2001). Since food oils contain a large variety of surface active components, it is likely that the association colloids are compositionally and structurally complex.

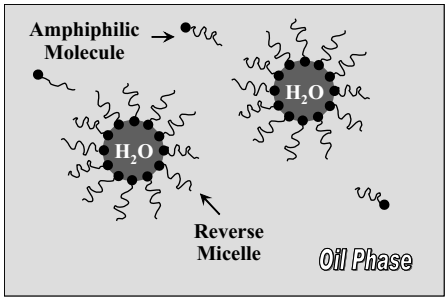


Figure 5 Schematic showing water core in a reverse micelle

Table 13 Influence of antioxidants on surface and interfacial tension of hexadecane as determined by Du Noüy Ring method at 30°C after 24 hours of equilibration

Antioxidant	Concentration (mmol/kg)	Surface Tension (mN/m)	Interfacial Tension (mN/m)
Control	0.0	26.0 ± 0.1	43.3 ± 0.4
α-Tocopherol	1.0	26.0 ± 0.1	41.5 ± 0.0
	2.5	26.0 ± 0.1	38.4 ± 0.4
	5.0	26.0 ± 0.1	35.0 ± 0.2
δ-Tocopherol	1.0	26.0 ± 0.1	37.7 ± 0.3
	2.5	26.0 ± 0.1	34.0 ± 0.0
	5.0	26.0 ± 0.1	27.9 ± 0.4
BHT	1.0	26.0 ± 0.1	43.7 ± 0.2
(butylated hydroxytoluene)	2.5	26.0 ± 0.1	43.6 ± 0.0
	5.0	26.0 ± 0.1	43.7 ± 0.0
3, 5 di-tert-4-hydroxy	1.0	26.0 ± 0.1	42.6 ± 0.3
benzyl alcohol	2.5	26.0 ± 0.1	40.7 ± 0.0
	5.0	26.0 ± 0.1	37.5 ± 0.4
TBHQ	0.25	26.0 ± 0.1	43.0 ± 0.1
(tertiary butyl hydroquinone)	0.5	26.0 ± 0.1	41.6 ± 0.2
	1.0	26.0 ± 0.1	40.0 ± 0.0
Trolox	0.2	26.0 ± 0.1	34.8 ± 0.0
	0.5	26.0 ± 0.1	30.4 ± 0.1
	1.0	26.0 ± 0.1	28.0 ± 0.1
	2.5	26.0 ± 0.1	–
Propyl gallate	1.0	26.0 ± 0.1	34.6 ± 0.1
	2.5	26.0 ± 0.1	–

– = Data not measured.

Research in our lab using X-ray diffraction has shown that lamellar structures exist in commercially available algal oil (data not shown).

There is a considerable body of evidence that supports the hypothesis that association colloids are the site of lipid oxidation in bulk oils. Numerous studies have supported the notion of the "antioxidant polar paradox," which states that hydrophilic antioxidants are more effective than lipophilic antioxidants in bulk oils. Several researchers have suggested that the increased effectiveness of hydrophilic antioxidants in bulk oils is due to their ability to migrate and concentrate at the oil-air interface where oxidation is prevalent. However, air is less polar than oil (dielectric constant of air is 1.0 compared to approximately 3.0 for food oils, CRC Press, 1982). Because air is less polar than oil, there would not be a major driving force for polar antioxidants to migrate to the air-oil interface and thus they would not be more likely to concentrate at the air-oil interface than hydrophobic antioxidants. This can be seen in Table 13 which shows that most antioxidants are unable to decrease surface tension of hexadecane meaning that the antioxidants do not concentrate at the air-oil-interface. In addition, Table 14 shows that the concentrations of antioxidants at the air-oil interface (collected by isolation of the top 1.5 mm of solidified oil and analysis of antioxidant concentrations) is not greater than the antioxidant concentrations in the bulk oil. While antioxidants do not seem to accumulate at the air-lipid interface, they are able to accumulate at water-lipid interfaces, as can be seen by their ability to decrease interfacial tension (Table 13). Therefore, it is more likely that surface active, hydrophilic antioxidants in bulk oil accumulate at the interface of association colloids (e.g. reverse micelles and lamellar structures). The reason that hydrophilic antioxidants are more effective in bulk oil could be due to their increased partitioning at the water-oil interface of association colloids where oxidative reactions could be more prevalent.

If the mechanism of lipid oxidation in oil-in-water emulsions is similar to bulk oils, then oxidation would be at least partially promoted by metal-catalyzed decomposition of lipid hydroperoxides. This hypothesis is supported by the fact that the metal chelator, citric acid, is an effective antioxidant in bulk oils. Since lipid hydroperoxides are surface active, they would likely migrate to the water-lipid interface of the association colloids where they could interact with metals in the water. Free fatty acids are well established as prooxidants in bulk oils. Free fatty acids can form complexes with transition metals and increase metal solubility (Frankel, 1998). In oil-in-water emulsions stabilized by emulsifiers such as SDS, iron will bind to the anionic surface of the lipid droplet, resulting in the acceleration of lipid hydroperoxide decomposition and fatty acid oxidation (Mancuso et al., 1999; Mei et al., 1998a, b). A similar situation could occur in bulk oil as free fatty acids migrate to the

Table 14 Partitioning of antioxidant at the air-oil interface collected by isolation of the top 1.5 mm of quick freezing hexadecane at −80°C after equilibration of antioxidant in oil for 24 hours at room temperature

	Antioxidant concentration (mmol/kg hexadecane)	
Antioxidant	Top layer	Bottom layer
δ-Tocopherol	0.171 ± 0.001	0.174 ± 0.001
Trolox	0.190 ± 0.001	0.200 ± 0.001

water-lipid interface where it creates an anionic surface that attracts transition metals and increases metal-lipid hydroperoxide interactions.

Another surface active component in bulk oil that impacts lipid oxidation is phospholipids. Phospholipids are known to increase the antioxidant activity of tocopherols. Koga and Terao (1995) observed that the presence of phospholipid enhanced the antioxidant activity of α-tocopherol in model bulk oil systems containing a trace amount of water (1% v/v). In the presence of 2,2′-azobis(2-amidinopropyl) dihydrochloride (AAPH), a water-soluble azo compound that generates free radicals in the aqueous phase of the association colloids, the presence of phospholipid increased the degradation of α-tocopherol more than in the absence of phospholipids. Degradation of α-tocopherol by the water-soluble free radicals increased as the phospholipid's hydrocarbon tail group size was increased, and thus the ability of the phospholipid to form association colloids was increased. The investigators suggested that the high rate of α-tocopherol consumption in the presence of phospholipids by water-soluble free radicals was due to the enhanced accessibility of α-tocopherol to the site of greatest oxidative stress. Thus, it is thought that surface active molecules, such as phospholipids, induce the concentration of antioxidants at the surface of association colloids, thereby increasing interactions between antioxidants and prooxidants by physically moving them within close proximity.

Further evidence that the observed increased antioxidant activity of α-tocopherol in the presence of phospholipids is a consequence of enhanced accessibility of the α-tocopherol to the site of greatest oxidative stress was obtained by comparing lipid oxidation and antioxidant loss rates in systems containing either water- or the lipid-soluble free radical generators. Unlike the water-soluble free radical generator, phospholipids did not enhance the interactions between α-tocopherol and lipid-soluble free radicals. These data suggest that phospholipids exert no observable effect on the action of α-tocopherol when the radical chain reaction is initiated in the lipid phase, which is consistent with the hypothesis that α-tocopherol is positioned within association colloids (Koga and Terao, 1995). Koga and Terao (1994) also found that the antioxidant activity of α-tocopherol could be increased when it was conjugated to the polar head group of phosphatidylcholine [1,2-diacyl-*sn*-glycero-3-phospho-2′-(hydroxyethyl)-2′, 5′, 7′, 8′-tetramethyl-6′hydroxychroman]. This increase in activity was postulated to be due to the increased partitioning of the reactive portion of α-tocopherol into the water phase of the association colloids in bulk oil (Koga and Terao, 1994).

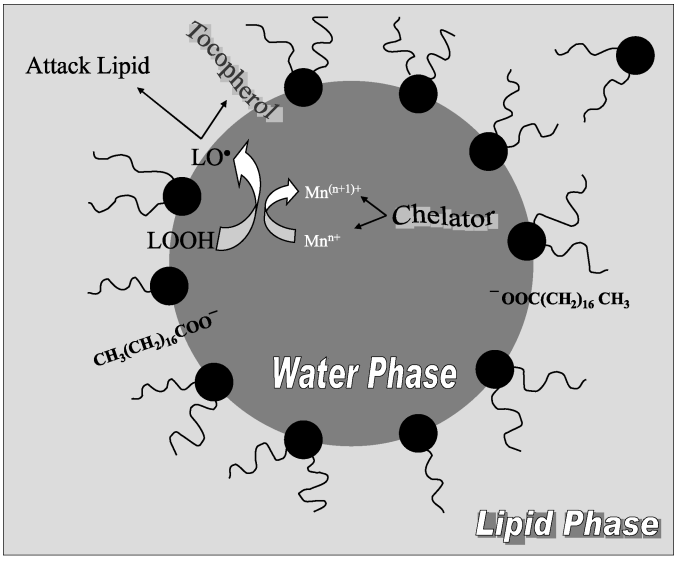
The role of water in bulk lipid oxidation has not been clearly established. The saturation level of water in edible oils is approximately 0.8%, however commercial oils should contain $\leq$0.3% water with most oils having 0.02–0.05% (Table 11). The water activity in foods is known to affect the rate at which lipid oxidation reactions occur (Frankel, 1998). In many foods, lipid oxidation rates are slowest at water activities of 0.2–0.4 with oxidation rates increasing above or below this water activity range. The impact of water activity on lipid oxidation rates has been postulated to be due to its effect on metal reactivity and lipid hydroperoxide stability. If association colloids are the site of oxidative reactions in bulk oil, then the physical properties of the dispersed water (e.g. water activity) could impact the kinetics of lipid oxidation. In a model system containing heptane and the surfactant sodium diisooctyl sulfosuccinate, NMR showed that small amounts of water were highly immobilized due to strong ion-dipole interactions between the water and the hydrophilic head group of the surfactant. Upon addition of water, water mobility increase until it was similar to pure water (Wong et al., 1977). The results show that water mobility can be altered in reverse micelles suggesting that the water activity of dispersed water in edible oils could be influenced by the composition of the oil, a factor that might influence lipid oxidation rates.

In general, we would expect the rate and mechanism of lipid oxidation in edible oils that contain association colloids to depend on:

- The total amounts of substrates, prooxidants, and antioxidants that can be concentrated at the water-lipid interface of the association colloids. This will depend on the amount of surface active components available to form association colloids (e.g. free fatty acids, phospholipids, and antioxidants).
- The location and orientation of reactants in association colloids. For instance, can lipid hydroperoxides extend into the water core where they interact with metals or is the interface of the association colloids anionic such that prooxidant metals are attracted and brought in close proximity with oxidizable lipids.
- Temperature which will change the structure of the association colloids as well as alter lipid oxidation rates.
- Water content and mobility which could influence the size and number of association colloids as well as the activity of reactants at the water-lipid interface or in the water core.
- The concentration and reactivity of prooxidants and antioxidants in the water inner core of the association colloids.
- Dimension of inner water core which will determine the type of molecule that can be incorporated into the association colloids.

CONCLUSIONS

Due to recent requirement to label the *trans* fatty acids content of foods and continuing evidence that saturated fatty acids are unhealthy, food manufacturers are increasing the levels of unsaturated fatty acid in their products, a process that will increase lipid oxidation. Unfortunately, the number of antioxidants available to food manufacturers to control oxidative rancidity is limited and the approval of new antioxidants is unlikely due to economic barriers in obtaining government approval for new food additives. Thus, a major challenge for the food industry is to use existing antioxidants more efficiently by delivering them to the physical location where fatty acid oxidation is prevalent.



LOOH = Lipid hydroperoxide
LO• = Alkoxyl radical
Mn^{n+}, $Mn^{(n+1)+}$ = Transition metals in reduced and oxidized states
= Amphiphilic molecule e.g. phospholipid
$CH3(CH2)_{16}COO^-$ = Fatty acid e.g. stearic acid

Figure 6 Proposed mechanisms of lipid oxidation in bulk oil containing reverse micelles

In order to accomplish this goal, a better understanding of the physical location of oxidation chemistry in bulk oil is needed. Since bulk oils contain surface active components and small quantities of water, it is likely that bulk oils contain association colloids such as reverse micelles and lamellar structures. The interface of association colloids is a likely site of oxidation reactions since many prooxidant and antioxidants are also surface active and thus would concentrate at the water-lipid interface (Fig. 6). More research is needed to better understand if the interface of association colloids is involved in the oxidation of bulk oils so that novel antioxidant technologies can be developed to better inhibit oxidative rancidity.

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