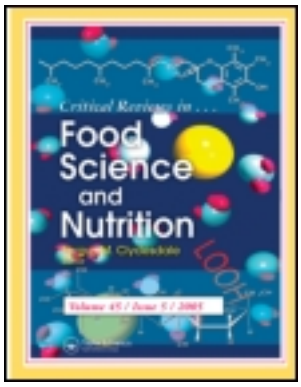

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Minor Components in Food Oils: A Critical Review of their Roles on Lipid Oxidation Chemistry in Bulk Oils and Emulsions

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Food oils are primarily composed of triacylglycerols (TAG), but they may also contain a variety of other minor constituents that influence their physical and chemical properties, including diacylglycerols (DAG), monoacylglycerols (MAG), free fatty acids (FFA), phospholipids (PLs), water, and minerals. This article reviews recent research on the impact of these minor components on lipid oxidation in bulk oils and oil-in-water emulsions. In particular, it highlights the origin of these minor components, the influence of oil refining on the type and concentration of minor components present, and potential physicochemical mechanisms by which these minor components impact lipid oxidation in bulk oils and emulsions. This knowledge is crucial for designing food, pharmaceutical, personal care, and other products with improved stability to lipid oxidation.

Keywords Lipid oxidation, minor components, association colloids, bulk oil, emulsions

INTRODUCTION

Food oils from a wide variety of sources are important to human health and the food industry since they are important components in a large variety of food products and since they are an important cooking medium (Salas et al., 2000). However, most oils are susceptible to oxidation as a result of their unsaturated fatty acids (Laguerre et al., 2007). The products formed in oxidized oil include numerous free radical species, primary oxidation products like lipid hydroperoxides and secondary oxidation products like aldehydes, hydrocarbons, ketones, and epoxides that negatively impact aroma (Frankel, 1980). In addition, lipid oxidation can produce toxic products that can negatively impact biological tissues. For instance, linoleic acid hydroperoxides are toxic to wild type *Saccharomyces cerevisiae* at a low levels (0.2 μM) (Evans et al., 1998). Oxidized palm oil has been shown to induce reproductive toxicity and organotoxicity of the kidneys, lungs, livers, and heart of rats (Ebong et al., 1999). High intake of a mixture of oxidized lard and cod liver oil caused impaired fertility in female rats and an increased incidence of morphologically abnormal spermatozoa in male rats (Zidkova et al., 2004). Oxidized lard, soybean oil, and particularly sardine oil increased spontaneous liver tumor development and the formation of 8-hydroxy-deoxyguanosine (8-OH-dG) in the liver DNA of mice (Ichinose et al., 2004). These results along with others suggest that the consumption of oxidized lipids should be avoided whenever possible.

How to prevent or retard lipid oxidation in food oil is a major focus of lipid research. In the past six decades, a lot of attention has been drawn on finding effective ways to extend the shelf life of oils. The addition of antioxidants is one effective way to retard lipid oxidation (Shahidi and Zhong, 2011). The most widely used antioxidants include free radical scavengers (also known as chain-breaking antioxidants) that inactivate free radicals formed in the initiation and propagation steps of lipid oxidation, and metal chelators. A number of natural or synthetic phenols can interact with hydroperoxyl (LOO•) and alkoxyl (LO•) radicals, producing hydroperoxides and alcohols, respectively, and low energy antioxidant radicals that do not readily promote the oxidation of unsaturated fatty acids (Frankel, 1980).

Among the free radical scavenging antioxidants, synthetic phenolic antioxidants, for example, butylated hydroxyanisole

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(BHA), butylated hydroxytoluene (BHT), and tert-Butylhydroquinone (TBHQ) normally exhibit higher antioxidative activity than non-synthetic antioxidants. However, the utilization of many effective synthetic antioxidants is being limited by consumer concerns of their negative impact on health. Research showed that large doses of both BHA and BHT (500 mg/kg body weight/day) result in certain changes in pathological (e.g., hypertrophy of the liver in rodents), enzyme (e.g., decrease in glucose 6-phosphatase and acid phosphatase), and blood lipid (e.g., increase in serum cholesterol and phospholipids) in both rodents and monkeys, and in some cases BHT has been reported to have teratogenic and carcinogenic effects in rodents (Branen, 1975).

Over the past several decades, food scientists have been mostly unsuccessful in their search for natural antioxidants which could possess similar antioxidant activity as synthetic antioxidants (Shahidi and Zhong, 2010b). The most common natural antioxidants in foods are tocopherol and rosemary extracts. Interestingly, rosemary extracts are not actually approved by the FDA for use as an antioxidant but instead as a flavor extract (FDA 21 CFR 182. (FDA, 2011)). Since the number of antioxidant options has not significantly increased in the past 30 years and in fact may be decreasing since food companies are reluctant to utilize synthetic antioxidants, new approaches are needed to fulfill the goal of retarding oil and foods from oxidation. The development of novel approaches to inhibiting lipid oxidation is highly reliant on our understanding of lipid oxidation mechanisms in variable lipid systems.

The mechanism of lipid oxidation in bulk oil has been studied for many decades (Decker, 2010). However, research has revealed that this reaction is extremely complex being a balance of the activity of numerous prooxidative and antioxidative factors (Decker, 2010). On top of these chemical effects, lipid oxidation is also impacted by physical properties of food and food components that influence factors such as partitioning of antioxidants, diffusion of oxygen, and interaction of prooxidants with lipid substrates. The impact of physical properties on lipid oxidation can be seen in heterogeneous food systems such as emulsions where the characteristics of the emulsion droplet interface are an important determinant in oxidative stability (McClements and Decker, 2000). Even bulk oils, which are often assumed to be a homogenous liquid, have numerous physical structures that impact lipid oxidation. This is because refined bulk oils contain numerous minor components that are amphiphilic, such as monoacylglycerols (MAG), diacylglycerols (DAG), phospholipids, sterols, free fatty acids (FFA), and polar products arising from lipid oxidation, such as lipid hydroperoxides, aldehydes, ketones, and epoxides. These surface active compounds in combination with water can form physical structures known as association colloids that can physically impact lipid oxidation (Chaiyasit et al., 2007a).

In this review, the source and general concentrations of minor components in bulk oil will be summarized. The impact of minor components on lipid oxidation in bulk oil and oil-in-water emulsions will be discussed. By better understanding how these minor components impact lipid oxidation, novel antioxidant strategies can be developed by using currently approved and available antioxidants and other food additives.

OIL REFINING

Crude vegetable oils predominantly contain triacylglycerols and small amounts of minor components that naturally occur in the plant component of their origin, such as proteins, free fatty acids, phospholipids, metals, tocopherols, pigments, and sterols. The effective removal of some minor components without sacrificing the loss of antioxidants is necessary to achieve a finished oil quality with acceptable standards for flavor, appearance, and stability. The oil refining process which includes degumming, neutralization, bleaching, and deodorization is therefore performed to produce oils suitable for use by the food industry and the consumer (Fig. 1).

Oil seed extraction will produce a crude oil that contains lipids such as phospholipids and sterols in addition to triacylglycerols. However, the extraction process will also produce conditions where triacylglycerols can react with enzymes such as lipase and lipoxygenase to form hydrolytic products of triacylglycerols (e.g., monoacylglycerols, diacylglycerols, and free fatty acids) and lipid oxidation products such as hydroperoxides. Oil refining is performed to reduce the concentration of these minor components as they can negatively impact the quality of the oil. For instance, caustic alkali is used to remove free

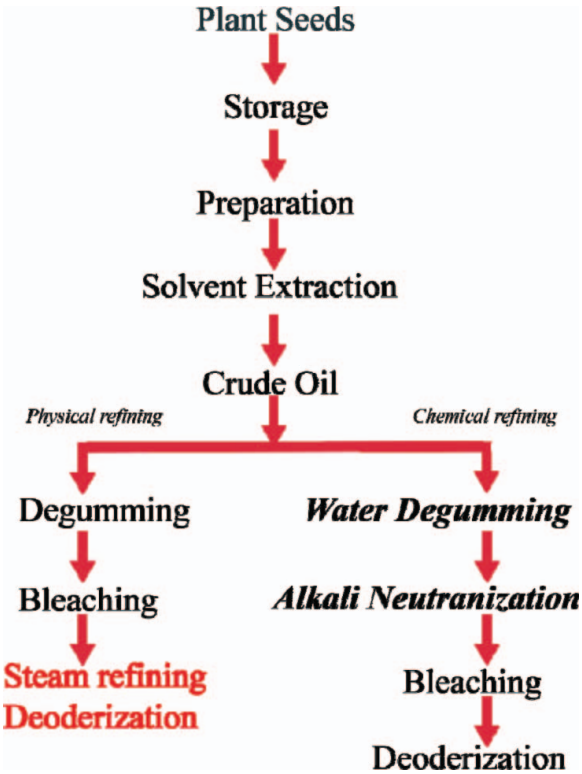

Figure 1 The schematic of oil refining process. (color figure available online.)

fatty acids in neutralization step since free fatty acids cause foaming and decreases the smoke point of oils (Bhattacharyya and Bhattacharyya, 1987). Phosphoric or citric acid is used to aid the removal of nonhydratale and hydratable phospholipids during the degumming step since phospholipids cause cloudiness and can form brown colors during heating (Smiles et al., 1988). Bleaching is performed with activated bleaching earth at relatively high temperatures around 100°C to decrease the concentration of pigments (e.g., chlorophyll), trace metals, and other polar compounds (e.g., phosphorus) that can accelerate lipid oxidation or damage flavor in refined oil. Finally, since the harsh conditions of these steps can produce off-flavors due to oxidation and since the oil can contain pesticides from the original oilseeds, the oil undergoes a deodorization step at high temperatures (200–260°C) under reduced pressure. Deodorization not only removes volatile off-flavors and pesticides but also decomposes lipid hydroperoxides, a potential lipid oxidation substrate. Overall, refining is designed to remove minor components that negatively impact oil quality. However, steps such as deodorization can also remove factors that improve oil quality such as tocopherols (lose one-third of tocopherols) and can cause the formation of *trans* fatty acids (e.g., 15-fold higher in deodorized corn oil than crude oil). While refining significantly decreases the concentration of the minor components, such as free fatty acid that impact the organoleptic quality of oil, one should realize that even at these lower concentrations, minor components can still impact oil chemistry such as lipid oxidation.

MINOR COMPONENTS IN BULK OIL

Free Fatty Acid

The reaction between water and triacylglycerols (TAG) results in the formation of free fatty acid (FFA) and diacylglycerol (DAG). TAG hydrolysis is accelerated by lipases, extremes in pH, and heat (Ohlson, 1976). The presence of FFA produces undesirable flavors, foaming during mixing and heating and causes a decrease in the smoke/flash point of oil thus reducing the maximum temperature to which they can be heated. FFAs in crude vegetable oils will increase with the age of the oilseeds and can be abnormally high if the oilseeds have been damaged or improperly stored. This is due to damage to cells in the seeds allowing lipase to interact with TAG. For instance, in oilseeds stored from 0 to 47 days, the FFA content in the extracted crude oil increased from 0.88 to 1.80 wt% (Lanser et al., 1991). Recent research from de Alencar and coworkers (2010) showed that FFA concentrations will also increase during crude oil storage.

There are several factors which can impact FFA concentrations in crude oils and during the refining process, such as the initial FFA content, water content, and processing temperatures, oil type, etc. The presence of FFA can catalyze the further hydrolysis of TAG, thereby increasing the total FFA concentration in oil. Some earlier results showed that the rate of TAG hydrolysis is proportional to the initial level of FFA (Gunstone and Padley, 1997). Another important factor is the water concentration since this is one of the required substrates for the hydrolytic reaction. Sarkadi (1959) showed that increasing of water content as a result of steam deodorization of peanut oil at 180°C increased FFA formation. Considering that both FFA and water are important factors in TAG hydrolysis, the following equation was used to estimate the formation of FFA over time (t) in the bulk oils containing water (Gunstone and Padley, 1997).

$$\frac{d[\mathrm{FFA}]}{dt} = k' \frac{[\mathrm{H_2O}]}{[\mathrm{H_2O}]_{\mathrm{Sat}}} [\mathrm{FFA}] \quad (1)$$

Here, k' is the rate constant, [FFA] is the free fatty acid concentration, $[H_2O]$ is the water concentration, and $[H_2O]_{Sat}$ is the water concentration at saturation.

The FFA content in deodorized food oils is required to less than 0.05% in the United States (Alimentarius, 1999; O'Brien, 2008). FFA are typically removed from oils by chemical neutralization which normally involves the conventional alkali (sodium hydroxide) neutralization process, precipitating the FFA as soap stock, and being removed by mechanical separation from the oil. Recently, some oil refineries are using physical refining. Physical refining is a high temperature, vacuum process that can remove both FFA and phospholipids at the same time effectively combining the neutralization and degumming steps. The choice of physical or chemical refining is highly correlated to the initial FFA concentration of the crude oil. When the FFA content is lower than 2.5% in the crude oil, physical refining can be employed without the neutralization step. In some cases physical refining is used on oils with >2.5% FFA but neutralization must be performed first (Decker, 2010). A major limitation of physical refining is that the high temperatures required can cause the formation of trans fatty acids (Maza et al., 1992).

FFA are produced at almost each step of refining since they often involve high temperatures and water (Farhoosh et al., 2009). Despite this, FFA concentrations as low as 0.005 wt% can be obtained (Ceriani and Meirelles, 2004). However, one should realize that these FFA concentrations cannot be maintained as even low FFA concentration can promote TAG hydrolysis. Therefore, the FFA content of retail bottled edible oil is higher than the concentrations measured immediately after refining process. For example, retail canola oil has a FFA concentration of approximately 0.1 wt%. Finally, free fatty acid concentrations can increase in refined oils during operations such as frying where the oils are exposed to high temperatures and water (Fritsch, 1981).

Table 1 Concentration of MAG and DAG in various oils as a function of refining (Gee, 2007; Sleeter, 1981)

Refining	Soybean oil		Palm oil	
Step	MAG (%)	DAG (%)	MAG (%)	DAG (%)
Crude oil	0.11	1.10	0.26	6.60
Degummed	0.10	1.44	0.17	6.70
Bleached	0.06	1.25	0.17	6.70
Deodorized	0.07	1.05	0.08	6.90

Monoacylglycerols and Diacylglycerols

Monoacylglycerols (MAG) are monoesters of glycerol in which one of the hydroxyl groups is esterified with fatty acids. There are two isomeric forms of MAG, that is, 1-MAG and 2-MAG, depending on the position of the ester bond on the glycerol group. Diacylglycerols (DAG) are esters of the glycerol in which two of the hydroxyl groups are esterified with fatty acids. They can exist in three structural isomers namely, 1,2-DAG, 2,3-DAG, and 1,3-DAG (Goñi and Alonso, 1999). DAG is a common precursor for the synthesis of both TAG and phospholipids in the oilseeds and oil bodies (Goñi and Alonso, 1999). Therefore, DAG that exists naturally in crude vegetable oils can be derived from the incomplete biosynthesis of TAG and phospholipids. Knowledge of the amounts of DAG naturally found in oilseeds is scare due to the lack of in situ measurements.

MAG and DAG are also formed from the partial hydrolysis of TAG (Coleman and Lee, 2004). The amount of DAG and MAG reported in the crude oil are therefore composed of two parts, inherent concentrations in the seeds and those formed after crushing the seeds and during refining. The formation of DAG and MAG depends on oilseeds storage conditions, temperature, and moisture as was discussed previously for FFA.

Table 1 lists the amount of DAG and MAG in crude and refined soybean oil and palm oil. After bleaching and deodorization, MAG concentrations decrease while DAG concentrations remain similar to crude oil or even increase (Gee, 2007; Ruiz-Méndez et al., 1997; Sleeter, 1981). Farhoosh and coworkers (2009) recently showed the DAG concentration in crude soybean oil (1.66%) decreased to 1.35% after the neutralization step. However, after deodorization, the DAG concentrations (1.74%) increased and reached around the initial amount in the crude soybean oils. They also observed the similar trend in the canola oil. Possible reasons for the increased in DAG in these reports is the existence of lipase in the crude oil which could form DAG or from TAG hydrolysis by high temperatures and water in the deodorization step (Huang, 1992).

Phospholipids

Phospholipids (PLs) are integral elements of all cellular membranes in living organisms and possess unique chemical structures containing both lipophilic and hydrophilic groups. Crude oil contains substantially high amount of PLs due to the solvent extraction of cell membranes. Phospholipids in oils include phosphatidylcholine (PC), phosphatidylethanolamine (PE), phosphatidylserine (PS), phosphatidylinosital (PI). Different species of seeds have different compositions of phospholipids but in general PC is predominant.

The amount of phospholipids in the oilseeds is small compared to animal tissues (Johnson, 2000). PLs in food oils cause foaming, cloudiness, and darkening during thermal processing. Normally, there are two types of PLs in crude oil, hydratable and non-hydratable. The degumming step removes hydratable PLs by washing them into the water phase. Non-hydratable PLs are not affected by water washing alone so citric or phosphoric acid are often added to the wash water to bind divalent cations thus making non-hydratable PLs hydratable. Physical refining can also be used to remove phospholipids as discussed above. Like other minor components, only trace amount of PLs will remain in the final refined oil with concentrations ranging from 20–2000 ppm with variations among different oilseeds species and refining methods (Koprivnjak et al., 2008; Verleyen et al., 2002).

Tocopherols

Tocopherols are the major oil soluble vitamin in crude oil. When the oilseeds are crushed, the tocopherols are extracted along with the oil. Natural tocopherols are mixtures consisting of α-, β-, γ-, δ- tocopherols. The volatility of tocopherols is above free fatty acids but below triacylglycerols. Thus, during the refining processing, tocopherols are partially removed during deodorization, thus decreasing their concentrations in the refined oil. Gogolewski and coworkers (2000) found that after the refining of rapeseed oil the tocopherol losses amounted to 30%. Two-thirds of the loss resulted from distillation and thermal degradation during deodorization, while one-third was caused by the combined effects of neutralization and bleaching. Rossi and coworkers (2001) reported that steam deodorization removed 200–300 ppm of tocopherols out of the original ~1000 ppm in crude palm oil.

The initial concentration and type of tocopherols in bulk oil vary with different oilseeds species. For instance, soybean oil has a high tocopherol concentrations with more than 65% γ-tocopherols and 20% δ-tocopherols while there is almost no δ-tocopherols in grape seeds oil (Kim et al., 2008). During storage tocopherol concentrations decrease which is accompanied by the generation of oxidized tocopherols. This is because tocopherols act as hydrogen donors and react with free radicals.

Pigments

The intensity of the bulk oils color mainly depends on the presence of coloring pigments such as carotenoids and chlorophyll. Vegetable oils with a minimum color index are considered to be more suitable for edible and industrial purposes (Latif and

Anwar, 2009). In addition, some of them have a prooxidative effect to the oil stability (Vide infra). Thus, pigments in crude oil are partially removed during the degumming, refining, and bleaching steps of the refining process.

Carotenoids are pigments in many vegetable oils and particularly in palm oil. They contain a long conjugated polyene chains and are yellow/orange/red in color. Crude palm oil normally contains 500–700 ppm of carotenes. These are mainly a-carotene (24–42% of total carotene) and β-carotene (50–60%) along with low levels of several other carotenes (Boon et al., 2010).

Chlorophylls are also found in vegetable oils. Chlorophyll includes chlorophyll a, chlorophyll b, and the Mg-free chlorophyll derivatives pheophytin a and pheophytin b. Some studies have reported no detectable chlorophylls in soybean oil after deodorization (Jung et al., 1989). However, other groups showed the existence of chlorophyll and pheophytins in refined oils. Pheophytin was reported to be the predominant chlorophyll, being about 0.06 and 0.10 ppm in refined soybean oil and corn oil, respectively (Usuki et al., 1984).

Miscellaneous Compounds

Nonsaponifiable Minor Components

Nonsaponifiable minor components in food oils include sterols, polycyclic aromatic hydrocarbons (PAHs), and hydrocarbons (e.g., alkanes, alkenes, and squalene) (Guillén et al., 2008b). Most vegetable oils contain 700–1100 mg/100 g of sterols, partly as free and partly as esterified sterols. High levels are present in rapeseed oil and in corn oil (Kmiecik et al., 2009). Sitosterol is generally the major phytosterol (50–80% of total sterol) with campesterol, stigmasterol, and Δ5-avenasterol also frequently attaining significant levels. Brassicasterol is virtually absent from the major seed oils except for rapeseed oil where it comprises 10% of the total sterols.

Food oils can be contaminated with PAHs due to the wide distribution of PAHs in the environment, their lipophilic nature, and the migration from contaminated packaging materials (Moret and Conte, 2000). Sekeroglu and coworkers (2007) tested 40 vegetable oil samples from Turkey for PAHs and found the total PAHs were above 25 ppb in most of the oils samples. More significantly, total PAHs levels in virgin olive oil always were 54.4–110.8 ppb (Speer et al., 1990). However, the refined food oils only occasionally exceeded the 25 ppb limit. Recently, Guillen and coworkers confirmed the occurrence of PAHs during the sunflower oil oxidation stored in the close container at room temperature for 112 months (Guillén and Goicoechea, 2008; Guillén et al., 2008a).

Squalene ($C_{30}H_{50}$) is a highly unsaturated open-chain triterpene. Olive oil is the major commercial oil with significant amounts of squalene (Bondioli et al., 1993). In refined food oils, new nonsaponifiable compounds are also formed as a consequence of the reactions occurring during the refining process (Moreda et al., 2001). These include steroidal compounds, arising from the dehydration of sterols, terpenic from terpenic alcohols, and other compounds deriving from squalene isomerization.

Polar Triacylglycerol Polymers

Polar triacylglycerol polymers (TGP) are formed during vegetable oil refining (Ferrari et al., 1996; Gomes et al., 2003). TGP are generally formed during the high temperature refining steps, for example, during bleaching and especially deodorization. An early study on the evolution of TGP in vegetable oils during physical refining reported a 1–2 wt% increase of TGP concentrations at physical refining temperatures less than 240°C. When physical refining temperatures were increased to 270°C, a sharp increase in TGP cocnentration to 3.0 wt% was observed. TGP formation also depends on the degree of saturation of the oils. For more saturated oils, such as palm oil, TGP increases were restricted to 2 wt%, even at temperatures of 270°C (deGreyt et al., 1997). Gomes (1992) used high-performance size exclusion chromatography to quantify the amount of oligopolymer in refined oils and found that refined olive oil had 0.7 wt% of oligopolymer twice of that in refined olive pomace oil. The final amounts of TGP found in food oils are generally $\sim$1 wt% depending on the fatty acid composition, initial quality, and refining technology used (de Greyt et al., 1997).

Oxidized Triacylglycerols

Oxidized triacylglycerols (ox-TG) are generally nonvolatile oxidation products left in the oil after deodorization. Oxidized triacylglycerols include cyclic carbon-to-carbon linked dimers and trimers, noncyclic hydroxy dimers, dimers, and trimers joined through carbon-to-carbon or carbon-to-oxygen linkage. Initial reports suggested that ox-TG concentrations ranged from 4.55 wt% in crude oil to 9.29 wt% after oil refining (de Greyt et al., 1997). However, more recently Hopia (1993) investigated the impact of oil refining on the ox-TG contents in three vegetable oils, that is, sunflower oil, soybean oil, and low erucic acid rapeseed oil. The results showed that the concentration of ox-TG ranged from 0.53 to 0.90% oil in the crude oils. After refining, ox-TG concentrations were decreased in bulk oil and ranged from 0.29% for sunflower oil to 0.78 wt% for soybean oil. The loss was attributed to the adsorption of ox-TG by the activated earth during bleaching. Farhoosh and coworkers (2009) found ox-TG concentrations in crude soybean oil and canola oil at 4.2 and 2.8 wt%, respectively. After oil refining, ox-TG decreased to 2.8 and 2.0 wt% in soybean oil and canola oil, respectively. They also noticed the level of the ox-TG in the refined oils was proportional to its original level in the crude oils.

Water

Since water and oil have opposite polarities and they tend to spontaneously phase separate because of the hydrophobic effect one might not expect to find water in bulk oil (Bell, 2004).

However, as discussed in the preceding sections, refined oils contain many surface active compounds such as free fatty acids (FFA), monoacylglycerols (MAG), diacylglycerols (DAG), and phospholipids (PLs). These surface active compounds have the ability to emulsify water into bulk oils. This could also be the reason that refined oil contains trace amounts of transition metals which are able to further deteriorate oil quality. The water content in freshly-opened, commercially available vegetable oils range from 200–2000 ppm (Chaiyasit et al., 2007a). Water concentrations in oil can change after opening since oil can absorb water from atmosphere or water in the oil can evaporate.

Water in refined oil is derived in two ways. The first is from the original water in the oilseeds. Sorption isotherm experiments showed water with three levels of affinity in soybean seeds: (i) a region of strongly bound water at moisture concentrations below 8%; (ii) a region of weakly bound water at moisture concentrations between 8 and 24%; and (iii) a region of very loosely bound water at concentrations greater than 24% (Vertucci and Leopold, 1984). When soybeans are dried for storage, the moisture content is ∼10 wt%. That water is likely the strongly bound water in the oilseed but it is possible that some of this water ends up in the crude oil. The second possible source of water is the water used to wash oils and remove the free fatty acids and phospholipids during the neutralization and degumming steps. The majority of this water is removed by centrifugation. The remaining water is removed by a vacuum dryer that controls the moisture content of the washed oil to below 1000 ppm, most often in the range of 500 ppm (O'Brien, 2004).

Oxygen

Oxygen is a primary reactant in lipid oxidation reaction which fuels the fatty acid decomposition pathway that causes rancidity. There are two types of oxygen in bulk oil systems, dissolved oxygen (DO) and non-dissolved oxygen. Dissolved oxygen is incorporated into food while non-dissolved oxygen stays in the headspace (Garcia-Torres et al., 2009). The solubility of oxygen and the rate of its diffusion in the bulk oil affect the rate and extent of lipid oxidation. Oxygen is as about 3–10 times more soluble in bulk oil than water (saturation occurs at 5–10 ppm in pure water at 20°C) (Montgomery et al., 1964; Windrem and Plachy, 1980). Schrader and coworkers (1979) determined that the diffusion coefficient of oxygen in soybean oil was 0.6×10–$9\ m^2.s^{-1}$ at 20°C which is lower than that of olive oil. Some researchers suggested that oxygen solubility was related to fatty acid chain length with oxygen solubility decreasing with increasing the hydrocarbon chain length (Battino et al., 1983).

Another form of oxygen associated with bulk oil is non dissolved oxygen or headspace oxygen. The air space above the oil, for example, in the oil tank or commercial oil bottle, is where headspace oxygen located. The headspace oxygen content in olive oil and marine oil at temperature lower than 60°C increases with the increase of temperature, which follows the rule of the Henry's Law, that is, the solubility is proportional to the partial pressure of headspace gas (Ke and Ackman, 1973). In other words, as temperatures increase, oxygen in the oil moves into the headspace. At temperatures higher than 60°C there is a large variation in the solubility of oil, especially in marine oil presumably due to heat accelerated oxidation which consumes oxygen. The mass transfer between headspace oxygen and oxygen in the oil is influenced by: (i) the rate of absorption; (ii) the oxygen concentration in the headspace; (iii) the headspace surface area to volume ratio; and (iv) agitation. With those factors being considered, an equation was developed to describe the absorption rate of oxygen between bulk oil and oxygen in the headspace (Gunstone and Padley, 1997).

$$\frac{dC}{dt} = \frac{KA}{V}(C_O - C) \tag{2}$$

Here, C_o is the equivalent solubility of oxygen in the bulk oil; C is the oxygen content in bulk oil after t times; K is the mass transfer coefficient; A/V is the area to volume ratio.

THE EFFECT OF MINOR COMPONENTS ON BULK OIL OXIDATION

The Effect of Oxygen on the Chemical Stability of Bulk Oil

Lipid oxidation is not a spontaneous reaction. Thermodynamically, oxygen cannot react directly with double bonds because the spin states are different. Ground state, atmospheric oxygen is in a triplet state, whereas the double bond of unsaturated fatty acids is in singlet state. Quantum mechanics requires that spin angular momentum be conserved in reactions. Therefore, interactions between triplet oxygen and unsaturated fatty acids demands that either the double bond be excited into a triplet state or oxygen is converted to a singlet state. The former seems impossible due to the requirement of prohibitive amounts of energy. The triplet oxygen also cannot convert to singlet states itself, thus direct reaction occurs between the oxygen and double bonds in oil do not occur unaided (Schaich, 2005). However, under the assistance of other minor components in bulk oil, several reactions can happen. For example, photosensitizers such as chlorophylls can produce singlet oxidation by mechanisms 3–5 outlined below.

$$\mathrm{Sen} + h\nu \rightarrow \mathrm{Sen}^* \tag{3}$$

$$\mathrm{Sen}^* + {}^3\mathrm{O}_2 \rightarrow {}^1\mathrm{O}_2^* \tag{4}$$

$${}^1\mathrm{O}_2^* + \mathrm{LH} \rightarrow \mathrm{LOOH} \tag{5}$$

In addition, oxygen along with iron can generate alkyl radicals (L•) as shown in reactions 6 and 7. Schafer and coworkers (2000) proposed that iron-oxygen complexes ($[Fe^{2+}\text{-}O^2]$) are one route by which iron can promote lipid oxidation in cell membrane.

$$\mathrm{Fe}^{2+} + \mathrm{O}_2 \rightarrow [\mathrm{Fe}^{2+-}\mathrm{O}_2] \tag{6}$$

$$[Fe^{2+-}O_2] + LH \rightarrow L\bullet \quad (7)$$

Triplet oxygen is directly involved in lipid oxidation propagation through its ability to react with alkyl radicals in diffusion controlled radical-radical reactions to form peroxyl radicals as shown in reactions 8 and 9 (Frankel, 2005):

$$L\bullet + O_2 \leftrightarrow LOO\bullet \quad (8)$$

$$LOO\bullet + RH \rightarrow LOOH + R\bullet \quad (9)$$

Because of these multiple pathways that oxygen can be involved in lipid oxidation, it is not surprising that many studies have shown that reduction of oxygen in packaged bulk oil can extend shelf life (Masella et al., 2010; Parenti et al., 2007). An 18-months shelf life test, performed on virgin olive oil indicated that the slowest oxidation rates occurred at the lowest initial dissolved oxygen concentration (Parenti et al., 2007). The same group also reported that the removal of oxygen from extra virgin olive oil by nitrogen purging lowered peroxide values (Masella et al., 2010). Packaging technologies such as oxygen scavenging film can also improve the oxidative stability of bulk oil (Maloba et al., 1996; Tawfik and Huyghebaert, 1999).

The Effect of Water on the Chemical Stability of Bulk Oil

Despite being present at relatively low levels, water could have an impact on the rate, extent, and mechanism of lipid oxidation in bulk oils since it may act as a solvent for hydrophilic or amphiphilic antioxidants and prooxidants (such as transition metals, free fatty acids, or lipid hydroperoxides). Recently, we studied the impact of water on lipid oxidation in stripped soybean oil (SSO) produced by adsorption chromatography. The soybean oil used initially had ~200 ppm of water. After stripping, the oil with silicic acid and activated charcoal the water content was reduced to less than 50 ppm. This is thought to be due to the removal of both water and polar surface active compounds by the stripping procedure. Water was then added back at concentrations up to 1000 ppm. Increasing water concentrations had very little impact on the lag phase of lipid oxidation as determined by hexanal formation during storage at 55°C (Fig. 2). However, there was a small trend suggesting that increasing water concentrations in this range decreased the extent of lipid oxidation.

The Effect of Free Fatty Acid on the Chemical Stability of Bulk Oil

Generally, FFA with unsaturated bonds showed a lower oxidative stability than their corresponding methyl esters and triacylglycerols (Miyashita and Takagi, 1986). In addition, FFA themselves have been reported to accelerate the oxidation of triacylglycerols in vegetable oils. FFA have been shown to have

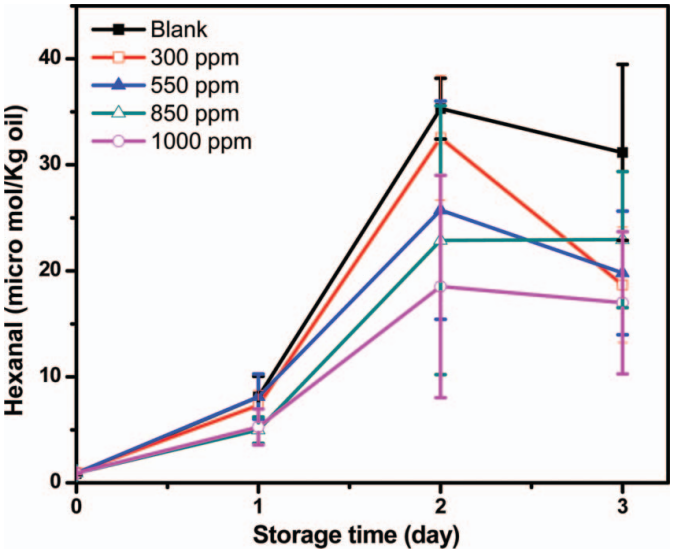

Figure 2 Formation of hexanal in stripped soybean oil (SSO) containing different concentrations of water at 55°C. (color figure available online.)

several different prooxidative tendencies. Yoshida and coworkers (1992) demonstrated that FFA (i.e., caprylic, capric, lauric, myristic, palmitic, or stearic acid) in microwaved stripped soybean oil increased oxidation with shorter the chain length and the higher the levels of FFA being more prooxidative (Yoshida, 1993). Aubourg (2001b) later showed similar results in marine oil with a higher degree of oxidation seen in the presence of short chain (lauric and myristic) than long chain (stearic and arachidic) fatty acids at 30°C. Paradiso and coworkers (2010) recently reported that low amounts of FFA caused an increase in the formation of oxidized triacylglycerol and triacylglycerol oligopolymers again showing the prooxidant activity of FFA. The prooxidant activity of FFA is associated with its free acid group since methyl esters of fatty acids do not accelerate oxidation. Proposed mechanisms of FFA include their ability to accelerate the decomposition of hydroperoxides and bind metals to make them more prooxidative (Miyashita and Takagi, 1986).

Obviously, it is very critical to control the levels and formation of FFA in crude, refined, and stored oils. While most commercial oils have FFA concentrations less than 0.05 wt%, there may be additional benefits if these levels could be even lower. Minimizing FFA formation during storage can be accomplished by decreased water exposure, minimizing temperatures, preventing contact with lipases, and avoiding exposure to extremes in pH.

The Effect of MAG and DAG on Chemical Stability of Bulk Oil

Different impacts of MAG and DAG on the oxidative stability of bulk oils has been reported. Mistry and Min (1987; 1988) found that 0–0.5 wt% of monostearin, distearin, monolinolein, or dilinolein acted as prooxidants in soybean oil. Colakoglu

(2007) found that soybean oil containing 1 wt% monoolein increased the rate of oxygen consumption. Wang and coworkers (2005) observed that randomized corn oil contained higher levels of MAG and DAG (0.3 and 5.1%, respectively) oxidized much faster than natural corn oil with no detectable MAG and 1.4% of DAG. On the contrary, Gomes et al. (2010) found that 1–3 wt% MAG decreased oxidation in stripped olive oil at 60°C. The effect of combinations of MAG or DAG with antioxidants in the bulk oil has also been studied. MAG or DAG in combination with citric acid resulted in greater antioxidant activity than the MAG or DAG itself (Aubourg, 2001a). In addition, as the chain length of the fatty acids on MAG or DAG was increased, the more effective the citric acid became.

The Effect of Phospholipids on the Chemical Stability of Bulk Oil

The impact of phospholipids (PLs) on bulk oil oxidation is also controversial. Dipalmitoyl phosphatidylcholine (DPPC) and dipalmitoyl phosphatidylethanolamine (DPPE) were reported to have poor antioxidant activity at 50°C and showed no synergistic effect with a-tocopherol in methyl linoleate (Husain et al., 1986). Phosphatidylcholine (PC) and phosphatidylethanolamine (PE) from egg yolk accelerated the oxidation of methyl linoleate (Husain et al., 1986). Takenaka and coworkers (2007) also found that PC and PE promoted bonito oil oxidation in the absence of α-tocopherol. However, they found that PE showed synergistic antioxidant activity with α-tocopherol, while PC did not.

Alternatively, Bandarra and coworkers (1999) showed that 0.5% PC was an effective antioxidant in sardine oil at 40°C. In addition, a high synergistic effect was observed in the same system with a mixture of α-tocopherol and PE. Others have reported similar results that PLs can increase the activity of tocopherols in bulk oils (Hahnel et al., 1999a; Hildebrand et al., 1984; Koga and Terao, 1995; Sugino et al., 1997). For the researchers who observed the antioxidant activity of PLs in bulk oil, metal chelating, free radical scavenging, and the formation of Maillard reaction products were given as the mechanisms by which PLs inhibit oxidation (Hahnel et al., 1999b; Khan and Shahidi, 2000; Koga and Terao, 1994).

The Effect of Tocopherols on the Chemical Stability of Bulk Oil

Tocopherols are the most common free radical scavenging antioxidants found in vegetable oils. Vegetable oils normally contain tocopherols concentrations in the range of 200–1000 ppm which originate from the seeds. After refining, almost 70% of the tocopherols remain in the bulk oil with 30% being removed during deodorization. Overall, tocopherols are probably the most important antioxidants in vegetable oils (for review see refs (Kiokias et al., 2008; Seppanen et al., 2010)). The antioxidant mechanisms of tocopherols (TOC) are shown below.

$$\mathrm{LOO\bullet + TOC \rightarrow LOOH + TOC\bullet} \quad (10)$$

$$\mathrm{LOO\bullet + TOC\bullet \rightarrow LOO - TOC} \quad (11)$$

However, under certain conditions the antioxidative ability of α-tocopherols is less effectiveness when increase its concentration. This is thought to be due to their ability to reduce endogenous transition metals naturally occurring in the oil or metals resulting from contamination during processing. These reduced metals can then promote the decomposition of pre-existing lipid hydroperoxides as shown in pathways 12 and 13. Yoshida and coworkers (2003) found that both α-tocopherol (100 μM) and α-tocotrienol (100 μM) reduced cupric iron (300 μM) and the concomitant formation of α-tocopheryl quinone and α-tocotrienyl quinone was observed by UV absorption spectrum and also by HPLC analysis in methyl linoleate. Interestingly, the β, δ-, and γ- forms of tocopherols were not found to reduce cupric iron in the same system.

$$\mathrm{TOC + Mn^{2}+ \rightarrow TOC^{+} + Mn^{+}} \quad (12)$$

$$\mathrm{LOOH + Mn^{+} \rightarrow LO\bullet + HO^{-} + Mn^{2+}} \quad (13)$$

The decreased activity of tocopherols has also been proposed to be due to the ability of the tocopherol radical to promote fatty acid oxidation especially when tocopherol radical concentrations are high (Decker, 1997; Yoshida et al., 2003, 1994).

$$\mathrm{LOOH + TOC\bullet \rightarrow LOO\bullet + TOC} \quad (14)$$

$$\mathrm{LH + TOC\bullet \rightarrow L\bullet + TOC} \quad (15)$$

Trace amounts of oxidized tocopherol exist in bulk oil after refining. Min and coworkers reported that oxidized α-, γ-, and δ-tocopherols promote the oxidation of purified soybean oil in the dark at 55°C (Jung and Min, 1992; Kim et al., 2007). Since it is possible that oxidized tocopherols occur naturally in bulk oil and that tocopherol ingredients could contain oxidized tocopherols, this could be a source of prooxidants in oils. More work is needed to determine if and how oxidized tocopherol could impact the antioxidant/prooxidant activity of tocopherols.

The Effect of Pigments on the Chemical Stability of Bulk Oil

The two major pigments that can impact lipid oxidation in oils are cholorophyll and carotenoids. Chlorophyll, a photosensitizer, is prooxidative when exposed to light due to its ability to promote the formation of singlet oxygen (Choe and Min, 2009). As described previously, singlet oxygen is formed by chlorophyll photosensitization by energy transfer from light to a sensitizer and then to triplet oxygen (Lee and Min, 1990). Singlet oxygen can then initiate lipid oxidation because it can directly react with the double bonds of unsaturated fatty acids

to form lipid hydroperoxides (Carlsson et al., 1976). In the bulk oil, it is important to remove as much chlorophyll as possible during refining since most retail oils are stored in transparent plastic packages.

Unexpectedly, chlorophyll and its degradation product, pheophytin, have also been reported to inhibit lipid oxidation in the rapeseed and soybean oils at 30°C during storage in the dark. This has been proposed to be due to their ability to scavenge peroxyl and other free radicals (Endo et al., 1985).

Carotenoids can be efficient singlet oxygen and excited photosensitizers quenchers that reduce oxidation by converting excited photosensitizers or singlet oxygen to their less reactive states (Jung and Min, 1991). Burton (1989) also proposed that under low oxygen partial pressure conditions, β-carotene can act as a lipid soluble chain breaking antioxidant. They also found that at oxygen pressures of 20 kpa or higher, β-carotene and related compounds are prooxidants in a methyl linoleate model system possibly due to the formation of carotenoids oxidation products (Burton and Ingold, 1984). During high temperature oil refining, carotenoids can also become thermally degraded. Thermally degraded carotenoids were reported to accelerate lipid oxidation in soybean oil at concentration of 50 ppm (Steenson and Min, 2000). More research is needed to elucidate how chemical changes of carotenoids impact the oxidative stability of oils.

The Effect of Miscellaneous Compounds on the Chemical Stability of Bulk Oil

Small amounts of squalene (200 ppm) were reported to have a limited impact on the oxidative stability of stripped olive oil 40 and 62°C in the dark, whereas higher concentration (7000 ppm) of squalene showed an antioxidative effect at the same system (Psomiadou and Tsimidou, 1999). In rapeseed oil, Malecka (1991) found that squalene (4000 ppm) increased the oxidative stability of oil heated at 170°C for 10 h. No significant impact of squalene (0–8000 ppm) on stripped sunflower oxidation was observed by Mateos and coworkers (2003b). Conversely, squalene was found to accelerate oxidation of stripped olive oil in a Rancimat apparatus at 100°C (Mateos et al., 2003a).

The effect of sterols on the oxidation of olive oil was studied at 180°C by Gordon and Magos (1983). They found that Δ5-avenasterol and fucosterol were effective as antioxidants at concentration of 0.1 wt%, while other sterols, including cholesterol and stigmasterol, were ineffective. The proposed mechanism was that lipid free radicals could react rapidly with sterols at unhindered allylic carbon atoms (Gordon and Magos, 1983). Phytosterols have also been reported to act as antioxidants in soybean, rice bran, and sunflower (Nyströ et al., 2007; Wang et al., 2002; Winkler and Warner, 2008).

Yoon and coworkers (1988) found that the oxidized triacylglycerol fractions obtained by thermal oxidation of soybean oil acted as prooxidant when it was added to stripped soybean oil. Gomes et al. (2008) found that oxidized triacylglycerol oligopolymers, a class of oxidation compounds present in refined vegetable oils, were the most prooxidative in vegetable oil amongst all the oxidized triacylglycerol fractions tested.

ASSOCIATION COLLOIDS AND LIPID OXIDATION IN BULK OILS

Evidence for the Presence of Association Colloids in Bulk Oil

As discussed briefly above, one of the major issues that is often overlooked in bulk oil oxidation is the physical properties of minor components (Xenakis et al., 2010). Bulk oil minor components, such as monoacylglycerols (MAG) and diacylglycerols (DAG), phospholipids (PLs), sterols, free fatty acids (FFA), and polar products arising from lipid oxidation are surface active compounds. These surface active molecules have the ability to form physical structures in the bulk oils in the presence of the small quantities of water ($\sim$300 ppm) typically found in refined oils (Chaiyasit et al., 2007a; Xenakis et al., 2010). These structures are known as association colloids. Recent research suggests that association colloids could participate to lipid oxidation and act as reaction sites in bulk oils.

Previous studies have demonstrated that surface active molecules can self-assemble in non-polar solvents (e.g., benzene, isooctane, cyclohexane, toluene, free fatty acid, and triacylglycerols) in the presence of water to form a variety of association colloids such as reverse micelles, micro-emulsions, lamella structures, and cylindrical aggregates (Fig. 3) (Chen et al., 2008; Lutton, 1965; Monduzzi et al., 2000; Srisiri et al., 1998). For instance, Ichikawa and coworkers formed reverse micelle systems using soybean phospholipids as a surfactant with fatty acids or fatty acid ethyl esters as the organic solvent (Ichikawa et al., 2000). Abraham and coworkers recently formed nutrient delivery systems consisting of water-in-oil nanoemulsions using oleic acid embedded in canola oil (Abraham and Narine, 2009). Chen and Terentjev (2009; 2010) identified ordered lamellar structures in hazelnut oil in the presence of monoglycerols (MAG). These studies suggest that the amphiphilic molecules in refined vegetable oils have the ability to form association colloids (Kasaikina et al., 1999).

There are several lines of evidence that association colloids occur naturally in refined and crude oils. The complete removal of water from refined oil is very difficult even at temperatures up to 200°C. This suggests that some of the water in oil is bound to polar compounds possibly in association colloids. We have indirectly seen this in our research since water content in oil is reduced by the removal of polar compounds. In addition, it was observed by research groups using ultrafiltration (UF) that only a small portion of the phospholipids in oils penetrates through UF membranes with a pore diameter of the order of 4 nm (Manjula and Subramanian, 2006; Subramanian and Nakajima, 1997; Subramanian et al., 1998). The proposed reason for the rejection of phospholipids by these non-porous membranes was suggested to be due to the formation of phospholipids reverse micelles, swollen in the presence of small quantities of

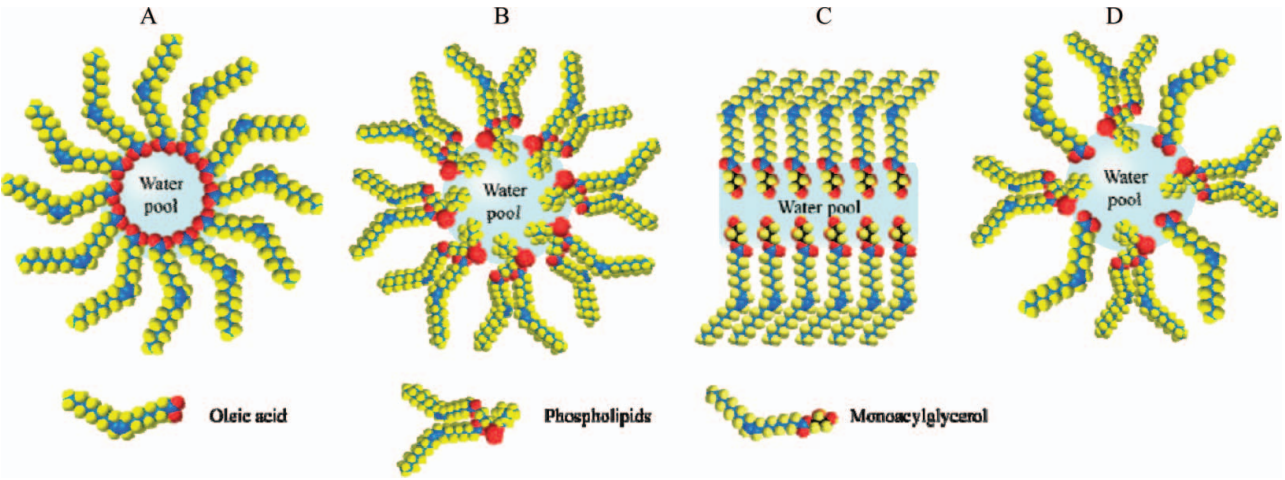

Figure 3 Schematic representation of the association colloids formed by minor constituents in bulk oil (A) a reverse micelle formed by oleic acid; (B) a reverse micelle formed by phospholipids; (C) Inverse lamella structure formed by monoacylglycerol; (D) a mixed reverse micelle formed by free fatty acids and phospholipids. (color figure available online.)

water plus containing other minor components such as pigments, which are then rejected by size exclusion. The amount of rejection phsopholipids closely depended on the amount and the size of reverse micelles formed during solvent extraction (Badan Ribeiro et al., 2008; Bottino et al., 2004; de Morais Coutinho et al., 2009).

Research in our lab found that when 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) was added to stripped soybean oil above its critical micelle concentrations (650 μM) it was able to form reverse micelles as determined by small angle x-ray scattering (SAXS; Fig. 4). This was not true for 1000 μM PC with shorter chained fatty acids (1,2-dibutyryl-sn-glycero-3-phosphocholine, DC_4PC). Increasing water levels in the stripped soybean oil with DOPC (950 μM) increased SAXS intensity suggesting that more reverse micelles were formed until eventually high water levels change the scattering pattern from isotropic to an anisotropic system indicating that the shape of the reverse micelles had changed (Chen et al., 2010).

Do Association Colloids Impact Lipid Oxidation?

Many of the compounds involved in lipid oxidation reactions such as lipid hydroperoxides, free fatty acids, and antioxidants are surface active. Previous research with oil-in-water emulsions has shown that the physiochemical property of the water-oil interface plays a very important role in lipid oxidation chemistry since it can impact the location and reactivity of both prooxidants and antioxidants (Waraho et al., 2011). This suggests that the water-oil interface of association colloids could also impact lipid oxidation chemistry by acting as nano-reactors. Some of the first research in this area was by Koga and Terao (1995) who observed that the presence of phospholipids enhanced the antioxidant activity of α-tocopherol in stripped oil containing a trace amount of water (1%). This study found that the presence of phospholipid increased the degradation of α-tocopherol in the presence of the water soluble free radical generator, 2,2-azobis(2-amidinopropyl) dihydrochloride (AAPH) suggesting that the phospholipids increased the exposure of α-tocopherol to the water phase. This could also be due to the fact that the reduction potential of α-tocopherol is lower in polar environments which could make tocopherol a more efficient free radical scavenger (Laranjinha, 2001). Degradation of α-tocopherol by the water-soluble free radicals decreased as the phospholipid's hydrocarbon tail group size was decreased, and thus the ability of the phospholipid to form association colloids was lost. Koga and Terao (1994) also found that the antioxidant activity of α-tocopherol could be increased in bulk oil when it was conjugated to the polar head group of phosphatidylcholine (PC). This increase in activity was again thought 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. This pioneering work was the first to suggest that the presence of physical structure in bulk oils could impact lipid oxidation chemistry by altering the activity of free radical scavenging antioxidants.

Recent research in our lab also showed that phospholipid reverse micelle impacts the activity of free radical scavenging antioxidants (Chen et al., 2011). In this study, the activity of non-polar (α-tocopherol) and polar (Trolox) antioxidants in stripped soybean oil (SSO) was determined in the presence and absence of DOPC reverse micelles. The activity of low α-tocopherol or Trolox concentrations (10 μM) was increased by DOPC reverse micelles; but when antioxidant concentrations increased to 100 μM their effectiveness decreased. Fluorescence steady state and lifetime decay studies showed that Trolox was highly concentrated in the reverse micelles which could explain why it was a more effective than α-tocopherol (Fig. 5). It is still unclear why the reverse micelles could both increase and decrease the activity of the antioxidants.

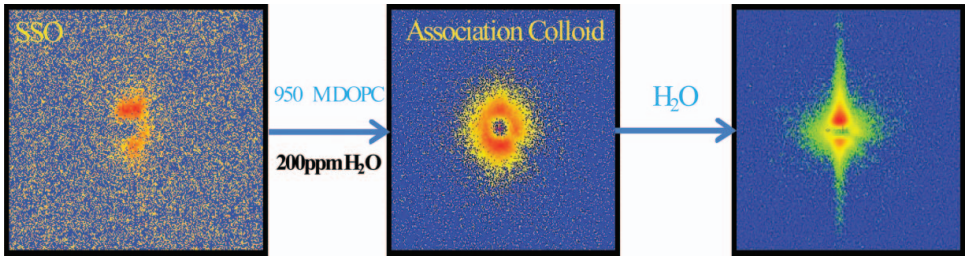

Figure 4 The formation of reverse micelles resolved by Small Angle X-ray Scattering (SAXS). (color figure available online.)

Chaiyasit and coworkers evaluated the ability of water, cumene hydroperoxide, oleic acid, and phosphatidylcholine to influence the structure of reverse micelles in a model oil (n-hexadecane) system containing sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles. This study found that water, cumene hydroperoxide, oleic acid, and phosphatidylcholine can alter reverse micelle size and lipid oxidation rates (Chaiyasit et al., 2007b; 2007c). Kasaikina and coworkers (2010; 2006; 2008; 1999) found the decomposition of cumene hydroperoxides into free radicals was accelerated by the existence of reserve micelle formed by cationic surfactants in organic media (Trunova et al., 2007). In addition, they found the oxidation stability of sunflower oil at 80°C in the presence of 0.1 μM 2,6-di-tert-butyl-4-methylphenol (BHT) was decreased in the presence of fatty alcohols, such as 1-tetradecanol, 1-octadecanol, and the MAG, 1-monopalmitoylglycerol. This result was explained by the so-called "micellar effect": the relatively higher concentration of polar species such as hydroperoxide and peroxyl radicals within and nearby the reverse micelles formed in the presence of these fatty alcohols and MAG, leading to an increase of the rate of chain initiation via an acceleration of the hydroperoxides decomposition (Kortenska et al., 2002).

Research in our lab also studied the impact of association colloids on lipid oxidation rates (Chen et al., 2010). This study utilized two PLs DOPC and DC_4PC which could be added to stripped oil with DOPC forming structure while the shorter acyl chains in DC_4PC resulted in no formation of physical structures. When the lipid oxidation rates were monitored, it was found that DOPC accelerated oxidation while DC_4PC had no effect. Since both PCs had the same head group, this suggests that the structures formed by DOPC were the cause of increased lipid oxidation rates.

THE EFFECT OF MINOR COMPONENTS ON THE OXIDATIVE STABILITY OF OIL-IN-WATER EMULSIONS

Many lipids in foods exist as oil-in-water emulsions (McClements, 2005). Unlike association colloids in bulk oil, an oil-in-water emulsion is a thermodynamically unstable system. The extremely large interfacial area in oil-in-water emulsions facilitates interactions between lipids and water soluble prooxidants (Waraho et al., 2011). This large interface is thought to be responsible for oil-in-water emulsions being much less oxidatively stable than bulk oil. While the mechanisms and factors that can potentially influence lipid oxidation in oil-in-water emulsions have been studied comprehensively in the past years, very little has been published on how minor components impact these pathways (Shahidi and Zhong, 2010a). This could be an important area since the minor components could directly influence oxidative stability by themselves or indirectly through the alteration of the physical properties of the emulsion droplet due to their surface activity.

The Effect of FFA on the Oxidative Stability of Oil-In-Water Emulsion

Free fatty acids have been shown to promote the lipid oxidation of stripped soybean oil-in-water emulsions. Oleic acid (0–5.0 wt% of oil) in Tween 20 stabilized emulsions increased lipid hydroperoxides and headspace hexanal formation (Waraho et al., 2009). At the same time, the negative charge of the emulsion droplets increased with increasing of oleic acid concentrations. In addition, the ability of FFA to decrease the negative

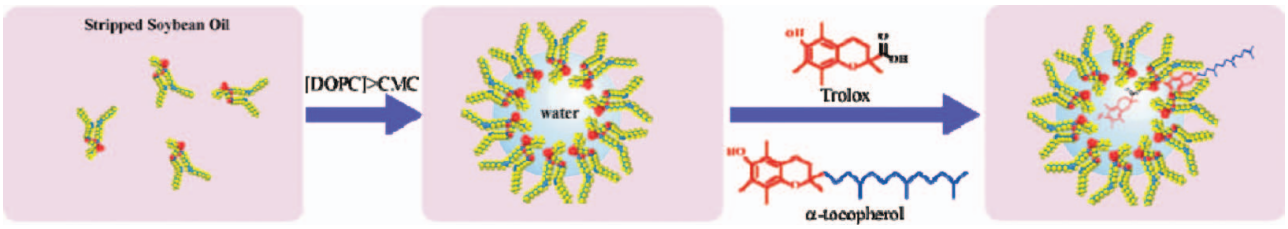

Figure 5 Schematic representation of the location of Trolox and α-tocopherol in SSO containing 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) reverse micelles. (color figure available online.)

charge of emulsion droplets and promote lipid oxidation decreased with decreasing pH, especially when the pH was below the pKa value of FFA. Since the prooxidant activity of free fatty acids is inhibited by EDTA, it is thought that they promote oxidation by making emulsion droplets negatively charge which in turn attracts metals to the droplet surface where they are very effective at promoting lipid oxidation.

The Effect of Phospholipids on the Oxidative Stability of Oil-In-Water Emulsion

Tsai and Smith (1971) found that the impact of phospholipids on the oxidation of methyl linoleate emulsions varied as a function of phospholipid type. Both the antioxidative and prooxidative activity of PLs with variable phosphoryl bases were observed in SDS stabilized methyl linoleate emulsions. They proposed that PLs may remove free radicals or hydroperoxides from the emulsion system and act thereby as antioxidants, or PLs may decompose hydroperoxides to new radicals and thus act as prooxidants. Recently, our group found that 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) inhibited lipid oxidation in 1 wt% stripped soybean oil-in-water emulsions at pH 7.0, while at pH 3.0 DOPC was prooxidative (Cardenia et al., 2011). DOPC did not affect the emulsion droplet charge or size at either pH 3.0 or 7.0. The antioxidant activity at pH 7.0 was observed in a series of phospholipids (PLs) that varied in fatty acid unsaturation level and chain length as well as type of phosphate head group. Overall, phosphatidylcholine with either oleic or palmitic acid aliphatic side chain were the most effective at inhibiting lipid hydroperoxide and hexanal formation of all of the PLs tested. The antioxidant activity of PLs was speculated to be due to their ability to form structures within the lipid phase of the emulsions droplets or to chelate metals.

The Effect of DAG on the Oxidative Stability of Oil-In-Water Emulsion

Unlike bulk oils, there is little information about the effect of diacylglycerol (DAG) on the lipid oxidation in oil-in-water emulsions. However, there are studies on how DAG can impact the physical properties of oil-in-water emulsions. In a comparison of the properties of β-lactoglobulin (β-LG) stabilized oil-in-water emulsions containing either DAG (88.3% of DAG in total) or TAG (97.4% of TAG in total) at pH 7, the β-LG was found to possess the higher susceptibility of adsorbed on the DAG oil droplet surface than on the TAG oil droplet surface (Sakuno et al., 2008). On the basis of their results, the comparably high density of protein emulsifier will be expected in the oil-water interface. The increasing of interface protein thickness could inhibit interactions between prooxidants in the aqueous phase and oxidizable lipids in the emulsion droplet core (Klinkesorn et al., 2005). In addition, protein emulsifiers have been demonstrated to serve as antioxidants (Elias et al., 2008). Thus, the incorporation of DAG in the protein stabilized bulk oil emulsions may not accelerate emulsion oxidation.

The Effect of Polar Compounds on the Oxidative Stability of Oil-In-Water Emulsion

Lipid hydroperoxides would be expected in oil-in-water emulsions since they are found in the bulk oils from which they are derived. For example, lipid hydroperoxides in oil-in-water emulsions are approximately 0.5 μM which is 1000 times higher than high density lipoproteins (HDL) (Bou et al., 2008). The addition of lipid hydroperoxides to oil-in-water emulsions increases lipid oxidation rates (Nuchi et al., 2001; 2002). Interfacial tension measurements show that linoleic acid, methyl linoleate, and trilinolein hydroperoxides are more surface-active than their nonperoxidized counterparts (Mancuso et al., 2000). This suggests that hydroperoxides could concentrate at the oil-water interface where they could react more readily with aqueous phase metals this increasing their decomposition into free radicals.

The other polar compounds that have been studied in oil-in-water emulsions oxidation are phytosterols (Cercaci et al., 2007). Cercaci and coworkers found that phytosterols were oxidized during storage in corn oil-in-water emulsions and formed phytosterols oxidation products (POPs). Corn oil-in-water emulsions containing ~900 ppm of phytosterols oxidized faster than the bulk corn oil containing ~6000 ppm of phytosterols. Interfacial tension measurements showed that phytosterols had a high degree of surface activity, which would allow them to migrate to the oil-water interface of the emulsion droplets where oxidative stress is high.

CONCLUSIONS AND FUTURE PERSPECTIVE

In a quest to make food healthier, the food industry would like to produce products with higher levels of polyunsaturated fatty acids. However, these products are more susceptible to lipid oxidation resulting in loss of quality and shelf-life. Unfortunately, the goal of increasing the level of unsaturated fatty acids in foods has become even more difficult in recent years since many companies do not want to use synthetic antioxidants and very few new antioxidants have been introduced into the market. Therefore, to overcome the challenge of developing foods with nutritionally significant amounts of unsaturated fatty acids, new antioxidant technologies need to be developed. This requires having a better understanding of the factors that impact lipid oxidation chemistry in foods.

The composition and concentration of the minor components in bulk oils and emulsions is a major factor in oxidative stability. Although more research is needed, there is some research on the impact of individual minor components on oxidative stability. Unfortunately, there are very few studies looking at how combinations of minor components impact lipid oxidation

chemistry. This could be one of the reasons for the often conflicting data on how minor components impact lipid oxidation. For instance, many studies utilize refined oil in their experiments meaning that the oil already contained a large number of minor lipid components. Therefore, in these studies the effect of minor components on lipid oxidation is not just due to the minor component being added but also its interaction with other inherent minor components in the refined oil. It might be more useful for studies to utilize oils stripped of their minor components and then add minor components back, both individually and in combination, to gain a better understanding of the mechanisms of lipid oxidation.

In addition, most studies on the impact of minor components on lipid oxidation have focused on their chemical properties. However, it is now evident that the minor components that are surface active can form physical structures in oils. The physical structures, or association colloids, are potentially a reaction site in oils where lipid oxidation is prevalent. Therefore, to understand how minor components impact lipid oxidation, we need to know how they impact both physical and chemical properties.

Oils refining operations are optimized to improve many quality parameters. However, not all of the specifications for oil quality are focused on lipid oxidation. Therefore, it is possible that oil refining could be altered in ways that could make oils more oxidatively stable. However, there is still not a good understanding of the optimal specifications for minor components required to maximize oxidative stability. In addition, it is possible that minor components could be added to oils at concentrations higher than seen in crude oils such that they inhibit oxidation themselves or that they could improve the antioxidant activity of other minor components. Overall, more research is needed to better understand the mechanisms of minor lipid components on lipid oxidation pathways in order to design oils with improved oxidative stability.

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