Approaches of lipid oxidation mechanisms in oil matrices using association colloids and analysis methods for the lipid oxidation

Won Young Oh[1] · Mi-Ja Kim[2] · JaeHwan Lee[1]

Abstract

Lipid oxidation is one of the key chemical reactions in foods containing fats and oils during production and storage. For several decades, many researchers have tried to understand the mechanisms of lipid oxidation and ways to control the rates of lipid oxidation. Theories of autoxidation or free radical chain reaction have been developed to successfully explain the phenomenon observed in oxidized lipids. Many studies have been conducted to explain the other factors that can affect the lipid oxidation such as food matrix, oxidation time and temperature, transition metal ions, pigments with sensitizing abilities, and surface-active compounds such as phospholipids, free fatty acids, monoacylglycerols, and diacylglycerols. Several strategies were developed to evaluate the degree of oxidation and oxidative stability. This review provides crucial information on the mechanism of lipid oxidation affected amphiphilic compounds and association colloids. This review article will extensively discuss about the methods for determining the oxidative stability.

Keywords Lipid oxidation · Association colloid: oil matrix · Analysis method · Emulsion

Introduction

Foods containing high fats and oils or those subjected to high temperature treatment undergo lipid oxidation during production and storage. The oxidized products significantly decrease consumers' acceptance of the food products. Also, intake of oxidized lipid products may have possible negative health effects (Huang and Ahn, 2019).

Depending on the factors, mechanisms of lipid oxidation in foods can be categorized such as autoxidation, photosensitization, and enzyme-catalyzed oxidation (Choe et al., 2005; Choe and Min, 2006; Laguerre et al., 2007). Autoxidation or the free radical chain reaction is the most basic theory

to explain lipid oxidation and all other theories share the pathways of autoxidation. In many cases, several mechanisms are needed to explain the oxidation of foods. Based on the theories of oxidation, diverse controlling strategies to extend the oxidative stability in foods have been developed including the increases of saturation through partial hydrogenation, reduction of prooxidant factors such as oxygen, light exposure, high temperature, and transition metal ions, or addition of antioxidant compounds including free radical scavengers, metal chelators, and quenching compounds for reactive oxygen species (Choe and Min, 2009; Decker, 2002; Lee et al., 2004). However, some of these strategies may cause unexpected health effects in the final food products and the availability of some strategies is limited depending on the environmental and economic conditions. For example, partial hydrogenation can cause an increase in the *trans* fatty acid content after processing, which has been positively associated with high risks of cardiovascular diseases (Horani et al., 2006; Lemaitre et al., 2006). Increasing health concerns on the consumption of *trans* fat in diets have resulted in the development of new regulations that require the contents of *trans* fat in foods to be labeled. The food industry is trying to develop less *trans* fat producing processes to meet the guidelines of regulation and the expectation of consumers (Edward and Hunter, 2005).

✉ JaeHwan Lee
s3hun@skku.edu

Won Young Oh
wyoh@skku.edu

Mi-Ja Kim
mijakim@kangwon.ac.kr

1   Department of Food Science and Biotechnology, Sungkyunkwan University, 300 Cheoncheon-dong, Jangan-gu, Suwon, Gyeonggi-do 440-746, Republic of Korea

2   Department of Food and Nutrition, Kangwon National University, Samcheok, Republic of Korea

The addition of antioxidants and/or the reduction of prooxidants are practical approaches to control the oxidation stability and shelf life of processed foods. However, the addition of antioxidants does not ensure the expected antioxidant capacity in foods due to the diverse range of factors that can affect oxidation. Chemical potentials and physical properties are major two factors controlling the mode of free radical scavenging antioxidants or free radical scavengers (FRSs) in foods (Chaiyasit et al., 2007; Choe and Min, 2009). The physical properties deal with locations, mobility, and interfacial properties of FRSs in the colloidal structures of oil systems. Also, the type of food matrix (bulk oil or emulsions) and environmental factors such as pH, types of surfactants, and presence of transition metal ions greatly influence the performance of antioxidant capacity of FRSs (Boon et al., 2009; Chaiyasit et al., 2007; McClements and Decker, 2000). A combination of 2 or more antioxidants can have synergistic, antagonistic or merely addictive effects (Choe and Min, 2009; Decker, 2002; Laguerre et al., 2007). Also, the antioxidant capacity of FRSs in model and food systems is greatly influenced by the analysis methods (Alamed et al., 2009). All these factors need to be considered when evaluating the antioxidant capacity of FRSs.

The proposed hypotheses on antioxidant capacity need to be tested and objectively supported by scientific evidence. However, the availability of assays limits the validation of the concept of antioxidant capacity. Most reported methods have focused on analyzing oxidation products from lipids or substrate loss in model systems, and direct and clear conclusions on the antioxidant capacity of FRSs cannot be made in many cases (Decker et al., 2005; Huang et al., 2005; Laguerre et al., 2007; Niki, 2010). The antioxidant capacity of FRSs depends on the applied methods, which have different principles. Choosing the proper methods and their combinational usages are needed to evaluate the antioxidant capacity of FRSs.

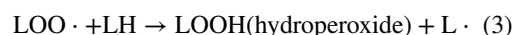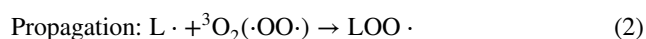## Mechanisms of lipid oxidation using chemical points of view

Autoxidation

Lipid oxidation is a reaction between lipids and oxygen molecules. Fats and oils are mainly composed of triacylglycerols (TAGs), which have a glycerol backbone and three esterified fatty acids. Also, minor compounds such as free fatty acids (FFA), monoacylglycerol (MAG), diacylglycerol (DAG), phospholipids (PLs), pigments, trace metals, moisture, air, and oxidized lipid products have been observed in commercially available fats and oils (Chaiyasit et al., 2007). Most minor compounds have amphiphilic characters with hydrophilic and lipophilic moieties in one molecule and have

been reported to influence the rates of lipid oxidation, either promoting or delaying the oxidation (Chaiyasit et al., 2007).

Atmospheric oxygen is a triplet oxygen in a di-radical state, while lipids are in a non-radical state. To react with triplet oxygen, lipids need to change into radicals from a non-radical state, which requires the abstraction of a hydrogen atom from one of the carbon atoms through energy consumption. Bond dissociation enthalpy (BDE) between hydrogen and carbon located near double bonds is relatively low and the hydrogen atom is an easy target for radical formation. Autoxidation is a radical chain reaction that involves initiation, propagation, and termination steps, which can be explained using the concepts of radical formation from lipids (Eq. 1), radical generation from lipid hydroperoxides (Eqs. 2, 3), and non-radical formation from combining radicals (Eqs. 4, 5, 6), respectively. The initiation step, which requires substantial energy to break the covalent bond between hydrogen and carbon, takes time and diverse factors can contribute the initiation steps. Singlet oxygen, transition metals, photosensitizers, high temperature, UV irradiation, and enzymes in biosystems can act as initiating factors from unsaturated fatty acids (Choe and Min, 2006; Laguerre et al., 2007; Domínguez et al., 2019).

Once lipid (LH) converts to alkyl radical (L·) through the help of initiators (Eq. 1), a triplet oxygen can react at a rate of $2-8 \times 10^9$/M/s (Zhu and Sevilla, 1990) (Eq. 2) to form peroxyl radical (LOO·), which abstracts a hydrogen atom (H·) from another lipid (LH) to form hydroperoxide (LOOH) (Eq. 3). Therefore, peroxyl radical (LOO·) acts as a kind of an initiator to generate alkyl radicals (L·), which is also called the free radical chain reaction (Choe and Min, 2006; Min and Boff, 2002a; 2002b).

$$\text{Initiation: } LH \rightarrow L \cdot + \cdot H(\text{help of diverse initiator}) \quad (1)$$

$$\text{Propagation: } L \cdot +{}^3O_2(\cdot OO\cdot) \rightarrow LOO \cdot \quad (2)$$
$$LOO \cdot +LH \rightarrow LOOH(\text{hydroperoxide}) + L \cdot \quad (3)$$

$$\text{Termination: } LOO \cdot +LOO\cdot \rightarrow LOOL + {}^3O_2 \quad (4)$$
$$L \cdot +LOO\cdot \rightarrow LOOL \quad (5)$$
$$L \cdot +L\cdot \rightarrow LL \quad (6)$$

Lipid radicals including alkyl (L·), alkoxyl (LO·), and peroxyl (LOO·) can react with each other to form a non-radical state, which is the termination steps (Eqs. 4, 5, 6).

Usually, primary oxidation refers to the steps needed for the formation of hydroperoxides. Hydroperoxides (LOOH) are decomposed into alkoxy radical (LO·) and hydroxyl radical (·OH), which is one of the most powerful radicals in biosystems. Secondary oxidation includes the steps that occur after the decomposition of hydroperoxides and the formation of volatiles from lipids. The decomposition of

hydroperoxides involves autoxidation, photosensitization, and enzyme-catalyzed oxidation.

In the case of linoleic acid (18:2), the BDE of hydrogen at C11 is 75–80 kcal/mol, while those at C8 or C14 is 88 kcal/mol and at C17 or C18 is 101 kcal/mol (Choe and Min, 2006; Min and Boff, 2002a; 2002b). Once a hydrogen atom is removed from C11, the radical at C11 shifts to adjacent carbons and forms a more stable condition. Migration of double bonds convert from natural *cis* forms into *trans* forms, which is a more stable form of double bonds. During this step, the original 9*cis* 12*cis* non-conjugated linoleic acid becomes 9*cis* 11*trans* conjugated linoleic acid or 10*trans* 12*cis* conjugated linoleic acid. Conjugated linoleic acid radicals can react with a triplet oxygen to form a hydroperoxide. Depending on the types of unsaturated fatty acids, types and relative amounts of hydroperoxides vary (Choe and Min, 2006; Min and Boff, 2002a; 2002b). The decomposition of hydroperoxides or β-scission reaction produces a hydroxyl radical ($\cdot$OH) and alkoxyl radical (LO$\cdot$). Volatiles with a small molecular weight including aldehydes, hydrocarbons, ketones, and acids can be formed from oxidized lipids (Frankel, 1985). These low molecular and volatile compounds are the secondary oxidation products responsible for the rancidity in oxidized foods.

Single oxygen oxidation mechanisms

In addition to autoxidation, photosensitization by singlet oxygen and enzymatic lipid oxidation are also common oxidation mechanisms. Photosensitization is a lipid oxidation process caused by visible light irradiation in the presence of photosensitizers, including chlorophylls, riboflavin, methylene blue or rose Bengal (Min and Boff, 2022a; 2022b). The ground and singlet state of photosensitizers (^{1}Sen) become excited singlet state (^{1}Sen*) upon light irradiation at the rate of 2×10^8/s, which can return to ground state via emission of fluorescence or generation of heat. The excited singlet state can become excited in the triplet state (^{3}Sen*) through intersystem crossing at a rate of 1–20×10^8/s. The excited triplet state (^{3}Sen*) can emit phosphorescent at a rate of 10^1–10^4/s and drop back to the ground and singlet state (^{1}Sen) or participate in a reaction through type I or type II pathways. Photosensitizers can abstract a hydrogen or electron through the type I pathway or transfer its high energy into a triplet oxygen ($^3O_2$) to form a singlet oxygen ($^1O_2$) at a rate of 1–3×10^9/s, through the type II pathway. Also, superoxide anion ($\cdot O_2^-$) can be formed at a rate of 2×10^8/s. Depending on the types of photosensitizers and availability of triplet oxygen, photosensitizers can go through either the type I or type II pathways or both pathways. Generally, riboflavin is known to prefer the type I pathway and chlorophyll and methylene blue prefer the type II pathway (Min and Boff, 2022a; 2022b; Yang et al., 2008). Singlet oxygen

has a relatively short half-life (2 μs in water − 700 μs in carbon tetrachloride) depending on the surrounding solvent. However, it can diffuse about 270 nm (Skovsen et al., 2005) and react rapidly with substrates containing an electron-rich moiety. Due to the vacant 2pπ orbital and other paired orbitals, the singlet oxygen is a non-radical and can react with non-radical state unsaturated fatty acids. Therefore, singlet oxygen oxidation or the type II pathway of photosensitizers does not require other initiators for the initiation step (Bacellar and Baptist, 2019). Singlet oxygen directly reacts with double bonds, which have a high electron density, and can generate conjugated or non-conjugated hydroperoxides. Secondary oxidation after the decomposition of hydroperoxides shares the same patterns with those of autoxidation. Due to the different hydroperoxides from unsaturated fatty acids, the profiles of oxidized volatiles through β-scissions by singlet oxygen oxidation are different from autoxidation (Frankel, 1985; Lee and Min, 2010).

Mechanisms of lipid oxidation using association colloid concept and matrix effects

Antioxidant polar paradox

The antioxidants sometimes show paradoxical behavior in different environment. Lipophilic chemicals exhibit higher antioxidant activity than hydrophilic chemicals under more moisture-rich conditions, such as in oil-in-water (O/W) emulsion, whereas the reverse phenomenon can be observed in bulk oil environments. These unexpected phenomena can be explained by the antioxidant polar paradox theory and association colloid structures (Chen et al., 2012; Laguerre et al., 2015). The presence of moisture and amphiphilic compounds has been proposed to lead to the formation association colloids; the O/W interface in association colloids has been suggested to act as a major site for lipid oxidation. Hydrophilic antioxidants might be concentrated inside association colloids in bulk oils, whereas lipophilic chemicals are located in oil droplets of the O/W emulsions. Therefore, chemicals that are properly positioned near the O/W interface might act efficiently as antioxidants in either bulk oil or the O/W emulsion matrix (Chen et al., 2010; Chen et al., 2012; Decker et al., 2017).

Bulk oil matrix

Many theories have been developed to explain the antioxidant polar paradox in bulk oil systems (Chaiyasit et al., 2005; Chaiyasit et al., 2007; Frankel et al., 1994; Richards et al., 2002; Schwarz et al., 2000). Interfacial characteristics and surfactant effectiveness of antioxidants have been

suggested as one of major factors determining the antioxidant capacities and to explain the antioxidant polar paradox. Most dominant lipid oxidation occurs at the interface of air-oil and water–oil. FRSs possess some degree of amphiphilic characteristics and FRSs located on the surface may efficiently prevent lipid oxidation. Proposed mechanisms of lipid oxidation in bulk oil using reverse micelle moisture structure are shown in Fig. 1(A). Moisture in bulk oil may be present in reverse micelles or lamella structures with the aid of amphiphilic compounds, which are called as association
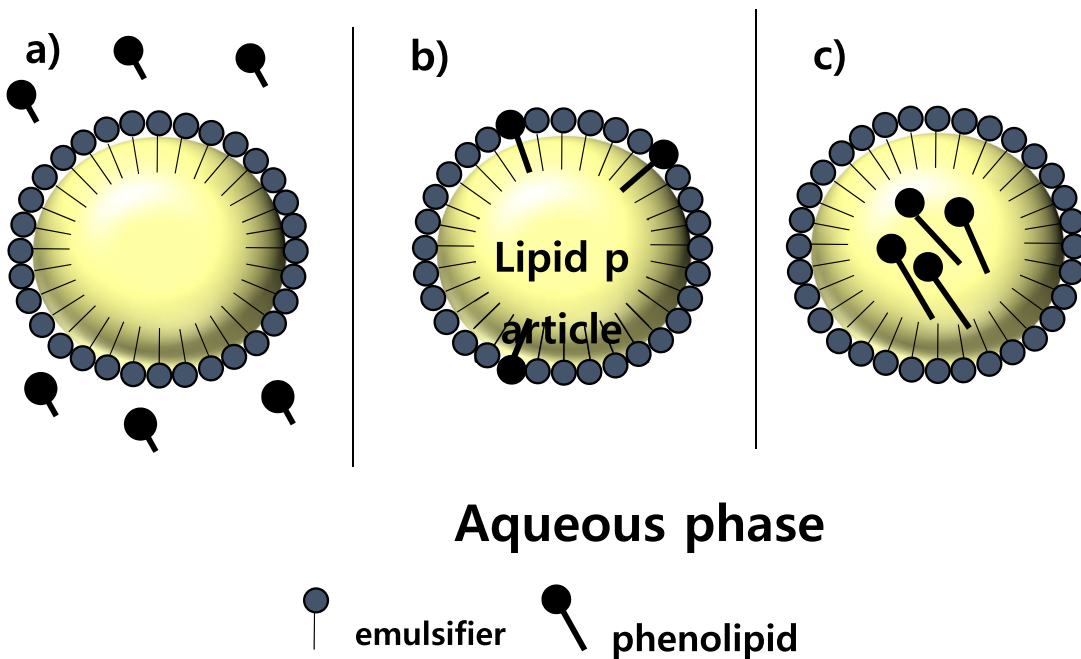
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(A)
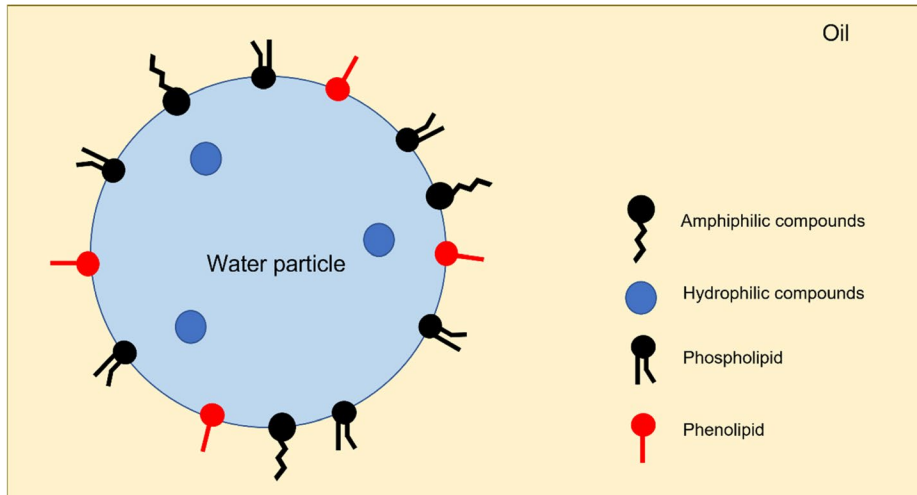
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3   Inspired from Chaiyasit et al. (2007)

4   (B)

5

6   Inspired from Lucas et al. (2010) and Lee and Oh (2022)

Fig. 1 Proposed physical locations of FRSs in bulk oil (**A**) and oil-in-water emulsion systems (**B**)

colloids (Fig. 1(A)). Moisture is one of main component for association colloidal structure in bulk oils and present from 200 to 800 ppm depending on the condition (Chaiyasit et al., 2007; Kim et al., 2018b). As oxidation time increases, the moisture content in oils increase up to certain point (Budilarto and Kamal-Eldin, 2015; Park et al., 2014), which could be due to the harvesting effects of amphiphilic compounds for the moisture. Antioxidant efficiency of α-tocopherol and ascorbic acid were substantially affected by the content of moisture in bulk oils during oxidation (Kim et al., 2015a; Kim et al., 2015b). Moisture itself could act as substrate for the formation of volatile compounds from lipid oxidation which was confirmed by the studies using deuterium oxide (Kim et al., 2014; Lee et al., 2018; Oh et al., 2017).

The major components of vegetable oil are TAGs and the contents of TAGs in crude oil and refined, bleached, and deodorizied (RBD) soybean oil range from 95 to 97% and > 99%, respectively. Minor compounds including phospholipids, MAGs, DAGs, FFAs, phytosterols, transition metal ions, and even FRSs are found in RBD vegetable oil depending on the refining process. Transition metals such as iron, copper, manganese, and nickel significantly accelerate the lipid oxidation and copper and iron are two major metal ions found in oils. The iron content is higher than the copper content in oil and the cuprous (Cu$^+$) and ferrous (Fe^{2+}) are much more effective than the cupric (Cu^{2+}) and ferric ion (Fe^{3+}) in lipid oxidation (Chaiyasit et al., 2007).

Bulk oil contains various minor amphiphilic components even after refining, bleaching, and deodorizing processes. Except for TAGs, almost all minor compounds have amphiphilic characteristics. The hydrophilic–lipophilic balance (HLB) of FFAs, DAGs, MAGs, and phospholipids have been reported to be 1.0, 1.8, 3.4–3.8, and 8.0, respectively, which can migrate to the interfacial region and form reverse micelles or lamella structures or association colloids (McClements, 2004). Hydrophilic antioxidants may migrate to the water–oil interface of the association colloids in bulk oil and increase the concentration of antioxidants at the interface, where lipid oxidation takes places. This will result in higher antioxidant capacities than lipophilic antioxidants, which are dispersed evenly in bulk oil (Chaiyasit et al., 2007; Figueroa-Espinoza and Villeneuve, 2005). The addition of hydrophilic antioxidants does not change the surface tension of the air-oil-interface in the hexadecane model system but decrease the interfacial tension of the water–lipid interface, which implies that hydrophilic FRSs in bulk oil accumulate at the interface of association colloids (Chaiyasit et al., 2007).

In addition, oxidation products including aldehydes and polar materials are amphiphilic compounds, which affect the integrity of association colloids and oxidative stability of oils. Total polar compounds from oxidized oils (Choi et al., 2018) and aldehydes like propanal, hexanal, and nonanal (Jo and Lee, 2021) acted as prooxidants. As oxidation products increased, critical micelle concentration of lecithin decreased in bulk oil implying oxidation products participate the association colloidal structures with moisture (Kim et al., 2018b). In addition, lecithin near its critical micelle concentration increases oxidative stability of non-stripped corn oil but not stripped corn oil (Kim et al., 2018a). Presence of phospholipid also change the antioxidant activities of tocopherol and ascorbyl palmitate through changing molecular mobility (Kim et al., 2023). Using NMR relaxation technique, added DOPC decreased the mobility of hydrogen atom in ascorbyl palmitate, which could help to enhance antioxidant activities (Kim et al., 2023). Interestingly, presence of amphiphilic compounds especially phospholipid can affect oxygen solubility in lipid matrix (Kim et al., 2022). Overall, amphiphilic compounds including FFA, MAG, phospholipids, even oxidation products affect the formation of association colloids with moisture and oxidative stability in bulk oil matrix.

Emulsion matrix

Emulsion matrices consist of two immiscible liquids (usually water and oil) and emulsifiers. One liquid act as the continuous phase and the other liquid is dispersed in the continuous phase. Emulsifiers, which are surface active compounds with both hydrophilic and hydrophobic moieties, adsorb to the surface of dispersed liquid, decrease the interfacial tension and kinetically prevent the aggregation of dispersed liquid. Emulsion systems that contain oil droplets dispersed in the aqueous phase are called oil-in-water (O/W) emulsion, while water-in-oil (W/O) emulsion consists of water droplets that are dispersed in an oil phase (McClements and Decker, 2000). The rate of lipid oxidation in W/O emulsions is similar to the bulk oil system, whereas the O/W emulsions showed faster oxidation rate than bulk oil (McClements and Decker, 2000; Schroën and Berton-Carabin, 2022). The oxidative stability depends on exposure to the air, transition metal ions and polar antioxidants located in the dispersed water phase, etc. Compared to bulk oil, O/W emulsions have notably higher water content and surface-active emulsifiers besides TAGs. Therefore, more factors affect the rates of lipid oxidation in emulsion systems including the chemical structures of lipids, oxygen concentration, the presence of antioxidants and prooxidant transition metal ions, droplet characteristics, interfacial characteristics, and interactions with aqueous phase components such as salts, sugars, polysaccharides, amino acids, proteins, and surfactants. The presence of transition metal ions is a critical parameter that controls the oxidative stability in O/W emulsions (Boon et al., 2009; McClements and Decker, 2000). The effects of the above factors on lipid oxidation in oil-in-water emulsions

are not discussed in this review but the information is available elsewhere (McClements and Decker, 2000).

Antioxidant activities of FRSs in emulsions are not the same as those in bulk oil (Alamed et al., 2009; Richards et al., 2002; Schwarz et al., 2000). The food matrix influences the physical stability of FRSs and partitioning of antioxidants, hydrogen bonding, interphase transport, surface accessibility. The interaction of emulsifier with antioxidants are important parameters that affect the antioxidant capacity in lipid-containing systems.

Studies using "phenolipids" showed that the length of the non-polar moiety of FRSs may be a critical factor dictating antioxidant capacity in O/W emulsion. Proposed antioxidant mechanisms of FRSs in O/W emulsion are shown in Fig. 1(B). Phenolipids are FRSs with different lengths of non-polar alkyl esters. The non-linear antioxidant capacities in O/W emulsions were observed and were shown to be dependent on the amphiphilic properties of phenolipids such as hydroxytyrosol fatty acid esters, rosmarinate alkyl esters, and chlorogenic acid alkyl esters (Laguerre et al., 2009; Laguerre et al., 2010; Lucas et al., 2010). The length of the non-polar chain of the phenolipids needs to fit the surface of the emulsions (Fig. 1(B)). If the length of the non-polar tail is too short, the phenolipid cannot be anchored and the antioxidant capacity will decrease (Fig. 1(B-a)). If the length is too long, then phenolipid may be immersed inside the lipid particle in the emulsion and the chance for FRSs to meet peroxyl radical (ROO•) will decrease (Fig. 1(B-c)). Antioxidants containing the proper non-polar chain length can fit into the interface and maximize antioxidant capacity (Fig. 1(B-b)). The proper length of non-polar tails varies depending on the types of antioxidants. In the case of hydroxyltyrosol fatty acid esters, octanoate showed the highest antioxidant efficiency (Lucas et al., 2010). Chlorogenate (Laguerre et al., 2009) and rosmarinate (Laguerre et al., 2010) showed the highest antioxidant capacities against dodecyl and octyl esters, respectively, than the other alkyl ester derivatives. Rutin and dihydrocaffeic acid possessed better antioxidant capacities with laurate and octyl ester chains, respectively, than other alkyl chain esters (Shahidi and Zhong, 2011). These reports imply that emulsions are much more complicated systems than bulk oil and it is not easy to simplify and to predict the antioxidant capacity of FRSs. Also, the antioxidant polar paradox should be modified to include the effects of the alkyl chain length when predicting the antioxidant capacities in FRSs (Shahidi and Zhong, 2011).

Pickering emulsions have shed a spotlight in recent years. Pickering emulsions are stabilized by solid particles such as silica, clay, chitosan, and cyclodextrins, not surface-active compounds (Berton-Carabin and Schroën, 2015; Yang et al., 2017). The solid particles can provide high stability of emulsion by preventing coalescence and this can be achieved by the formation of a steric barrier at the interface of oil and water. Also, these offer useful characteristics such as conductivity, responsiveness, and porosity (Yang et al., 2017). The examples of food grade solid particles used in Pickering emulsions are summarized in Table 1. The solid particles can interact with both oil and water and characteristics are very important to determine the emulsion type. For example, if the solid particles possess more wettability to water, it forms O/W emulsion (Hossain et al., 2021). In the emulsion, the solid particle, dispersed phase, and continuous phase have a three-phase boundary, and the contact angle (θ) is the angle at the three-phase boundary. The angle less than 90° forms an O/W emulsion while W/O is produced when the angle is higher than 90°. Either way, a more stable Pickering emulsion needs the angle that is close to 90° and this is due to the balance of solid particles in both phases (Hossain et al., 2021). Besides the contact angle, particle size can also play an important role in Pickering emulsions by impacting the energy (ΔE) required to desorb a particle at the interface (Berton-Carabin and Schroën, 2015):

$$\Delta E = \pi r^2 \gamma (1 - |\cos\theta|)^2,$$

where r and γ are particle radius (m) and interfacial tension (N/m), respectively.

Methods for determining the oxidative stability in edible oil

Numerous assays have been developed to assess the antioxidant capacity of compounds in foods and biological systems (Decker et al., 2010). Some in vitro assays have been developed to determine the antioxidant capacity of a molecule with the goal of reducing the stable artificial free radical through hydrogen or electron transfer, which are indirect approaches (Munteanu and Apetrei, 2021). Several direct methods have been developed involving oxidizable substrates including individual or blended fatty acids, TAGs, or oils. Depending on the purposes of the study, proper assays have been chosen to assess the antioxidant capacity of FRSs.

Methods for determining degree of oxidation

Representative oxidation steps and assays according to the oxidation products are shown in Fig. 2. Generally, the formation of hydroperoxides is regarded as the primary oxidation step and the decomposition of hydroperoxides into small volatile molecules is considered secondary oxidation. Formation of dimers and polymers can be observed in high temperature treatment such as during the deep-fat frying process.

Table 1 Solid particles possessing antioxidant activity in Pickering emulsion matrix

Type of particle	Overview	References
Polysaccharides		
Cellulose		
Cellulose nanocrystals	Z-average diameter 111.7 nm	Chen et al. (2018)
	Zeta (ζ)-potential -26.7 mV	
	Contact angle 51.7°	
Cellulose nanofibrils	Hydrodynamic diameter 29.39 to 575.8 nm	Tang et al. (2019)
	ζ-potential -38.1 to 22.4 mV	
	Contact angle 46.10 to 71.32°	
	Droplet size of emulsion: < 35 μm	
Starch		
Quinoa starch	Particle size distribution 4 to 10 μm	Rayner et al. (2012)
	Droplet size of emulsion 9 to 70	
Waxy maize starch	Particle size (d_{43}) of octenylsuccinylation treated soluble starch nanoparticle 27.9 μm	Ye et al. (2017)
	Particle size (d_{43}) of H_2SO_4 treated soluble starch nanoparticle 38.8 μm	
	Droplet size of emulsion 10 to 100 μm	
Chitosan		
Self-aggregated chitosan particles	Contact angle of 42.47°	Asfour et al. (2017)
	Particle size 287.3 nm	
	ζ-potential -48.1 to 78.4 mV	
	Droplet size ($d_{4,3}$) 5.8 to 18.7 μm	
Proteins		
Soy		
Soy lipophilic protein nanoparticles	Hydrodynamic radius (R_h) 136 ± 0.8 nm	Gao et al. (2013)
	ζ-potential -20 mV, at pH 7.0	
	Droplet size of emulsion < 1 μm	
Corn		
Zein	Contact angle 133.75°	Dai et al. (2018)
	ζ-potential 43 mV	
Hybrid particles		
Polysaccharide–polysaccharide		
Chitosan/gum Arabic (CH/GA = 1:1) nanoparticles	Particle size 108.6 nm	Sharkawy et al. (2019)
	ζ-potential $+56.3$ mV	
	Contact angle 89.2°	
	Polydispersity index 0.218	
Protein-polysaccharide		
Zein-gum Arabic complex colloidal nanoparticles	Contact angle 88.95°	Dai et al. (2018)
	ζ-potential -38 mV	
	Droplet size ($d_{4,3}$) around 22 to 88 nm	
	Droplet size ($d_{3,2}$) around 12 to 68 nm	

The conjugated dienoic acids (CDA), peroxide values (POV), *p*-anisidine values (*p*-AV), volatile compound analysis, total polar material (TPM) analysis, and 2-thiobarbituric acid reactive substances (TBARS) determine specific lipid oxidation products (Table 2) (Alamed et al., 2006; Estevez and Cava, 2006; Shahidi and Wanasundara, 2017; Shahidi and Zhong, 2020). Some assays including HOD, CDA, and POV are good for determining primary oxidation stages, while *p*-AV, volatile analysis, TPM, and TBA values are suitable for determining products produced from secondary oxidation (Fig. 2).

UV absorbance for conjugated diene or triene is another tool that has been used to determine the oxidation degree of polyunsaturated fatty acids. CDA analyzes the conjugated

dienes in polyunsaturated fatty acids from the migration of *cis* double bonds into *trans* conjugated forms. The conjugated autoxidizable triene assay uses tung oil containing ~86% eleostearic acid, which is an octadecatrienoic acid that is conjugated to trienes and exhibits strong UV absorption at 273 nm (Laguerre et al., 2008). The absorbance from conjugated triene decrease as oxidation proceeds and this method could also be used in O/W emulsions (Laguerre et al., 2010).

POV has been used to determine the amount of primary oxidation products or peroxides. *p*-AV measures the 2-alkenals content, which are one of the secondary oxidation products produced from the *β*-scission of hydroperoxides. Volatile analysis determines total or individual volatiles such as hexanal, propanal, or *t*-2-heptenal as secondary oxidation products (Alamed et al., 2006; Lee et al., 2007b; Lee and Min, 2010; Lee and Decker 2011). Depending on the types of major fatty acids and mode of oxidation, target volatiles could be chosen. Hexanal and *t*-2-heptenal are commonly observed volatiles produced from oxidized linoleic acid through thermal oxidation and 1-octen-3-ol could be a useful volatile to determine the effects of singlet oxygen oxidation on linoleic acid (Lee and Decker, 2011). Propanal is one of the main volatiles produced from thermally oxidized linolenic acid (Frankel, 1985). Volatile analysis requires a specific apparatus to trap and concentrate the volatiles such as solid phase microextraction and gas chromatography coupled with a flame ionization detector or a mass selective detector for separation and quantification of isolated volatiles. TPM determines the carbonyl compounds or oxidized lipid containing oxygen.

Edible bulk oils, which can be treated with or without a stripping process to reduce all minor oil components, can be thermally oxidized at 60 °C in the dark (AOCS oven storage test for accelerated aging of oils, Cg5-97) (Decker et al., 2005) or thermally oxidized under desired processing conditions ranging from 90 to 180 °C in the dark (Yeo et al., 2010). Combinations of assays determining primary and secondary oxidation products have been recommended for use to measure the antioxidant capacity of FRSs or to determine the degree of lipid oxidation. Totox, which involves both POV and *p*-AV assays, was introduced to predict lipid oxidation. Totox (or oxidation value) $= 2 \times (POV) + p$-Anisidine (Kochhar, 2000).

In the case of emulsion systems, emulsifiers with low hydroperoxides and minimal concentration should be added to produce stable emulsions and the oxidation temperature needs to be lower than 60 °C. Oil should be recovered from sampled emulsion and lipid hydroperoxides for primary oxidation and headspace volatile analysis by gas chromatography for secondary oxidation can be used (Alamed et al., 2009; Decker et al., 2005; Lee and Decker, 2011).

In general, non-volatile lipid oxidation products do not contain chromophores or fluorophors, thus selective detection techniques are unavailable (Steenhorst-Slikkerveer et al., 2000). Gas chromatography (GC) and GC–mass spectrometry (MS) are options to measure oxygenated fatty acids. However, to use these techniques, the oxygenated lipid must undergo hydrolytic and/or derivatization. On the other hand, liquid chromatography (LC)–MS (or LC–MS/MS), another way to measure lipid oxidation, does not need laborious sample preparation. This provides information on intact oxygenated TAGs with differentiation of homologs and geometric isomers (Xia and Budge, 2017). LC–MS is particularly used for epoxides produced by hydrogen abstraction-independent pathways. Also, it can determine a balance between hydroperoxide (formed by hydrogen abstraction-dependent pathway) and epoxide (Grüneis et al., 2019). According to Grüneis et al. (2019), total epoxide value was decreased while heating temperatures and treatment time were increased. On the other hand, peroxide value at 180 °C was higher than that of 25 and 80 °C. The authors claimed that considering only peroxide value could underestimate early-stage lipid oxidation and suggested that epoxide value might also be used as an indicator for early-stage lipid oxidation.

Nuclear magnetic resonance (NMR) is also frequently used to analyze fatty acids, TAGs, adulteration of oil, and oxidation products including alcohols, epoxides, and ketones (Xia and Budge, 2017). Detailed information on the chemical shifts of oxidative products is available elsewhere (Martínez-Yusta et al., 2014; Xia and Budge, 2017). The advantage of using NMR is that the technique is a reliable quantitative method and well correlated with standard methods such as TBARS and acid values (Xia and Budge, 2017). The pretreatment of NMR is simply dissolving oil or lipid in deuterated solvents. A single run will provide a simultaneous determination of oxidation products. Although ^{1}H, ^{13}C, and ^{31}P NMR can be used for lipid analysis, ^{1}H NMR plays an important role due to its higher sensitivity (Xia and Budge, 2017).

Methods for predicting the oxidative stability

Headspace oxygen depletion (HOD) method

The HOD method determines the oxygen contents in an air-tight sealed vial containing lipid system. As the degree of lipid oxidation increase, the headspace oxygen decreases due to the consumption of headspace oxygen by lipids (Lee and Min, 2010). Quenching mechanisms and kinetics of antioxidants including *α*-tocopherol, riboflavin, and *β*-carotene for singlet oxygen were determined by measuring the depletion of headspace oxygen content (Huang et al., 2004; Yang et al., 2002). Changes in

headspace oxygen were compared in elaidic *trans* fatty acid and oleic *cis* fatty acid under methylene blue photosensitization and thermal autoxidation (Lee et al., 2010a).

Rancimat

The Rancimat method, an accelerated oxidation test, determines the induction period (IP) via the measurement of conductivity changes by volatile compounds formed (Félix-Palomares and Donis-González, 2021). The Rancimat equipment exposes the oil to high temperature and air bubble in a vessel until short-chain fatty acids (SCFAs) are generated (Félix-Palomares and Donis-González, 2021; Pawar et al., 2014). The SCFAs produced are immediately transferred to a separate vessel containing distilled water and the conductivity is monitored at room temperature (Mendez et al., 1996; Pawar et al., 2014).

The IP means the resistance of lipids against oxidation, thus this method establishes the relative stability of fats. The results obtained are well correlated with other methods measuring oxidative stability and one possible way to carry out this is by comparing the IP determined by EN 14112 (Flitsch et al., 2014). Also, the method provides reproducible oxidation conditions (e.g., temperature and air) as well as cheap, timesaving, and devoid of toxic reagents. It offers various applications such as edible oils, fats, nanoemulsions, and plant extracts (Tinello et al., 2018).

Oxidation test (OXITEST)

The OXITEST (AOCS Cd 12c-16) is another accelerated oxidation test measuring IP. The equipment controls temperature (ambient to 110 °C) and oxygen pressure (0–8 bar) and reads the oxygen uptake, which is used to generate IP value (Tinello et al., 2018; Tsao et al., 2021). The method does not require any sample preparation such as oil extraction and it can assess any type of food (solid, powder, or liquid) (Tinello et al., 2018). Inside the equipment (oxidation chambers, sample holders, and covers) is made of titanium to prevent chemical corrosion (Comandini et al., 2009). Also, the OXITEST system offers a well-controlled environment from light and oxygen, which can affect the shelf-life of food lipids (Tsao et al., 2021). By measuring the accelerated oxygen absorption inside the chamber, it provides information on the intrinsic resistance of food and renders to predict the shelf-life (Comandini et al., 2009).

Radical scavenging compounds from oxidized lipids (RSOL) and antioxidant prooxidant balance (APB) value using DPPH

The DPPH radical is very stable and commercially available, therefore it is frequently considered the first step of measurement of antioxidant activity. The purple color of the DPPH radical turns yellowish when the radical is donated hydrogen atoms or electrons by the antioxidant. The antioxidants in lipids can be extracted by using methanol and the antioxidant capacity of these can be measured by the color change of DPPH radical (Cheng et al., 2006; Hristeac et al., 2006; Ionita, 2005; Ozcelik et al., 2003).

The DPPH method was modified to evaluate the degree of lipid oxidation and antioxidant capacity of a FRS in thermally oxidized vegetable oils (Lee et al., 2007a), sesame seed oil (Lee et al., 2010b), and lard model systems (Yeo et al., 2010). Isooctane was used as a solvent to dissolve DPPH and lipid instead of alcohols. The results of the modified DPPH method using oxidized oils showed that some radical scavenging compounds from oxidized lipid, which are designated as "RSOLs", were continuously formed during lipid oxidation (Yeo et al., 2011).

When FRSs including tocopherol, BHA, TBHQ, or sesamol were added to oil, the DPPH absorbance increased at a certain time, which may be due to the depletion of FRSs, and started to decrease at later times, which may have been related to the formation of RSOLs. One of the main disadvantages of using the modified DPPH method is not only FRSs but also RSOLs can react with DPPH and decrease the absorbance. If the ratio between FRSs and RSOLs for DPPH is determined correctly, the antioxidant capacity can be predicted during lipid oxidation. For this, a new concept recently proposed, the antioxidant prooxidant balance (APB) value can be used (Choi et al., 2018; Song et al., 2016).

$$APB = DPPH\ loss\ in\ methanol/DPPH\ loss\ in\ isooctane,$$

$$DPPH\ loss(mole/g)$$
$$= Conversion\ of\ DPPH\ absorbance\ into$$
$$DPPH\ concentration(mole/L)$$
$$\times sample\ volume(L)/sample\ weight(g)$$

The APB value is varied depending on the type of lipids. Since DPPH loss in methanol indicates the level of FRSs in the lipid, low APB value (< 0.5) means that the lipid is highly oxidized. On the other hand, if the APB value is higher than 1, this indicates that the lipid is fresh (Choi et al., 2018).

Representative steps of lipid oxidation   Representative assays for each step
                                                of lipid oxidation

RH

$\downarrow$ $-\quad \cdot H$

Alkyl radical   R·

$\downarrow$ $+\quad O_2$ $\longrightarrow$ **Headspace oxygen depletion**

Peroxyl radical   ROO·

RH   FRS(AH), free radical scavengers

R·   FRS· (A·) radical from FRS

Hydroperoxide   ROOH $\longrightarrow$ UV absorbance for **conjugated diene**
                                              if RH are polyunsaturated fatty acids

                                              Peroxide value

Hydroperoxide
decomposition $\downarrow$

Volatile compounds   **TBA value, *p*-AV value**
(malonaldehydes, aldehydes,   **Total volatile analysis**
alcohols, acids, ketones,   (hexanal, *t*-2-heptenal etc)
hydrocarbons, and so on)

Carbonyl group addition   **Polar compound analysis**
and polar compound   **Total carbonyl compounds**
formation

Polymer formation in oil with   **Polymer analysis**
deep-fat frying process

Adapted from Lee and Oh (2022)

Fig. 2 Assays used to determine the degree of lipid oxidation and their oxidized targets in oil matrices

Chemical and physical factors in bulk oil matrix

Lipid oxidation is influenced by the chemical and physical characteristics of lipids. The chemical nature of lipids includes degree of unsaturation, degree of oxidation, and antioxidants, and physical factors are moisture content and viscosity. The consideration of these factors renders the prediction of oxidative stability. The chemical factor can give a brief idea of oxidative stability while considering both chemical and physical aspects provide a more accurate

Table 2 Summary of methods for the evaluation of lipid oxidation in oil matrix

Method	Principle/compounds	Technique	Comments	References
Analysis of primary oxidation products				
Peroxide value	Reduction of ROOH with KI and measurement of I_2 Titration with $Na_2S_2O_3$	Iodometric titration	$\approx$ 0.5 meq/kg fat	Dobarganes and Velasco (2002), Shahidi and Zhong (2020)
Conjugated dienes and trienes analysis	Isomeric hydroperoxides will make conjugated dienes with the removal of oxygen and determine 1,4-dienes produced	UV–Vis spectrometry Absorption at 233 nm	$\approx$ 0.2 meq/kg lipid Suitable for PUFA-containing foods	Abeyrathne et al. (2021)
Analysis of secondary oxidation products				
Thiobarbituric acid reactive substances (TBARS)	Detect the production of chromogen due to the reaction of malonaldehyde and thiobarbituric acid	UV–Vis spectrometry (absorption at 532 nm), HPLC, GC–MS, and fluorometer	Simple and fast detection Easy to detect and low cost. Reproducible well and correlate well with sensory attributes	Abeyrathne et al. (2021)
p-Anisidine	Aldehydes, mainly alkenals	UV–Vis spectrometry Absorption at 350 nm	Application to fats and oils	Dobarganes and Velasco (2002), Shahidi and Zhong (2020)
Carbonyls	Total carbonyls or specific carbonyl compound formed	Spectrometry technique and HPLC	Application to fats and oils	Dobarganes and Velasco (2002), Shahidi and Zhong (2020)
Oxidative stability instruments	Volatile organic acids	Rancimat	Monitoring changes in conductivity Rapid and automated Application to fats and oils	Dobarganes and Velasco (2002), Shahidi and Zhong (2020)
Hydrocarbons	E.g., ethane, pentane	GC or GC–MS	Direct headspace Rapid analysis Application to all samples	Dobarganes and Velasco (2002), Shahidi and Zhong (2020)
Volatile aldehydes	E.g., propanal, hexanal	GC or GC–MS	High sensitivity Application to fats and oils	Dobarganes and Velasco (2002)
Sensory analysis	Use trained or untrained human panelist to determine the level of oxidation through sensory attributes, such as odor, taste, and acceptability	–	Application to all animals and plant-based foods, cereals	Abeyrathne et al. (2021)
Analysis of both primary and secondary oxidation products				
Total oxidation index (TOTOX)	Determine the total oxidized products	–	Simple calculation Application to fats and oils	Abeyrathne et al. (2021)

Adapted from Abeyrathne et al. (2021), Dobarganes and Velasco (2002), Shahidi and Zhong (2020)

prediction of oxidative stability. The proposed predictive model of oxidative stability can be achieved by following equation (Lee and Oh, 2022):

Predictive model of oxidative stability

= chemical factors × physical factors

$$\left\{ \frac{\text{Oxidizability} \times \text{TOTOX value} \times \text{acid value}}{\text{DPPH loss in methanol}} \right\}$$

$$\times \left\{ \frac{\text{Moisture content}}{\text{Viscosity}} \right\}$$

Above prediction equation has antioxidative factors in denominator while prooxidative factors locate in numerator. Degree of unsaturation of fatty acid could determine basic properties of oxidative stability in lipids. Presence of other antioxidative or prooxidative factors should be considered to predict the oxidative stability more accurately.

To determine oxidizability, a study on fatty acid composition needs to be carried out to evaluate the degree of unsaturation. The rates of oxidation in oils can be predicted differently depending on the model systems and previous reports. For example, the ratios of oleate, linoleate, and linolenate used to calculate the oxidizability of oils at 1:27:77 (Min and Boff, 2002a; 2002b), 1:50:100 (Neff et al., 1992), 1:3:12 (Kerrihard et al., 2015) or 1:12:25 (Hu, 2018). If an oil contains 50% oleic acid, 25% linoleic acid, and 5% linolenic acid, then the oxidizability of this oil is calculated as 185 ($50 \times 1 + 25 \times 3 + 5 \times 12$) when using the rate of 1:3:12.

From the above prediction equation, the degree of oxidation is considered by TOTOX value (primary and secondary oxidation products) and acid value. Also, the presence of antioxidant can be achieved by DPPH loss in methanol. With respect to the physical factors, the moisture content plays an important role in the surface area of association colloids (Kim et al., 2018b), which are considered the major site for lipid oxidation and substrates for the formation of volatiles, thus the moisture content act as a prooxidant. On the other hand, the higher viscosity could retard the chemical reaction including lipid oxidation. However, the effect of each factor on lipid oxidation may be different, thus the weight of each factor should be considered, which needs further investigation.

In conclusion, this review introduces the concept of lipid oxidation based on the mechanism and food matrix (bulk oil or emulsions) and methods to determine the degree of lipid oxidation. In addition, this article proposes a new way to predict oxidative stability in lipids based on chemical and physical factors. This contribution will be of interest to newcomers to the food lipid area, industry, and consumers.

Declarations

Conflict of interest The authors have declared no conflict of interest.

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