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LIPID OXIDATION IN OIL-IN-WATER EMULSIONS: A MINI REVIEW

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ABSTRACT

Emulsion technology has been emerged into food industries widely. Researches in emulsion and its application have been done intensively particularly to understand emulsion behavior in relation to its stability. Stability of emulsion indicates stability of food products therefore attempt to identify the causes of instability increases. This mini review underlines lipid oxidation in oil in water emulsion including emulsion definition, factors involved in determining the rate of lipid oxidation, common cause of oxidative instability and some case examples of lipid oxidation in emulsion.

1. EMULSION DEFINITION

An emulsion is dispersion of two immiscible liquids, in which one is dispersed in the other (usually oil and water, with droplet size in a range of 0.1 to 100 μm) and thermodynamically unstable due to different densities of oil and water (McClements, 2005). This property needs positive free energy to increase the surface area between water and oil phase. In order to increase the emulsion stability for a period of time, emulsifiers are usually added prior to homogenization. Emulsifiers are surface-active molecules that absorb to the surface of oil droplets immediately after homogenization and have the ability to form

a protective membrane to prevent droplet aggregation. Many food lipids are in the form of this type of emulsion, such as milk, dressings, mayonnaise, beverages, sauces, etc., while margarine and butter are two examples of a water-in-oil emulsion (Dickinson, 1992; McClements, 2005).

2. OIL IN WATER EMULSION (O/W EMULSION)

Theoretically, an oil-in-water emulsion consists of three regions: the interior of the oil droplets, the aqueous or continuous phase, and the interfacial layer. The interfacial layer is a few nanometer-thick layer surrounding each droplet in the emulsion, and this narrow region consists of a mixture of emulsifier molecules, oil, water and any other surface-active compounds attracted toward this region. For relatively small droplets with thick interfacial layers, the volume occupied by the interface is quite significant. Thus, it is highly possible that low concentrations of

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molecules (few μM to mM) such as antioxidants, pro-oxidants, and hydroperoxides are localized within the interfacial region. Molecule position in the emulsion depends on their polarity and surface activity. Polar molecules are usually located in the aqueous phase, non-polar ones in the oil phase, and amphiphilic molecules at the interface (Dickinson and McClements, 1995).

Type and concentration of molecules present in the interface determine its characteristic and most importantly have a great impact on the rate of lipid oxidation in the emulsion (Dickinson and McClements, 1995). Another factor that must be taken into account is the lipid molecules orientation at the interfacial layer, whether parallel or perpendicular to the interface. This orientation will affect molecule accessibility to the water-soluble antioxidants or pro-oxidants. If oxidation occurs, oxygen can increase the polarity of fatty acids, and this will change the emulsion properties as well as the susceptibility of fatty acid to oxidation (Hiemenz, 1997).

3. THE RATE OF LIPID OXIDATION

McClements and Decker (2000) highlight the importance of molecular environments providing details and causes of lipid oxidation in oil-in-water emulsions. They describe the factors involved in determining the rate of oxidation as follows:

1. Chemical structure of lipids

The number and location of double bond in a lipid molecule determine its susceptibility to oxidation. The rate of fatty acid oxidation increases as the degree of unsaturation increases (Nawar, 1996). The closer the double bonds to the methyl end of a fatty acid, the greater its stability with respect to oxidation (Miyashita *et al.*, 1995).

2. Oxygen concentration

In food oils, oxygen is reported three times more soluble than in water, thus oxygen can act as a fuel to accelerate lipid oxidation unless an action is taken to exclude oxygen (Ke and Ackman, 1973).

3. Antioxidants

The effectiveness of chain-breaking antioxidants is determined by their chemical properties and physical location within a system. Lipophilic antioxidants are more effective in oil-in-water emulsions than the hydrophilic ones. Similarly, non-polar antioxidants work better in emulsions than in bulk oil compared to the polar antioxidants. Tocopherols are examples of

lipophilic and non-polar antioxidants while Trolox and ascorbic acid are in the group of hydrophilic and polar antioxidants. The effectiveness of tocopherols in emulsion increases as their polarity decreases or their surface activity increases. This is due to their position will be at the oil-water interface when oxidation occurs (Huang *et al.*, 1996). EDTA and phytate are transition metal chelators that retard oxidation by binding and removing iron from the droplet surface (Mei *et al.*, 1998a; Mancuso *et al.*, 1999b).

4. Interfacial characteristics

The rate of lipid oxidation in emulsion is highest if the droplets are negatively charged (because they can attract the positively charged iron ions electrostatically to the droplet surface), and fairly similar for uncharged and positively charged droplets (Mancuso *et al.*, 1999a; Mancuso *et al.*, 1999b). Oxidation rate is significantly lower when the lipid droplets are cationic at a pH below the isoelectric point (pI) of the emulsifying proteins (Hu *et al.*, 2003a; Donnelly *et al.*, 1998). The oxidation is lowest in the system where the droplets are stabilized by surfactants with longest polar head groups because they can act as a thick physical barrier to separate the lipid from pro-oxidants (Silvestre *et al.*, 2000). Protein also has the ability to build thick and viscoelastic membranes surrounding the oil droplets, thus partly inhibiting oxidation (Donnelly *et al.*, 1998).

5. Droplet characteristics

Contradictive findings exist with regard to the role of droplet size in the emulsion. If a system has excess of reactants, decreasing droplet size means doubling their concentration, thus the oxidation rate increases. In contrast, if there is only a small amount of hydroperoxides on the surface of the oil droplets, decreasing the droplet size means that there is no effect of free radicals on oxidation (Roozen *et al.*, 1994).

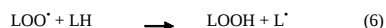
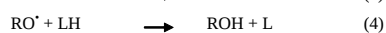
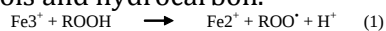
6. Interaction with aqueous phase components

Casein has the ability to form an interfacial layer of up to 10 nm around oil droplets, which is very thick compared to the 1-2 nm for whey protein (Dickinson and McClements, 1995). A thick interfacial membrane may explain why an emulsion stabilized by casein is more stable to oxidation than an emulsion stabilized by whey protein (Hu *et al.*, 2003b). Proteins were also reported as effective transition metal chelators that reduce iron and hydroperoxide interaction (Cho *et al.*, 2003; Hu *et al.*, 2003a; Hu *et al.*, 2004b;

Hu *et al.*, 2003b; Hu *et al.*, 2004a; Guzun-Cojocar *et al.*, 2010). However, recent research shows that the protein function as an iron chelator might be changed during food processing if the protein chain is unfolded, and its denaturation may alter the metal-binding properties (Pitkowski *et al.*, 2009). Polysaccharides may have a dual function in emulsion as thickening agents and as antioxidants by chelation of metal ion and by hydrogen donation (Gohtani *et al.*, 1999).

4. COMMON CAUSE OF OXIDATIVE INSTABILITY IN EMULSION

Previous studies regarding oil-in-water emulsion emphasized that the common cause of oxidative instability in this system is the interaction between transition metal originated in the aqueous phase and the hydroperoxides located on the surface of the oil droplets. Iron is chemically reactive and has become one of the main pro-oxidants in foods (Cho *et al.*, 2003). As an oxidation accelerator, iron can promote lipid oxidation by coming into close proximity to the lipid substrate (McClements and Decker, 2000). Transition metals or pro-oxidants have the ability to decompose hydroperoxide (ROOH) into peroxy (ROO[•]) and alkoxyl (RO[•]) radicals, which are highly reactive (eq.(1) – eq. (6)). If within the oil droplets and at the oil-water interface these radicals react with unsaturated fatty acids (LH), the lipid radical (L[•] and LOO[•]) will be formed. Further reactions of lipid radicals with other unsaturated fatty acids will regenerate the oxidation chain reaction (Mei *et al.*, 1998a; Mei *et al.*, 1998b). Moreover, formation of alkoxyl radical leads to the reaction of β -scission, which results in the development of rancidity indicators such as ketones, aldehydes, alcohols and hydrocarbon.



McClements and Decker (2000) also underlined the importance of the physical location of reactive molecules within the emulsion. Hydroperoxides and free radicals are usually present on the surface of droplets and are surface active, whereas the transition metals and enzymes, as lipid oxidation accelerators, originate from the aqueous phase of the emulsion. If the free radicals are formed on a droplet surface, they can easily react with unsaturated fatty acids within the same droplet surface and oxidation occurs. Therefore, the rate of oxidation depends on the speed of free

radicals, hydroperoxides or unsaturated fatty acids when diffusing within a droplet from one region to another (McClements and Decker, 2000).

5. EXAMPLE OF LIPID OXIDATION IN EMULSION

A recent study reveals that iron is a cause of oxidation. Choi *et al.* (2009) isolated iron from fish oil emulsion and observed the rate of oxidation. Iron was encapsulated within the internal aqueous phase of the water-in-oil-in-water (W/O/W) emulsion. The first aqueous phase system was prepared by dispersing 15 wt% whey protein isolate and 0.1 wt% iron into a 20 mM phosphate buffer solution at pH 7.0. The oil phase was prepared by mixing 8 wt% polyglycerol polyricinoleate (PGPR) into corn oil. Then the first aqueous phase was mixed with the oil phase to form a W/O emulsion and subsequently dispersed into 80 wt% of an aqueous surfactant solution (0.5 wt% Tween 20, 20 mM phosphate buffer, 0.02 wt% sodium azide) at pH 7.0 using a membrane homogenizer. The final W/O/W emulsion was finally combined with a pre-mix 16 wt% fish oil with 84 wt% aqueous surfactant solution. The results show that the TBARS formed decreased compared to fish oil emulsion only and depended on the concentration and location of iron, i.e., no added iron < iron in external < aqueous phase < iron in internal aqueous phase (Choi *et al.*, 2009).

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