

COMPREHENSIVE REVIEW

Oxidation and oxidative stability in emulsions

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Abstract

Emulsions are implemented in the fabrication of a wide array of foods and therefore are of great importance in food science. However, the application of emulsions in food production is restricted by two main obstacles, that is, physical and oxidative stability. The former has been comprehensively reviewed somewhere else, but our literature review indicated that there is a prominent ground for reviewing the latter across all kinds of emulsions. Therefore, the present study was formulated in order to review oxidation and oxidative stability in emulsions. In doing so, different measures to render oxidative stability to emulsions are reviewed after introducing lipid oxidation reactions and methods to measure lipid oxidation. These strategies are scrutinized in four main categories, namely storage conditions, emulsifiers, optimization of production methods, and antioxidants. Afterward, oxidation in all types of emulsions, including conventional ones (oil-in-water and water-in-oil) and uncommon emulsions in food production (oil-in-oil), is reviewed. Furthermore, the oxidation and oxidative stability of multiple emulsions, nanoemulsions, and Pickering emulsions are taken into account. Finally, oxidative processes across different parent and food emulsions were explained taking a comparative approach.

KEYWORDS

antioxidant, emulsifier, emulsion, oxidation, oxidative stability

1 | INTRODUCTION

Emulsions are complex systems comprising of two or more liquids with one being dispersed in the other one. There are different types of emulsions (Figure 1) such as oil-in-water (O/W) emulsions where oil is dispersed in water phase (McClements, 2016), water-in-oil (W/O) emulsions where an aqueous phase is dispersed in a lipid phase (Kirkhus et al., 2015), and multiple emulsions that consist of an emulsion within another emulsion (Muschiolik

& Dickinson, 2017). Furthermore, emulsions are divided in terms of the size of droplets such as regular emulsions, microemulsions, and nanoemulsions (Gutiérrez et al., 2008). Emulsions can also be categorized according to their method of stabilization, that is, regular emulsions and Pickering emulsions where solid particles are adsorbed at the interface between two phases of the emulsion (Yang et al., 2017). Emulsions are applied in various areas including food science (Murray, 2019), cosmetics (Peito et al., 2022), medicine (Chen et al., 2022), and construction

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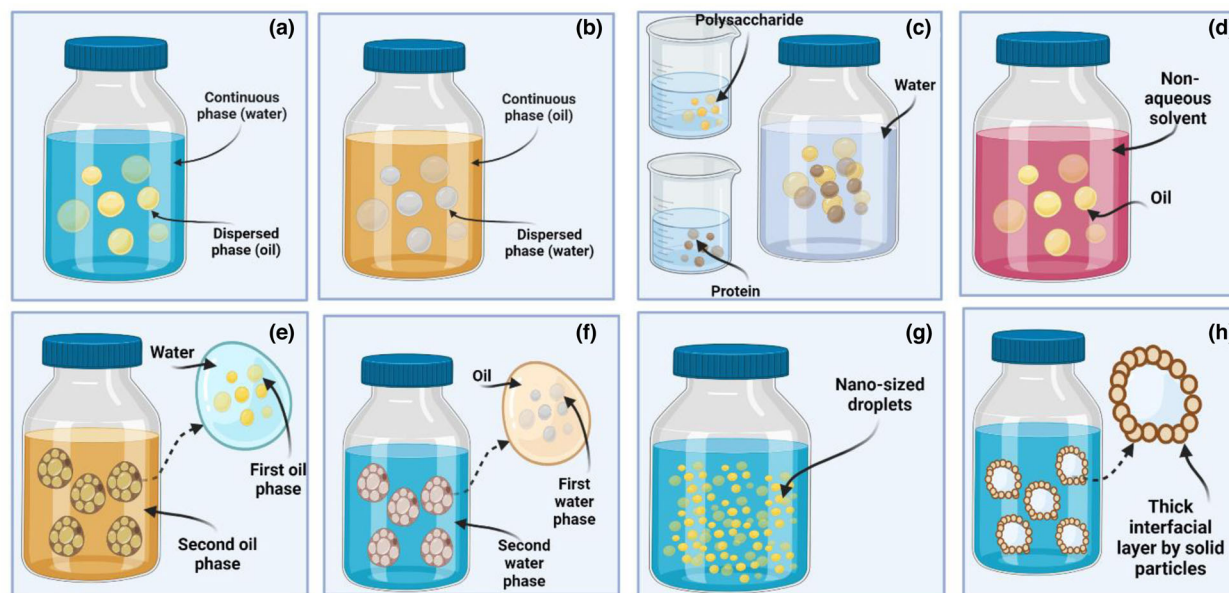


FIGURE 1 Different emulsions: (a) oil-in-water emulsion; (b) water-in-oil emulsion; (c) water-in-water emulsion; (d) oil-in-oil emulsion; (e) oil-in-water-in-oil emulsion; (f) water-in-oil-in-water emulsion; (g) nanoemulsion; and (h) Pickering emulsion.

(Fang et al., 2022), among others. In food science, emulsions are used in the production of variety of foods such as sausages (Schopfer et al., 2022), margarines (Silva et al., 2021), mayonnaise (Yesiltas et al., 2021), dairy products (Ahn et al., 2022), seafood (Ghelichi et al., 2018), among others. However, adoption of emulsions in different applications is restricted by some barriers such as instability of emulsion during processing, packaging, and/or storage. In this regard, one of the most important limiting factors in the use of emulsions, especially in food science, is the oxidative degradation of emulsions, which results in detrimental effects in the final products.

The initial lipid oxidation processes are the same in emulsions as in neat oils. However, emulsions are more complex systems than neat oils. For that reason, lipid oxidation products can react with, for example, the emulsifier and other ingredients present in the emulsion. For example, if proteins are present, Strecker aldehydes can be formed and this will not happen in neat oils (Hidalgo & Zamora, 2004; Thomsen et al., 2013). In most cases, oxidation occurs faster in emulsions than in bulk oils. This can be ascribed to either the emulsification conditions and/or the larger interfacial area available in emulsions compared with neat oil. During the emulsification process, the oil may be exposed to air (oxygen) or high temperature, which will increase oxidation as further discussed below. If sonication is used as the emulsification method, acoustic cavitation can lead to direct production of free radicals (Jana et al., 1990; Riesz & Kondo, 1992).

Lipid oxidation is an interfacial phenomenon as it is initiated at interfaces between oil and water, where unsat-

urated fatty acids in the oil phase and prooxidants such as trace metal ions in the aqueous phase can interact. Thus, the large interfacial area between the oil and the aqueous phase created during emulsification will lead to increased interactions between reactants, which in turn may increase the rate of lipid oxidation. Importantly, prooxidant metals, oxygen, and water-soluble antioxidants have to diffuse through the aqueous phase to reach the oil droplets or the o/w (oil/water) interface. For that reason, oxidation is significantly affected by differences in solubility properties, mobility, and mass transfer rates of transition metals and antioxidants through different phases (Mickaël Laguerre et al., 2017).

In the light of the above, this review aims to review different strategies in order to render oxidative stability to emulsions and to shed light on oxidation in various types of emulsions.

2 | LIPID OXIDATION REACTIONS AND THEIR ASSESSMENT

2.1 | Lipid oxidation reactions

Lipid oxidation happens in lipids containing at least one double bond no matter whether they are found as free fatty acids (FFAs) or are bound in triacylglycerides or phospholipids. Lipid oxidation happens in the presence of oxygen, but the direct oxidation of unsaturated fatty acids by ground state oxygen (triplet oxygen 3O_2) is spin forbidden. However, oxidation can be initiated by initiators that

can produce free radicals by different mechanisms. One of the mechanisms involve enzymes (lipoxygenases), but since these enzymes are usually not present in oils used for emulsion production, this type of lipid oxidation will not be further discussed here. The most common form of lipid oxidation is autoxidation, which is a reaction between free lipid radicals and oxygen. The other common form is photooxidation resulting from exposure of lipids to light in the presence of photosensitizers. Autoxidation is initiated in the presence of initiators (e.g., metal ions, heat or already existing lipid radicals), which causes unsaturated fatty acids (LH) to form alkyl radicals (L·). These radicals react fast with oxygen to form peroxy radicals (LOO·). Thereafter, the peroxy radical reacts with a new unsaturated fatty acid to form lipid hydroperoxides (LOOH) and a new lipid radical, whereby the lipid oxidation reaction can propagate until two free radicals join and form a non-radical product. The lipid hydroperoxides are regarded as the primary oxidation products and are nonvolatile and therefore odor and tasteless. Lipid hydroperoxides can easily decompose to alkoxy and peroxy radical intermediates (LO· and LOO·) by thermal dissociation or by the presence of trace metals such as iron and copper. These free radicals can further propagate the free radical chain to form new hydroperoxides. Alkoxy radicals can also further decompose via β -scission, whereby a range of nonvolatile (core-aldehydes) and volatile secondary oxidation products are formed (Frankel, 1991). Volatile oxidation products include aldehydes, ketones, alcohols, acids, and hydrocarbons and they lead to rancid and other off-odors and off-flavors.

2.2 | Lipid oxidation assessment

The extent of lipid oxidation can be assessed by a wide range of methods such as peroxide value (PV), anisidine value (AV), thiobarbituric acids reacting substances (TBARS), as well as instrumental methods such as high-performance liquid chromatography, gas chromatography–mass spectrometry (GC–MS), near infrared spectroscopy, nuclear magnetic resonance (NMR), Fourier-transform infrared spectroscopy, and differential scanning calorimetry. Sensory evaluation of oxidative flavor deterioration is another important method that should be used to understand how lipid oxidation impacts sensory properties of food emulsions.

Primary oxidation products can be determined by spectrophotometric measurement of conjugated diene hydroperoxides at 234 nm or by determination of the so-called PV. Before measurement, the lipids must be extracted from the emulsions. The reader is referred to Schaich (2016) for an overview of extraction methods. The

analytical principle of all wet-chemical methods for the determination of PV is the ability of the lipid hydroperoxides to oxidize either ferro or iodide ions, which then react with another reagent and form a colored complex, which in most cases is determined by spectrophotometry (Nielsen et al. 2003).

Some secondary oxidation products can also be measured spectrophotometrically. Thus, the anisidine test is a method commonly used in the oil industry as a measure of the level of carbonyl compounds. The principle of the anisidine test is that carbonyls react with *p*-anisidine to form a colored complex that absorbs at 350 nm. It primarily measures 2-alkenals, but other carbonyl compounds are also able to react with *p*-anisidine. Different 2-alkenals give rise to different color intensities of the formed anisidine complex. Therefore, different 2-alkenals have different contributions to the final AV. Determination of TBARS is another commonly used method for the determination of secondary oxidation products. This test measures the colored pigment formed as a result of the reaction between thiobarbituric acid (TBA) and oxidation products from poly unsaturated fatty acids (PUFAs) (Guillén-Sans & Guzmán-Chozas, 1998). Neither the TBA nor the anisidine method are sensitive or specific, but this problem can be overcome by the use of gas chromatographic (GC) methods to determine secondary volatile oxidation products (aldehydes, hydrocarbons, ketones, and alcohols). GC can be combined with MS to increase the degree of certainty of the identification and quantification of the volatile oxidation products. Before the volatile oxidation products can be analyzed by the GC–MS, they must be collected from the sample matrix. The most common methods to collect the volatiles are: static headspace, solid phase micro extraction (SPME), and dynamic headspace method/purge and trap (Thomsen et al., 2016). NMR is an alternative method to determine secondary volatile oxidation products, but it does not offer the same ability to measure a large range of different volatile oxidation products, but primarily measures selected aldehydes (Merckx et al., 2018).

3 | METHODS TO RENDER OXIDATIVE STABILITY TO EMULSIONS

3.1 | Storage conditions

Lipid oxidation increases with increasing temperature. At moderate temperatures, heat primarily promote oxidation by breaking the O—O bonds in traces of lipid hydroperoxides. This gives rise to formation of alkoxy and hydroxyl radicals, which can initiate oxidation. For that reason, emulsions rich in unsaturated lipids should

be stored at as low temperature as possible. When studying lipid oxidation, one may wish to increase temperature to accelerate oxidation and thereby shorten the length of the experiment. It should, however, be borne in mind that already at temperatures above 40°C, oxidation kinetics will change for oils rich in long-chain (LC) omega-3 fatty acids (Sullivan et al., 2011). Reactions taking place at high temperature may thus be different from those taking place at lower temperature. High temperature may lead to breakage of emulsions depending on the emulsifier/stabilizer used to stabilize the emulsion. Lipid oxidation kinetics will be different in a broken emulsion compared with an unbroken emulsion.

During storage of emulsions, lipid oxidation will also be affected by the presence of light. If a photosensitizer such as chlorophyll or riboflavin is present in the emulsion, light is particularly detrimental because this will lead to photooxidation, which happens ca. 1000 times faster than autoxidation (Frankel, 2005). Oxygen is needed for lipid oxidation to occur, so by removing oxygen it is possible to slow down lipid oxidation. For instance, the use of a commercial packaging aiming to scavenge oxygen was found to significantly reduce oxidation in O/W emulsion as evidenced by the values of hydroperoxides and TBARS regardless of pH, concentration of oil, and/or presence of sodium chloride in the system (Johnson et al., 2018). In practice, it is however very hard to remove all oxygen completely. Three types, or species, of oxygen are involved in oxidation: triplet oxygen ($^3\text{O}_2$), reactive oxygen species (ROS), and singlet oxygen ($^1\text{O}_2$). The oxidative deterioration of edible oils through exposure to triplet oxygen is unlikely to occur due to electronic spin restrictions. However, these restrictions are overcome by ROS contributing to the initiation, for example, by hydroxyl ($\text{HO}\cdot$) that receives hydrogen from a lipid and forms a carbon-centered radical on the alkyl chain, or propagation, for example, by peroxy ($\text{ROO}\cdot$) and alkoxy ($\text{RO}\cdot$), phases of oil oxidation process. Singlet oxygen, which is formed by transfer of energy from a photosensitizer to oxygen, causes oil oxidation independent of temperature owing to low activation energy required and therefore, can cause oxidation even when the storage temperature is reduced. For more details on the role of oxygen in oil oxidation, reader is referred to Johnson and Decker (2015).

3.2 | Emulsifiers

Emulsifiers are surface-active substances, which are able to rapidly adsorb at the oil–water interface of emulsions, decreasing interfacial tension and preventing droplet aggregation (McClements, 2016). Adsorption of emulsifier molecules at oil–water interfaces happens during homoge-

nization, when the droplets are freshly formed, and create an interfacial layer allowing the oil droplets to disperse in the aqueous phase. Emulsifiers have a crucial role in forming and stabilizing emulsions, thereby providing physicochemical stability. Emulsifiers are commonly used in commercial emulsion-based food products such as milk, yoghurt, mayonnaise, salad dressings, and coffee cream. With the increasing awareness of environmental sustainability and healthy food consumption, the demand for using natural instead of synthetic emulsifiers is increasing (McClements et al., 2017). This urges researchers to investigate the characteristics of novel emulsifiers, which are sustainable and have high potential in stabilizing food emulsions. Furthermore, emulsifiers with multifunctionality, such as those with both antioxidant and antimicrobial activities, are of high interest (García-Moreno et al., 2020; Ghelichi et al., 2017; McClements & Decker, 2018; McClements & Jafari, 2018; Yesiltas et al., 2021). Thus, emulsifier peptides might also hinder lipid oxidation at the oil–water interface due to their radical scavenging and metal ion chelating activities or prolong shelf life of foods due to their antimicrobial activities in emulsions.

Emulsifiers can be classified as high-molecular-weight emulsifiers (e.g., amphiphilic biopolymers such as proteins and polysaccharides), low-molecular-weight emulsifiers (LMWEs; e.g., small-molecule surfactants), and solid particles (e.g., silica). Emulsifiers adopt a conformation locating their hydrophilic parts in the aqueous phase and their lipophilic parts in the oil phase, reducing oil/water interfacial tension. Proteins and some polysaccharides are examples of amphiphilic biopolymers. Proteins consist of amino acids, which vary according to their polarity, dimensions, chemically reactive groups, and interactions with other molecules (McClements, 2016). Polysaccharides mainly consist of hydrophilic parts. Therefore, they are not sufficient when used as emulsifiers alone due to low interfacial activity. However, some natural (guar or Arabic gums) and modified polysaccharides (modified starches) contain nonpolar groups (e.g., nonpolar proteins, phenolic groups, and lipids) covalently or noncovalently attached to polysaccharide backbone, which increase their ability to decrease interfacial tension at the oil–water interface (Dickinson, 2009; Yesiltas, García-Moreno, et al., 2018). Their use in emulsions contribute to physical stability either via emulsification with their interfacial activity due to the hydrophilic/hydrophobic parts or via stabilization with their ability to thicken the aqueous phase of O/W emulsion (Dickinson, 2003). Some starches can also act as Pickering agents and stabilize emulsions through Pickering stabilization, which is further described later in this review.

Proteins are complex molecules and act as emulsifiers but their adsorption mechanism is different from small

surface-active molecules due to their individual molecular structures (Dalglish, 1997). The hydrophobic amino acids (e.g., in Gly, Ala, Val, Leu, Ile, Pro, Phe, Met, and Trp) or side chains lie on the oil phase, whereas the hydrophilic amino acids (e.g., Ser, Thr, Cys, Asn, Gln, and Tyr) or side chains dissolve in the water phase of the emulsion. Proteins are classified as globular and random-coil according to their configuration adopted in aqueous mediums. Examples of these protein types are whey protein and casein, respectively, both of which are milk proteins and widely used in food industry. Common milk proteins used as food emulsifiers are (i) caseins (α_{s1} , α_{s2} , β , κ -caseins) and sodium caseinate with flexible structures and (ii) whey proteins (α -lactalbumin, β -lactoglobulin, bovine serum albumin, immunoglobulins) and whey protein concentrate (WPC) or isolate with rather rigid structures (Dalglish, 1997). Various configurations of proteins may give them flexibility when adsorbed at oil–water interface of an emulsion. It was reported that compact and globular proteins such as β -lactoglobulin form dense and interconnected interfacial films, whereas flexible and disordered proteins such as caseins form thicker yet less densely packed interfacial films. When casein is present in sufficient amount, multilayered interfaces of casein molecules can be formed (Dickinson, 1999). Thick interfacial layer provided by proteins (e.g., casein) contributes to the physical stability of the emulsions by providing steric repulsion forces (McClements, 2016). Multilayers, stacking of molecules, and interaction between emulsifiers lead to thicker, denser, and less permeable oil–water interfacial layers, which may result in improved oxidative stability by acting as a physical barrier hindering prooxidant diffusion into the oil phase (Berton-Carabin et al., 2018; McClements & Decker, 2018).

Plant-based proteins are also becoming popular as a sustainable source for the replacement of animal proteins among the consumers and the food industry. Proteins were extracted from soybeans (Huang L. et al., 2019), peas (Burger & Zhang, 2019; Geerts et al., 2017; Lam et al., 2018), and chickpeas (Felix et al., 2019), among others. Furthermore, proteins from potato starch production side stream (García-Moreno et al., 2020), spent grain (Negi & Naik, 2017), and winery waste (Pavlou et al., 2019) showed emulsifying activity in emulsions. Benjamin et al. (2014) showed that legume (pea, lupin, and soy) proteins had comparable emulsifying properties to β -lactoglobulin and Tween 20 (commercial name of polysorbate 20, a nonionic surfactant), reducing interfacial tension (46–55% with respect to the bare oil/water interface) and leading to physically stable O/W emulsions with negative surface charge (~ -35 mV), and small particle diameter ($D[3,2] < 0.4 \mu\text{m}$). It is noteworthy that Tween surfactants are in fact polysorbate molecules with a hydrophilic head

group of oligo(ethylene glycol) chains and a hydrophobic tail of fatty acid ester moiety (Shen et al., 2011) and the common Tween surfactants are Tween 20, 40, and 80, which stand for polysorbate 20, 40, and 80, respectively. Gumus et al. (2017) reported that legume proteins (pea and faba bean) were used to emulsify oils and their ability to limit oxidation was found to be higher than that of whey protein when the nonadsorbed proteins were washed away in emulsions, which could be attributed to their enhanced interfacial layer or better antioxidant activity at the oil–water interface. Emulsifying and antioxidant activities of plant-based peptides were also reported in several other studies (e.g., Ashaolu, 2020; Cheng et al., 2014; García-Moreno et al., 2020). Sensory properties such as bitterness or some characteristic flavors of plant-based proteins and peptides can be a major challenge, which needs to be investigated further and taken into account when applied in food products (Görgüç et al., 2020; Gumus et al., 2017).

Polysaccharides are mostly added as thickeners to the aqueous phase of the emulsions to increase viscosity, thereby enhancing the physical stability of O/W emulsions. Natural or modified polysaccharides with amphiphilic character were reported to be sufficient in stabilizing O/W emulsions either alone or used in combination with other emulsifiers such as proteins (Charoen et al., 2011; Liu et al., 2016; Yesiltas et al., 2017; Zhang H. et al., 2019). Examples of polysaccharides with emulsifying activities are gum Arabic, pectin, galactomannan, modified starches, and cellulose (Dickinson, 2003; McClements & Gumus, 2016). However, a larger amount of polysaccharides is typically required to form an emulsion compared with proteins or biosurfactants (McClements et al., 2017). Djordjevic et al. (2008) reported that the oxidative degradation of citral was equal at pH 3 or less at pH 7 in gum Arabic stabilized emulsions compared with whey protein isolate (WPI) stabilized emulsions. However, the formation of *p*-cymene, a citral oxidation product, was greater in the gum Arabic stabilized emulsion than in WPI stabilized emulsion at pH 3 and 7. This was attributed to the formation of a cationic droplet interface at pH 3.0 for WPI stabilized emulsion that can repel prooxidative metals and/or the ability of amino acids in WPI to scavenge free radical and chelate prooxidative metals.

LMWEs are mainly surfactants that are relatively smaller compounds compared with biopolymers. They can be synthetic or natural. Examples of synthetic LMWEs are derivatives of mono- and diglycerides (e.g., DATEM (diacetyl tartaric acid ester of mono and diglycerides), CITREM (citric acid esters of mono- and diglycerides)), sucrose esters, and polyoxyethylene derivatives (e.g., Tween 20, Tween 80). Phospholipids (e.g., lecithin), glycolipids (e.g., rhamnolipids, sophorolipids), and saponins are examples of natural surfactants. Tween 20 was used

by Narkiewicz-Michalek et al. (2019) to test the antioxidative effect of incorporated trans-resveratrol (TRES), a natural polyphenol found in different plants with anti-inflammatory, cardio-protective, antioxidant, and anti-cancer properties, into stripped corn O/W emulsions and results showed that more than 85% of the TRES was at the oil–water interface. It was reported that an increase in Tween 20 concentration promoted the incorporation of TRES into the interfacial layer. However, the concentration of TRES at the interface decreased due to the increase in interfacial volume because of a higher number of molecules adsorbed. On a side note, stripped oils are obtained when minor constituents of the oils are removed by different methods such as chromatography. Triacylglycerols (TAGs) comprise approximately 95% of edible oils, whereas the minor constituents of these oil (ca. 5%) mainly include mono- and diacylglycerols, FFAs, pigments, phenolic compounds, and sterols (Abad & Shahidi, 2020).

3.2.1 | Combined use of emulsifiers

Even though using only one type of emulsifier can be sufficient to emulsify oils, combined use of different types of emulsifiers are quite common in food emulsions as a strategy to provide better physical stability as well as to protect lipids against oxidation (McClements & Decker, 2018). The efficiency of using more than one type of emulsifier in an emulsion depends either on the formation of emulsifier complexes that leads to enhanced interfacial layer or on the competitive adsorption of each emulsifier at the interface that originates interfacial displacement (Dickinson, 2009; McClements & Jafari, 2018). A pea protein and tannic acid complex was used for stabilization of flaxseed O/W emulsions by Li et al. (2020), where impact of the complex on oxidative stability and lipid digestion was investigated and found to be improved. Another study carried out by Yi et al. (2019) investigated the competitive adsorption of caseinate and Tween 20 in 5% walnut O/W emulsions at pH 7. Lipid oxidation was promoted when Tween 20 displaced the adsorbed caseinate, which indicated the antioxidant activity (e.g., metal ion chelating) of sodium caseinate. On the other hand, Tween 20 did not have any antioxidant activity when adsorbed at the interface where oxidation is initiated. This study demonstrated that the interfacial composition has a critical importance on the oxidative stability of emulsions when containing emulsifier mixtures with different antioxidant activities.

Amphiphilic biopolymers and/or surfactants may form thick interfacial layers and inhibit lipid oxidation by acting as a physical barrier with higher steric forces. Large molecules such as proteins tend to form thicker interfacial layers, which may retard the diffusion of prooxidants

toward the lipid phase (Berton-Carabin et al., 2018). Due to the amphiphilic character of the proteins, interaction with lipophilic molecules such as surfactants and lipids is likely to occur when used in complex food systems (Semenova et al., 2009). Likewise, surfactants with larger head groups may provide better oxidative stability due to providing a steric stabilization (physical barrier) compared with those with smaller head groups. Silvestre et al. (2000) showed that the increasing length of the hydrophilic head group on nonionic surfactants decreased the rate of lipid oxidation, which was attributed to a physical barrier for radicals' diffusion from the interfacial layer to the oil phase. Moreover, it was reported that lipid oxidation (PV and hexanal and propanal formation) in salmon O/W emulsions stabilized by polyoxyethylene 10 lauryl ether (Brij-lauryl) or polyoxyethylene 10 stearyl ether (Brij-stearyl) decreased when the hydrocarbon tail length of surfactants increased, which again was attributed to the ability of the surfactant layer to sterically hinder interactions between hydrophilic prooxidants and polyunsaturated fatty acids inside the droplets (Chaiyasit et al., 2000). Nevertheless, the length of the head had an influence on lipid oxidation to a higher extent compared with tail groups. Cho et al. (2017) incorporated ellagic acid into sodium caseinate, which was used in combination with high-methoxyl pectin or carboxymethyl cellulose in the emulsification of 10% fish O/W emulsions in order to increase oxidative stability. The authors reported a reduction in PV and volatiles content for emulsions containing ellagic acid compared with the control emulsions without it after 14 days storage at room temperature.

Kibici and Kahveci (2019) compared the physical and oxidative stability of emulsions produced with proteins (sodium caseinate and WPI) or LMWEs (CITREM and lecithin) in combination with stabilizers (maltodextrin and β -cyclodextrin). They reported that emulsions fabricated using CITREM and lecithin had better creaming stability with lower droplet size. However, these emulsions had lower viscosity compared with proteins as emulsifiers. Physical stability was improved for the CITREM emulsion when β -cyclodextrin was added, whereas oxidative stability was inferior based on TOTOX (total oxidation value) ($2 \times PV + AV$) of 60 and 88 on days 1 and 15 compared with only CITREM emulsion with TOTOX values of 22 and 40 on days 1 and 15) during storage at 55°C. Zhang et al. (2020) reported that mixed use of almond protein isolate and *camellia* saponin provided better physical and oxidative stability by enhancing the resistance to droplet flocculation and preventing oxidation of lipids (hydroperoxides and TBARS) and proteins (carbonyl formation, sulfhydryl loss, intrinsic fluorescence loss, and electrophoresis). This was attributed to the presence of both emulsifiers at the oil–water interface due to electrostatic at pH 3 ($<pI$ of the

almond protein isolate, which is 4.5) and/or hydrophobic attractions at pH 7 ($>pI$ of the almond protein isolate) providing a steric barrier, which prevents both prooxidant diffusion into the oil droplets and droplet coalescence (Zhang et al., 2020).

3.2.2 | Conjugated emulsifiers

Zhang H. et al. (2019) showed that gum Arabic formed ternary complexes with calcium and whey protein to stabilize O/W emulsions, which improved the encapsulation of resveratrol at the oil–water interface. Resveratrol stability was also increased in the presence of CaCl_2 and improved the oxidative stability of sunflower oil. Liu et al. (2016) reported that polyphenol–protein–polysaccharide (chlorogenic acid (CA)–lactoferrin (LF)–dextran) ternary conjugate performed as a better emulsifier compared with single protein or binary conjugates (CA–LF or LF–dextran) for providing physical and chemical stability in 5% β -carotene added medium-chain triglyceride (MCT) O/W emulsion. It was shown that the composition of the ternary conjugates was an important factor for emulsifying activity. The mass ratio of 1:2 CA–LF conjugate to dextran was more effective in stabilizing O/W emulsions than ratios of 2:1 and 1:1 (Liu et al., 2016).

Yesiltas et al. (2017) used combination of sodium caseinate and sodium alginate for the physical and oxidative stabilization of 70% fish O/W emulsions. Results showed that the combined use of sodium caseinate and sodium alginate allowed the production of a stable emulsion, except when high ratio between sodium alginate and aqueous phase was employed. Both viscosity and droplet size of the emulsions were significantly influenced by fish oil content, and viscosity was affected by total stabilizer content, whereas droplet size was affected by the ratio between the two stabilizers. All emulsions had good oxidative stability during their storage of 4 weeks (peroxide value <1 meq peroxides/kg oil), which confirms the protecting effects of both compounds (Yesiltas et al., 2017). Same authors also investigated the combined effect of modified alginates (succinic anhydride and dodecyl succinic anhydride) and sodium caseinate on the oxidative and physical stability of 50–70% fish O/W emulsions and found that fish oil content and emulsifier type had significant effect on droplet size, viscosity, protein content in the water phase and PV (Yesiltas et al., 2018a). Moreover, modified alginate with longer chain length provided better physical stability compared with only sodium caseinate and sodium caseinate plus modified alginate with short chain. However, emulsions containing modified alginate with short chain provided better stability compared with the rest of the emulsions, when both

oxidative and physical stabilities were considered (Yesiltas et al., 2018a).

Recently, modified surfactants (DATEM and phosphatidylcholine) with caffeic acid covalently attached were investigated in combination with sodium caseinate for the stabilization of 70% fish O/W emulsions. The results indicated that the use of these modified surfactants affected physical stability of the emulsions by replacing sodium caseinate at the interface (e.g., DATEM) or interacting more at the oil–water interface (e.g., phosphatidylcholine). Nevertheless, longer chain length improved the oxidative stability of the emulsions when compared with control emulsions containing free caffeic acid as antioxidants (Yesiltas et al., 2019; Yesiltas et al., 2018b). These results, from the last three studies referred to, are illustrated in Figure 2. The illustration concerning sodium caseinate and phosphatidylcholine is a simpler expression of what was previously published in Yesiltas et al. (2019b).

3.2.3 | Emulsifiers used for stabilizing W/O emulsions

Emulsifiers with low hydrophilic lipophilic balance (HLB 3–6), which are predominantly hydrophobic and thus preferentially solubilize in the oil phase, are normally used for the stabilization of W/O emulsions (McClements, 2005). Nonetheless, it is worth mentioning that solubility of the emulsifier is not the main factor determining the type of emulsion stabilized, but the curvature of the monolayer formed at the o/w interface that allows the most efficient packing of the emulsifier molecules. The type of packing mainly depends on: (i) the geometry of the emulsifier molecules (e.g., volume and length of the hydrophobic tail and the cross-sectional area of the hydrophilic head group) and (ii) the temperature of the system (e.g., below or above the phase transition temperature) (McClements, 2005). The emulsifiers employed to stabilize W/O emulsions can be synthetic such as sorbitan esters (Spans, E491-5) and polyglycerol polyricinoleate (PGPR, E476), or natural such as lecithins, mono- and di-glycerides (Le Révérend et al., 2011). PGPR (HLB ~ 4.3) is the most widely used due to its superior emulsifying properties. For instance, W/O emulsions with reduced droplet size and thus higher physical stability have been obtained with PGPR instead of Spans as emulsifiers (Márquez et al., 2007). On the other hand, mono-, di-, or tri-glycerides crystals stabilize W/O emulsions by: (i) forming a fat crystal network in the continuous phase (nonsurface active crystals) that immobilize water droplets preventing coalescence and sedimentation (Hodge & Rousseau, 2005) and (ii) acting as Pickering particles, which sit at the w/o interface sintering together to form a crystalline fat shell that act as a steric

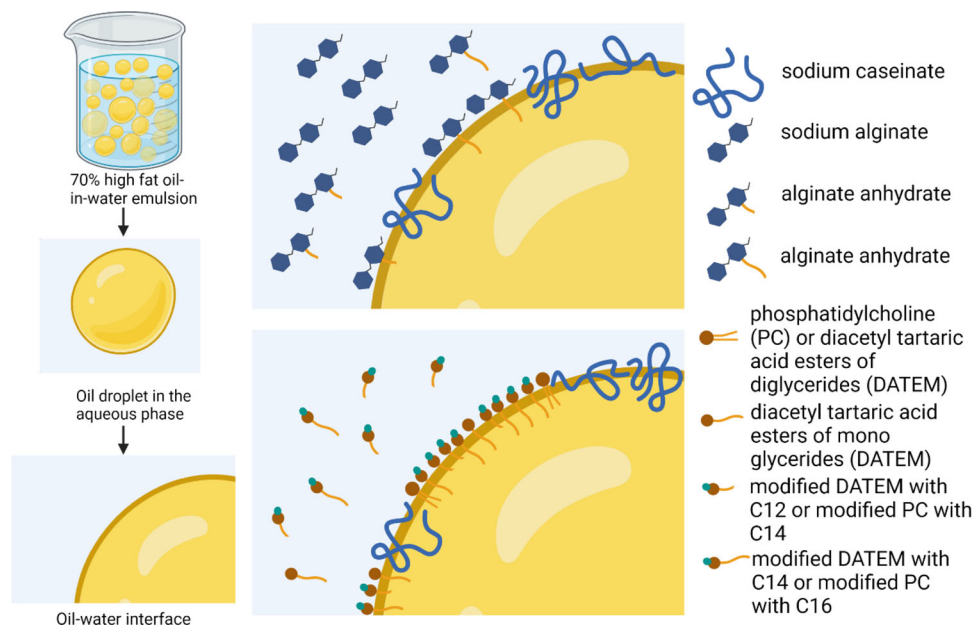


FIGURE 2 Simple illustration of the oil–water interfacial structure in 70% fish o/w emulsions stabilized with the combination of sodium caseinate and alginates (upper-right) and sodium caseinate and surfactants (lower-right).

barrier between adjacent water droplets (Ghosh & Rousseau, 2011; Norton et al., 2009). It should be mentioned that the type of surfactant used will strongly influence crystal properties, in particular, the crystal surface-activity, which determines how efficiently it anchors at the interface (Ghosh & Rousseau, 2011).

3.3 | Optimization of production methods

Lipid oxidation can occur during the emulsion production process, but the emulsification technology and conditions can affect lipid oxidation after the emulsion has been produced. Therefore, the type of emulsification technology has to be chosen carefully and the emulsification conditions must be optimized. A range of different emulsification technologies are available, for example high-pressure homogenization, microfluidization, mixing (e.g., rotor–stator principle), and membrane homogenization. High-pressure homogenization cannot be applied to prepare highly viscous emulsions and is usually not used for high fat emulsions.

Only few systematic studies have been carried out in which lipid oxidation has been compared in emulsions produced under similar conditions in different homogenization devices.

Horn et al. (2012) compared the effect of using a two-stage valve homogenizer or a microfluidizer on lipid oxidation in 10% fish O/W emulsions prepared with either whey

protein or sodium caseinate as emulsifier. Because previous studies have shown that lipid oxidation can be affected by the oil droplet size distribution, homogenization conditions were optimized for each type of equipment so that similar oil droplet size distributions were obtained irrespective of the type of equipment used. It was found that the type of homogenization equipment used influenced lipid oxidation when emulsions were prepared with whey proteins as emulsifiers, but not when prepared with caseinate. In the whey protein stabilized emulsions, the microfluidizer increased the oxidative stability compared with when emulsions were prepared by the two-stage valve homogenizer. Moreover, emulsification by microfluidizer resulted in more protein being present at the interface, which led to a better protection of the oil inside the oil droplet. It was also suggested that a more favorable composition of the proteins at the interface was obtained. The authors proposed that the type of homogenization equipment was less important for casein-stabilized emulsions because excess casein proteins with metal chelating properties are present in the aqueous phase no matter which homogenization technology was used. In casein-based emulsions, the actual composition of protein components at the interface may therefore be less important for the oxidative stability.

Other studies, by Horn et al. (2013), Sørensen et al. (2007), and Let et al. (2007), demonstrated that homogenization conditions could affect lipid oxidation in different types of emulsions with fish oil. Horn et al. (2013) studied the effect of two different homogenization pressures

(5 or 22.5 MPa), and two different temperatures (22 and 72°C) in fish O/W emulsions prepared with either a combination of α -lactalbumin and β -lactoglobulin or with a combination of sodium caseinate and β -lactoglobulin. It was found that an increase in pressure increased the oxidative stability of emulsions with caseinate and β -lactoglobulin. In contrast, oxidative stability decreased with increasing pressure in emulsions with α -lactalbumin and β -lactoglobulin. For both types of emulsions, the distribution of proteins between the interface and the aqueous phase appeared to be important for the oxidative stability. Similar conclusions were made in the studies by Let et al. (2007) and Sørensen et al. (2007) who studied the effect of homogenization pressure and temperature on lipid oxidation in fish oil enriched milk. Their studies also showed that a favorable partitioning of proteins between the aqueous phase and the interface was more important than the droplet size distribution.

Ramisetty and Shyamsunder (2011) compared the effect of using ultrasonication technique or mechanical agitation method on the droplet size of O/W emulsions containing Tween 20, Span 20, and glycerin. Results showed that the longer emulsification time provided narrower droplet size distribution for both homogenization, which also indicates better stability for emulsions. However, it was pointed that the temperature was increasing with longer emulsification times, which may initiate lipid oxidation for susceptible oils. They also reported that ultrasound technique (at low frequency, 20 kHz) provided more stable emulsions compared with the mechanical stirring technique (Ramisetty & Shyamsunder, 2011). Kobayashi et al. (2015) reported that ultrasound provided smaller droplet size (100–200 nm) compared with a mechanical homogenizer (250–3000 nm) for 1–10% toluene-in-water emulsions emulsified with Tween 20. On the other hand, Calva-Estrada et al. (2018) reported that the carrot carotene enriched canola oil-in-blackberry juice emulsion obtained by ultrasound had bimodal distribution, whereas the emulsion obtained by high-pressure homogenization showed unimodal distribution with particles smaller than 1 μ m diameter with greater uniformity of size. Results also revealed that β -carotene degradation is very dependent on the mean particle diameter and the antioxidant compounds in blackberry juice used conferred protection to carotenoid compounds during 60 days of storage at 25°C.

In emulsions prepared with a mixture of different emulsifiers, the distribution of emulsifiers between the different phases may depend on the order in which they are added as observed by Waninge et al. (2005). They assessed the distribution of proteins and phospholipids in emulsions of identical compositions, but prepared through varied procedures: (i) oil emulsification was performed in the presence of proteins, then phospholipids were added to

the emulsion; (ii) oil emulsification was performed in the presence of phospholipids, then proteins were added to the emulsion; or (iii) oil emulsification was performed in the presence of both proteins and phospholipids. They found that the composition of the interface was different up to 48 h after the emulsification and that it was dominated by the emulsifier present during the homogenization, that is, if the emulsifier was added after homogenization it was present to a lower extent at the interface.

3.4 | Antioxidants

Antioxidants are defined as compounds that delay the onset and prevent or decrease the rate of lipid oxidation. Compounds with antioxidant properties are divided into three different categories depending upon the mechanism of the compounds as antioxidants. The three categories are termed: primary, secondary, or multiple function antioxidants. Primary antioxidants are antioxidants that scavenge radicals. These antioxidants react directly with lipid, peroxy and alkoxy radicals to terminate the initiation and propagation steps of lipid oxidation. According to their mechanisms of action, these antioxidants are also referred to as chain-breaking antioxidants. In contrast, the category of secondary antioxidants are compounds that indirectly inhibit lipid oxidation. This include compounds with several different mechanisms such as oxygen scavenging, chelation of transition metal, singlet oxygen quenching, and synergism between antioxidants. Compounds that can act by several antioxidant mechanisms are termed multiple function antioxidants (Coupland & McClements, 1996; Frankel, 2005; McClements & Decker, 2000). Tocopherols, ascorbic acid, butylated hydroxytoluene (BHT), and phenolic compounds are common compounds with radical scavenging properties. Ascorbic acid is also known for its ability to work as an oxygen scavenger and to regenerate other antioxidants, for example, tocopherols. Depending on the molecular structure of phenolic compounds, they have the ability to chelate metal ions. Phenolic compounds with this property have a dihydroxy substitution to the phenolic ring. Other compounds known for their metal chelating property are ethylenediaminetetraacetic acid (EDTA) and citric acid. Carotenoids, for example, lycopene are known to be potent quenchers of singlet molecular oxygen. The application of antioxidants in emulsion systems is a commonly used approach to improve oxidative stability in these systems.

Overall, the efficiency of antioxidants in emulsified systems has been extensively studied and it depends not only on the molecular structure and reactivity, but also on factors such as physical location and presence of other compounds and environmental condition. Since, lipid

oxidation is initiated at the interface between oil and water phases, the location of antioxidants has been in focus when evaluating the efficiency of antioxidants (Coupland & McClements, 1996; Frankel, 2005; D.J. McClements & Decker, 2000; Sørensen et al., 2008). With the extensive research in antioxidant efficiency in emulsified systems, different hypotheses for the effect of antioxidants have been suggested including the polar paradox theory and the cut-off effect theory as described below.

The polar paradox hypothesis states that the efficiency of the antioxidants is related to their affinity toward the different phases in emulsions, that is, oil and water phases. In emulsified systems, lipophilic antioxidants are more efficient than hydrophilic antioxidants due to their ability to be located closer to the oil–water interface. This is also confirmed in studies with ascorbyl palmitate and tocopherols, which were shown to be more efficient in emulsion (O/W) than their hydrophilic counterparts ascorbic acid and trolox (Frankel et al., 1994; Frankel et al., 1996; Porter, 1993).

For the efficiency of antioxidative compounds in emulsions, the cut-off effect can be seen as an extension of the polar paradox hypothesis, since the cut-off effect is related to the degree of lipophilicity of the antioxidants for optimal antioxidant efficiency. According to the cut-off effect theory, an increased antioxidant efficiency is obtained with increased lipophilicity of the antioxidant until a certain degree of lipophilicity also denoted critical chain length (CCL). After reaching CCL, the antioxidant efficiency declines with increasing lipophilicity. The optimal antioxidant efficiency for obtained at CCL is explained by the partitioning of antioxidant into the different compartments of the emulsion. At CCL, the antioxidant is located at the interface between the oil and water phases. This cut-effect was observed with rosmarinic and CAs and lipophilized esters of these phenolic compounds, which were evaluated in model emulsion systems. It was found that dodecyl chlorogenate (C12) and octyl rosmarinate (C8) were the most efficient chain lengths, that is, CCL was C12 and C8 for chlorogenate and rosmarinate, respectively (Laguerre et al., 2009; Laguerre et al., 2010). In addition, studies of the efficacies of compounds with different lipophilicity (phenolipids) in more complex emulsion systems have elucidated that the CCL is not as “clear cut” in these systems rather several CCLs were observed, thus a broader range. Depending on emulsion composition a range from C1 to C4 and C4 to C12 was observed, respectively (Alemán et al., 2015). In complex emulsion systems, several components can interfere and affect the efficacy of the antioxidant (Sørensen et al., 2007). Therefore, selection of antioxidants should be tested carefully for the intended emulsion system. There is also a need to further investigate the potential of conjugating antioxidants with emulsifiers,

thereby incorporating the antioxidants into the interface as demonstrated by Yesiltas et al. (2019) and Yesiltas et al. (2018a).

Recently, a putative theory about mass transfer mechanisms for oxidants and antioxidants as determinant of lipid oxidation has been postulated (Laguerre et al., 2017). This has been considered to highly influence lipid oxidation and the inhibition by antioxidants in emulsions. The different mass transfer mechanisms suggested to influence lipid oxidation and antioxidants in emulsions are diffusion, collision exchange separation transfer, and micelle assisted transfer. Briefly, water-soluble molecules can be exchanged from one droplet to another by diffusion through the water phase. In contrast, mass transfer for hydrophobic molecules can occur through collision exchange separation, in which two lipid particles come into contact (collide) and exchange their content, which is a slower transfer than diffusion. The transfer rate of hydrophobic molecules can be increased when emulsifier is present in excess. Presence of excess emulsifier in the aqueous phase may lead to micelle formation that can act as a carrier to transfer hydrophobic molecules. Based on this putative mass transfer theory and the cut-off effect, it was suggested that transfer of antioxidants from one droplet to another is the most important factor governing their antioxidant action. The cut-off point (CCL) marks the hydrophobicity threshold and beyond the cut-off, an antioxidant can no longer be transferred through diffusion in the aqueous phase. Efficiency of more hydrophobic antioxidant molecules (above CCL) depends on mass transfer (i.e., collision exchange or micelle assisted transfer) to be localized close to the interface (Laguerre et al., 2017).

Since, the efficiency of an antioxidant is influenced not only by the type of emulsion, for example, O/W, W/O, multiple emulsions, and so on, but also the composition and concentration of different component in the system, it is crucial to evaluate antioxidants of interest in the emulsion system it finally has to be used in before final selection of antioxidants. Additionally, a consideration is also the property of the antioxidant selected. In some cases, it can be an advantage to add blends of antioxidants or extracts, such as green tea, rosemary, or seaweed extracts, to have components with several antioxidant properties present in the emulsion systems, for example, both radical scavenging and metal chelating antioxidants.

4 | OXIDATION IN EMULSIONS

This section presents a detailed and comprehensive overview of oxidation in different types of emulsions, namely O/W, W/O, O/O, multiple, nano, and Pickering

emulsions. Table 1 summarizes some studies on oxidation and oxidative stability in different types of emulsions.

4.1 | O/W emulsions

O/W emulsions contain two immiscible liquids (oil and water), with oil being dispersed as spherical droplets in water phase (Figure 1a) (McClements, 2016). Examples of commonly consumed foods as O/W emulsions are milk, mayonnaise, cream, dressings, cream cheese and soups. As most food emulsions are in the form of O/W, these emulsions are the most widely studied model systems in food science. Moreover, foods containing water as their continuous phase can easily be enriched with oil-soluble bioactive compounds, such as omega-3 polyunsaturated fatty acids, vitamins (A, D, E, and K), carotenoids, and phytosterols, through O/W delivery emulsions (McClements et al., 2017). Bioactive compounds are desired to be incorporated into food systems due to their positive contribution to human health (Hajfathalian et al., 2018).

O/W emulsions can be classified into two categories according to the dispersed phase (oil droplets) volume fraction; low fat (<30%) and high fat (>50%) emulsions. Low fat O/W emulsions have been studied intensely, whereas there are only a few studies reported on high fat O/W emulsions (Horn et al., 2011; Yesiltas et al., 2017, 2018a, 2019). Fat content has an impact on the final textural and microstructural properties of O/W emulsions. For instance, high fat content (e.g., mayonnaise) results in a thick or viscous emulsion, whereas low fat emulsions (e.g., milk) are thinner and less viscous. In addition to physical stability, fat content also influences the oxidative stability of O/W emulsions (Yesiltas et al., 2017, 2018a).

Physical instabilities, such as creaming, flocculation and coalescence, need to be prevented after the production of O/W emulsions. Moreover, chemical instabilities such as oxidation and hydrolysis reactions might also occur leading to quality deterioration of the final product (McClements, 2016). Lipid oxidation mechanisms have been elucidated in bulk fats and oils for decades. Even though the knowledge obtained from the lipid oxidation in bulk oils has been useful, understanding oxidation mechanisms in emulsions require different approaches and techniques due to higher complexity of these systems (McClements & Decker, 2000). Predicting and controlling lipid oxidation and antioxidant activity in food matrices are quite complex due to the fact that various factors may affect oxidative stability. Even in simpler systems such as O/W emulsions, it is challenging to understand the nature of the lipid oxidation and antioxidant activity occurrences. Therefore, investigating more effective strategies is necessary in order to control lipid oxidation in heterogeneous

matrices such as food emulsions (Jacobsen, 2015; Jacobsen et al., 2008; Villeneuve et al., 2018). Studies have shown that several factors affect lipid oxidation in O/W emulsions such as oil volume fraction, homogenizer type, surface charge, pH, droplet size, viscosity, interface structure (e.g., thickness and permeability), and the presence or addition of antioxidants (Berton-Carabin et al., 2018; Jacobsen, 2015; Jacobsen et al., 2008).

Traditional and advanced analytical techniques have been used to study physicochemical properties of O/W emulsions to keep quality parameters under control from the production of the food product to their digestion in the gastrointestinal system of consumers. Because food emulsions are complex O/W emulsions, understanding the dynamics in simplified O/W emulsions may help controlling the physicochemical changes in real foods. Droplet size distribution is one of the commonly studied properties in O/W emulsions. It usually varies in the range between 100 nm and 100 μm depending on oil volume fraction, type of the emulsifier, homogenization method used, as well as production conditions such as pH, ionic strength, pressure, and temperature (McClements, 2016). Droplet size is used for the calculation of specific surface area of the emulsion, which is often up to a few m^2 per g of oil (Berton-Carabin et al., 2018).

Oil–water interfacial tension is closely related to the emulsion system's free energy built between immiscible oil and water phases. Larger total interfacial area and higher level of free energy in the emulsion system are linked together, which then affect the physical instability and increase the affinity of the system to phase separate (Walstra, 1993). Composition, production method, and conditions of the O/W emulsion have an effect on the oil–water interfacial structure, composition, and mechanical properties (Berton-Carabin et al., 2018). Moreover, interface structure is important when physical stability and its relation to chemical stability is the main point of discussion (Berton-Carabin et al., 2014; Jacobsen, 2015). Safflower O/W emulsions stabilized with protein-coated O/W nanoemulsion droplets oxidized significantly slower compared with composition-matched conventional protein-stabilized emulsions, indicating that the interface structure of droplet-stabilized emulsion provides limited contact between prooxidant metals, oxygen, and lipid substrate (Okubanjo et al., 2019).

One of the richest sources of polyunsaturated fatty acids is fish oil, which represents a great nutritional value. However, fish oil is susceptible to oxidation, resulting in the formation of off-flavor and consequently, reduction of consumer acceptability in food products. Therefore, a huge body of studies has tried to find measures, such as emulsification (Ghelichi et al., 2017) and/or addition of natural antioxidants (Hajfathalian et al., 2018), to stop or

TABLE 1 Composition, means of production, storage characteristics, physical characteristics, and measurement of oxidative stability for different types of emulsions

Type of emulsion	Oil phase(s)	Solvent	Emulsifier (s)	Antioxidant (s)	Means of production	Droplet size ² (µm)	Zeta potential ² (mV)	Storage conditions	Measurement of lipid oxidation	Reference
Oil-in-water	Fish oil (FO) and a mixture of fish and rapeseed oil (1:1) (5 wt.%)	10 mM sodium acetate-imidazole buffer (pH 7)	Citrem and Tween 80	Caffeic acid and caffeates (C1-C20)	Ultra-Turrax + Two-valve table homogenizer/Microfluidizer	D _{3,2} = 0.101 –0.131	–	Dark, 20°C, 15 days	Peroxide value, tocopherols consumption, volatiles	(Sorensen et al., 2017)
Fish oil (1 wt.%)	10 mM sodium phosphate buffer (pH 7)	Lentil, pea, and faba bean, and whey proteins	High-pressure microfluidizer	D _{3,2} = 0.120 –0.409	–42 to –22	Dark, Fe ²⁺ addition/no added iron, 37°C, 21/33 days	Peroxide value, TBARS	(Gumus et al., 2017)		
Fish oil (5 wt.%)	10 mM sodium acetate –10 mM imidazole buffer (pH 7)	Potato peptides (0.2 wt.%)	Ultra-Turrax + Microfluidizer	D _{3,2} = 0.124 –0.228	–60 to +30	Dark, Fe ²⁺ addition, 20°C, 7 days	Peroxide value, tocopherols consumption, volatiles	(García-Moreno et al., 2021)		
Fish oil (5 wt.%)	Distilled water (pH 2 or 8)	Whey protein, soy protein, blue whiting protein hydrolysates (2 wt.%)	Ultra-Turrax + High pressure homogenization	D _{3,2} = 0.140 –0.160	–46.8 to +36.3	Dark, Fe ²⁺ addition, 20°C, 10 days	Hydroperoxides, amidine value, volatiles	(Padial-Dominguez et al., 2020)		
High fat (>50%)	10 mM sodium acetate-imidazole Buffer (pH 4.5 and 7.0)	Sodium caseinate, whey protein isolate, milk phospholipid concentrates (with either 20 or 75% phospholipids), soy lecithin (2.8 wt.%)	Stephan Universal mixer	D _{3,2} = 8.19 –50.81	–56.6 to +42.7	Dark, 19°C, 6 weeks	Peroxide value, volatiles	(Anna Frisenfeldt Horn et al., 2011b)		
Fish oil (50, 60, 70 wt.%)	Distilled water (pH 7)	Combinations of casein, DATEM, and DATEM modified with caffeic acid (2.8 wt.%)	Stephan Universal mixer	D _{3,2} = 2.20 –2.71	–75.3 to –60.6	Dark, Fe ²⁺ addition, 20°C, 12 days	Peroxide value, tocopherols consumption, volatiles	(Yesiltas, García-Moreno, et al., 2018)		

(Continues)

TABLE 1 (Continued)

Type of emulsion	Oil phase(s)	Solvent	Emulsifier (s)	Antioxidant (s)	Means of production	Droplet size _d (µm)	Zeta potential _d (mV)	Storage conditions	Measurement of lipid oxidation	Reference
	Fish oil (50, 60, 70 wt.%)	Distilled water (pH7)	Combinations of sodium caseinate and commercial sodium alginate/long chain modified alginate/short chain modified alginate (1.4 wt.% total emulsifier, the ratio of sodium caseinate to alginates is 1.2)	Stephan Universal mixer	D _{3,2} = 2 - 18	-	Dark, Fe ²⁺ addition, 20°C, 12 days	Peroxide value, tocopherols consumption, volatiles	(Yesilias, Sorensen, et al., 2018)	
	Fish oil (70 wt.%)	Distilled water (pH 7)	Combinations of sodium caseinate and commercial phosphatidyl-choline/modified phosphatidyl-choline with different alkyl chain lengths and covalently attached caffeic acid (2.8 wt.% total emulsifier, the ratio of sodium caseinate to phosphatidyl-cholines is 1.2)	Stephan Universal mixer	D _{3,2} = 0.7 - 11.1	-61.9 to 47.0	Dark, Fe ²⁺ addition, 20°C, 12 days	Peroxide value, tocopherols consumption, volatiles	(Yesilias, Sorensen, et al., 2019)	
Water-in-oil	Glycerol trioleate	Distilled water (3 wt.%)	SODIUM OLEATE/OLEIC ACID MIXTURE (0.5 WT.%, 20/80 MOL/MOL%)	Ultra-Turrax	D _{3,2} = 3.3 - 6.6	-	Exposure to UV light, 25°C, 25 h	Peroxide value	(Mosca et al., 2008)	
Palm stearin, coconut oil, sunflower oil	Water + salt	DISTILLED MONO-GLYCERIDE, LECITHIN, skim milk powder	-	Scraped-surface heat exchanger	-	-	5 and 25°C, 12 weeks	Peroxide value, tocopherols consumption, volatiles and sensory evaluation	(Hong Zhang et al., 2006)	

(Continues)

TABLE 1 (Continued)

Type of emulsion	Oil phase(s)	Solvent	Emulsifier (s)	Antioxidant (s)	Means of production	Droplet size ² (μm)	Zeta potential ² (mV)	Storage conditions	Measurement of lipid oxidation	Reference
Walnut oil	20 mM phosphate buffer (2 wt.%, pH 3)	PGPR (0.3, 0.5, 1 wt.%)	α-TOCOPHEROL, TROLOX, EDTA	Hand-held mixer + Microfluidizer	z-Average diameter = 0.320 ± 0.017	-	Dark, 45° C, 25 days	Peroxide value, volatiles (hexanal)	(Yi et al., 2015)	
Algae oil	Water (2 wt.%)	PGPR, Lecithin PC75 or PCS0, lyso-lecithin, mono-diglycerides	Green tea ex-TRACT, grape seed extract, rosmarinic acid, α-tocopherol, deferoxamine, ascorbic acid, EDTA	High-speed blender + Microfluidizer	-	-	Dark, 45° C, 10 days	Peroxide value, tocopherols consumption, volatiles (propanal)	(B. Chen et al., 2016)	
Fish oil and rapeseed oil (1:1)	10 mM-acetate-imidazole buffer (1 wt.%, pH 7)	PGPR (1 wt.%)	Ascorbic acid, ascorbic palmitate, ascorbic conjugated linoleic acid (CLA)	Hand-held homogenizer + Microfluidizer	z-Average diameter = 0.241 – 0.293	-	Dark, 37° C, 400 h	Peroxide value, volatiles (propanal, hexanal)	(Sorensen et al., 2011)	
Walnut oil	20 mM phosphate buffer solution (2 wt.%, pH 3 or 7). Containing 0.1–0.2 wt.% of DTAB, SDS, Tween 20, WPI	PGPR (0.5 wt.%)	-	Hand-held homogenizer + Microfluidizer	z-Average diameter = 0.2 – 0.4	-	Dark, 45° C, 25 days	Peroxide value, volatiles (hexanal)	(Yi et al., 2014)	
Walnut oil	20 mM phosphate buffer solution (10 wt.%, pH 7) with NaCl	PGPR (2.7 wt.%)	α-TOCOPHEROL, TROLOX, citric acid, EDTA, WPI	Hand-held homogenizer + Microfluidizer	z-Average diameter = 0.156 – 0.285	-	Dark, 45° C, 12 days	Peroxide value, volatiles (hexanal)	(Zhu et al., 2015)	
Multiple emulsions	Oil-in-water-in-oil (O ₁ /W/O ₂)	NaCl solution (60 g/kg)	E ₁ : NaCaS ₂ E ₂ : PGPR	-	Hand-held Homogenizer + Homogenizer	D (v, 0.5) O/W = 0.97 – 1.25	-	5° C, 80 days	Hydroperoxides, Anisidine value, Sensory	(O' Dwyer et al., 2013)

(Continues)

TABLE 1 (Continued)

Type of emulsion	Oil phase(s)	Solvent	Emulsifier (s)1	Antioxidant (s)1	Means of production	Droplet size ² (µm)	Zeta potential ² (mV)	Storage conditions	Measurement of lipid oxidation	Reference
	O ₁ : Mix of camelina and fish oils O ₂ : Mix of Palm and sunflower oils	NaCl solution (60 g/kg)	E ₁ : NaCas E ₂ : PGPR	GTE α-tocopherol	Hand-held homogenizer+ Homogenizer	D (v, 0.5) O/W = 1.05 – 1.13	-	5° C, 50 days	Hydroperoxides, Anisidine value	(S. W. Huang et al., 1994)
	O ₁ : Different ratio of camelina and tuna oils O ₂ : Mix of Palm and sunflower oils	NaCl solution (60 g/kg)	E ₁ : NaCas E ₂ : PGPR	-	Hand-held homogenizer+ Homogenizer	D (v, 0.5) O/W = 1.05 – 1.25	-	5° C, 80 days	Hydroperoxides, Anisidine value, Volatiles (SPME GC-MS)	(O'Dwyer et al., 2013)
Water-in-oil-in-water (W ₁ /O/W ₂)	Sunflower oil	W ₁ : Aqueous solution of ferrous sulfate heptahydrate (1 M) W ₂ : Glucose solution (2 M)	E ₁ : PGPR (10, 25, 50 and 70 g/kg oil) E ₂ : Tween 20 (5 g/kg)	-	Hand-held homogenizer (W ₁ /O) + Premix membrane emulsification system	D _{3,2} (W ₁ /O) = 0.21 – 3.33	-	Dark, Room temp., 7 days	Conjugated diene, Anisidine value	(Duque-Estrada et al., 2019)
	Sunflower oil	W ₁ : Aqueous solution of ferrous sulfate heptahydrate with hydrated gelatine lactose and postassium sorbate W ₂ : Aqueous solution with ferrous sulfate heptahydrate, lactose, guar gum, and postassium sorbate	E ₁ : PGPR E ₂ : Tween 80	-	Hand-held homogenizer	3.85 – 4.26 (W/O/W)	-50.1 – -20.9	4° C, 30 days	-	(Barbosa & Garcia-Rojas, 2022)

(Continues)

TABLE 1 (Continued)

Type of emulsion	Oil phase(s)	Solvent	Emulsifier (s)	Antioxidant (s)	Means of production	Droplet size ² (μm)	Zeta potential ² (mV)	Storage conditions	Measurement of lipid oxidation	Reference
	Olive, linseed, and fish oil (70:20:10)	W ₁ : NaCl solution W ₂ : NaCl solution	E ₁ : PGPR (6% w/w) E ₂ : Sodium caseinate (0.5% w/w)	W ₁ : Gallic acid (2.225 mg/kg) W ₂ : Quercetin (2–225 mg/kg)	W ₁ /O: Blender + High pressure homogenizer (W ₁ /O) W/O/W: Mixing (700 rpm) + Homogenizer	D _{4,3} = 2.47–8.65	–	4° C, 28 days	Hydroperoxides, TBARS	(W. Silva et al., 2018)
	Perilla oil (300 g/kg)	W ₁ : NaCl solution (0.584 g/100 mL) and sodium azide (0.04 g/100 mL) W ₂ : NaCl solution (0.584 g/100 mL) and sodium azide (0.04 g/100 mL)	E ₁ : PGPR (6 g/100 g) E ₂ : Sodium caseinate (0.5 g/100 mL)	W ₁ : Hydroxytyrosol (300 mg/kg)	W ₁ /O: Food processor + High pressure homogenizer W/O/W: Food processor + High pressure homogenizer	D _{4,3} = 2.03–2.47	–	4° C, 22 days	Malondialdehyd, TBARS, Lipid hydroperoxides	(Flairz et al., 2016)
Nanoemulsions	MCT or corn oil	Water (0.02% sodium azide) Span 80 and Tween 80	CURCUMIN	Magnetic stirrer	z-Average diameter \approx 100 nm for corn oil and \approx 50 nm for MCT	13.17 \pm 3.7 for corn oil and 6.177 \pm 1.77 for MCT	In glass vials at room temperature	DPPH radical scavenging of antioxidant in oil vs. in nanoemulsion	(Shah et al., 2016)	
	Olive oil	Deionized water	Olive oil endogenous phenolic compounds (vanillic caffeic and syringic acid)	High speed homogenizer	MDD varied from \approx 250 nm to \approx 600 nm	–	Ambient temperature (25 °C)	Oxidation reactor	(Katsouli et al., 2017)	
	Fish oil	5 mM buffer solution	Dispenser/ homogenizer + ultrasonic homogenizer	D _{4,3} varied from \approx 66 nm to \approx 700 nm depending on emulsification time	From –37.5 to +4.3 depending on droplet size	Dark, 4 and 25° C, 1 month	TBARS	(Nejadmansouri et al., 2016b)		

(Continues)

TABLE 1 (Continued)

Type of emulsion	Oil phase(s)	Solvent	Emulsifier (s)	Antioxidant (s)	Means of production	Droplet size ² (µm)	Zeta potential ² (mV)	Storage conditions	Measurement of lipid oxidation	Reference
Olive oil, soybean oil, and flaxseed oil	Phosphate buffer solution (5 mM, pH 7.0)	WPI	TOCOPHEROLS AND SESAMOL	Homogenizer	MDD varied between 225.29 and 251.46 nm	~34.28 to ~17.63 for tocopherol-enriched flaxseed oil emulsion	37°C, 35 days	Hydroperoxids and TBARS	(Guo et al., 2021)	
Pomegranate seed oil	Water	Polysorbate 80	α-TOCOPHEROL	Ultra-Turrax + ultrasonic homogenizer	α-Average diameter varied from ~36 nm to ~40 nm	~8.5	25°C, 50 days	Peroxide value and TBARS	(Sahafi et al., 2021)	
Sunflower oil	Water	CHITOSAN-STEARIC ACID NANOGELS, POLYSORBATE BATE 80	Homogenizer	Varied from ~35 to ~65 depending on pH	-	45°C, 20 days	Hydroperoxids, TBARS, MDA	(Aarjari et al., 2019)		
Sunflower oil	Distilled water	OSA MODIFIED STARCH PARTICLES, SDS, CTAB and Tween 20	High speed homogenizer	D ₁₀ varied from ~1 to ~90 for emulsions with different surfactants	-	Dark, 50°C, 14 days	Peroxide value and acid value	(Song et al., 2020)		
Corn germ oil	Deionized water	Zeln-hawthorn white pomace composite nanoparticles	High speed homogenizer	In µm range (exact numbers not provided)	-	Room temperature, 1 month	Hydroxyl radical scavenging ability, T-AOC, MDA content	(Jiang et al., 2020)		
Sunflower oil	Distilled water	Rutin hydrate, polysorbate 20, WPI, SDS	High shear mixer	D _{3,2} varied from ~5 to ~20 depending on stabilizer used	From ~17 to ~5 descending with pH	40°C, 7 days	Peroxide value and P-anisidine value	(Noon et al., 2020)		
Flaxseed oil	Water	Flaxseed protein, the soluble fraction of flaxseed mucilage, and polysorbate 80	THYMOL	Ultra-Turrax	D _{4,3} = 4.6-5	-	28 days in an incubator at 4°C, and in an oven at 50°C	Peroxide value and TBARS	(Nikbakhti Nasrabadi et al., 2020)	

DATEM: diacetyl tartaric acid ester of mono(diglycerides); PGP: polyglycerol polyricinoleate; DTAB: dodecyltrimethylammonium bromide; SDS: sodium dodecyl sulfate; Tween 20: polyoxyethylene sorbitan monolaurate; WPI: whey protein isolate; MCT: medium-chain triglyceride; MDD: mean droplet diameter; TBARS: thiobarbituric acid-reactive substances; OSA: octenyl succinic anhydride; CTAB: cetyltrimethyl ammonium bromide; T-AOC: the total antioxidant capacity; MDA: malondialdehyde; NaCas: sodium caseinate; GTE: green tea extract.

^a Lowercase denotes addition to the aqueous phase. Uppercase denotes addition to the oil phase, except for EDTA, WPI, and SDS. Italics denote that it could act as both emulsifier and antioxidant.

^b Range of droplet size and zeta potential of emulsions after production.

delay oxidative reactions in fish oil. Padial-Domínguez et al. (2020) compared the physical and oxidative stability of whey, fish (blue whiting), or soy protein hydrolysate stabilized 5% fish O/W emulsions during 10 days of storage. Results showed that the oxidative stability of the emulsions was highly affected by their physical stability; droplet size of the emulsion produced with fish protein hydrolysate increased during storage as well as the formation of volatile compounds compared with the other two emulsions. Nevertheless, it was also reported that the emulsion produced with fish protein hydrolysate had a significantly higher initial PV (11.44 ± 0.39 mmol O_2 /kg oil) compared with emulsions produced with soy protein or whey protein hydrolysate (2.3 and 3.3 mmol O_2 /kg oil, respectively). Even though physical instability has an influence on oxidative stability, initial levels of oxidation in emulsions has to be taken into account. Moreover, the oxidation level of the emulsifiers before emulsion production was shown to have an influence on the final oxidation status (Sørensen et al., 2010). Sørensen et al. (2010) substituted egg yolk as emulsifier in light mayonnaise with milk-based emulsifiers to eliminate the iron present in the egg yolk, which promotes lipid oxidation especially in the presence of susceptible oils rich in polyunsaturated fatty acids (e.g., fish oil). Results indicated that the initial quality (e.g., oxidation status) of the emulsifiers plays a more important role than the iron content in the emulsifier. In addition, the type of emulsifier and the presence of endogenous tocopherol also have an impact of on the oxidative stability and efficacy of added antioxidants (Sørensen et al., 2017). The oxidative stability of different emulsions was evaluated with the addition of caffeic acid or caffeates with different alkyl chain length, one stabilized with Tween 80 and another one stabilized with CITREM. In Tween 80 stabilized emulsions, the oxidative stability with caffeic acid and caffeates were accessed with and without endogenous tocopherol. Results showed that caffeic acid was the most efficient antioxidant in CITREM and Tween stabilized emulsions in the presence of endogenous tocopherols. In contrast, caffeic acid acted as a prooxidant in Tween stabilized emulsions and the caffeates as strong antioxidants in the absence of endogenous tocopherols. Moreover, partitioning of caffeic acid and caffeates was influenced by emulsifier type and the presence of endogenous tocopherols. The partitioning of caffeates in the aqueous phase decreased with increased alkyl chain (lipophilization) and after C4 the caffeates were in most cases not detected in the aqueous phase. For Tween stabilized emulsion, lower concentration of caffeic acid and methyl caffeates were measured in the aqueous phase compared with CITREM stabilized emulsions. Higher concentration of caffeic acid and methyl caffeate (CA C0 and CA C1) were detected in

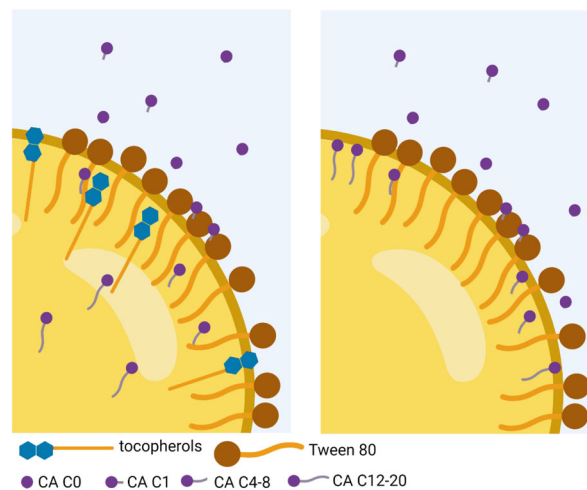


FIGURE 3 Illustration of the assumed partitioning based on measured concentration of caffeic acid and caffeates in the aqueous phase of Tween 80 stabilized emulsions with and without the presence of endogenous tocopherol.

the aqueous phase in Tween stabilized emulsions without endogenous tocopherols (Figure 3). The differences observed in antioxidant efficiency with the two emulsifiers and with and without endogenous tocopherols was explained by antioxidant–emulsifier and antioxidant–antioxidant interactions (Sørensen et al., 2017).

Viscosity of the aqueous phase also has effect on physical and oxidative stability of O/W emulsions. Shi et al. (2020) studied the potential application of enzymatic degraded polysaccharides from *Enteromorpha prolifera* (EEP) as antioxidants in preventing lipid oxidation in fish O/W emulsions emulsified with Tween 80, gum Arabic, or lecithin. Results showed that 1 wt% EEP provided the best oxidative stability when Tween 80 was used as an emulsifier and this was suggested to be due to increased viscosity upon EEP addition. In addition, the effect of increased viscosity of emulsion was explained as it slowed down the movement of dispersed droplets and prevented the aggregation of droplets, which resulted in an increase in the stability of emulsion. However, it was also discussed that the unadsorbed polysaccharides (when added at high concentrations) may lead to an osmotic attraction between the droplets, which could overcome repulsive interactions causing the flocculation of droplets (Shi et al., 2020). Moreover, other studies reported that the diffusion of the prooxidants is limited when the viscosity of the aqueous phase was increased in 50–70% fish O/W emulsions stabilized with a combination of sodium caseinate and various types of alginates, which affected the oxidative stability favourably (Yesiltas et al., 2017, 2018a). The oil–water interface characteristics, such as viscoelasticity, charge, and

structure, of fish O/W emulsions stabilized with potato peptides had an effect on physical and oxidative stability of the emulsions (García-Moreno et al., 2021). Peptides with a predominant α -helix conformation at the interface provided less stiff and more stretchable interfaces, whereas peptides with predominantly β -strand structures at the interface were equipped with stronger inter-peptide interactions, which led to the formation of stiffer interfaces. In addition, their results showed that the oxidative stability of fish O/W emulsions was mainly influenced by the peptides providing a positive surface charge, which repelled prooxidant cationic metal ions, independently of the interfacial structure and viscoelasticity of the interface.

The electrical charge of the emulsion droplets has an impact on physical and oxidative stability. Adsorbed emulsifier molecules such as ionic surfactants, phospholipids, proteins, and polysaccharides influence the magnitude and sign of the electrical charge, which largely depend on the type and concentration of surface-active molecules present at the oil–water interface (McClements, 2016). Besides, ionic composition and pH of the aqueous phase also contribute to the electrical charge of an emulsion droplet and this can be manipulated by choosing emulsifiers with desirable charge characteristics (e.g., sign, magnitude, isoelectric point) and controlling the aqueous phase properties (e.g., pH and ionic strength). Wu et al. (2016) investigated the physical and oxidative stability of self-emulsifying krill O/W emulsions at pH values between 3 and 7 and NaCl concentrations from 50 to 1000 mM, as krill oil naturally contains phospholipids, which can aid as emulsifiers. They found that the particle size increased with decreasing pH and it kept increasing during the storage at lower pH values. This was attributed to the decreasing negative charge of the droplets with decreasing pH as confirmed by the zeta potential results, which resulted in the reduction of the electrostatic repulsion between droplets, thereby leading to increased droplet interactions. As the physical stability was obtained for the 1 wt% krill O/W emulsion at pH values 5–7, further lipid oxidation investigations were carried out at pH 7. Wu et al. (2016) reported that both lipid hydroperoxides and TBARS increased after 1 day of storage when the oxidation is initiated with the addition of 50 μ M Fe²⁺ and oxidation could be controlled with the addition of antioxidants, for example, Trolox or α -tocopherol. The effect was more pronounced for α -tocopherol when added after emulsion production instead of addition prior to the homogenization. It was shown previously that the surface charge of the droplets plays an important role in the oxidative stability of the O/W emulsions (Mei et al., 1998). They suggested that the positively charged emulsifiers could be an effective way to control iron-catalyzed lipid oxidation. However, as the cationic surfactants are not common in foods, protein sta-

bilized emulsions at pH values below the isoelectric point could reduce lipid oxidation. Moreover, they suggested that the addition of NaCl might aid hampering lipid oxidation by releasing ions that compete for ion binding, thereby decreasing oxidation rates.

Physical stability and sensory properties of low-fat (15–20 wt%) O/W emulsions were investigated based on the use of ultra turrax, rotor–stator, and ultrasound homogenization methods (Cabrera-Trujillo et al., 2018). Results showed that ultrasound homogenization technique provided the most stable emulsions based on droplet size, zeta potential, viscosity, and phase separation during 7 days of storage followed by rotor–stator and ultra turrax. The smallest droplets were obtained when ultrasound was used, whereas the highest viscosity was provided by the rotor–stator homogenizer. Finally, the sensory preference test reported that the emulsions produced with rotor–stator had 43% acceptance, whereas ultrasound had 21% acceptance (Cabrera-Trujillo et al., 2018). Yesiltas et al. (2021) reported the effect of homogenization technique and emulsifier combinations on the physical and oxidative stability of high-fat (60%) O/W emulsions. A surfactant (PC or DATEM) was used in combination with sodium caseinate to investigate the effect of surfactant type on the stability of emulsions and it was found that emulsions containing DATEM provided smaller droplets, higher viscosity, and less creaming compared with emulsions containing PC. However, emulsions containing PC had better oxidative stability based on the formation of primary and secondary volatile oxidation products and consumption of alpha-tocopherols compared with emulsions containing DATEM. Better oxidative stability obtained with emulsions containing PC was attributed to its antioxidant properties (García-Moreno et al., 2014). When ultra turrax as the primary and colloid mill as the secondary homogenizer were used, smaller droplet sizes, higher viscosity, and less creaming instability were obtained compared with the use of Stephan Mixer.

Feng et al. (2021) tested the effect of additional excess protein on the oxidative stability of O/W emulsions stabilized with either Tween 20 or WPI as the two starting emulsions. Nonmodified or dextran-glycated soy protein isolate (SPI) was added to the continuous phase of the starting emulsions. Results showed that the addition of these compounds did not significantly affect the physical stability of emulsions, while the inhibition of lipid oxidation was the highest in the following order: glycated SPI mixture \approx SPI/dextran mixture > SPI > WPI. It was suggested that SPI ingredients and dextran have potential for inhibiting lipid oxidation in emulsions due to their iron-binding and free radical-scavenging activities; former effect being predominant by preventing transition metals from approaching the oil–water interface. More

importantly, the protecting effect of excess protein in Tween 20-stabilized emulsions was higher compared with WPI-stabilized emulsions, which was attributed to the interaction of surfactants with proteins leading to a protein conformational change and increase their ability to bind molecules involved in the reaction cascade (Feng et al., 2021).

O/W emulsions were shown to be stabilized using protein-coated nanoemulsion droplets at various concentrations from 2 to 16% (Ye et al., 2013). Lowest concentration (2%) was sufficient to prevent coalescence and the interface was almost totally covered by the added nanoemulsion. Moreover, it was reported that increased concentration of nanoemulsion yielded the formation of smaller droplets in the final emulsion. Nanoemulsion droplets adsorbed directly at the surface of the core oil were flattened in their shape compared with the others that are not directly in contact with the core oil, which had more spherical shape (Ye et al., 2013).

4.2 | W/O emulsions

W/O emulsions consists of an aqueous phase dispersed as spherical droplets in a continuous lipid phase (Figure 1b). Although these emulsion systems have been considerably less studied than O/W emulsions, they have a wide range of applications in: (i) the food industry, for instance in products such as butter, spreads, margarine (Kirkhus et al., 2015), and cocoa butter (di Bari et al., 2014) and (ii) the cosmetic and pharmaceutical industry, for example, in products such as sunscreen (Kwak et al., 2015) and lipstick (Le Révérend et al., 2011).

Lipid oxidation in W/O emulsions is one of the main causes of emulsion deterioration due to the easy access of prooxidants (e.g., oxygen) to the oxidizable continuous lipid phase (Mosca et al., 2008). As for other types of emulsions, the type and content of lipids determine the rate of oxidation in W/O emulsions. Sopolana et al. (2016) reported that lipid oxidation of light margarines (35–70% fat and similar fatty acid composition, mainly linoleic acid) decreased with increasing lipid content when heated at 180°C. The authors did not detect primary oxidation products by ¹H NMR, as a consequence of its fast degradation at the high temperature studied, but secondary volatile oxidation products such as aldehydes (e.g., n-alkanals and (E)–2-alkenals), epoxides (e.g., mono- and diepoxides), and alcohols. Moreover, the quality of the lipids used to produce W/O emulsions influences their oxidative stability. For instance, margarine produced with hardstock obtained by chemical interesterification (70 palm stearin/30 coconout oil) showed higher PV than margarine obtained with hardstock with same fatty acid composi-

tion and obtained by enzymatic interesterification. The authors stated that differences in PV for the margarines, but not in volatiles or sensory analysis, were attributed to further heating stages in the chemical interesterification process when compared with the process using lipases. Thus, initial oxidation status of the lipids used influenced the oxidative stability of margarines (Zhang et al., 2006). Furthermore, Yi et al. (2013) observed that increasing the content of FFAs in the lipid phase (e.g., from 0 to 1 wt.% oleic acid) significantly decreased the lag phase (from eight to one day(s)) for lipid hydroperoxides and hexanal formation in 2 wt.% water-in-walnut oil emulsions stabilized with 0.5 wt.% of PGPR at pH 7. The authors reported a higher prooxidant effect for short FFAs than medium FFAs (e.g., lauric vs. palmitic or steric acids). It was attributed to a higher surface activity of short FFAs, which was accumulated at the water droplet interface, making it more negatively charged (FFAs are negatively charged at pH 7). This attracted transition metals that promoted lipid oxidation by interacting with lipid hydroperoxides (also surface-active molecules located at the interface). The authors found that increasing the degree of unsaturation of the FFAs (e.g., linolenic vs. oleic acids), as expected, resulted in increased oxidation rates, favored by the higher oxidizability of the unsaturated FFAs. These results are in agreement with those studies that report the prooxidant effect of FFAs in bulk oils (Aubourg, 2001; Yoshida, 1993). Similarly, addition of FFA (oleic acid) to soybean O/W emulsions promoted lipid oxidation by increasing the negative charge of the oil/water interface, which favored attraction of prooxidant metal ions (Waraho et al., 2009).

Although lipid oxidation in W/O emulsions may be similar to that in bulk oil (i.e., due to direct exposure of the lipid phase to air), other factors such as the presence of prooxidants, antioxidants or emulsifiers in the water phase and at the w/o interface also play a significant role in the oxidative stability of W/O emulsions. In this regard, several research works have studied the influence of antioxidant addition on lipid oxidation in W/O emulsions. Yi et al. (2013) reported that the addition of 50 μM EDTA (a metal chelator) to the water phase of 2 wt.% water-in-walnut oil emulsions stabilized with 0.5 wt.% of PGPR at pH 7 significantly inhibited lipid oxidation based on hydroperoxides and hexanal measurements. Likewise, Yi et al. (2015) observed that addition of metal chelators such as EDTA or deferoxamine retarded lipid oxidation in 2 wt.% water-in-stripped walnut oil emulsions stabilized with 0.3 wt.% of PGPR at pH 3. The authors reported a dose-dependent effect for both chelators in the concentration range of 5–50 μM, whereas increasing concentration to 100 μM did not further improve oxidative stability (based on hydroperoxides and hexanal measurements). Moreover, EDTA was found to be a stronger chelator than

deferoxamine, which was attributed to the ability of EDTA to chelate both iron and copper. Chen et al. (2016) also reported a strong antioxidant effect of EDTA (50 μM) in 2 wt.% water-in-algae oil emulsions stabilized with 0.5 wt.% PGPR at pH 7. Overall, the results from these studies denote the importance of endogenous transition metals such as iron and copper to catalyze lipid oxidation in W/O emulsions by decomposing lipid hydroperoxides into reactive radicals (e.g., alkoxyl and peroxy radicals).

Other works have investigated the effect of radical scavengers on the oxidative stability of W/O emulsions. Sørensen et al. (2011) studied the influence of the polarity of radical scavengers on the oxidative stability of 2 wt.% W/O (fish oil:rapeseed oil, 1:1) emulsions stabilized with 1 wt.% PGPR at pH 7. The authors reported that, although all antioxidants tested (100 μM in emulsion) retarded lipid oxidation in W/O emulsions, addition of ascorbyl palmitate or ascorbyl lipophilized with conjugated linoleic acid was more efficient when compared with addition of ascorbic acid or conjugated linoleic acid. This was in agreement with the polar paradox indicating higher efficiency for amphiphilic antioxidants, which are preferably located at the w/o interface, in heterogeneous systems such as W/O emulsions. Similarly, Yi et al. (2015) studied the effect of the addition (0, 10, 100, 500, and 1000 μM in emulsion) of α -tocopherol or Trolox (its polar counterpart) on the oxidative stability of 2 wt.% water-in-stripped walnut oil emulsions stabilized by 0.3 wt.% PGPR at pH 3. The authors observed that both radical scavengers inhibited lipid oxidation in W/O emulsions, with the lowest formation of hydroperoxides and hexanal in those emulsions containing the antioxidants at the highest concentration assayed (1000 μM). Interestingly, the results indicated that Trolox was more efficient than α -tocopherol. Although both antioxidants are surface-active, the long alkyl chain of α -tocopherol may have favored the formation of reverse micelles in the lipid continuous phase reducing the migration of α -tocopherol to the w/o interface when compared with Trolox. Alternatively, Chen et al. (2016) investigated the oxidative stability of 2 wt.% water-in-algae oil emulsions stabilized with 0.5 wt.% PGPR at pH 7 containing 300 μM of grape seed extract (>90% polyphenols) or 300 μM of green tea extract (GTE) (>90% epigallocatechin gallate). The authors observed that W/O emulsions with added antioxidants showed higher oxidative stability (based on propanal measurement) compared with the control emulsion, although no significant differences were observed between extracts.

The characteristics of the oil-water interface in W/O emulsions, which highly affect oxidative stability, are determined to a great extent by the type of emulsifier employed. In addition to determining the interface structure, emulsifiers interact with prooxidants (e.g., transition

metals) and antioxidants influencing the location of pro- and antioxidants in emulsions and thus their role in lipid oxidation. Yi et al. (2015) observed a higher oxidative stability for 2 wt.% water-in-stripped walnut oil emulsions when increasing PGPR concentration (0.3, 0.5, and 1 wt.%), despite the lower droplet size obtained (i.e., increased surface area). This finding was explained by an interaction of the excess PGPR with lipid hydroperoxides, solubilizing them away from the droplet surface. This reduced the decomposition of lipid hydroperoxides by transition metals present in the aqueous phase, whereby lipid oxidation decreased. Chen et al. (2016) reported a significantly higher oxidative stability during 4 days of storage for 2 wt.% water-in-algae oil emulsions when stabilized with 0.5 wt.% defatted soy lecithin (PC75, 75% phosphatidylcholine) or 0.5 wt.% defatted lyso-lecithin (lyso-PC) instead of 0.5 wt.% PGPR. This was attributed to: (i) the larger droplet size of emulsions stabilized with PC75 and lyso-PC (i.e., reduced surface area) when compared with the emulsion stabilized with PGPR and (ii) the higher content of α -tocopherol in PC75 and lyso-PC when compared with PGPR. However, it should be mentioned that the emulsion stabilized with PGPR showed a higher physical stability compared with those stabilized with PC75 or lyso-PC. Yi et al. (2014) investigated how the addition of emulsifiers (0.1 wt.% in emulsion) such as dodecyltrimethylammonium bromide (DTAB), sodium dodecyl sulfate (SDS), polyoxyethylene sorbitan monolaurate (Tween 20), and WPI influenced the oxidative stability of 2 wt.% water-in-walnut oil emulsions stabilized with 0.5 wt.% PGPR at pH 7. Interestingly, the emulsion containing SDS presented a higher oxidative stability when compared with the control (only PGPR), whereas the addition of Tween 20 did not have any effect and the addition of DTAB had a prooxidant effect favoring the formation of hydroperoxides and hexanal. The authors attributed the protective effect of SDS to the formation of negatively charged micelles in the aqueous phase, contrarily to Tween 20 that is nonionic or cetyltrimethyl ammonium bromide (CTAB) that is cationic. The SDS negatively charged micelles were able to attract transition metals to the core of the water droplet reducing their concentration at the o/w interface and thus decreasing their interaction with lipid hydroperoxides. Likewise, the addition of WPI retarded lipid oxidation in W/O emulsions stabilized with PGPR, both at pH 3 and 7. Nonetheless, higher oxidative stability was found for the emulsion containing WPI at pH 7 compared with pH 3, as a consequence of the negative charge and thus higher chelating activity of WPI in the aqueous phase above its isoelectric point. Zhu et al. (2015) reported that the antioxidant activity of WPI in 10 wt.% water-in-walnut oil emulsions stabilized with PGPR at pH 7 was significantly affected by the ionic strength. Addition of low levels of salts (<50 mM)

enhanced oxidative stability, whereas addition of high levels of salts (500 mM) favored lipid oxidation when compared with the control emulsion. These findings were explained as follows: (i) low concentration of salt could remove trace of metals from the w/o interface where they were bound to anionic FFAs and (ii) high concentration of salt might shield the surface charge of WPI by counterions making it less negative and thus reducing its chelating properties.

4.3 | Oil-in-oil emulsions

Oil-in-oil emulsions, also known as water-free (or waterless) emulsions, anhydrous emulsions, and nonaqueous emulsions, are in fact mixtures of immiscible oils, for example, vegetable oil and silicone oil, stabilized by particles (Figure 1d) (Binks & Tyowua, 2016). These emulsions are also formed by dispersion of oil droplets in an immiscible nonaqueous liquid (Jaitely et al., 2004). The most important issue to consider in the formation of these uncommon emulsions is lack of information on the action of surfactants on the nonaqueous media (Riess et al., 2004). Oil-in-oil emulsions are mostly considered for drug delivery purposes where a given agent is incompatible with water (Zhang M. et al., 2019). They are also adopted in other sectors such as electronics, cosmetics, catalysts, and so on (Klapper et al., 2008 and references therein). However, very few reports are found on the application of oil-in-oil emulsions in food sector. For example, Patel et al. (2006) produced lecithin-based microemulsions where the aqueous phase was replaced with propylene glycol, a nonaqueous polar solvent. Moreover, Ceballos et al. (2014) produced propylene glycol-in-oil (MCT oil + soybean oil) emulsion to be added to foodstuff. They witnessed that the nonaqueous emulsion they manufactured had acceptable macroscopic stability within 1-month preservation at ambient temperature. They suggested that this emulsion could be considered for the production of foods with reduced fat content. It seems that more research should be devoted on the formation of oil-in-oil emulsions in food industry, especially when water-incompatible ingredients should be incorporated in foodstuffs.

Although oil-in-oil emulsions contain oil in their formulations, oxidation has not been studied in these emulsions yet. Most studies were centered on the pharmaceutical applications of these emulsions where oil oxidation was not considered. Instead, these studies mostly focused on stabilization of these emulsions in terms of coalescence or flocculation as well as rheological properties. For example, Atanase et al. (2015) adopted a triblock copolymer to stabilize a nonaqueous emulsion for preparing drug-loaded formulations for topical applications. Likewise, oxidative

stability of oil-in-oil emulsions in food sector has not been analyzed. It should be noted that very few studies considered stabilization of these emulsions designed for food production, but the stabilization process was solely based on physical properties of the emulsions. For instance, Ceballos et al. (2014) concluded that ethyl cellulose could stabilize propylene glycol-in-oil emulsions in terms of structure and flow properties. Future studies are encouraged to determine oil oxidation in oil-in-oil emulsions produced for food formulations and devise measures to give oxidative stability to these emulsions in the event of deteriorative oil oxidation.

4.4 | Multiple emulsions

Multiple emulsions, also referred to as double emulsions, consist of a complex system of an emulsion within another emulsion. Multiple emulsions are mainly of two types: oil-in-water-in-oil (O/W/O) and water-in-oil-in-water (W/O/W). O/W/O is oil dispersed in water and then this emulsion is dispersed in a second oil phase (Figure 1e), whereas in W/O/W emulsions, water is first dispersed in oil and then this emulsion is dispersed in a second water phase (Figure 1f). For O/W/O emulsions, the inner oil phase is also called O1 and the outer oil phase O2. Similarly, in W/O/W emulsions, the inner water phase is called W1 and outer water phase W2 (Dickinson, 2011; Lamba et al., 2015; Muschiolik & Dickinson, 2017). Multiple emulsions consist of three phases and two oil-water interfaces. Two different emulsifiers are typically required, since two different kinds of interfaces are present in these emulsion systems. Emulsifiers with low HLB value (higher ratio of nonpolar groups; 4–6) are considered good W/O emulsifiers, whereas emulsifiers with higher HLB value (higher ratio of polar groups; 8–18) function well as O/W emulsifiers. Hence, selection of different emulsifiers/surfactants is important for the formation of multiple emulsions (Dickinson, 2011; Lamba et al., 2015).

There are several commonly food grade hydrophobic emulsifiers. PGPR is a hydrophobic emulsifier predominantly used to prepare primary W/O emulsions of W/O/W emulsions. Other hydrophobic emulsifiers used for the formation and stabilization of double emulsions include sorbitan monooleate (Span 80), glycerol monooleate, and lecithin (Lamba et al., 2015; Muschiolik & Dickinson, 2017). A wider range of food grade hydrophilic emulsifiers and stabilizers are available compared with hydrophobic emulsifiers. The hydrophilic emulsifiers include small molecule surfactants such as Tween 20 and lecithin, hydrocolloids, for example, gum Arabic and gelatin, egg proteins, soy proteins, and other proteins such as WPI and

sodium caseinate as previously commented in Section 2.3 (Muschiolik & Dickinson, 2017).

Several parameters affect the stability of multiple emulsions such as composition and emulsification conditions. Composition is optimized to improve the stability of the system, for example, parameters such as addition of electrolytes, addition of gelling agents, and emulsifiers (Lamba et al., 2015; Muschiolik, 2007).

These multiple emulsion systems have potential for application in the food processing industry. The application possibilities are encapsulation or protection of sensitive bioactive compounds such as iron (Duque-Estrada et al., 2019; Ilyasoglu Buyukkestelli & El, 2019), catechin, curcumin and CA, n-3 fatty acids (Freire et al., 2017; O'Dwyer et al., 2013a,b) and to control release of flavor and aroma and to produce food with lower oil or fat content (Robert et al., 2019; Silva et al., 2018). The most popular application of multiple emulsions remain those concerned with encapsulation and release (Muschiolik & Dickinson, 2017).

Most of the research done on multiple emulsions have focused on encapsulation of bioactive compounds, the stability and release of the encapsulated compounds rather than the oxidative stability of the emulsion system. Only few studies with multiple emulsions (W/O/W and O/W/O) have paid attention to the oxidative stability of the lipid phase(s).

Different types of oils have been applied in multiple emulsion systems and the selection of oils depends on the purpose. If the emulsion system is intended as encapsulation of other bioactive compounds than LC omega-3 poly PUFAs, oils such as linseed (Dima & Dima, 2018; Poyato et al., 2013), soybean (Arab et al., 2019), and sunflower (Arab et al., 2019; Duque-Estrada et al., 2019; O'Dwyer et al., 2013; Simiqueli et al., 2019) have been applied. For LC omega-3 PUFA, fish oil and omega-3 PUFA perilla oil (65% 18:3) have been used as fat replacer (e.g., meats) or as delivery emulsion for incorporation in foods for producing healthier foods (Flaiz et al., 2016; O'Dwyer et al., 2012, 2013a,b; Silva et al., 2018). With the use of lipid source with higher concentration of unsaturated fatty acids, the risk of oxidative instability is increased due to several interfacial in multiple emulsions. However, the oxidative stability are also affected by process condition, emulsifier type and concentration, interaction of other ingredients in the systems, and concentration of prooxidants and antioxidants.

Some researchers studied the incorporation of iron into multiple emulsions (W/O/W) for delivery of iron (Duque-Estrada et al., 2019; Buyukkestelli & El, 2019; Simiqueli et al., 2019). Iron is a prooxidant and can have a great impact on the oxidative stability. Hence, this might challenge the design of the emulsion system. Duque-Estrada et al. (2019) evaluated the effect of PGPR concentration

(10–70 g/kg) on the resulting lipid oxidation in double emulsions with iron encapsulated in the inner aqueous phase of the W/O/W emulsions. All double emulsions underwent lipid oxidation and in particular those with highest PGPR concentration. It was assumed that it was due to the small inner droplet size, which promoted contact between oil and the internal aqueous phase containing the iron (Duque-Estrada et al., 2019). In addition, the resulting oxidative stability of yoghurt fortified with the iron-loaded emulsions was evaluated. Iron in the aqueous phase resulted in significant lipid oxidation during storage (Hosseini et al., 2019). A combination of rice bran oil and rice bran stearin as oil phase and hydrophilic quillaja saponin surfactant in the aqueous phase of iron-loaded W/O/W emulsions was produced to evaluate the oxidative stability of the lipids. Results showed that incorporation of rice bran stearin in the oil phase could retard lipid oxidation in the emulsions. Thus, changing the oil phase from liquid to semi-solid oil significantly retarded lipid oxidation. This was explained by the formation of fat crystals when rice bran stearin was added, where the formed crystals reduced diffusion of compounds including oxygen. Moreover, a lower level of unsaturated fatty acids in the emulsion with rice brain stearin could also explain the reduced oxidation observed. Furthermore, the authors concluded that the fabricated double emulsion could not only be used for delivery of iron, but also of other hydrophilic bioactive compounds for fortification of foods (Prichapan et al., 2020).

In addition, W/O/W emulsions can be applied as fat replacer (Robert et al., 2019; Silva et al., 2018) for a healthier fat profile or for n-3 PUFA enrichment (Flaiz et al., 2016; Hwang et al., 2017; Poyato et al., 2013). In these later cases, more unsaturated lipids are used, for example, perilla oil (65% C18:3) and fish oil, which increases the susceptibility to lipid oxidation. Therefore, antioxidants are used to improve the oxidative stability of these emulsions. The addition of quercetin and gallic acid in the internal and external aqueous phase of W/O/W containing a blend of olive, linseed, and fish oils (70:20:10) as oil phase and stabilized with PGPR and sodium caseinate was investigated. There was no significant effect on the oxidative stability of W/O/W by adding gallic acid; however, quercetin significantly improved the oxidative stability (Silva et al., 2018). The effect of adding hydroxytyrosol on the oxidative stability of normal and gelled W/O/W emulsions has been evaluated. The oxidative stability was maintained in both systems by the addition of hydroxytyrosol. However, the gelled double emulsion was more stable than the normal double emulsion. Antioxidant loss progressed faster in the more compartmentalized systems (double emulsion and gelled double emulsion) compared with more simple O/W emulsion and double emulsion compared with gelled

double emulsion. This was attributed to the larger surface area in the double emulsions and the decreased movement in the gelled double emulsions (Flaiz et al., 2016). Olive leaf extract incorporated in the internal aqueous phase also improved the oxidative stability of W/O/W containing a blend of olive, linseed, and fish oils (70:20:10) and stabilized with PGPR and sodium caseinate (Robert et al., 2019) similar to Silva et al. (2018). Another study revealed that the oil type (olive and linseed oils) used in the W/O/W systems affected the efficacy of the applied antioxidants (dried leaf extract and butylated hydroxyanisole (BHA)). High oxidative stability was observed in the emulsions produced with olive oil and with no differences between the antioxidants applied. Nevertheless, in emulsion produced with linseed oil, the more lipophilic antioxidant, BHA, was more efficient in delaying lipid oxidation than the more hydrophilic extract (Poyato et al., 2013). The oxidative stability of W/O/W emulsion with CA stabilized with nonionic emulsifiers and lecithin in the presence of chitosan in the internal and external aqueous phase was studied. The oxidative stability was improved with CA in the internal aqueous phase. Based on results of this study, oxidative stability of W/O/W in the presence of CA is influenced by many factors such as location of antioxidants in the different regions of the emulsion, surfactants, the presence of metal ions, presence of chitosan, antioxidant concentration, and temperature (Dima & Dima, 2018). Different concentrations of WPC in the external aqueous phase and vitamin E and C in the oil and internal aqueous phase, respectively, in W/O/W emulsions with fish oil has also been evaluated. Combined use of vitamin E and C improved the oxidative stability and the oxidation decreased with increasing WPC concentration in the external aqueous phase (Hwang et al., 2017).

A few studies have been carried out with O/W/O containing n-3 fatty acids (blend of camelina and tuna oils in different ratio) and stabilized with PGPR and sodium caseinate for incorporation into spreads (high oil content products). The degree of unsaturation influenced the oxidative stability, where tuna oil (more unsaturated) reduced oxidative stability compared with camelina oil (O'Dwyer et al., 2013b). In addition, the application of water soluble antioxidant (GTE), oil soluble antioxidant (alpha-tocopherol), or both reduced lipid oxidation in n-3 enriched table spreads prepared using O/W/O technology using a blend of camelina and fish oils (75:15) and stabilized with PGPR and sodium caseinate. The content of hydroperoxides measured differed with antioxidant applied. GTE in the emulsions resulted in the lowest PV measured followed by the combination of GTE and alpha-tocopherol. No significant difference in AV in the spreads containing antioxidants was observed (O'Dwyer et al., 2012).

The studies above indicate that W/O/W and O/W/O emulsions can be produced with addition of antioxidants in order to improve the oxidative stability. However, the composition of the system and location of the antioxidants are important parameters for producing oxidative stable double emulsion systems for different purposes.

4.5 | Nanoemulsions

Nanoemulsions are thermodynamically unstable systems with small droplet sizes ranging from 20 to 200 nm (Figure 1g) (Gutiérrez et al., 2008). Other droplet size ranges have also been introduced for nanoemulsions; for example, Morales et al. (2003) recommended a range between 50 and 500 nm. However, other criteria seem to outweigh droplet size in importance when comparing nanoemulsion and microemulsion. McClements (2012) stated that thermodynamic stability is the most important distinguishing factor in comparison between microemulsion and nanoemulsion where the former is thermodynamically stable, whereas the latter is not. Nevertheless, nanoemulsions possess a very high level of kinetic stability, which is defined by their great stability against droplet coalescence, dilution, and temperature changes (Anton et al., 2008). Nanoemulsions are used in different areas such as cosmetics and healthcare (Bouchemal et al., 2004), agrochemical applications (Gutiérrez et al., 2008), and food industry (Li et al., 2016).

Two general methods can be considered for the production of nanoemulsions, namely high-energy and low-energy emulsification methods: the former are carried out using devices (e.g., high pressure homogenizers and ultrasound generators) to prepare very large interfaces while the latter are obtained by modifying physicochemical characteristics of emulsion components such as surfactants (Anton et al., 2008). Two very common low-energy methods to form nanoemulsions are spontaneous emulsification (Bouchemal et al., 2004) and phase inversion (Fernandez et al., 2004). Nanoemulsification approach can be adopted to produce various kinds of nanoemulsions: O/W nanoemulsions (e.g., Li et al., 2016), W/O nanoemulsions (e.g., Katsouli et al., 2018), and even multiple (W/O/W) nanoemulsions (Huang H. et al., 2019). It seems that most of the studies have focused on the production of O/W nanoemulsions and future studies may work on the production and analysis of other types of nanoemulsions to be used in food industry, cosmetics, healthcare, and so on.

Shah et al. (2016) determined the antioxidant effect of curcumin in nanoemulsion (with MCT and corn oil as the oil phase and Span80 and Tween 80 as the surfactants) and found that the incorporation of the antioxidant

in nanoemulsion improved oxidative stability of the emulsion due to enhancement of radical scavenging activity of curcumin in the nanoemulsion. Relkin et al. (2008) determined α -tocopherol stability in O/W nanoemulsion stabilized with protein during storage for 8 weeks at ambient temperature and found that mixtures of α -tocopherol and stearin-rich fraction in nanoemulsified phase reduced α -tocopherol degradation compared with that in bulk phase. Incorporation of phenolic compounds in nanoemulsions could also prolong oxidative stability in the emulsions. Katsouli et al. (2017) reported that incorporation of caffeic acid, an endogenous phenolic compound in olive oil, in W/O nanoemulsion (with extra virgin olive oil as the oil phase and Tween 20 as the emulsifier) rendered oxidative stability to the nanoemulsion for over 33 h at room temperature. It is noteworthy that oxidative stability of the W/O nanoemulsion is greatly influenced by the amount of aqueous phase, where increased water phase will accelerate oil oxidation. This is explained by higher surface area of the emulsions with more water, which accelerate oil oxidation by providing a better condition for interaction of water-soluble transition metals and lipids (Yi et al., 2014a). In line with this, Katsouli et al. (2017) uttered that higher amount of water in their W/O nanoemulsion accelerated oil oxidation and emulsion degradation.

Some studies revealed that oil is better protected in nanoemulsions than in conventional emulsions. For instance, Nejadmansouri et al. (2016b) reported that fish O/W nanoemulsion stabilized with WPI had significantly higher oxidative stability than conventional fish O/W emulsion. They assumed that such a higher oxidative stability in the nanoemulsion could be attributed to thicker layers of protein at the interface. Lee et al. (2011), however, asserted that oxidation rate in O/W nanoemulsion stabilized with WPI was higher than that in conventional emulsion due to the increased surface area in the nanoemulsion, more impurities in greater content of protein, and/or weaker light scattering in the nanoemulsion. The discrepancy between the inferences of these studies may illuminate the fact that more in-depth studies are required to shed light on the interfacial circumstances in nanoemulsions. In other words, it should be studied whether larger interface obtained by nanoemulsification could increase the risk of oil oxidation even at the presence of thicker layers of protein. The different results of these two studies may also be explained by the different methods adopted to produce the nanoemulsions (sonication in the former and high-pressure homogenization in the latter), influencing interface area and antioxidant properties of the protein. It should be noted that these studies determined oil oxidation solely based upon TBARS method, which is an index of secondary oxidation, especially based on the formation of certain aldehydes such as malondialdehyde.

Nevertheless, a more comprehensive analysis of oil oxidation is required to evaluate oxidative behavior in O/W nanoemulsions.

The production of fish O/W nanoemulsions is known as a rather novel method to better impede oxidation in fish oil. Nejadmansouri et al. (2016b) reported that nanoemulsification of fish oil through sonication could considerably decrease oil oxidation in storage compared with conventional emulsions. However, in another study, these authors reported that incorporation of nonionic surfactants in nanoemulsions prepared through ultrasonic method increased oxidation rate compared with conventional emulsions (Nejadmansouri et al., 2016a). In contrast, Karthik and Anandharamakrishnan (2016) obtained oxidatively stable fish O/W nanoemulsions through microfluidization using Tween 40 as an emulsifier. These differences in findings of the studies could be due to the different approaches adopted to fabricate the nanoemulsions. This theory, however, was refused by Walker et al. (2015) who observed no significant difference in oxidative stability of fish O/W nanoemulsions produced by low- and high-energy methods (i.e., spontaneous emulsification and microfluidization, respectively). Incorporation of certain ingredients such as carrier oils and/or natural antioxidants may also prevent oil oxidation in nanoemulsions. Walker et al. (2017) determined the protective effect of carrier oils (MCT, lemon oil, and thyme oil) against oxidation in fish O/W nanoemulsion stabilized with Tween 80. They found that these carrier oils had considerable role to delay fish oil oxidation in the nanoemulsions with MCTs having the strongest effect. Antioxidant added to the oil phase of nanoemulsions may lead to longer lag phase in the induction period during the autoxidation of the oil. Therefore, the propagation stage of the oxidation process is hindered when antioxidant neutralizes the free radical by donation of a hydrogen atom. This interpretation of oxidation hindrance in nanoemulsions by adding antioxidant to the oil phase was observed when α -tocopherol was incorporated into the oil phase of nanoemulsion before emulsification (Guo et al., 2021; Sahafi et al., 2021). It should be noted that the formation of nanoemulsions containing antioxidants may also exert protective effect against degradation of ingredients other than oil. For instance, Yang et al. (2011) stated that formation of nanoemulsions containing natural antioxidants (β -carotene, tanshinone, and black tea extract) could improve stability of citral (α,β -unsaturated aldehyde with one additional double bond, which is responsible for lemon-like aroma in some food products and cosmetics) during storage.

Overall, it is not still clear whether nanoemulsification is superior to other methods to increase oxidative stability of susceptible oils. For example, Chen et al. (2017)

reported that flaxseed oil droplets were more stable against oxidation when encapsulated in microgels than in nanoemulsions. Future studies, thus, should focus on optimization of nanoemulsification process to yield more oxidative stable nanoemulsions. The optimization could be performed in terms of the approach adopted for fabrication of nanoemulsion, emulsifier and surfactants used, antioxidants, and storage conditions.

4.6 | Pickering emulsions

Pickering emulsions are formed by use of solid particles that adsorb at the interface between two phases of the emulsion (Yang et al., 2017). In other words, they are the emulsions stabilized by solid particles by which thick interfacial layers are created around droplets (Figure 1h) (Kargar et al., 2011). Pickering emulsions shield droplets at high concentrations of dispersed phase by rendering stabilization against coalescence and Ostwald ripening (Wen et al., 2014). They are formed by means of different solid particles such as silica, alumina, wax, chitin, clay particles, titanium oxides (Song et al., 2015 and references therein), as well as cellulose nanocrystals, phytosterol, modified starch, zein, and gliadin colloid particles (Zhou et al., 2018 and references therein). Xiao et al. (2016) summarized three main characteristics in order for a particle to act as Pickering agent: wettability by and insolubility in both phases of emulsion, preservation of partial wettability to increase interface adsorption efficiency, and being smaller than emulsion droplets. For comprehensive information on particles used to fabricate Pickering emulsions, reader is referred to Yang et al. (2017).

Although the notion of Pickering particles was proposed over 100 years ago, it has recently turned into a hot research tag in different areas including pharmaceutical and food sciences. Regarding the application of Pickering emulsions in foods, it should be noted that a large number of studies on these emulsions cannot be taken into account for food applications because the particles used (especially inorganic ones) are not allowed in the production of foods (Fu Liu & Tang, 2013).

While Pickering emulsions are mostly characterized by their improved physical stability (Yang et al., 2017), some studies highlighted the heightened oxidative stability of emulsions stabilized with Pickering particles. For instance, Nikbakht Nasrabadi et al. (2020) suggested that a blend of Pickering stabilization (by using flaxseed protein and polysaccharides) and addition of thymol to the oil phase could retard oxidative reactions in highly unsaturated oils.

As mentioned above, the number of particles to yield Pickering emulsions meant to be used in food industry is limited because not all the particles are allowed in food

production. Therefore, recent studies have tried to explore the possibility of adopting existing particles that can play the role of Pickering particles. In one of these efforts, Song et al. (2020) examined the stability of emulsions fabricated by octenyl succinic anhydride-modified starch particles as Pickering agents and small molecular surfactants as stabilizers. They concluded that the hydrophobically modified starch particles and the surfactants (SDS, CTAB, and Tween 20) together could enhance the oxidative stability of the emulsions (by using sunflower oil) as evidenced by the reduction in the formation of lipid hydroperoxides in the treated emulsions. Jiang et al. (2020) also adopted an antioxidant polysaccharide to fabricate stable Pickering emulsions. They produced composite nanoparticles using zein and pectin derived from hawthorn wine pomace. The composite was used to form Pickering emulsion by using corn oil showing considerable oxidative stability. In another research, Atarian et al. (2019) stabilized O/W emulsions using chitosan-stearic acid nanogels as Pickering particles. They stated that the stability of these Pickering emulsions fabricated by using sunflower oil is a function of pH, chitosan-to-stearic acid ratio, and oil-to-nanogel ratio and claimed that the most oxidatively stable Pickering emulsion was obtained when pH was set at 8 and the above-mentioned ratios were adjusted to 0.5:1 and 20:1, respectively. They also compared the oxidative stability of this emulsion with that of the emulsion stabilized using Tween 80 and reported that the former showed higher stability than the latter against oil oxidation.

Despite the reports claiming the positive effect of Pickering particles in food emulsions in order to retard oil oxidation, a study performed by Schröder et al. (2019) showed that this is not always the case. These authors stated that colloidal lipid particles, when used as Pickering particles, could improve physical stability of emulsions prepared by using sunflower oil. However, when they compared the oxidative stability of such emulsions with that of conventional sodium caseinate-stabilized emulsions containing only liquid oil, they realized that colloidal lipid particles have limited capability to render oxidative stability to emulsions. These authors attributed this to the presumption that these particles are unable to form a homogenous interfacial barrier, which leads to the diffusion of small prooxidant molecules causing oil oxidation. In another study on the stability of Pickering emulsions manufactured with rutin hydrate and sunflower oil, Noon et al. (2020) reported that the use of rutin hydrate as Pickering particle could render oxidative stability to the emulsions compared with the emulsions containing polysorbate 20 and sodium dodecyl sulfate as conventionally used emulsifiers. However, when ferrous ion was added to the emulsions, the oxidative stability of the Pickering emulsion decreased substantially. This observation

reveals that Pickering particles with prooxidant nature, like rutin hydrate, might not be able to protect the emulsions against oil oxidation at higher concentrations of iron ion.

5 | OXIDATION ACROSS DIFFERENT TYPES OF PARENT AND FOOD EMULSIONS

What we presented so far mainly focused on oil oxidation within different types of emulsions, whereas this section compares oil oxidation and its underlying factors across emulsions. One of the most influencing factors in differentiating oxidative behavior across emulsions is interface where oxidation is inherently initiated and where most of oxidation stabilizing measures essentially target. It is generally hypothesized that the structure of oil–water interface may predict oxidative stability of emulsions. Droplet size is regarded as an important predicting factor in oxidative fate of the system where smaller droplet size accounts for physical stability of emulsion, but on the other hand, for oxidative instability due to larger surface area (Kampa et al., 2022). Nevertheless, disparities in oxidative destiny of nanoemulsions with far smaller droplet sizes than conventional emulsions (refer to Section 4.5) point to the fact that the myth “the smaller droplets, the more oxidation” is not always the case. It seems that a holistic approach should be taken in discussing oxidation in emulsions based on oil–water interface, for instance by considering the type of oil, antioxidant and/or surfactant used, concentration of metal ions, and the method of emulsification. As explained in Section 2.1, metal ions such as iron ion can act as initiators of autoxidative reactions leading to the formation of free radicals. Fenton reaction (formation of hydroxyl radical caused by the reaction of Fe^{2+} and hydrogen peroxide) and oxidation initiation at optimum ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ (1:1) were proposed theories for the role of iron ion in oxidation, which have been reported not to be always the case for iron-induced oxidation. This was the reason some studies considered the influence of other factors such as pH, particle size, and of course emulsifiers on iron-induced oxidation (Daoud et al., 2021). Antioxidant addition is one of the most common methods of rendering oxidative stability to emulsions regardless of emulsion type. The so-called polar paradox and its extension, that is, cut-off or nonlinearity theory (refer to Section 3.4), have been widely considered to explain stabilizing efficiency of antioxidant. However, the interrelation of oil–water interface properties with oxidative stability has mostly been elucidated based upon O/W emulsions and therefore, studies should be performed to examine that in

other types of emulsions. For instance, cut-off effect was recently found to be a determining factor of oil oxidation in W/O emulsions as in O/W emulsions, whereas the initial droplet size of the emulsions did not bring about significant differences in initial oxidation rate in these emulsions (Zhang et al., 2023). It could be generalized that no matter what type of emulsion is considered, the events taken place at the interface of oil and water has the final say in oxidative circumstances of emulsions. This is further supported by the finding of above-mentioned study where CCL of antioxidant in W/O, as in O/W, emulsions is responsible for the overall efficiency of antioxidant used and eventually the oxidative stability of emulsions.

In addition, it should be analyzed whether antioxidant immobilization techniques and their efficiency to locate antioxidant at the interface of oil and water is a function of type of emulsion or not. It was explained that antioxidant–protein conjugations bound by covalent bonds could aggregate at the interface and inhibit oil oxidation (Zhang et al., 2022). Similarly, conjugation of polyphenols to a common emulsifier (sodium caseinate) was claimed to increase oxidative stability of emulsions, no matter what type, by locating at the interface (Gong et al., 2022). Therefore, it can be speculated that the components that are expected to be located at the interface of immiscible liquids at any type of food emulsions will define the destiny of the system. The tradeoffs of components including emulsifiers, surfactants, antioxidants, radicals, and any other reactive molecule at the interface and between interface and other regions of emulsions will govern the chemical reactions at the interface (Costa et al., 2021). Future academic efforts are encouraged to highlight these tradeoffs in different types of emulsions to shed light on how the dynamics of emulsion droplets and reactive molecules between the interface and other regions would elucidate oxidative events.

One important difference in oil oxidation between O/W and W/O emulsions could be the fact that interfacial area to analyze oxidative behavior in the former emulsion should not be directly and confidently considered for the latter, because the much higher oil content in W/O emulsion compared with its counterpart could prevent from the surfacing of the oxidation products and therefore mask oxidative differences between these two emulsions as a result of particle size and interfacial area. This would invalidate the unanimously accepted theories of oil oxidation for O/W emulsions based upon the formation of the interface and ensuing interfacial area (Zhang et al., 2023). The same conclusion might be applied to multiple emulsions that are actually emulsions of emulsions where differences in the amount of phases and the resulting disparity in interfacial area are evident. Therefore, future studies should

scrutinize the role of interfacial kinetics in the oxidative stability of other emulsions than the conventional O/W, especially given the above-mentioned differences in the formation of oil–water interfaces.

Oxidative differences across different emulsions could also be considered with regard to the phenomena related to the transport of reactants through different emulsion phases, which is known as mass transport (refer to Section 3.4). Overall, three theories have been put forward for the explanation of the transport of reactants such as oxidants and antioxidants in emulsions, namely diffusion, collision-exchange-separation, and micelle-assisted transfer, which consider molecule transport among particles (i) through the aqueous phase of emulsion, (ii) collisions of particles, and (iii) molecule stabilization in micelles, respectively (for detailed explanations of these mechanisms, the reader is referred to Laguerre et al., 2017). In terms of oxidation differences across different emulsions, it is apparent that the mass transport behavior of peroxyradicals is a function of their water-solubility or hydrophobicity. For instance, in O/W emulsions where water is the continuous phase, hydrophobic radicals such as lipoperoxyradicals cannot move from one oil droplet to another through diffusion through the aqueous phase and therefore, in order for them to spread oxidation in the emulsion, they should wait for the collision of oil droplets transferring their contents to each other (collision-exchange-separation theory) or to be stabilized in the micelles formed by the excess of surfactants (micelle-assisted transfer theory). The shift from collision-exchange-separation pathway to micelle-assisted transfer pathway is considered to accelerate oxidation in O/W emulsions and this shift is even compared with the so-called shift of oil oxidation from the initiation phase to propagation phase. The above-mentioned shift in mass transport pathways is governed by the concentration and particle size of the oil droplets and formed micelles (Laguerre et al., 2017b). Therefore, a microemulsion with larger oil droplets and excessive amount of surfactant than needed, for example, should probably experience accelerated oxidation as a result of micelle-assisted transport of radicals, whereas a nanoemulsion with considerably smaller droplets and with less amount of surfactant should encounter prooxidant transfer through oil particle collisions and therefore, will not be shifted from the initiation to propagation phase as fast as the former emulsion. However, this generalization should be adopted prudently because Kloster et al. (2023) recently reported that different molecules may show different behavior regardless of the excess of surfactants. They found that TAG-bound hydroperoxides were not transported from one droplet to another by surfactant micelles, whereas the opposite was observed for 2-alkenals, alkadienals and

4-hydroperoxy-2-alkenals. One may consider a similar destiny for water soluble radicals in W/O emulsions where the radical cannot be transported through the continuous phase (oil) through diffusion. Surfactant micelles present in the aqueous phase in W/O emulsions do not affect mass transport of lipid oxidation products (which propagate oxidation easily in the continuous lipid phase in these emulsions). However, it has been observed that negatively charged surfactant micelles in the aqueous phase in W/O emulsions attract metal ions reducing their concentration at the W/O interface and thus reducing the oxidation of lipid hydroperoxides located at the interface (Yi et al., 2014b). In addition, the role of micelles themselves as a host of oxidative reactions as nanoreactors should be taken into consideration (Villeneuve et al., 2021). The mass transport pathways explained here have been presented based on the structure of O/W emulsions. Research is required to elucidate prooxidant and antioxidant transport in other types of emulsions such as W/O and multiple emulsions with regard to the hydrophobicity of the molecules to be transported as well as emulsion-specific factors such as particle size and surfactant concentration.

As a general rule to rationalize the oxidative differences across different types of emulsions, it can be said that oxidation in any type of emulsion is a function of events taken place at the interface of oil and water that are governed by the interactions between different components such as emulsifiers, surfactants and/or antioxidants, and the oil–water interface. These factors along with the composition of continuous phase of emulsion (water in O/W and oil in W/O) determine interfacial parameters such as electrostatic status and thickness, which not only account for the physical stability of emulsions but also for oxidative fate of the whole system (Costa et al., 2021). Oxidative differences across various types of emulsions may also be taken into account when they are stabilized using solid particles at their interfaces, which are called Pickering emulsions (refer to Section 4.6). Since Pickering emulsions are obtained by altering or modifying the interfaces of conventional emulsions using a wide array of solid particles, oxidative fate of such emulsions will again be a function of interfacial factors influenced by manipulation of the interface of oil and water. Pickering particles are also designed to be a reservoir of antioxidants, thus locating antioxidants at the o/w interface and enhancing oxidative stability of emulsions (Schroder et al., 2020). In a recent study, interfacial layer properties, droplet size, and pH were introduced as three main factors influencing oxidation in O/W Pickering emulsions (Keramat et al., 2022). Nevertheless, by considering another study focusing on O/W, W/O, and multiple emulsions stabilized with Pickering particles (Mwangi et al., 2020), it can be concluded

that the role of solid particle administered to render stability to emulsions overshadows the type of emulsion to be particle stabilized.

In addition to what explained hitherto, oxidation and oxidative stability in food emulsions, for example, milk and mayonnaise, could be more complicated to anticipate because of various ingredients incorporated to produce food emulsions, which would undermine the expected oxidative status as influenced by factors like pH of the food emulsion. For instance, lipid oxidation in a fermented milk product enriched with pre-emulsified omega-3 oil exceeded that of parent emulsion due to acidic pH of food emulsion that caused iron release from the phospholipid stabilizer leading to the increased rate of oxidation in the food emulsion (Lu et al., 2013). Affinity of antioxidant toward the oil–water interface in food emulsion could be considered a determining factor in the oxidative stability of the food. The role of antioxidant orientation toward the oil–water interface in the oxidative stability of food emulsion was observed in a study on milk containing omega-3 fatty acids where ascorbyl palmitate was found to be a more efficient antioxidant than tocopherol at least partly due to its higher affinity to locate at the interface (Let et al., 2005). It is assumed that emulsions with smaller droplets are more prone to oxidation due to higher interfacial area. However, this is not a silver bullet explain oxidation in all kinds of parent and food emulsions. For instance, milk with smaller droplets owing to the application of higher homogenization temperature and pressure was more stable than the one with larger droplets and thus less interfacial area (Let et al., 2007). This was explained by the role of homogenization temperature in β -lactoglobulin unfolding and partitioning between the interface and aqueous phase (Sørensen et al., 2007), which improves oxidative stability of food emulsion via two possible pathways, one through providing a better coverage of oil droplets and another by the role of amino acids with sulfhydryl groups (Ghelichi et al., 2021). Differences between food emulsions in terms of oxidative stability could occur on account of componential variations. Such a difference is noticeable between two common food emulsions, that is, milk and yogurt, where the latter is generally presumed as more stable than the former because of antioxidant peptides released during milk fermentation by lactic acid bacteria as well as higher oxygen levels in milk (Farvin et al., 2010). Furthermore, mayonnaise, an O/W food emulsion, is severely susceptible to oxidation. The underlying mechanism of oxidation in this food emulsion is attributed to its low pH, which triggers the phosvitin-bound iron in egg yolk leading to the appearance of free radicals (Jacobsen et al., 2001).

In light of lipid oxidation on the basis of characteristics of emulsions and underlying factors and mechanisms

elucidated herein, it can be concluded that interfacial properties of various types of emulsions and their interconnections with emulsion components such as emulsifiers and antioxidants are like a rollercoaster that cannot be unified into a unique unanimously accredited framework to predict oxidative behavior in these systems. Nor can a magic panacea be devised for the anticipation of oxidative circumstances in food emulsions with regard to plethora of factors influencing lipid oxidation in these systems such as pH, varied affinity of antioxidants toward the interface, oxygen content, interactions of components, to name a few. It seems that there is still and probably always a long way to be paved to attain a comprehensive picture of oxidation within different types of parent and food emulsions, let alone across them.

6 | CONCLUSIONS AND FUTURE REMARKS

Emulsions have a wide array of applications in food technology and myriad of studies have been carried out on various aspects of these food systems. The most area of concern in the use of emulsions in food science is their instability in terms of physical and/or oxidative circumstances. When producing foodstuffs based on emulsions, one might wish to render oxidative stability to the system by incorporating commercially available antioxidants; however, studies have indicated that different measures are there to be taken so as to stabilize an emulsion to prevent from the oxidative degradation of the system. These measures, which vary from the selection of emulsifiers to optimization of manufacture and storage conditions, might turn out to be even more efficient and economical. It should be noted that most of these methods have been examined in O/W, W/O, and multiple emulsions, which are of higher applicability in food production compared with O/O emulsions. On the other hand, manipulation of droplet size or the interface structure is found to be a promising strategy to fabricate more oxidatively stable emulsions than conventional ones, which may justify the recent tendency of academia to study different aspects of nanoemulsion and Pickering emulsion.

Oxidation and oxidative stabilization of emulsions is an extremely extensive field of study where every new study carried out brings along new questions and pathways for future research. It is in fact so dynamic and fast-growing field that current theories on various oxidative processes and underlying factors are constantly being revised and completed by new studies. Research is and will be going on to discover different processes and factors influencing oxidation in different emulsions with regard to interface characteristics, surfactants and emulsifiers, antioxidant

agents, properties of continuous and aqueous phases, role of micelles both as nanoreactors for the initiation of oxidative reactions and transport of prooxidants/antioxidants, among others. For instance, more research is required regarding the role of interaction between emulsifiers, between emulsifiers and antioxidants, between emulsifier and prooxidants and so on, formation and structure of the interface, sustainable ingredients in emulsions, and type of the surfactant and antioxidant, among others, in the pathways of prooxidant and antioxidant molecule transport in the emulsion and therefore, propagation of oxidation. Majority of strategies adopted hitherto to oxidatively stabilize emulsions were invasive by, for instance, manipulating the interface for achieving more stable emulsions. Furthermore, synthetics agents are added to emulsions to render oxidative stability, but their use is advised against due to their adverse health effects and the clean-label trend. A budding trend in the stabilization of emulsions against oxidation is the growing tendency toward less invasive methods for instance by removing prooxidants using protective packaging systems, or application of optimized methods of emulsification that would guarantee less deterioration caused by oxidation. For instance, one may consider the optimization of production methods for achieving physically stable emulsions with low or even devoid of excess surfactants in order to reduce the formation of micelles. Moreover, incorporation of agents such as surfactants, emulsifiers, and antioxidants of natural origin that can both exert health promoting effects via their bioactivities and oxidatively stabilize emulsions is considered one tickle to get two giggles. A balance, however, should be aimed between the efficiency of novel emulsion stabilizing strategies and their cost effectiveness and operability at a large scale so that the outcomes of this ongoing research area appear not merely in publications but also on dinner tables.


AUTHOR CONTRIBUTIONS

Sakhi Ghelichi: Conceptualization; Visualization; Writing-original draft; Writing-review & editing. **Mona Hajfathalian:** Conceptualization; Writing-original draft; Writing-review & editing. **Betül Yesiltas:** Conceptualization; Visualization; Writing-original draft; Writing-review & editing. **Ann-Dorit Moltke Sørensen:** Conceptualization; Writing-original draft; Visualization; Writing-review & editing. **Pedro J. Garcia-Moreno:** Conceptualization; Writing-original draft; Visualization; Writing-review & editing. **Charlotte Jacobsen:** Conceptualization; Writing-original draft; Writing-review & editing.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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