Progress in Lipid Research 94 (2024) 101275

Contents lists available at ScienceDirect

Progress in Lipid Research

journal homepage: www.elsevier.com/locate/plipres

Lipid oxidation in emulsions: New insights from the past two decades

Marie Hennebelle [a,*], Pierre Villeneuve [b,c], Erwann Durand [b,c], Jérôme Lecomte [b,c], John van Duynhoven [d,e], Anne Meynier [f], Betül Yesiltas [g], Charlotte Jacobsen [g], Claire Berton-Carabin [f,h,**]

[a] Laboratory of Food Chemistry, Department of Agrotechnology and Food Sciences, Wageningen University, Wageningen, Netherlands
[b] CIRAD, UMR Qualisud, Montpellier F34398, France
[c] Qualisud, Univ Montpellier, Avignon Université, CIRAD, Institut Agro, IRD, Université de La Réunion, Montpellier, France
[d] Laboratory of Biophysics, Wageningen University & Research, Wageningen, the Netherlands
[e] Unilever Food Innovation Centre, Wageningen, the Netherlands
[f] INRAE, UR BIA, Nantes 44300, France
[g] Research group for Bioactives – Analysis and Application, Technical University of Denmark, National Food Institute, Kgs. Lyngby DK-2800, Denmark
[h] Laboratory of Food Process Engineering, Department of Agrotechnology and Food Sciences, Wageningen University, Wageningen, Netherlands

ARTICLE INFO

Keywords:
Lipid oxidation
Emulsions
Lipid droplets
Interface
Antioxidants
Colloids
Co-oxidation

ABSTRACT

Lipid oxidation constitutes the main source of degradation of lipid-rich foods, including food emulsions. The complexity of the reactions at play combined with the increased demand from consumers for less processed and more natural foods result in additional challenges in controlling this phenomenon. This review provides an overview of the insights acquired over the past two decades on the understanding of lipid oxidation in oil-in-water (O/W) emulsions. After introducing the general structure of O/W emulsions and the classical mechanisms of lipid oxidation, the contribution of less studied oxidation products and the spatiotemporal resolution of these reactions will be discussed. We then highlight the impact of emulsion formulation on the mechanisms, taking into consideration the new trends in terms of emulsifiers as well as their own sensitivity to oxidation. Finally, novel antioxidant strategies that have emerged to meet the recent consumer's demand will be detailed. In an era defined by the pursuit of healthier, more natural, and sustainable food choices, a comprehensive understanding of lipid oxidation in emulsions is not only an academic quest, but also a crucial step towards meeting the evolving expectations of consumers and ensuring the quality and stability of lipid-rich food products.

1. Introduction

Lipid oxidation plays a critical role in the sensory quality, nutritional value and shelf-life of lipid-rich food products. It is therefore important to control this phenomenon, in particular in products containing a high amount of (poly)unsaturated fatty acids that are especially sensitive to oxidation [1,2]. Lipid oxidation can occur through three major pathways: enzymatic oxidation via the action of enzymes such as

Abbreviations: A•, antioxidant radical; ABTS, 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonate); AFM, atomic force microscopy; AH, antioxidant; AMVN, 2,2′-azobis (2,4-dimethylvaleronitrile); AV, anidisine value; BHT, butyl hydroxytoluene; CCL, critical chain length; CLSM, confocal laser scanning microscopy; CLP, colloidal solid lipid particles; CMC, critical micelle concentration; cryo-TEM, cryo-transmission electron microscopy; DLPC, dilauroylphosphatidylcholine; DMSN, dendritic mesoporous silica nanospheres; DPPH, 2,2-Diphenyl-1-picrylhydrazyl; EDTA, ethylenediaminetetraacetic acid; FFA-OOH, free fatty acid hydroperoxide; FID, flame ionization detector; GA, gallic acid; GC, gas chromatography; HLB, hydrophilic-lipophilic balance; HSAB theory, hard and soft acid and base theory; IMAC, immobilized metal ion affinity chromatography; L•, lipid alkyl radical; LC, liquid chromatography; LDL, low-density lipoprotein; LH, unsaturated fatty acid; LMWE, low molecular weight emulsifier; LO•, lipid alkoxyl radical; LOO•, lipid peroxyl radical; LOOH, lipid hydroperoxide; MCP, metal chelating peptide; MRP, Maillard reaction product; MS, mass spectrometry; NMR, nuclear magnetic resonance; OH•, RO•, hydroxyl radical; OSA, octenyl succinic anhydride; O/W emulsions, oil-in-water emulsions; PA, phosphatidic acid; PC, phosphatidylcholine; PE, phosphatidylethanolamine; PG, phosphatidylglycerol; PI, phosphatidylinositol; PS, phosphatidylserine; PV, peroxide value; R•, alkyl radical; ROO•, peroxyl radical; SDS, sodium dodecyl sulfate; SPI, soy protein isolate; SPME, solid phase microextraction; SPR, surface plasmon resonance; switchSENSE®, electrically switchable nanolever technology; TAG, triacylglycerol; TBARS, thiobarbituric acid reactive substances; WPI, whey protein isolate..

* Corresponding author.
** Corresponding author at: INRAE, UR BIA, Nantes 44300, France.
E-mail address: marie.hennebelle@wur.nl (M. Hennebelle).

https://doi.org/10.1016/j.plipres.2024.101275
Received 23 October 2023; Received in revised form 19 January 2024; Accepted 22 January 2024
Available online 26 January 2024

lipoxygenases, photooxidation via the activation of a sensitizer by light and autooxidation. While the first two are usually well controlled in food products through heat treatment and packaging, autooxidation remains a challenge, in particular to answer the increased demand by the consumers for more sustainable and natural products (i.e., clean label). Current methodologies to prevent lipid oxidation (i.e., cold chain storage, vacuum- or controlled atmosphere packaging, addition of synthetic antioxidants) need to be reconsidered and new trends are appearing, including the use of more natural antioxidants from plant extracts, the development of upcycled ingredients from food industry side streams, the introduction of low or mildly processed ingredients, or the increased use of plant-based emulsifiers.

Although the mechanisms of lipid oxidation have been extensively studied in bulk oils and fats, most of the lipids consumed by the population are in the form of emulsions, in particular oil-in-water (O/W) emulsions, a generic structure found for example in various beverages, milk, infant formulas, dairy-based goods, mayonnaises, dressings, as well as pharmaceuticals, cosmetics, and personal care products. Such emulsions consist of oil droplets dispersed within a continuous aqueous phase and stabilized by surface-active molecules, which adsorb at the oil-water interface. The oil-water interface is known to play a crucial role by being the location where lipids, oxygen, and pro-oxidants enter into contact (for reviews, see [3,4]). The large interfacial area typically found in emulsions promotes the exposure of lipids to pro-oxidant agents, and thus accelerates lipid oxidation compared to bulk oils. Many factors, such as the droplet size, interfacial composition, emulsifier type, partitioning and reactivity of pro- and antioxidants can impact the lipid oxidation process in emulsified foods, making it a challenge to fully understand and control the reactions, and therefore, to rationalize formulation strategies.

In 2000, a review by McClements and Decker [3] provided a foundational framework for comprehending lipid oxidation in emulsified

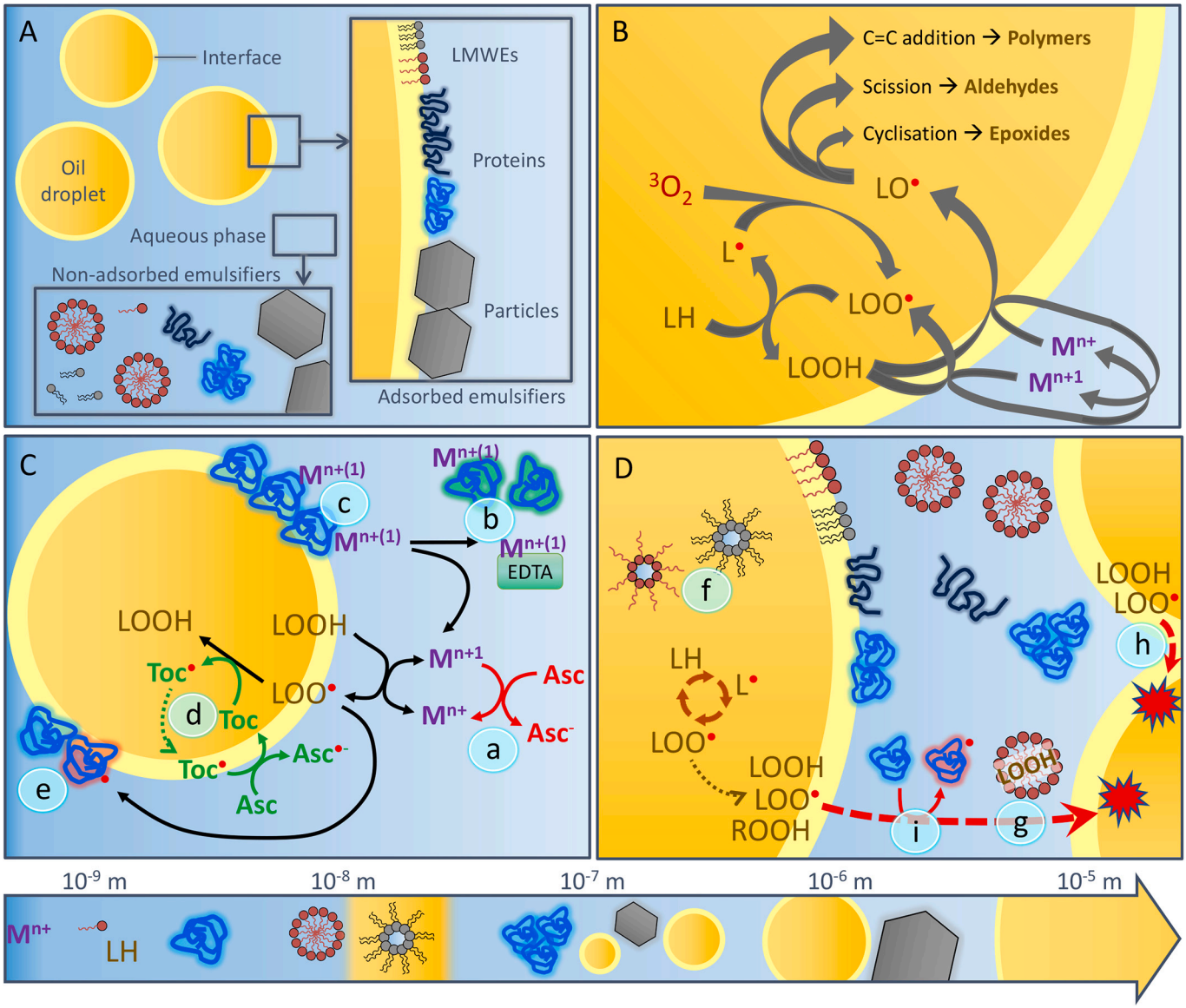

Fig. 1. (A) General structure of an O/W emulsion and of various types of food emulsifiers. (B) Simplified overview of dominant chemical pathways of lipid oxidation in emulsions, with an emphasis on the redox cycling engine involving transition metals (reduced form M^{n+}, oxidized form M^{n+1}). (C) Pro- (red) and antioxidant (green) mechanisms as influenced by the surface of oil droplets. (D) Possible transport routes (red arrows) of lipid oxidation intermediates (e.g., lipid oxidation products bearing a hydroperoxide group) between emulsion droplets. LH, unsaturated lipid; L•, alkyl radical; LOO•, peroxyl radical; LOOH, lipid hydroperoxide; LO•, alkoxyl radical; ROOH, molecule bearing a hydroperoxide group (e.g., hydroperoxy-alkenal); Asc, ascorbate; Toc, tocopherol. The letters (a) to (i) point to mechanisms referred to and further explained in the text. The large arrow at the bottom depicts typical dimensions (m) of the molecules and structures discussed. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

systems, highlighting the role of interfacial and droplet characteristics, and interactions with components from the aqueous phase. Since then, advancements in analytical techniques (for reviews, see [5–9]) have provided new insights in the mechanisms of lipid oxidation in emulsified systems, the distribution and reactivity of pro- and antioxidants, the arrangements of molecules at the interface and the role of colloidal structures and transport of lipid oxidation intermediates. Additionally, new insights into the role and reactivity of the emulsifiers (e.g., proteins, phospholipids, or surfactants) have been proposed.

The present review provides an update on our understanding of lipid oxidation in O/W emulsions focusing primarily on autooxidation reactions. After briefly summarizing the classical lipid oxidation pathways, the contribution of less studied oxidation products and the spatiotemporal resolution of these reactions will be discussed. Then, the impact of emulsion formulation and structure will be presented with a focus on the importance of the interfacial layer and emulsifiers. Finally, novel antioxidant strategies that have emerged over the past two decades will be highlighted.

2. Lipid oxidation mechanisms in oil-in-water emulsions

2.1. General properties of emulsions and oil-water interfaces

Due to the molecular incompatibility between oil and water, emulsions tend to undergo physical destabilization to minimize the interfacial area, ultimately leading to complete phase separation if the system is not appropriately physically stabilized. Yet, it is possible to produce metastable emulsions that maintain their physical attributes and structure for relevant periods compared to typical storage times. This can be achieved using physical stabilizers, among which emulsifiers, which are molecules – or, sometimes, supramolecular structures – capable of adsorbing at the oil-water interface. Regarding O/W emulsions, which are the focus of this review, three primary categories of food emulsifiers exist (Fig. 1A): (i) low molecular weight emulsifiers (LMWEs), often termed surfactants, which are molecules constituted of a polar or fully charged hydrophilic headgroup and one or more hydrophobic alkyl chains. Examples encompass lecithins (i.e., a mixture containing polar lipids, in particular phospholipids, obtained by degumming of crude vegetable oils) [8], polysorbates, mono- and diacylglycerols, and other fatty acid esters [10,11]; (ii) amphiphilic biopolymers, which are larger molecules made of distinct hydrophilic and hydrophobic segments; in food applications, proteins are a prominent representative of such emulsifiers [12,13]; (iii) colloidal particles possessing surface characteristics that confer them with partial wettability by both oil and water. This allows them to strongly anchor at the oil-water interface, resulting in so-called Pickering emulsions [14–17].

Selecting an appropriate emulsifier is not a simple task, as the implications stretch beyond preserving the structural integrity of individual droplets. The properties of the formed interfacial layer directly depend on the type of emulsifier [18,19]. For LMWEs, the interface thickness closely aligns with the size of individual molecules (1–3 nm), surface load (Γ) ranges from <1 to 1–2 mg/m^2, the formed layer is highly mobile and viscous, and adsorbed molecules display substantial lateral mobility and rapid exchange with excess surfactants in the surrounding aqueous phase [20]. Protein-based interfacial layers, on the other hand, exhibit varying interfacial thicknesses (1 to >15 nm), which is contingent on the protein type, structure, aggregation state, and homogenization conditions. The surface load for proteins varies as well, from 1 to 2 mg/m^2 for monomeric proteins to >10 mg/m^2 for aggregates or multiple layers [19]. Adsorbed proteins can establish lateral interprotein interactions, thereby forming a network that imparts mechanical strength and a viscoelastic character to the interfacial film [21,22]. Adsorbed colloidal particles, forming Pickering emulsions, have interfacial thickness and surface load directly tied to the size and density of the adsorbed particles. These values may significantly surpass those of LMWEs and biopolymers by orders of magnitude. These particle layers can modify droplet density, potentially leading to droplet sedimentation rather than creaming. Attractive lateral capillary forces between trapped particles within the interfacial film stem from the deformation of the fluid interface around particles, granting the interfacial layer high mechanical stability and rigidity. This, combined with the high desorption energy of the particles once adsorbed, confers such emulsions with a high physical stability, in particular regarding resistance to coalescence [15,23].

An important aspect to consider is that food emulsions are often formulated with an excess of emulsifiers, i.e., the amounts used are generally beyond what is strictly necessary for interface coverage and physical stabilization [4]. Consequently, only a fraction of emulsifier actually stabilizes the oil droplets, whereas the excess remains in the continuous phase. This excess fraction might exist as soluble monomeric molecules, or form colloidal structures such as micelles or aggregates, that may even incorporate a fraction of oil [24]. Although often overlooked, the occurrence of these structures has critical implications for the physicochemical stability of emulsions. For instance, high biopolymer concentrations in the continuous phase can induce depletion flocculation [25], and excess surfactant micelles can promote compositional ripening, favoring the droplet-to-droplet transfer of lipophilic molecules [26–28]. This emulsifier-driven ability to solubilize and segregate components may play a significant role in the chemical reactivity of emulsions, particularly in terms of lipid oxidation, as discussed in further detail in sections 2.4 and 3.3.

2.2. Global overview of lipid oxidation pathways

Lipid oxidation is a complex radical chain reaction (Fig. 1B) that is classically divided into three main stages: initiation, propagation, and termination [29–31]. During the initiation step, an alkyl radical (L•) is formed following the abstraction of a hydrogen atom from a (poly)unsaturated fatty acid (LH) in the presence of a catalyst (e.g., heat, light, metals). This hydrogen abstraction occurs mostly on the carbon next to or between double bonds in mono- and polyunsaturated fatty acids, respectively, which are the C—H bonds with the lowest dissociation energies (74 and 65 kcal.mol^{-1}, respectively) [32]. During the propagation phase, the highly unstable alkyl radicals quickly react with oxygen ($k > 10^9$ L.mol^{-1}.s^{-1}) to form peroxyl radicals (LOO•) that in turn, attack neighboring unsaturated fatty acids to form on the one hand, new alkyl radicals that feed the propagation cycle, and on the other hand, lipid hydroperoxides (LOOHs), the first metastable oxidation products, also referred to as primary oxidation products. These lipid hydroperoxides can next degrade, leading to the formation of secondary oxidation products, including volatile compounds that contribute to the characteristic off-flavors of lipid oxidation [33]. The primary pathway of lipid hydroperoxide degradation involves the cleavage of the weak O—O bond in the lipid hydroperoxide structure to form an alkoxyl radical (LO•). Scission reaction of this LO• radical results in the formation of a variety of volatile compounds, such as aldehydes, ketones, alcohols and esters. Finally, during the termination phase, radicals react together to form non-radical products (e.g., dimers and polymers), putting an end to the reaction.

Transition metal ions such as iron and copper play a key role in lipid oxidation and constitute one of the main pro-oxidant factors in foods [34]. Trace amounts of these transition metals can indeed hardly be avoided during food production, whether they come from the raw material itself, contamination during processing, and/or are added for nutritional purposes. Metal ions can contribute to the initiation reaction and as shown in Fig. 1B, they are also key catalysts for the degradation of lipid hydroperoxides, leading to the formation of LOO• or LO• radicals through the reaction of M^{n+1} (e.g., ferric (FeIII) and cupric (CuII)) or M^n (e.g., ferrous (FeII) and cuprous (CuI)) transition metal ions, respectively, with hydroperoxides [34–37]. These radicals can catalyze hydrogen abstraction much faster than the ab initio hydrogen abstraction from LH [38] and are therefore important contributors to the

propagation cycle of lipid oxidation. The metal redox cycle in Fig. 1B is also strongly modulated by the presence of water-soluble reducing agents, such as ascorbic acid, that aid regenerating bivalent transition metals (mechanism (a) in Fig. 1C) and thus display a pro-oxidant effect [39], or metal chelators (mechanism (b) in Fig. 1C), thus having an antioxidant action in the latter case.

In order to control or prevent lipid oxidation reactions, antioxidants are often used, as previously extensively reviewed [7,40]. Briefly, antioxidants can be divided into two main categories depending on their mode of action: primary antioxidants or chain-breaking antioxidants, which act as radical scavengers, and secondary antioxidants, which block the action of pro-oxidants (e.g., metal chelators, oxygen scavengers). For instance, phenolic compounds that contain a benzene ring with one or more hydroxy groups are effective primary antioxidants, as they can give away one of their protons to stabilize a radical while becoming metastable radicals themselves [41,42]. Ethylenediaminetetraacetic acid (EDTA) is strong metal chelator, well-known for its strong antioxidant efficacy in food emulsions [43]; water-soluble proteins that have affinity for metal ions are also known to act as antioxidants [4,44]. Furthermore, covalent and non-covalent binding of reactive secondary lipid oxidation products to water-soluble proteins has been proposed as an antioxidant route [4,45]. Assessing the activity and efficiency of antioxidants is not trivial, as they might have multiple modes of action, act in synergy with other molecules, and be highly influenced by their environment and partitioning.

2.3. Beyond the classical pathway of lipid oxidation

In most studies revolving around lipid oxidation in model, real food and biobased systems, hydroperoxides and aldehydes have been considered as the main markers for primary and secondary oxidation, respectively. However, several other oxidation products have been described, as highlighted by Schaich [46], that received attention only recently. Among them, epoxides (Fig. 1B) have been proposed as an important missing piece of the lipid oxidation puzzle.

Epoxy fatty acids have been identified and quantified in fresh and thermally oxidized oils [47–50], as well as in other food matrices (e.g., crisps, meat, mayonnaise, biscuits) [51] by gas chromatography-flame ionization (GC-FID) or gas chromatography–mass spectrometry (GC–MS) following transmethylation and separation (e.g., by solid phase extraction or adsorption chromatography) steps. Methodological advances in liquid chromatography-mass spectrometry (LC-MS) allowed for the semi-quantitative assessment of intact epoxidized triacylglycerols (TAGs), which have been proposed as an early marker for lipid oxidation in canola oil and margarines [52,53]. This claim was, however, not substantiated by a quantitative NMR study showing that in oils and mayonnaise, epoxides should be considered as a reaction product of alkoxyl radicals competing with the formation of aldehydes and therefore as a secondary product of lipid oxidation [54]. In these systems, the concentration of epoxides could reach considerable levels (e.g., higher than aldehydes), but kinetically, these compounds appeared after the formation of lipid hydroperoxides. These observations discard epoxides as minor compounds and also as early markers for lipid oxidation.

In theory, alkoxyl radicals could also lead to the formation of non-volatile fatty alcohols and ketones [46]. However, despite the increased sensitivity in methodology, only little information on the presence of these oxidized products has been reported, and mostly in vegetable or marine oils after a hydrolysis step of the TAGs [48,55–61]. Recent work reported the detection of acetone by headspace solid phase microextraction (SPME)-GC–MS as a degradation product of epidioxides formed upon lipid oxidation in margarines [53]. Since epidioxides are expected to be cyclization products of hydroperoxides, acetone would therefore be also a late marker for lipid oxidation.

Besides evaluating the contribution of “minor” lipid oxidation markers, it is important to note that most analyses in food products are carried out on total lipid fractions or TAGs, the most abundant lipids in food products. However, as will be highlighted in further detail in the following sections, the oil-water interface in O/W emulsions plays a critical role and it would be of interest to gain more insights into the oxidation susceptibility and pathways of surface-active lipids, such as phospholipids or di- or monoacylglycerols, which are commonly used as emulsifiers. The formation of hydroperoxides and aldehydes, but also of epoxides, alcohols, and ketones has been reported following thermal oxidation of pure phospholipids [62,63] or of phospholipids in egg yolk [64]. However, only one mention of phospholipid hydroperoxides in food emulsions (mayonnaise, in this case) was found [65]. More work is therefore required to better understand the contribution of these minor, yet reactive surface-active lipids in the process of lipid oxidation in foods.

2.4. Spatiotemporal resolution of lipid oxidation in emulsions

Although we have so far focused on the chemical dimension of lipid oxidation, the spatiotemporal framework of the reaction is also of utmost importance in multiphase and interface-dominated systems such as O/W emulsions [66]. In the following section, we will develop these aspects (Fig. 1C and D).

2.4.1. The central role of the interface between oil and water

As briefly introduced earlier, the oil-water interface plays a key role in the oxidation of O/W emulsions; its composition and structure can influence the contact between oxygen, pro- and antioxidants and lipids. For instance, negatively charged proteins have some affinity for metal cations dissolved in the continuous phase [67], which are key catalysts for the degradation of hydroperoxides as described in section 2.2. When used as emulsifiers, such proteins can contribute bringing these catalytic ions at the oil-water interface close to the dispersed oil phase and therefore catalyzing lipid oxidation reactions (mechanism (c) in Fig. 1C). Similarly, the charge of the surfactants at the interface was reported to influence the extent of iron-catalyzed lipid oxidation [68]. The role of specific emulsifiers will be discussed in more details in section 3.

Primary or chain-breaking antioxidants act by scavenging radicals generated at the oil-water interface (see Section 2.2). A well-known example relates to the lipophilic antioxidant α-tocopherol (mechanism (d) in Fig. 1C). The efficacy of such radical scavengers is enhanced by making them more amphiphilic and therefore partitioning closer to the oil-water interface, a route that will be reviewed in more detail in section 5.1.

It has also been demonstrated that proteins adsorbed at droplet interfaces co-oxidize with lipids [69–71] (mechanism (e) in Fig. 1C). Whether the oxidation of proteins at the interface can prevent the subsequent oxidation of lipids via a shielding effect or, on the contrary, trigger interfacial radical oxidation reactions involving lipids needs, however, to be resolved. The evidence for the occurrence of these events was largely circumstantial until imaging techniques recently provided direct visual underpinning, mainly relying on the use of lipophilic radical-sensitive fluorescent probes [72], protein autofluorescence and fluorescent spin traps [73,74]. The use of fluorescent spin traps revealed the appearance of protein radicals upon oxidation of lipids. This provides a clue for scavenging of lipid radicals near the oil-water interface by surface-active proteins (mechanism (e) in Fig. 1C). The role of protein co-oxidation will be discussed in more detail in section 4.3.

Finally, the structural heterogeneity of the interfacial layer has also been put forward as a modulating factor of lipid oxidation in food emulsions [75,76]. Evidence was based on indirect measurements in model emulsions and on reconstituted Langmuir monolayers. Further insights in the impact of interfacial layer heterogeneity on lipid oxidation in complex food emulsions may be obtained by the deployment of super-resolution light microscopy methods, which can spatially resolve the location of proteins at the surface of oil droplets [77,78].

2.4.2. Modulation of oxidation kinetics by the formation of colloidal structures within the oil phase

Small colloidal structures are critical to consider when discussing lipid oxidation reactions in oils and in emulsions [79]. In that respect, bulk oils should not be considered as structurally homogeneous liquids. They are dynamic multiphase systems, which evolve over time in terms of structure, composition and reactivity as the oxidation process progresses. The presence of surface-active species at a concentration above their critical micelle concentration (CMC) can give rise to the presence of colloidal particles, also coined as reverse micelles and association colloids (mechanism (f) in Fig. 1D). Such colloidal particles can also be formed by lipid oxidation products such as lipid hydroperoxides (in particular the ones formed from small lipids such as free (i.e., unesterified) fatty acids), which are more surface-active than their non-oxidized counterparts and can contribute to the formation of reverse micelles on their own. The appearance of colloidal structures has been associated with oxidation phenomena in bulk oils [80–85], as they can carry pro-oxidants such as e.g., metals [79]. They might also enhance the solubility of oxygen [86]; however, to which extent this may play a relevant role remains to be demonstrated. Formation of reverse micelles typically triggers acceleration of lipid oxidation reactions, even though direct observations of reverse micelles in oxidizing oils and emulsions are still scarce [82,87]. Evidence for their relevance mostly stems from the acceleration of lipid oxidation kinetics when a critical concentration is reached [79]. A model has been described for determining the CMC of lipid hydroperoxides in oil [88]; this concept has been applied to establish a predictive model for lipid oxidation in mayonnaise [89].

2.4.3. Transport through the continuous aqueous phase

The radicals initially generated at the interface do not only promote further reactions at the droplet interface or in the oil phase, but might also be transported through the aqueous phase to proteins or neighboring oil droplets [79,90]. The proposed mass transport phenomena have recently been detailed and discussed in reviews [66,79,90], which suggest that the mechanisms in liquid food emulsions could occur along three pathways that depend on the molecule and droplet size, composition and rate of diffusion: non-assisted diffusion through the continuous phase ($\sim 10^{0}$ nm, $\sim 10^{-9}$ $m^2.s^{-1}$), micelle-assisted transfer ($\sim 10^{1}$ nm, $\sim 10^{-10}$–10^{-11} $m^2.s^{-1}$) (mechanism (g) in Fig. 1D) or inter-droplet collision ($> 10^{1}$ nm, $\sim 10^{-11}$–10^{-12} $m^2.s^{-1}$) (mechanism (h) in Fig. 1D). Thus, water-soluble molecules could easily be exchanged between droplets via the diffusion pathway in the aqueous phase of emulsions, whereas more hydrophobic species are thought to be transferred either by the collision of adjacent droplets or by micelle-assisted mechanisms. The transfer rate would then be faster via the micelle-assisted pathway and would depend on the size and micelle concentration [79].

Using the peroxyl radical-sensitive dye BODIPY665/676, inter-droplet molecular exchanges of lipid radical species in Tween 20-stabilized emulsions were also demonstrated after formation of peroxyl radicals induced by the lipophilic initiator AMVN (2,2′-azobis (2,4-dimethylvaleronitrile) [91]. Yet, the same team did not find any spreading of oxidation to neighboring lipid droplets when alkoxyl radicals were generated with di-tert-butyl peroxide [92]. Using a comparable yet complementary imaging approach that allows the spatially resolved excitation by singlet oxygen, a similar observation was reported in cod liver O/W emulsions stabilized with casein [93,94], as well as in high fat (70%) emulsions stabilized by phospholipids [95]. The explanation for this phenomenon may lie in the difference in the respective lifetime of the two radicals: alkoxyl radicals (10^{-6} s) being much less stable than peroxyl radicals (0.5–7 s) [96]. These lifetime values can be directly converted to a diffusion distance [97], leading to the estimation that a peroxyl radical may travel over a distance of about 0.2 μm to 140 μm (depending on the viscosity), whereas alkoxyl radicals may travel only over 0.1 nm to 0.1 μm. Conversely, studies have shown that non-radical lipids, including long-chain hydrocarbons such as octadecane [26,28,98,99], specific secondary lipid oxidation products bearing a hydroperoxide group (e.g., 4-hydroperoxy 2-nonenal), free fatty acids (e.g., linoleic acid), as well as secondary oxidation compounds (e.g., 2,4-decadienal), can diffuse through the emulsion system and may propagate oxidative reactions to neighboring lipid droplets [27,99–101]. Experiments performed using flow cytometry suggested that micelle-facilitated transport is an active transport mechanism in model O/W emulsions [100]. Studies using carefully prepared model emulsions confirmed that these transport mechanisms are limited to specific lipid oxidation products; for instance, hydroperoxides bound to a TAG backbone are not prone to transport, probably because their insertion into the hydrophobic core of surfactant micelles is not sterically possible, whereas smaller hydrophilic molecules are [27].

2.4.4. Oxidation reactions within the continuous aqueous phase

As described in section 2.1, food emulsions are typically stabilized with emulsifiers that are used in excess. Thus, non-adsorbed emulsifiers (e.g., LMWEs, proteins) can be present in the water phase in considerable concentrations. These excess emulsifiers can greatly influence lipid oxidation, either by acting as pro- or antioxidant themselves, or by being co-oxidized in the water phase. These aspects will be described in further detail in sections 3.3 and 4.

All these aspects related to the presence and contribution of colloidal structures in both the oil and aqueous phases highlight another interesting aspect that is the definition of interfacial region of emulsified food systems. Should we say that a molecule, either integrated in or just nearby (physically adsorbed) the interfacial layer of a lipid droplet (oil-water), or within surfactant micelles in the aqueous phase, or within association colloids in the lipid phase, belongs to the same “interfacial region”? Moreover, is there a dynamic exchange between all these interfacial domains, which is much faster than the rates of relevant chemical reactions (antioxidant and pro-oxidant), so that each time a molecule undergoes a chemical transformation it is immediately replaced by another molecule to maintain the domains of this interfacial region in thermodynamic equilibrium?

2.5. Modelling approaches

Modelling lipid oxidation reactions in food systems has attracted a lot of attention in the past two decades. Mathematical modelling approaches can indeed be very valuable to help with the interpretation of the data and/or to predict the extent and rate of lipid oxidation. This could help food manufacturers determine the shelf-life of their products and evaluate antioxidant activity in their systems. Various modelling approaches have been employed in that respect.

Statistical models, such as response surface methodology (RSM) and regression analysis, have been applied to identify significant factors affecting lipid oxidation. For example, such models have been applied to estimate the impact of heat treatment temperature and time of the degradation of α-tocopherol and the formation of TAG polymers during frying [102], of phytic acid and/or α-tocopherol concentration on lipid oxidation inhibition in ground chicken meat [103], of pH, ionic strength, iron and temperature on the oxidation of phospholipid liposomes [104] or to evaluate the role of fatty acid composition on the oxidative stability of various fats and oils [105]. These models can be helpful to identify optimal conditions to prevent oxidation. However, their simplicity often does not fully capture the complex nature of lipid oxidation reactions, in particular in complex multiphasic systems, which might limit their predictive accuracy.

Several (semi-) empirical models have been proposed to describe the accumulation of oxidation products in oils and emulsions (for review, see [106]). These models are based on the experimental observation that the formation of e.g., hydroperoxides usually follow a sigmoidal curve, and can therefore be described with a mathematical function, such as Gompertz, Foubert, Weibull or logistic functions [88,89,107–113]. These models describe well the experimental data, allow the comparison

between samples with specific variations (e.g., different concentrations of antioxidant) and have even been used to predict the shelf-life of emulsions, such as mayonnaise [114]. On the other hand, the interpretation of their parameters can be complex as they do not relate directly to parameters from the system itself (e.g., composition of the samples or conditions of incubation) and they do not consider the full cascade of reactions involved. More recently, a more extensive mechanistic kinetic model has been proposed in bulk oils, taking into consideration the multiple reactions involved in lipid oxidation, the oxygen mass transfer, as well as the initial composition of the oil [115]. This model presents the advantage of enabling the shelf-life prediction of different vegetable oils stored under different oxygen conditions, but remains limited to bulk oils. In O/W emulsions, a kinetic model incorporating reaction kinetics and mass transfer was shown to well describe the oxidation process in emulsions stabilized with five different emulsifiers [116].

Despite the numerous advances in modelling approaches over the past two decades, modelling lipid oxidation in complex multiphase systems such as O/W emulsions remains a challenging task. This is largely due to the high complexity of the systems. First, the conditions of storage or treatment during the shelf-life might differ. A well-known example are the fluctuations in the temperature used. To deal with that, Arrhenius equations have been used in combination with kinetic model to adjust the temperature-dependent kinetic rate constant, in particular in bulk oils [117–120]. Such models should, however, be applied with caution; e.g., Sullivan et al. [119] highlighted that the Arrhenius model can only be applied up to 40 °C on fish oil. Then, as already highlighted in previous sections and discussed in further details later, multiple factors inherent to the studied systems (e.g., droplet size, (non-)adsorbed emulsifiers, pH, pro- and antioxidants, partitioning of the molecules, transport phenomenon) can influence lipid oxidation and therefore need to be considered to develop robust predictive models. To evaluate the partitioning of different antioxidants in emulsions, a pseudophase kinetic approach, based on the reactivity of a 4-hexadecylarenediazonium probe [121,122] has been developed. Note that since arenediazoniums are cationic species, this model has only been validated with non-ionic surfactants. This is an interesting technique, as it can be performed directly in an opaque emulsion. Yet, this model implies that the system is already at thermodynamic equilibrium, with the rate of the chemical reaction being much slower than the rates of the dynamic processes. Although these two criteria might not necessarily be met depending on the food [123], this is a good approach to evaluate how emulsifiers are affecting distribution of molecules (e.g., phenolic antioxidants) in simple O/W emulsions, and then attempt to link this change to the antioxidant efficiency. For other factors, in particular the transport phenomenon and interactions between multiple factors (e.g., the impact of pro-oxidant concentration in the aqueous phase will be influenced by the droplet size and the pH of the emulsion), a better understanding is needed in order to incorporate them properly in modelling approaches. This brings us to another limitation, namely the availability of a complete dataset that provides the information required to do so.

3. Impact of emulsion formulation and structure on lipid oxidation

3.1. Effects of emulsion processing and structural properties on lipid oxidation

In industrial settings, high-pressure homogenizers and rotor-stator systems are commonly employed for emulsification, and the number of passes required depends on the degree of recoalescence, and vice versa [19]. High-pressure homogenizers use a narrow constriction to generate turbulent shear forces, which can yield submicron droplets in large-scale equipment. Conversely, lab-scale homogenizers often operate under laminar flow conditions, making it challenging to extrapolate results to larger-scale processes. Colloid mills utilize the velocity difference between rotating and stationary elements to induce shear for droplet breakup, but they typically have low energy density, making it difficult to create small droplets. Other emulsification methods, such as membrane emulsification, exist but are currently impractical for most commercial applications [124]. Costa et al. [125] highlighted that homogenization, particularly when involving intense mechanical forces, can impact emulsifier molecules or supramolecular structures. The combined influence of temperature and shear on emulsifiers is often overlooked in emulsion research. For example, high pressures can alter the tertiary structure of globular proteins, leading to protein unfolding even when the product temperature remains below the protein denaturation temperature, potentially resulting in protein aggregation. The conditions of emulsification, including the type of equipment and energy input, are also important as they determine the specific droplet size distribution, which directly influences the emulsion's ability to resist oxidation due to variations in total surface area [126,127]. In principle, smaller droplets, and thus a larger oil-water interfacial area, should promote lipid oxidation. While this effect has often been observed experimentally, there have been conflicting reports, possibly stemming from the challenges of altering droplet size without affecting other emulsion properties [4]. Several studies, in particular by C. Jacobsen's group, have demonstrated that the homogenization conditions can impact lipid oxidation in various types of emulsions containing fish oil [128–130]. Horn et al. [128] investigated the effect of different homogenization pressures and temperatures on fish O/W emulsions. These emulsions were prepared using either a combination of α-lactalbumin and β-lactoglobulin or a combination of sodium caseinate and β-lactoglobulin. The study found that increasing pressure enhanced the oxidative stability of emulsions containing caseinate and β-lactoglobulin, but conversely, it decreased oxidative stability in emulsions with α-lactalbumin and β-lactoglobulin. In both cases, the distribution of proteins between the interface and the aqueous phase played a crucial role in determining oxidative stability. Let et al. [129] and Sorensen et al. [130] conducted similar studies on the effect of homogenization pressure and temperature on lipid oxidation in fish oil-enriched milk. These studies also emphasized that achieving a favorable partitioning of proteins between the aqueous phase and the interface was more critical for oxidative stability than the droplet size distribution.

It has been frequently suggested that emulsifiers capable of forming a dense layer around lipid droplets might protect against lipid oxidation by creating a steric barrier against pro-oxidants. Early support for this idea came from e.g., Hu et al. [131], who found that emulsions stabilized with casein, a protein known for its ability to create thick and compact interfacial layers, exhibited greater resistance to oxidation compared to emulsions stabilized with other proteins, such as whey proteins. It was also reported that the oxidative stability of soy protein-stabilized emulsions improved when the protein surface coverage was increased through physical treatments such as heat treatment or the addition of salt [132]. Other attempts to modulate the connectivity and thickness of the interfacial layer in emulsions encompassed the enzymatic cross-linking of adsorbed proteins [133] or the design of multilayered films by layer-by-layer deposition [134–136]. The former route did not lead to clear effects on lipid oxidation; the latter did show some effects, but which seemed mostly related to the electrostatic charge of the most external biopolymer layer, rather than to the number of layers. Besides, the layer-by-layer technique presents a major drawback in terms of potential applications due to the difficulty to scale up the preparation process. It is also important to note that all these studies often did not measure the actual interfacial thickness, leaving some of these effects as largely speculative. As highlighted by McClements and Decker [137], experimental approaches aimed at modifying interface thickness often involve other changes, such as alterations in amino acid composition, conformational changes, and the distribution of proteins between the interface and the aqueous phase. Furthermore, the molecular size of pro-oxidants (such as metal ions and reactive oxygen species) is typically much smaller than the typical structural elements at the interface

(biopolymer loops, pores), raising doubts about whether this parameter plays a decisive role in the oxidation of emulsions.

Because the interface is an area with a high local concentration of solutes, including emulsifiers, it can exhibit enhanced incompatibility, non-miscibility, repulsive interactions, and phase separation when compared to more diluted phases within the bulk [19,138]. Regarding this incompatibility, the impact on lipid oxidation in emulsions stabilized by such layers was analyzed. For example, oil droplets were stabilized by dairy proteins used either alone or in combination with a pure phospholipid (dilauroylphosphatidylcholine, DLPC), with a careful selection of ratios to prevent the displacement of proteins [75]. The microstructure and topography of the interfacial layers, reconstructed as Langmuir-Blodgett (LB) films and investigated using atomic force microscopy (AFM), revealed that the incorporation of DLPC into the casein layer increased the structural heterogeneity of the films. Interestingly, the rate of lipid oxidation in the emulsion stabilized by the casein-DLPC mixture was higher than in the emulsion stabilized solely by the protein. This suggests that the homogeneity of pure protein layers, as opposed to mixed layers, could provide some protection against lipid oxidation. However, this effect likely depends on the type, purity, and quantity of the phospholipid used. García-Moreno et al. [139] found that the incorporation of soybean lecithin (a mixture of phospholipids) as a co-emulsifier in caseinate-stabilized emulsions reduced lipid oxidation compared to emulsions with only caseinate. However, this effect was not observed when using pure phospholipids instead of lecithin. In that case, incorporating phospholipids led to a substantial increase in the concentration of non-adsorbed caseinate (more than a 2-fold increase), so a concurrent effect of non-adsorbed caseinate on lipid oxidation cannot be excluded.

The effect of incorporating a co-surfactant into Tween 20-stabilized interfaces on lipid oxidation in emulsions was also investigated [76]. Lipid oxidation occurred earlier in emulsions stabilized with Tween 20-co-surfactant mixtures than in emulsions stabilized solely with Tween 20. This effect was attributed to the non-ideal interfacial behavior of Tween 20-co-surfactant mixtures, as indicated by surface-pressure isotherms. Such structural heterogeneity of the interfacial layer might enhance the accessibility of the lipid substrate to pro-oxidants present in the aqueous phase. This observation may hold general importance, as most technical emulsifiers used in food applications consist of complex mixtures of molecules (e.g., WPI, sodium caseinates, lecithins, etc.). A challenge in that respect is the difficulty to assess the structural homogeneity/heterogeneity of interfacial films in situ in O/W emulsions – model interfaces are of great help, but inevitably raise the question of whether or to which extent the observed structures will also be found at the surface of real emulsion droplets. As suggested earlier (section 2.4.1), the recent advances based in microscopy techniques will certainly be instrumental in making progress on this matter [73,74,77]. The use of scattering techniques or synchrotron radiation circular dichroism (SR-CD) (in the case of protein-based emulsifiers) can also further advance the area [140,141].

3.2. New trends in food emulsifiers

Over the past decade, a large amount of research has been conducted to identify and characterize new emulsifiers with potential for current applications in biobased systems and notably food products. This progress has been largely driven by the current clean-label trend aiming to favor the use of natural, ideally plant-based and minimally processed ingredients [142]. Among the noticeable trends that have emerged accordingly, two seem of particular interest: plant-derived protein fractions, and biobased particles (forming so-called Pickering emulsions). These two new categories of emulsifiers have undoubtedly occupied an increasing part of the research on food emulsions lately; for instance, in 2022, the number of publications with the topic and/or keywords “food emulsion, plant protein” or “food emulsion, Pickering” represented 15% and 22%, respectively, of all the publications on food emulsions (Fig. 2). Twenty years ago, these percentages were only around 0–3%. Therefore, it seems important to take a closer look at how these new emulsifiers can modulate the sensitivity of the resulting emulsions to oxidation.

3.2.1. Plant protein-based emulsions

As mentioned earlier, amphiphilic biopolymers such as proteins have been widely used as emulsifiers. Conventional proteins for this purpose used to be largely represented by dairy proteins. However, in the current context of the protein transition, increasing interest has been encountered in using plant-based protein ingredients as alternatives [12,143–145]. This has opened a fascinating research field since, from a functionality perspective, this transition is extremely challenging. Indeed, the properties of most of the current plant protein ingredients drastically differ from those of dairy proteins. This is primarily due to the fundamentally different physiological roles of both types of proteins: when dairy proteins are well-soluble in aqueous media, plant storage proteins present in pulses and oilseeds are not. This has consequences on the processes required to yield subsequent ingredients (concentrates, isolates), which may include severe thermomechanical steps and drastic chemical modifications of the proteins. Milder processes (e.g., dry fractionation) are therefore gaining attention as they lead to protein ingredients with less chemical damage and better functionality, even though they cannot yield fractions with a very high protein content [146]. Quite surprisingly, among the plethora of articles that have been published in the past decade on plant protein-stabilized emulsions, only very few investigated lipid oxidation in such systems. Moreover, when checking the available works, some of them did not compare the oxidative stability of such emulsions to that of reference emulsions (e.g., dairy protein-based), making it difficult to assess how and to which extent plant protein ingredient may constitute a mitigating solution to lipid oxidation. To the best of our knowledge, the first articles that addressed this question were by Hu et al. [131] and Faraji et al. [147], who investigated lipid oxidation in emulsions stabilized by soy protein isolate (SPI), sodium caseinate and WPI. Although from the same group, both studies did not lead to a unilateral conclusion regarding the effect of SPI on lipid oxidation in emulsions. In the former study, at pH 3.0, SPI-based emulsions oxidized more than the dairy protein-based ones; conversely, in the second study, at pH 7.0, the opposite effect was found. In the latter case, the protective effect of SPI was particularly marked when excess proteins were present in the continuous phase of the emulsions, pointing at the pivotal role of non-adsorbed proteins, as discussed in detail in section 3.3. This agrees with Feng et al. [148], who also highlighted an antioxidant effect of SPI added to the continuous phase of O/W emulsions at pH 7.0. Apart from soy-based proteins, a few other plant-based protein ingredients have been investigated regarding their effect on lipid oxidation in emulsions. For instance, a better oxidative stability of pea protein isolate-based emulsions compared to a control emulsion with WPI was also recently reported [149]. In another study, lipid oxidation was compared in emulsions prepared with lentil-, pea-, faba bean protein ingredients or WPI [44]. The performance of these different protein ingredients for preventing lipid oxidation was dependent on the addition of exogenous iron – in iron-catalyzed conditions, the WPI-stabilized emulsion was slightly more stable than the plant protein-based ones, whereas without added iron, the onset of lipid oxidation was delayed in the emulsions stabilized by pea or faba bean protein ingredients, compared to the other two. These results suggest that the endogenous content of iron (and/or of metal chelators such as phytates, often found in pulse- and oilseed protein ingredients) is certainly of importance. In addition, this study highlighted that the non-adsorbed protein fraction in these emulsions exhibited a great antioxidant effect, for all tested protein sources. Finally, a few studies showed that the oxidative stability of plant protein ingredient-based emulsions may be modulated by physicochemical treatments applied to the ingredients prior to emulsification. For instance, Shao and Tang [132] found that heat-treating soy proteins improved the oxidative stability of

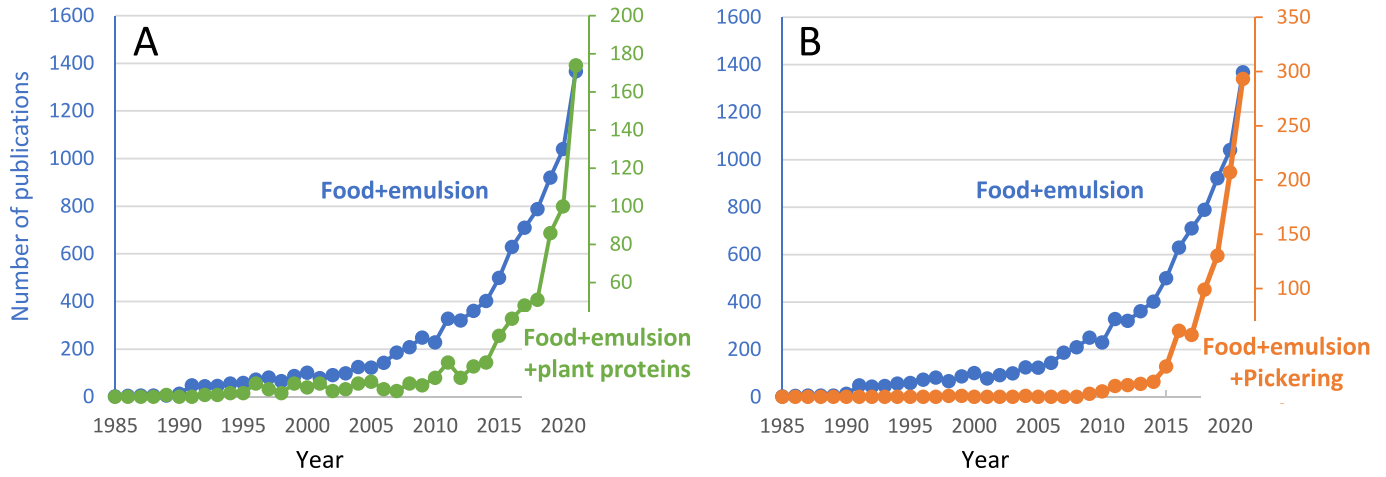

Fig. 2. Evolution of the number of publications (terms appearing in the title, keywords and/or abstract) related to (A) plant protein-based food emulsions (green curve, secondary Y-axis) and (B) food Pickering emulsions (orange curve, secondary Y-axis). In both graphs, for comparison purposes, the number of publications for food emulsions is shown as the blue curve (primary Y-axis). Source: Web of Science, August 2023. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the resulting emulsion, and Liu et al. [150] showed that a moderate degree of hydrolysis of faba bean proteins was also beneficial in that respect.

Despite the increasing use of plant protein ingredients in model systems and in real food products, a great research gap regarding these ingredients still exists as their detailed composition (in particular, regarding the non-protein constituents) is generally not determined in emulsion studies [151]. Plant protein concentrates and isolates used for food applications typically contain 50–60%wt and > 70%wt of proteins, respectively, the rest consisting of a mix of lipids (notably phospholipids), carbohydrates (including residual amounts of starch for starch-containing pulses, such as pea) phytochemicals, trace metals, fibers, and ash. This is not only a blind spot when it comes to the technological (e.g., emulsifying) properties of these ingredients, but we expect that these non-protein constituents could largely drive the oxidative fate of emulsions prepared thereof. For example, C. Berton-Carabin's group recently showed that commercial pea and lupin protein ingredients contain high amounts of lipids, including polar lipids, polyunsaturated fatty acids and highly variable amounts of tocopherols [151]. Other components such as phenolics or phytates may also be present in highly variable amounts depending not only on the botanical source and variety, but also by the processes applied to prepare the ingredients, and are also known to affect lipid oxidation in emulsions [152]. We thus foresee that progress in systematically establishing comprehensive compositional characterization will be key for the future development of oxidatively stable plant protein-based emulsions.

3.2.2. *Pickering emulsions*

As mentioned earlier, Pickering emulsions refer to emulsions physically stabilized by solid or semi-solid colloidal particles that anchor at the oil-water interface. In the past decade, the interest in biobased particles for this purpose has boomed [153] and a plethora of particles have been identified as potent in that respect. We will not extensively review all the work done in this area as it would reach outside the scope of the present article, and several dedicated reviews are readily available on this topic [15,16,154–158]. Yet, it may be important to recall (i) that such particles may be constituted of various macroconstituents (proteins, polysaccharides, lipids) and of various combinations thereof, along with endogenous or purposely added bioactive components; and (ii) that suitable particles may be built purposely by combined selected ingredients through a controlled process ("bottom-up" route), or may exist endogenously in biobased materials, including certain by-products from the agri-food industry ("top-down" route) [159].

The first investigations into lipid oxidation in Pickering emulsions were conducted in the early 2010s [160,161], i.e., at the onset of the 'neoPickering era' [153]. These first studies showed that a Pickering emulsion stabilized by silica particles was more stable to lipid oxidation compared to a conventional Tween 20-stabilized emulsion. Yet, another control emulsion stabilized by caseinate showed even superior oxidative stability, which was attributed to the protein's metal chelating properties. The differences in oxidative stability among these emulsions were thought to be associated with interfacial microstructure, possibly due to a physical barrier created by the silica particles. However, this explanation appears unlikely given the size of aqueous phase pro-oxidants (typically around 0.075 nm for iron ions) compared to the particle size (12 nm in diameter in this study) and the pore size of such a layer (maximum pore diameter around 1.9 nm, assuming a packed layer of uniform spheres) [161]. A subsequent study by this group [160] explored lipid oxidation in Pickering emulsions stabilized by two types of biobased particles: microcrystalline cellulose and octenyl succinic anhydride (OSA) starch granules. The former system was more stable to lipid oxidation, which was hypothesized to be due to factors such as the free radical scavenging properties of microcrystalline cellulose particles, the formation of a thick interfacial layer, and the formation of a network in the continuous phase which would reduce reactant mobility. However, this study did not include a comparison with conventional emulsions, making it challenging to assess the potential advantages of Pickering particles in mitigating lipid oxidation.

In a later study, another group reported a protective effect of sorghum protein particles used as Pickering stabilizers against lipid oxidation compared to a Tween 80-stabilized emulsion [162]. Although the control emulsion had smaller droplet size than the Pickering emulsion, making definitive conclusions difficult, the authors suggested that the positive charge of kafirin (the main protein present in sorghum seeds) and its content in antioxidant amino acids could explain their findings. Similarly, particles made of caseinophosphopeptide and chitosan (a chitin-derived polysaccharide) with positive charge and endogenous antioxidant properties were found to contribute to the oxidative stability of high internal phase Pickering emulsions [163]. Another study from C. Berton-Carabin's group examined the oxidative stability of a Pickering emulsion stabilized by solid fat particles and compared it to two reference emulsions: a conventional caseinate-stabilized emulsion and another caseinate-stabilized emulsion containing high melting point fat within the oil droplet core (referred to as the control emulsion) [164]. The advantage of the control emulsion was its identical overall composition to that of the Pickering emulsion but with

a completely different structure, lacking interfacial particles. The findings indicated that the Pickering particles did not, per se, prevent lipid oxidation compared to caseinate-stabilized emulsions, suggesting that these particles did not induce a physical barrier effect at the interface. However, the Pickering emulsion exhibited higher oxidative stability compared to the control emulsion with high melting point fat in the droplet core. This was attributed to intra-droplet lipid crystallization in the latter system, which expelled labile polyunsaturated fatty acids from inside the droplets to the surface, facilitating their contact with aqueous phase pro-oxidants. Other researchers also explored the use of various lipid-based particles to stabilize Pickering emulsions [165]. They highlighted the importance of the lipid type used to form the particles in influencing the oxidation of the oil droplet core. For example, Pickering emulsions made with trimyristin or olive oil particles showed greater resistance to lipid oxidation compared to a conventional protein-stabilized emulsion, whereas those made with palm olein particles did not exhibit a clear advantage. Interestingly, the protective effect of the former particles was only observed when they were present during emulsion homogenization, not when added post-emulsification, which is an important control to ascribe the protective effect of the particles to their interfacial localization. Furthermore, the physical state (crystalline vs. liquid) of the lipid material within the particles did not appear to be a dominant factor affecting the protective effect of the particle layer [165].

Considering these findings, it is questionable whether Pickering particle layers may exert a purely physical barrier effect in preventing lipid oxidation. Achieving a defect-free interface at the scale of the involved reactants is highly challenging, especially without post-emulsification modifications. To our knowledge, such modifications have not been tested specifically for preventing lipid oxidation, although they have been demonstrated to delay other reactions related to the lipid phase, such as the gelatinization of adsorbed starch granules in Pickering emulsions induced by post-emulsification heat treatment, which was effective in delaying oil digestion [166].

These examples underscore several pivotal questions regarding the selection of promising Pickering particles for preventing lipid oxidation in emulsions. First, the choice of the reference or control system is crucial, as some studies have used bulk oil for comparison, whereas others have employed conventional emulsions (protein- or surfactant-stabilized). Second, it is important to consider not only the interfacial role of the particles but also their presence and structuring effect within the continuous phase of the emulsion. Lastly, the greatest promises of Pickering emulsions with regard to controlling lipid oxidation seem to lie in the potential of the particles to be functionalized with antioxidants; this aspect is further developed and exemplified in section 5.3.

3.3. *Trade-off between adsorbed/non-adsorbed emulsifiers*

As evoked in section 2.1, only a fraction of the emulsifier used to prepare emulsions does locate at the surface of lipid droplets (“adsorbed”), whereas the rest (“non-adsorbed”) remains in the continuous aqueous phase, as free molecules or as aggregates (e.g., micelles in the case of surfactants) when their concentration exceeds a critical value. Another often overlooked option is the possibility that emulsifiers are embedded either free or in the form of aggregates into the lipid droplets (“non-adsorbed”). Indeed, as described in section 2.4.2, it is now recognized that bulk oil systems are not necessarily homogeneous and that lipid oxidation occurs mainly at the surface of association colloids in bulk oils. It is currently unknown whether the association colloids are preserved when the oil is emulsified. There are two possible scenarios: they could be lost if the surface-active molecules move to the surface of the lipid droplets, or, on the contrary, be maintained or newly formed if some of the emulsifier and water migrate and associate into the lipid droplets during emulsification. To date, almost nothing is known about the relationship between the emulsifier and the existence of those association colloids in the oil phase on the oxidative stability and antioxidant activity in food emulsions.

The mode of addition of the antioxidant during the preparation of food emulsions is also important [167–169]. For example, the addition of α-tocopherol either in the oil (pre-emulsification), or in the aqueous phase (post-emulsification) causes, in the presence of an excess of surfactant (>CMC), differences in its antioxidant activity, which can be correlated with a profound change in its distribution within the interfacial region [170]. Since the beginning of the 2000’s, many studies have confirmed the importance of the interfacial region on lipid oxidation and the preponderant role of the surface activity of a molecule in modulating its antioxidant capacity.

Amphiphilic molecules present in emulsion systems (e.g., lipids, proteins, phenolics, etc.) may associate with emulsifiers surrounding the emulsion droplets or those present in the form of aggregates. The total concentration of added surfactant as well as its nature and partitioning between the droplets and micelles have a significant impact on the oxidative stability because this affects (i) the structure of the oil-water interface, (ii) the distribution/interaction/mobility of molecules, and thus (iii) the chemistry of oxidation and antioxidant pathways (Fig. 1). Point (i) was already discussed in sections 2.1 and 3, therefore this section will focus on the influence of non-adsorbed emulsifiers with respect to (ii) and (iii). As most emulsions contain emulsifiers in quantities above their CMC, the “non-adsorbed” part is readily available to self-assemble or co-assemble in the aqueous phase in the form of (co-) micelles or aggregates, which may then affect the distribution and mobility of molecules, thus orienting the oxidative stability. This effect is the result of a change in the balance of the antioxidant and pro-oxidant pathways. For instance, small aggregates such as micelles are highly dynamic structures, which may alter the partitioning of molecules present in the system, concentrate specific molecules or assist the rapid exchange/transfer of components, as described in section 2.4.3, which may be either pro-oxidants (lipid hydroperoxides, metals, etc.) or antioxidants (phenolics, proteins, etc.).

In this context, an excess of emulsifiers made it possible to intensify the inter-droplet molecular exchange phenomenon of (non-) radical lipids described in section 2.4.3, likely by concentrating and assisting the diffusion of pro-oxidant lipids [28,100,171]. For lipid radical species, the diffusion capacity remains low and inversely proportional to their reactivity, therefore we would not expect a major effect of non-adsorbed emulsifiers to accelerate the oxidation of LO• and LOO• by assisted diffusion. This is especially true when the oil contains high levels of unsaturated fatty acids, when the food viscosity is high, or when the alkoxyl and peroxyl radicals are bound to TAG, since the oxidation reactions will readily propagate through the interior/surface of the oil droplet under these conditions, instead of spreading to an adjacent and neighboring droplet [91,93]. Regarding non-radical lipid molecules, not all of them can be transferred between droplets, as seems to be the case with TAGs. For example, Coupland et al. [98] found that while hexadecane or octadecane can be relocated in different lipid droplets with an excess of emulsifiers (i.e., compositional ripening), corn oil TAGs cannot. Similarly, it has been shown that saturated and unsaturated TAGs did not mix in mayonnaises containing surfactant micelles [172], and that barely any TAG-bound hydroperoxides were able to transfer from one droplet to another, even with an excess of emulsifiers [27]. It turns out that TAGs cannot diffuse between droplets in O/W emulsions, whether through the continuous phase or associated into micelle structures. This is likely due to their large molecular dimension, making the slow inter-droplet collision pathway their single mode of diffusion. In summary, the bulkier and more hydrophobic a molecule is, the weaker its ability to propagate oxidation to the surrounding droplets. Similarly, the smaller and more polar a molecule is, the greater its ability to be transferred through to a surrounding droplet. Considering that oxidation may decrease the molecular size of lipids via e.g., scission reactions, while making them more polar (addition of oxygen atoms), one would expect that non-adsorbed emulsifiers could concentrate lipid oxidation intermediate species and influence their mobility, which may

participate in accelerating the oxidation of surrounding droplets during the propagation step. Conversely, in the case of very lipophilic lipids (e.g., TAG-OOH, etc.), one may suspect that their potential diffusion will be restricted, which would limit the influence of non-adsorbed emulsifiers and inter-droplet pro-oxidant activity in the early stage of oxidation [27,98]. Finally, hydroperoxides from free fatty acids (FFA-OOH) are more surface-active than their homologues formed on higher molecular weight lipids (TAGs, diacylglycerols, etc.) and more stable than their radicals (FFA-OO•), which have a limited half-life time, making them a serious candidate in the inter-droplet pro-oxidant activity [100]. However, it is unclear whether such a micellization can be achieved by FFA-OOH alone or whether an excess of non-adsorbed emulsifiers would be necessary (co-micellization).

Aggregates formed by non-adsorbed emulsifiers can also affect the partitioning, the solubilization of pro-oxidant metals, as well as the metal-ligand interactions [173]. In general, the factors which promote the presence of metals at the oil-water interface increase oxidation rates (e.g., negatively charged emulsifiers). A well-known example are phosvitins, which are proteins abundantly present in egg yolk, the main emulsifier in mayonnaise [174]. Phosvitins have a low affinity for ferrous ions at the low pH of mayonnaise [175], which promotes the formation of peroxyl radicals at the droplet interface. Also for other emulsifying proteins, a low affinity for transition metal ions has been associated with pro-oxidant activity [137]. For example, emulsions prepared with caseins have a higher oxidative stability [176] than those prepared with whey proteins [177], which has been attributed to the higher affinity of caseins for transition metals [137]. The difference in oxidative stability of O/W emulsions prepared with caseinate and bovine serum albumin has also been attributed to the metal affinity of these two proteins [178]. On the contrary, factors that remove metals from the interface (e.g., positively charged emulsifiers or aqueous phase metal chelators) decrease oxidation rates [69]. On the one hand, the solubilization of pro-oxidant metals in micelles or aggregates formed by the non-adsorbed emulsifiers could inhibit lipid oxidation by segregating them away from the sensitive lipid droplets. On the other hand, and in view of the previous observations, this phenomenon could promote oxidation by allowing an individual lipid droplet that is undergoing oxidation to transfer pro-oxidative factors to a second droplet, or to concentrate (bring close together) metals and pro-oxidant lipids (e.g., FFA-OOH) thus accelerating the formation of free radicals. In addition, since transition metal ions at lower valence states (e.g., Fe^{2+}) can decompose lipid hydroperoxides much faster than those at higher valence states [34], a co-concentration of a low-redox potential antioxidant with metals (e.g., Fe^{3+} and Cu^{2+}) could trigger the formation of LO• and LOO• radicals [39]. This is an explanation why, especially when the pH decreases, antioxidants may act as pro-oxidants.

Small aggregates formed by non-adsorbed emulsifiers in the continuous aqueous phase of emulsions may also get involved in the inhibition of oxidation propagation. For example, excess emulsifying proteins can provide an antioxidant route by scavenging radicals (mechanism (I) in Fig. 1D) [4,179]. Another example is the case when those dynamic structures modify the distribution of antioxidant molecules, which will positively influence their activity. For instance, while eicosyl rosmarinate (i.e., rosmarinate esterified with a C20 alkyl chain) was shown to be weakly antioxidant in an O/W emulsion of purified soybean oil, the addition of an excess of Tween-20 emulsifier beyond its CMC led to a strong improvement in its antioxidant capacity [180]. This modification in antioxidant action was due to a change in antioxidant location. Indeed, the formation of co-micelles with eicosyl rosmarinate and emulsifiers shifted the distribution of antioxidant towards the interfacial region of emulsion, therefore improving its efficacy. This result was not observed with butyl and dodecyl rosmarinates, likely because the non-adsorbed emulsifiers did not significantly change their partitioning. The pseudophase kinetic approach developed to assess the location of antioxidants (see Section 2.5) confirmed the effect of excess emulsifiers on the antioxidant distribution, since the percentage of antioxidant molecules such as tocopherols in the interfacial region increased rapidly with increasing surfactant concentration [181,182]. These results, along with a multitude of others [101,173,183,184], highlight the role of micelles on the antioxidant efficacy. According to the literature, for the most lipophilic antioxidants, micellization would promote their effectiveness by improving their diffusion and/or concentration in interfacial region meaning also that the oxidized form at the interface of the lipid droplets could be more quickly replaced. For antioxidants of intermediate polarity and amphiphilic nature, micellization will tend to reduce their action, likely by reducing their concentration at the oil-water interface ("dilution effect"). For highly water-soluble antioxidants, there does not seem to be any definite trend, likely because the effect on antioxidant distribution will be less important than the inter-droplet pro-oxidant effects of lipids and metals.

Another important area of research that is currently poorly understood lies in the impact of the excess of emulsifiers and the ratio of free-to-adsorbed emulsifiers on the competition effects between molecules (e.g., antioxidants vs emulsifiers, emulsifiers vs emulsifiers, etc.). For instance, phenolic-protein [185,186] or tocopherol-phospholipid [187] interactions, either at the oil-water interface or in the continuous aqueous phase, could affect their tridimensional structure (in the case of proteins), their respective partitioning, or/and their antioxidant activity in food emulsions, which may alter oxidative stability.

Last but not least, the raw materials' selection and the energy level for the preparation of emulsions could alter the physicochemical properties of the system, which may significantly alter the oxidative stability. This is particularly the case when proteins are used as emulsifiers to stabilize emulsions [130,188,189]. The most likely reason lies in the ability of the proteins to change the location of the pro-oxidant metal ions, either close to the oil-water interface or away from it. Thus, lipid oxidation is inhibited by adsorbed proteins at pH values below their isoelectric point due to their capacity to electrostatically repel transition metals, but may be promoted above their isoelectric point due to their aptitude to attract metals [190]. Yet, for non-adsorbed proteins, the opposite effect is expected since negatively charged proteins can pull transition metals away from the droplet surfaces when binding them. Thus, the ratio of free-to-adsorbed proteins and their ionization state, as well as the capacity to bind and alter the electron density of transition metals, are important points that must be better investigated. Also, very often, the preparation of emulsions with very small droplet size requires a great energy input, which can have an importance on both the concentration of oxidized compounds (e.g., hydroperoxides) at "time 0" and the ratio of free-to-adsorbed emulsifiers. In addition, small and large droplets do not have the same interfacial properties nor the same curvature properties on their surface, which can alter the accumulation of emulsifiers (e.g., proteins), and the part of non-adsorbed fraction. Finally, at fixed lipid concentration, an increase in droplet size will simultaneously increase the concentration of non-adsorbed emulsifiers, which, depending on their capacity to form aggregates (e.g., micelles), could alter the mechanisms that has been previously detailed, while reducing the average distance between oil droplets. With a reduced distance, one can expect that the exchanges of species (hydroperoxides, radicals, oxidizing species, antioxidants) between neighboring droplets are more noticeable. Finally, since the composition of emerging plant protein ingredients is highly complex, it would be essential to better elucidate the role of minor surface-active components, along with the mechanisms underlying their accumulation during protein fractionation processes in their functional properties (emulsifying properties), and the impact on oxidative stability of processed foods [191]. For instance, Keuleyan et al. [151] found that in commercial pea and lupin protein ingredients, a high pressure homogenization treatment can strongly affect colloidal structures by disrupting large powder aggregates, enhancing the protein solubility and the release of endogenous lipids as small colloidal suspensions. This notion of species diffusion and interactions of the many substances involved in lipid oxidation pathways is very complex and requires further research.

In conclusion, in food emulsions, it is obviously very difficult to predict these behaviors since they are dependent on the composition, concentration of all the molecules present, food processing, etc. and the only rule that seems to prevail is that of case by case. Thus, the effect of emulsifiers, and the trade-off to be found between adsorbed and non-adsorbed fractions, must be apprehended in a systemic way, taking into consideration the multivariate molecular interactions and the resulting variation of oxidation, pro-oxidant and antioxidant mechanisms.

4. Sensitivity of the emulsifiers themselves to oxidation

As already discussed in section 3, the different parameters influencing the oxidative stability of emulsions are numerous. Among them, one that is not so often considered is the sensitivity of emulsifiers themselves to oxidation and how it can impact lipid oxidation.

4.1. Low molecular weight surfactants

As early as the seventies, the potential oxidation of non-ionic polysorbates esters (Tween) was demonstrated [192,193] as well as the presence of peroxide contaminants in polyether surfactants (e.g., Triton, Tween and Brij series) [194]. In the nineties, the accumulation of peroxides in Tween surfactants (i.e., polysorbates) during storage was confirmed [195]. This accumulation was also observed by Mancuso et al. [196] who showed that non-ionic surfactants containing polyoxyethylene units (Tween or Brij) could accumulate higher peroxide contents (4.0 to 34 μmol of peroxide/g of surfactant) than ionic surfactants (0.40 to 13.0 μmol of peroxide/g measured for SDS surfactant). Ha et al. [197] also found that peroxides can be easily generated in Tween surfactants upon light exposure, while storage in the dark and reducing oxygen contact could prevent it. Other authors suggest solvent washing to remove peroxides in surfactants before use [198] or the addition of synthetic antioxidants such as butyl hydroxytoluene (BHT). The oxidation mechanism of polysorbates is partly related to their ethylene oxide moieties [192,199]. However, these surfactants may contain unsaturated fatty acids as their lipophilic tail, which are more prone to oxidation compared to their ethylene oxide moieties [200]. Yao et al. [201] observed that Tween 80 (oleate) was 2.65 times more sensitive to oxidation than Tween 20 (laurate). A deeper mechanistic study was performed by Kishore et al. [202] who showed that radical formation occurs at the polyoxyethylene as well as the olefinic sites. In Tween 80, radical initiation at the olefinic site precedes initiation at the polyoxyethylene site. Later, the oxidative degradation products of Tween 80 were studied by ^{1}H NMR and LC-MS/MS and hydroxyl, ketone or epoxy derivatives from oleic acid were identified [203,204]. Very recently, the presence of secondary oxidation compounds such as aldehydes was also detected in Tween 80 [205]. Using electron paramagnetic resonance spectroscopy, radicals such as HO•, R•, RO• and ROO• could be identified in bulk polysorbates [206]. Concerning the physical properties of oxidized polysorbates, it is worth noting that some authors showed that oxidation could modify their surface properties, making them more surface-active, but this seems to have little impact on their CMC [207]. Moreover, the extra- and intra-micellar oxidation of polysorbates seems to be independent of the nature of the buffer in which they are added [208].

The presence of peroxides or radicals in surfactants can favor lipid oxidation in emulsions as shown by Nuchi et al. [209]. These authors evaluated the influence of Tween peroxides on the lipid oxidation kinetics in two different systems. In a methyl linoleate micellar system, when using increasing quantities of Tween containing 3.5 and 14.7 μmol hydroperoxide/g surfactant, a reduction of the lag phase of hexanal formation was observed. The addition of ferrous ion in the presence of surfactant containing the lowest quantities of peroxides (3.5–6.0 μmol/g) did not accelerate the formation of secondary oxidation compounds, whereas such an acceleration was observed for Tween with higher quantities (14.7 μmol/g). Different results were found when using a salmon oil-in-water emulsion. In that case, the addition of ferrous ions in the emulsion made with low levels of Tween 20 hydroperoxides increased the oxidation kinetics (primary and secondary oxidation compounds). For Tween 20 with high levels of hydroperoxides, the addition of pro-oxidant metals did not significantly modify the lipid oxidation kinetics. The authors suggested that as ferrous ions can promote both the breakdown and formation of hydroperoxides, the balance of these reactions could be influenced by the concentrations of hydroperoxides brought by Tween 20. Similarly, Schwarz et al. [210] also showed a pro-oxidant effect of Tween 20 that was attributed to pro-oxidant properties of the methyl glucose headgroup of the surfactant [211].

Although not directly correlated to their sensitivity to oxidation, a substantial amount of research has been made to evaluate the interaction of surfactant micelles with pro-oxidants metals or reactive oxidation products and the related impact on lipid oxidation. For example, it was observed [173] that Brij micelles in emulsions were capable of trapping ferric ions and thereby limiting their pro-oxidant effect. Similar metal trapping capacities were also envisaged by Haahr and Jacobsen [212] when studying the oxidative stability of fish oil emulsions stabilized by a nonionic surfactant (Tween 80, i.e., a polysorbate) or an anionic one (Citrem, i.e., a fatty acid ester of citric acid).

Surfactant micelles may also interact with oxidation products. Kasaikina et al. [213] and Uluata et al. [214] showed that surfactants could associate with hydroperoxides as co-micelles. Once the association is made, depending on the charge of the surfactants, this would either favor the decomposition of hydroperoxides into more reactive radical species (acceleration of lipid oxidation kinetics), or, conversely, favor the stabilization of hydroperoxides resulting in a delay in the formation of secondary oxidation products.

4.2. Phospholipids

Emulsions can also be physically stabilized by lecithins that are recovered during oil refining from the degumming process of vegetable oils (soy, rapeseed, sunflower) or from animal products (egg yolk or milk fat) [215]. Lecithins correspond to a complex mixture of lipids including TAGs, fatty acids, sterols, glycolipids, and phospholipids. Phospholipids are the main lipid species in lecithins (phosphatidylcholine (PC), phosphatidylinositol (PI), phosphatidylethanolamine (PE), phosphatidylserine (PS), phosphatidylglycerol (PG), and phosphatidic acid (PA)) [215]. Depending on the source and method of production, lecithins have various phospholipid contents. Typically, soy lecithins are the richest in phospholipids (60 to 70%), whereas other sources such as sunflower oil, rapeseed oil or dairy fat have lower contents [216]. Crude lecithins can also be fractionated by solvent processes to increase their phospholipid concentration and remove residual TAGs. Depending on the source, lecithins also have varying phospholipids distributions. Crude soybean lecithin mainly contains PC, PE and PI, whereas egg yolk lecithins are particularly rich in PC and PE and dairy lecithins are characterized by the presence of sphingomyelin [216–218]. Lecithins can play a particular role in the oxidative stability of emulsions as phospholipids are known to possess antioxidant activities through different mechanisms [83]. For example, phospholipids are known for their metal chelating properties that can be attributed to the negative charges present on their phosphate headgroup. The iron-binding capacity of individual phospholipids from egg yolk as reported by Dacaranhe and Terao [219] was in the order PA $\geq$ PS $\geq$ PG $>$ PE $=$ PC, but contradicting results have been reported in literature. For example, García-Moreno et al. [139] reported that pure PC had a higher metal chelating activity than pure PE and both were better than lecithin. However, these metal chelating properties are dependent on the pH conditions. When using a soybean O/W emulsion at pH 3.0 [220], which is below the pK_a of PC, PC was not charged and thus could not chelate pro-oxidant metals. In contrast, at pH 7.0, a combination of caseinate with either PC, PE or lecithin as

emulsifiers improved the oxidative stability of 10% fish O/W emulsions compared to when caseinate was used alone [139]. Phospholipids are also well known for their synergistic interactions with tocopherols [221–223]. For example, both PE and PS were shown to prolong the oxidation lag phase of perilla oil in the presence of tocopherols, whereas when the oil was depleted in tocopherols, these phospholipids had no antioxidant activity [224]. Similarly, others found that neither PC nor PE had antioxidant activity when added to canola oil depleted from tocopherols, whereas upon the addition of α-tocopherol, synergistic activities were observed [225]. The synergistic interactions between phospholipids and tocopherols are generally attributed to the capacity of phospholipids to convert the oxidized form of tocopherols (tocopherylquinone) back to tocopherols [226]. Similarly to the metal chelating properties of phospholipids, their potential regenerative activity on tocopherols is dependent on the phospholipid type. Doert et al. [227] showed that both PE and PS could form complexes with the quinone form of tocopherols. These complexes would then undergo various rearrangements that would regenerate tocopherols. On the contrary, no tocopherol regeneration was observed with PC, which was attributed by the authors to the absence of a primary amino group in PC. The absence of synergistic effect between PC and tocopherols was also reported elsewhere [83,228], whereas others did observe a synergistic effect of this phospholipid with tocopherols [221,223]. These contradictory conclusions could be due to different experimental conditions, different types of tocopherols, phospholipids (or lecithins) and oils used as oxidizable substrate. It is also worth noting that sphingomyelin, which is found in dairy lecithins, may also have synergistic effects with tocopherols, which can be even more pronounced than the ones observed with phospholipids [229]. The formation of Maillard reaction products with phospholipids containing a primary amine group (PE) and secondary lipid oxidation products (aldehydes) is also possible. Indeed, Hidalgo et al. [230] showed that PE could react with 4,5-epoxy-2-heptenal and that the resulting non-enzymatic browning products, in particular pyrroles, contributed to delaying lipid oxidation. Such a reaction was not observed with PC, which does not have a primary amine group but a tertiary one. The formation of pyrroles in the case of PE was also suspected by Bandarra et al. [231] in sardine oil or by Lu et al. [232] to explain the remarkable oxidative stability of marine phospholipids. In biological systems, the reactivity of the polar headgroup of phospholipids such as PE with secondary lipid oxidation products such as hydroxyalkenals has also been shown [233], and could be of relevance in food systems, although this aspect has not been well-documented yet. However, in some studies, phospholipids have also been described as molecular species that can favor lipid oxidation. This pro-oxidant effect could be partly attributed to the high concentration in PUFA in animal and marine phospholipids, but also to a more indirect effect. Indeed, phospholipids would contribute to the modification of the physical structure of the system and/or of the partitioning of molecular species involved in the lipid oxidation pathway [79]. For example, the negative charge of phospholipids could attract metals at the surface of emulsion droplets, favoring their pro-oxidant effect [69].

Due to the presence of unsaturated fatty acids in their structure, lecithins are also prone to oxidation themselves. For example, soy and rapeseed lecithins are particularly rich in linoleic acid, whereas rapeseed phospholipids are rich in oleic acid [234]. Marine phospholipids are known to contain significant amounts of long chain omega-3 fatty acids [235]. The oxidation of phospholipids corresponds to well-known pathways in biology leading to the formation of oxidized phospholipids which are largely documented for their biological activities [236–238]. In terms of chemical mechanisms, the phospholipid oxidation is very comparable to the one of TAGs containing unsaturated fatty acids. Therefore, phospholipid oxidation also leads to the formation of radical species (peroxyl, alkoxyl), hydroxyperoxides, secondary oxidation compounds, or oxypolymers. Moreover, besides the formation of pyrroles that has been already discussed above, non-enzymatic browning reactions from phospholipids can also lead to the formation of Strecker aldehydes. Intermediate products formed in this reaction pathway include epoxy keto fatty esters, epoxyalkenals and hydroxyalkenals [235,239]. The patterns and kinetics of phospholipid oxidation are largely documented when dealing with liposomal systems for food, pharmaceutical or cosmetic applications. The oxidative stability of liposomes is greatly influenced by their size and molecular composition as well as the molecular composition of their surrounding medium [240]. For example, for marine phospholipids, this transformation is so fast that the usual formation of lipid hydroperoxides and aldehydes evaluated by measurement of peroxide value (PV), anisidine value (AV) or thiobarbituric subtances (TBARS) cannot be detected, which can lead to the erroneous conclusion that no lipid oxidation is taking place [241]. Concerning emulsions that are stabilized by lecithins, to the best of our knowledge, no research work exists where the oxidation kinetics of phospholipids versus the ones of TAGs were compared. Still, in such emulsions, as phospholipids locate either at the interfacial area or as colloidal structures in the continuous phase, one can assume that, compared to the lipid droplets, phospholipids would be more in contact with pro-oxidants and could be then oxidized faster. By analogy, one can cite the various studies made on the study of oxidative stability in model meat system. Igene et al. [242] evaluated the effect of TAGs and phospholipids on development of rancidity using lipid-free muscle fibers in combination with added TAGs or phospholipids. Results showed that both TAGs and phospholipids contribute to development of rancidity, although phospholipids were the first to oxidize. Later, the same research group showed that PE and PC were particularly sensitive to oxidation in frozen meat [243]. Others confirmed this observation and found that 70–77% of total malondialdehyde in phospholipids was formed from PC and PE, followed by 16–25% from PI and PS in chicken meat [244]. This logically arises from the relative abundance of the different phospholipids, as PC and PE are the major ones in chicken meat. Yet, some deviations from a strict proportionality between the relative abundance of the different phospholipids and their contribution to MDA formation were also noticed; for instance, proportionally, the highest amount of MDA was formed in PI [244]. As mentioned above, very few data exist regarding the impact of oxidized lecithins on the oxidative stability of emulsions. One can cite Pan et al. [245] who showed that free-radical permeation across the surface of lecithin-stabilized oil droplets occurred more quickly with pre-oxidized lecithin than with fresh lecithin. This resulted in shorter oxidation lag phase in the case of emulsion stabilized by pre-oxidized lecithin.

4.3. Proteins

Many food emulsions are also stabilized by proteins as emulsifiers [246–248]. Just like phospholipids, proteins are known to possess antioxidant activity through radical scavenging or metal chelating mechanisms. Through physicochemical mechanisms or interactions with other compounds present in the emulsion, proteins can also contribute to a better oxidative stability of the emulsion concerned. These antioxidant effects of proteins have been widely documented and are discussed later in this review (section 5.2). Moreover, we recommend interested readers consulting the following reviews on the topic [4,249–251]. Proteins are also prone to oxidative degradation themselves. Protein oxidation can occur during production and storage of the protein ingredients or within the emulsion when used as emulsifiers [252,253]. Protein oxidation leads to chemical and structural modifications of proteins with amino acid group modifications, peptide bond breakage, and protein cross-linking reactions. Such modifications modulate their solubility, emulsifying properties and the resulting physical stability of the concerned emulsion [254–258] as well as their digestibility [259–261]. Protein oxidation has also an impact on the overall oxidative stability of emulsions. In fact, protein oxidation and lipid oxidation are now known to be interdependent as proteins can react with lipid oxidation products such as radicals, hydroperoxides or with secondary lipid oxidation products such as aldehydes [262–264].

In addition, protein radicals can also react with other proteins, lipids or oxygen to generate protein hydroperoxides. Many research studies showed that protein oxidation occurs at an early stage in emulsions, suggesting a sacrificing role of proteins to protect lipids. For example, Yang and Xiong [265] investigated the relative reaction rate of protein and lipid oxidation in an emulsion containing myofibrillar proteins. When oxidation was induced by a hydroxyl radical, protein oxidation markers (tryptophan fluorescence intensity, carbonyl formation) exhibited significant changes within 2 h, whereas no lipid oxidation markers were found (hydroperoxides) within the same period; it should be pointed out that this may also depend on the different sensitivities of the applied methods. For example, using different analytical techniques, Baron et al. [266] could detect volatile lipid oxidation products before protein carbonyls. Moreover, proteins adsorbed at the oil-water interface seem to be more sensitive to oxidation than non-adsorbed proteins, as suggested by Yan et al. [267] for an O/W emulsion stabilized by a SPI. Similarly, Yi et al. [268] added Tween to a caseinate-stabilized emulsion to induce displacement of the adsorbed proteins from the interface to the continuous aqueous phase. Emulsions stabilized solely by caseinate exhibited relatively slow lipid oxidation, whereas caseinate was rapidly oxidized. Competitive removal of caseinate by the surfactant reduced protein oxidation, but then lipid oxidation was faster. The authors also concluded that adsorbed proteins were more sensitive to oxidation themselves, but also more efficient at protecting lipids. The same research group made a comparable study with an O/W emulsion stabilized by whey protein isolate (WPI) (0.5% *w/v*) and increasing amounts of Tween 20 (0 to 0.4%) at pH 3.0 and pH 7.0 [269]. Upon addition of Tween, whey proteins were displaced from the interface more readily at pH 3.0 than at pH 7.0. Protein oxidation was faster, whereas lipid oxidation was slower at both pH conditions. Here again, the authors observed that the displacement of whey proteins from the interface reduced protein oxidation but promoted lipid oxidation, indicating that adsorbed proteins are more prone to oxidation than non-adsorbed proteins. The kinetics of protein and lipid oxidation at the interface are also dependent on the nature of the protein itself. For example, Sorensen et al. [130] studied the effect of homogenization conditions of fish oil-enriched milk emulsions on the changes in the protein composition of the milk fat globule membrane and the oxidative stability of the systems. High pressure and high temperature resulted in less lipid oxidation, whereas low pressure and low temperature resulted in faster lipid oxidation. This intriguing result was explained by analyzing the interfacial protein composition (SDS-PAGE) and emulsion microstructure (confocal laser scanning microscopy, CLSM), which showed that high temperature resulted in an increase in β-lactoglobulin adsorbed at the oil-water interface, whereas casein, which is more prone to oxidation, was present at the oil-water interface with increasing pressure. The addition of non-protein compounds at the interface can also modulate the oxidative fate of emulsions. For example, the addition (0.2–0.6 g/kg) of konjac glucomannan (KGM), a neutral plant polysaccharide, to walnut O/W emulsions coated by WPI inhibited lipid oxidation, yet promoted protein oxidation [270].

Protein-based emulsifiers may also contain small amounts of lipids, which may be oxidized before emulsion formulation. This was observed by Sørensen et al. [271], who found that replacing high-quality egg yolk (PV < 0.1 meq/kg) with a milk protein-based emulsifier (PV $= 9.8$ meq/kg) led to an increased degree of oxidation in light mayonnaise, even though the milk protein-based emulsifier contained only 7.3 μg/g iron versus 51 μg/g in egg yolk. Previous work had demonstrated that the high concentration of iron in egg yolk in combination with the low pH of mayonnaise catalyzes lipid oxidation [39]. The higher degree of oxidation in mayonnaise with the milk protein-based emulsifier was therefore most likely due to the presence of oxidized lipids in the emulsifier.

The quantitative and spatiotemporal mapping of lipid and protein co-oxidation was recently evaluated in mayonnaise with the use of CLSM and fluorescent lipophilic dye BODIPY 665/676 [74]. CLSM analysis revealed a heterogeneous distribution of protein oxidation at the interface pointing towards lipoprotein granules that are typically present in egg yolk. Finally, in the absence of tocopherols (stripped oil), protein oxidation was enhanced both at the interface and in the continuous phase. This enhanced protein oxidation upon removal of tocopherol was attributed to the transport of lipid radicals from the oil droplets to the interface and continuous phase. The authors also evaluated the effect of ascorbic acid on lipid and protein oxidation. In the presence of tocopherols, ascorbic acid showed an antioxidant effect towards lipids, whereas in the absence of tocopherols, it behaved as a pro-oxidant. However, other studies have shown that ascorbic acid acts as a strong catalyst of lipid oxidation in mayonnaise prepared with a mixture of rapeseed oil and fish oil, which contained tocopherols [272]. Concerning protein oxidation, ascorbic acid acted as a pro-oxidant for adsorbed proteins at the interface as well as for the ones in the continuous phase. Interestingly, contrasting behaviors with other antioxidants regarding lipid or protein oxidation were also reported. For instance, Raes et al. [273] showed that α-tocopherol and the polyphenol quercetin were able to lower lipid oxidation while their effect on protein oxidation was not clear, whereas carnosic acid (a phenolic diterpene) did not have any effect on lipid oxidation and tended to promote protein oxidation. In an O/W emulsion stabilized by whey proteins, Tian et al. [274] showed that high concentrations of tea polyphenols could inhibit lipid oxidation but promoted protein oxidation. Polyphenols are known to be able to bind to proteins through non-covalent interactions, in a pH-dependent manner. Such a binding impacts the physicochemical properties of proteins [275,276]. In particular, their structure and surface chemistry could be altered by the formation of these polyphenol-protein conjugates, thereby increasing their susceptibility to oxidation [277].

Very recently, concomitant lipid and protein oxidation reactions were further studied at multiple scales in mayonnaises [73]. Protein radicals were localized at the interface and in the continuous phase using a fluorescently labelled, free radical spin trap. Cryo-transmission electron microscopy (cryo-TEM) and bright-field light microscopy were used to observe low-density lipoprotein (LDL) particles at the nanometric scale in a time-resolved manner. The accumulation of fluorescent spin traps precedes the local appearance of protein autofluorescence and therefore is an early and sensitive marker of protein oxidation. Therefore, thanks to the use of a water-soluble fluorescent spin trap (CAMPO-AFDye 647), early lipid and protein radical formation at the oil-water interface could be detected and confirmed that protein oxidation is faster at the interface than in the continuous phase. This is due to the presence of lipid radicals at the interface. Similar observations were made by Chen et al. [188] who found that whey protein oxidation was faster at the oil-water interface compared to the oxidation of non-adsorbed proteins. Yang et al. [73] also showed that the pathway for protein oxidation in the continuous phase is independent from lipid oxidation in oil droplets. In that case, lipid oxidation in LDL particles produces lipid radicals that induce protein free radical formation and protein oxidation. Notably, upon addition of a metal chelator such as EDTA, protein oxidation was more effectively inhibited at the interface than in the continuous phase.

5. Novel antioxidants from model systems to real food applications

Since the early 2000's, the paradigm of antioxidant efficiency in O/W emulsions has substantially evolved, while at the same time, exploration of various routes has greatly progressed to yield antioxidants that are not only optimally efficient, but also meet criteria that have become increasingly important, such as the natural origin of the ingredients to meet the clean-label trend.

Two decades ago, the prevalent theory was that of the polar paradox, suggesting that polar antioxidants would be more effective in bulk lipids, while nonpolar antioxidants would perform better in O/W emulsions. However, new findings in the 2000's challenged this model,

prompting a revaluation of the polar paradox and the introduction of new concepts and hypotheses [278]. For instance, in bulk oil, as explained earlier (section 2.4.2), it was demonstrated that the critical site of oxidation is not the air-oil interface, as previously proposed in the polar paradox. Instead, oxidation occurs at association colloids formed by traces of water and surface-active molecules such as phospholipids. At the same period, it was demonstrated that in O/W emulsions, a nonlinear relationship between hydrophobicity and antioxidant capacity applies [279]. This effect, referred to as the cut-off effect, was then amply further studied and confirmed, as detailed in the following (section 5.1).

In the past decade, another huge trend has been the quest for antioxidant solutions efficient in O/W emulsions while based on natural ingredients. Among the plethora of related literature, often relying on empirical approaches, some recent trends include the aid of bioinformatics to yield antioxidant peptides, and the controlled localization of natural antioxidants using Pickering particles as interfacial reservoirs. These aspects are reviewed below, with a focus on how they can be tuned to potentialize biobased, natural ingredients, and even by-products from the agro-food industry.

5.1. *Phenolipids and the cut-off effect*

In emulsions, the effectiveness of antioxidants at reducing lipid oxidation is highly dependent on their intrinsic chemical reactivity and their ability to localize at the oil-water interface. While the former is based on their capacity to donate hydrogen atoms or electrons, i.e., their redox properties, the latter may be related to their hydrophilic-lipophilic balance (HLB). Since natural antioxidants such as phenolics are relatively polar molecules, their amphiphilic character can be adjusted by lipophilization. This structural modification, consisting of the covalent attaching of one or more hydrophobic tails, can be achieved by various chemical or enzyme-catalyzed reactions such as esterification, amidation or etherification. For example, lipophilization has been successfully applied to phenolic acids [280,281], and to tyrosol/hydroxytyrosol [282], by esterifying either the free carboxyl group with aliphatic alcohols or the primary hydroxyl with aliphatic carboxylic acids respectively. Thus, by preserving the phenolic hydroxyl, the resulting molecules, called “phenolipids,” retained all their reactivity with free radicals. Chemical lipophilization by esterification, usually carried out under harsh conditions with strong acid catalysts (hydrochloric acid, sulfuric acid, paratoluene sulfonic acid, sulfonic acid resins), is quite efficient and quantitative, and can be driven to completion by continuous drying of the medium when water is produced. Conversely, enzymes allow the synthesis of phenolipids under milder conditions with better selectivity and fewer side reactions. However, enzymatic catalysis is often much slower, potentially subject to inhibition phenomena, and, as recently described in several reviews, requires the fine-tuning of numerous parameters to be effective [283–285].

In any case, although natural phenolipids can be found in many plants [286–291], the above-mentioned hemisyntheses offer the advantage of easy and quantitative access to a wide range of tailor-made molecules, particularly suitable for investigating the effects of amphiphilicity on antioxidant activity in lipid systems. In this section, we focus more specifically on alkyl ester series of hydroxybenzoic acids, hydroxycinnamic acids, tyrosol and hydroxytyrosol (Fig. 3), which were particularly studied over the last two decades and have led to major advances in the field.

In 2009, Laguerre et al. [279] reported the first systematic evaluation of the effect of increasing the hydrophobicity of phenolipids on their antioxidant activity in a model emulsion. By testing alkyl chlorogenates (from C1, methyl to C20, eicosyl) in a stripped tung O/W emulsion, they found that antioxidant activity increased as the alkyl chain lengthened up to a threshold corresponding to the C12 ester, followed by a collapse in antioxidant capacity for longer alkyl chains. The authors described this behavior as a cut-off effect, referring to the general phenomenon of the same name observed for various biological activities in series of amphiphilic homologues; in addition, the alkyl chain at which the threshold occurred was referred to as the “critical chain length” (CCL). To explain these unexpected results, insofar as the polar paradox rule was only partially fulfilled, Laguerre et al. [279] hypothesized that a different distribution of antioxidants into the different phases of the

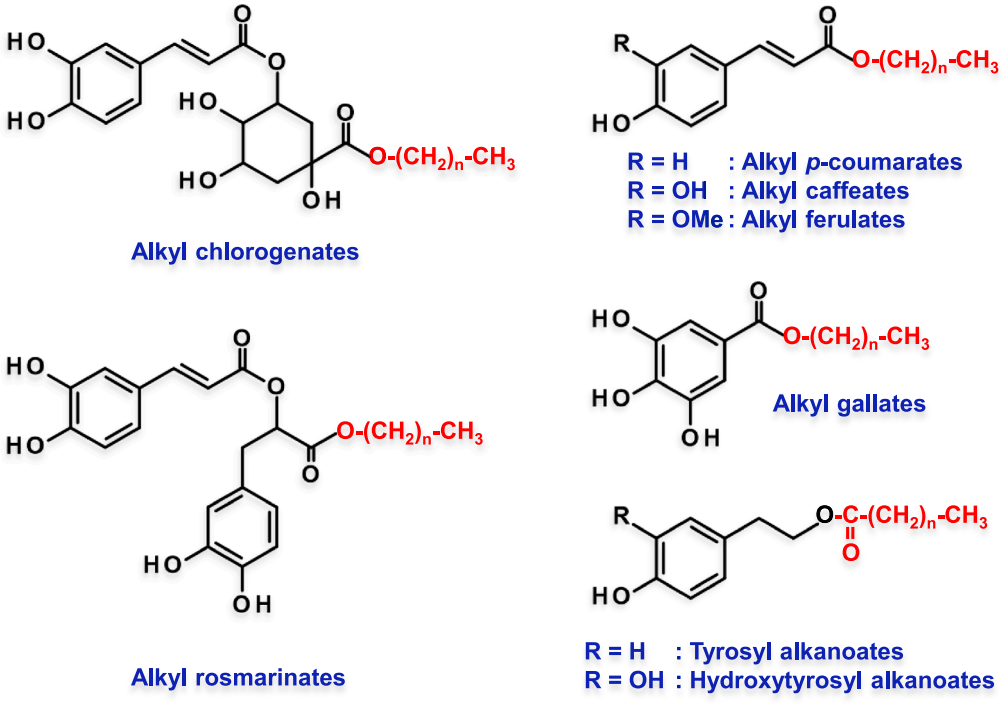

Fig. 3. Chemical structure of the phenolipids discussed in this section.

emulsion, according to both their hydrophobicity and emulsifier concentration, influences their antioxidant activity.

In the following years, the antioxidant activity of other phenolipids series was investigated in different emulsions. In addition to systematically confirming the presence of a cut-off effect, these studies also showed that the associated threshold intensity (relative to the activity of the unmodified starting phenolic) and critical chain length (CCL) were specific to each system evaluated, as shown in Table 1.

Key findings from these studies were that the efficacy of phenolipids (and corresponding CCL) depends not only on their own reactivity (i.e., lipophilization has little or no effect on the efficacy of weak antioxidant molecules), but also on the physicochemical characteristics of the emulsion. Thus, physicochemical characteristics such as wet versus dry emulsions, droplet size, charge, phases and interface composition, emulsifier type and concentration, etc. and the phase in which antioxidants are added have been suggested to play a critical role in the partitioning of antioxidants in the emulsion and especially their location at the oil-water interface. During the same period, the hypothetical relationship between the surface properties of phenolipids and their distribution formulated by Laguerre et al. [279] was experimentally tested in several studies.

Following the observation of Medina et al. [292] of a cut-off effect in the antioxidant capacity of some hydroxytyrosol-based phenolipids in fish O/W emulsions, the same group investigated the surface-active properties of two series of tyrosyl and hydroxytyrosyl alkanoates in water [300]. In each series, esters with HLB of 8–11 were effective surfactants, but hydroxytyrosol homologues performed better than tyrosol ones. Interestingly, the surfactant effectiveness, as measured by the surface tension at the CMC, γ_{CMC}, followed a non-linear pattern as a function of the alkyl chain length with a threshold corresponding to C8 ester in both series, i.e., the same as the CCL found for antioxidant activity of hydroxytyrosyl alkanoates in emulsion. Three years later, a foundational paper by Romsted and Bravo-Díaz [122] introduced the pseudophase kinetic model described in section 2.5, a powerful thermodynamic-based approach that allows access to the reactivity and partitioning of antioxidants in O/W emulsions according to different physicochemical properties of the system and its components.

Using this pseudophase kinetic model, Losada Barreiro et al. [301] studied (i) the partitioning of gallic acid (GA) and some alkyl esters (C3, propyl; C8, octyl; C12, octadecyl) (Fig. 3) in stripped olive or corn oil-in-water emulsions of different oil:water (*v*/v) ratios and emulsifier (Tween 20) contents, and (ii) the ability of each phenolic compound to retard lipid oxidation in the emulsions. A positive correlation was found between the antioxidant efficacy of gallates and their concentration in the interfacial region, with a cut-off effect centered on propyl ester (C3 > GA > C8 > C12). Moreover, the same antioxidant ranking was observed regardless of the type of oil, the oil:water ratio (1:9 to 1:1, v/v), and the volume fraction of the surfactant (from 0.005 to 0.04). Later, the same correlation was obtained when applying the model to alkyl gallates in various stripped O/W emulsions [302–304], as well as to other phenolipids such as alkyl caffeates [305,306] or hydroxytyrosyl alkanoates [307] (Fig. 3). One of the main conclusions of these studies is that the accumulation of antioxidants in the interfacial region is a dynamic and evolving process depending on both their HLB and surfactant volume fraction. On one hand, the highest incorporation of the antioxidant occurs when their HLB is in the medium range, usually 8–11, and of the same order of magnitude as the interface. On the other hand, the interface volume fraction depends on the initial emulsifier content and the number of antioxidant molecules that incorporated into the interfacial region. As a result, increasing the surfactant volume fraction favors the incorporation of the antioxidant into the interfacial region and modifies its overall HLB, but as the interfacial volume simultaneously increases, the effectiveness of the antioxidants may be reduced due to dilution effects or, conversely, enhanced. In addition, increasing the surfactant content results in a decrease of the intensity of the cut-off effect, which may disappear completely with a large excess of emulsifier.

This is consistent with the formation of micelles of excess surfactant which act as reservoirs capable of solubilizing antioxidants [308] and modifying their partitioning in the emulsion with, as a consequence, a drastic change in their apparent antioxidant capacity. This can lead to a decrease in antioxidant capacity when amphiphilic phenolipids are extracted from the interface by surfactant micelles or, conversely, to an improvement when the more lipophilic species are transferred from the core of the oil droplets to the aqueous or interfacial phases [79].

As the pseudophase model cannot distinguish the interfacial region from emulsion droplets or micelles, this phenomenon was experimentally revealed in various studies. When evaluating alkyl rosmarinates (C4–20) in a stripped tung O/W emulsion stabilized with Brij 35 at a

Table 1
Critical chain lengths (CCL) within phenolipid series.

Phenolipids	Alkyl chains tested[a]	Lipid system	Emulsifier	CCL[b]	Remarks	Reference
Hydroxytyrosyl alkanoates	0, 2, 4, 8, 12	Fish O/W emulsions	Lecithin	8		[292]
Alkyl rosmarinates	0, 1, 4, 8, 12, 16, 18, 20	Tung O/W emulsion	Brij 35	8		[293]
Alkyl rosmarinates	0, 4, 8, 12, 18, 20	Soybean O/W emulsion	Tween 20	4		[180]
Alkyl coumarates	1, 4, 8, 12, 16, 18, 20	Tung O/W emulsion	Brij 35	12	Very weak antioxidant activity of all phenolics	[294]
Alkyl ferulates	1, 4, 8, 12, 16, 18, 20	Tung O/W emulsion	Brij 35	4–12		[294]
	0, 1, 4, 8, 12, 16, 20	Fish oil-enriched milk	–	1	Pro-oxidant effect of C12 and C8; C16 and C20 almost inactive	[295]
	1, 4, 8, 12, 16, 18, 20	Tung O/W emulsion	Brij 35	8		[294]
Alkyl caffeates	0, 1, 4, 8, 12, 18	Fish oil-enriched mayonnaise	–	4–12	Rapeseed oil-based mayonnaise	[296]
	0, 1, 4, 8, 12, 16, 20	Fish oil-enriched milk	–	1–4		
Alkyl protocatechuates	1, 2, 4, 6, 8, 10, 12, 14, 16, 18	Tung O/W emulsion	Brij 35	2–4	C2-C6 acted as chain-breakers, while C12-C20 as retarders	[297]
Natural rye bran alkylresorcinols	17, 19, 21, 23, 25	Algae O/W emulsion	Brij L23	21	All alkyl resorcinols were more effective than orcinol	[298]
Alkyl gallates	0, 3, 8, 12, 16	Spray-dried emulsion (WPI + caseinate + sunflower and fish oils)	–	8	Very slight cut-off effect. Hydrophobic gallates (≥C8) are more effective in encapsulated fat than in surface free fat	[299]

[a] Number of carbon atoms in the alkyl chain.
[b] Critical chain length: number of carbon atoms in the alkyl chain at the maximum antioxidant capacity.

concentration lower than its CMC (no surfactant micelles), Laguerre et al. [293] found that the amphiphilic C8 ester, preferentially located at the interface, was the best at preventing lipid oxidation, whereas highly hydrophobic C16-C20 esters were almost inactive due to their concentration within the oil droplets. They further showed that C16-C20 esters were gradually solubilized in the aqueous phase when increasing Brij 35 amount way above its CMC. The same phenomenon was later observed with alkyl rosmarinates in Tween 20-stabilized soybean O/W emulsion where, at low surfactant concentration, the C20 ester appeared to be the least efficient antioxidant and the C4 ester the best [180]. They showed that increasing the amount of Tween 20 micelles in emulsions resulted in a dramatic increase in the concentration of C20 ester in the aqueous phase (>7.5-fold) and a concomitant enhancement in its antioxidant activity. Finally, another study [169] found consistent results when investigating the effects of SDS concentration (below and above its CMC) and mode of incorporation (i.e., before or after high-pressure homogenization of a coarse emulsion) of alkyl gallates (C3-C16) on the oxidative stability of SDS-stabilized rapeseed O/W emulsions. They observed that regardless of the situation, the antioxidant capacity of gallates increased with the length of the alkyl chain until a plateau was reached for C16 ester. However, the incorporation of phenolipids before homogenization had a significant positive effect on the efficacy of all the esters, especially the most hydrophilic ones (C0-C3), this effect being much more pronounced in the presence of SDS micelles. In addition to the amount, the nature of the surfactant is also of paramount importance in establishing a cut-off effect and the associated CCL. For example, when alkyl gallates were used as antioxidants in stripped O/W emulsions, replacing the emulsifier Tween 20 (polyoxyethylene-sorbitan monolaurate) with Tween 80 (polyoxyethylene-sorbitan monooleate) increased the CCL from 4 to 8, all other things being equal [301–303]. Gonzalez et al. [309] also evaluated alkyl gallates in non-stripped fish O/W emulsions stabilized with anionic (Tween 20) or charged (lecithin) emulsifiers. While a clear cut-off effect occurred at CCL = 6–12 for lecithin-stabilized emulsions, no such behavior was observed for Tween 20, for which the antioxidant efficacy gradually increased with alkyl chain lengthening. Finally, all gallates showed a pro-oxidant behavior with SDS as emulsifier. Sørensen et al. [310] investigated the efficacy of caffeate esters (C0-C16) in fish O/W emulsions stabilized with Tween 80 or Citrem. In the presence of endogenous tocopherols, no cut-off effect was observed in both Tween 80- and Citrem-stabilized emulsions, whereas alkyl caffeates were the most efficient antioxidants in stripped-based O/W emulsions stabilized with Tween 20, with a cut-off effect centered on the C16 ester. The authors suggested that the presence of tocopherols may have favored the micellization of caffeates by the emulsifier, thus reducing or eliminating their antioxidant activity.

From the above, it can be concluded that the cut-off effect of the antioxidant activity of phenolipids in emulsions is a generic phenomenon, but one that occurs under specific conditions. It reflects the complexity of the reactions and interactions of antioxidants with system components, first and foremost the emulsifier, whose type and concentration are particularly critical. It is therefore difficult to predict exactly which antioxidant will perform best and at what level in a given system, much less in complex real food systems, and to date experiment remains the most effective means of addressing this issue.

5.2. Peptides (e.g., derived from by-products)

During the last decades, there has been an increasing focus on the production of antioxidant peptides from various protein sources such as aquatic, terrestrial plants, terrestrial animals and dairy resources [311,312]. In addition, many recent studies have focused on the use of protein-rich side-streams from food production to yield antioxidant peptides. In a similar fashion to antioxidant phenolics, antioxidant peptides can function either as free radical scavengers by hydrogen transfer or electron donation and/or they can chelate metal ions.

5.2.1. Top-down approach to obtain antioxidant peptides

Traditionally, a top-down approach has been used to produce antioxidant protein hydrolysates/peptides. This approach is based on a trial-and-error process starting with the evaluation of the ability of a range of different proteases to produce hydrolysates with different degrees of hydrolysis. Enzymes are added individually, or in combination in different concentrations. Subsequently, the hydrolysates are tested directly, or they are fractionated before being assessed for their antioxidant activity to determine the optimal conditions in that respect. Most studies have evaluated the antioxidant activity of the hydrolysates/peptides using different in vitro assays such as 2,2-Diphenyl-1-picrylhydrazyl (DPPH) scavenging activity, reducing power, 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS) scavenging activity and/or Fe^{+2} chelating activity.

It has been suggested that the number and location of hydrophobic amino acids (Leu, Val, Ala, Pro, Phe), aromatic amino acids (Tyr, Trp, His), sulfur amino acids (Cys, Met), acidic (Glu), and basic (Lys) amino acids influence the antioxidant capacity of peptides. Particularly, hydrophobic amino acids have been suggested to play a large role for the peptides' ability to scavenge free radicals [313]. Likewise, the ability of Phe, Tyr, and Trp residues to act as chelators of metal ions has been reported [314]. However, the antioxidant activity of peptides is not only dependent on the individual amino acids, but also on the amino acid sequence, length, structure and charge of the peptides as will be further touched upon below.

Moreover, peptides may exert different antioxidant properties than observed in in vitro assays when added into complex food systems. Some studies have investigated the ability of hydrolysates/peptides obtained by the top-down approach to inhibit lipid oxidation in O/W emulsions (e.g., [315–317]), but only few studies, if any, on the application in real food emulsions are available.

5.2.2. Bottom-up approach to obtain antioxidant peptides

Recently, a novel methodological approach was developed for discovering antioxidant peptides using peptidomics and bioinformatics tools [318]. This new approach implies that the amount of work and resources allocated for this process can be reduced using computational approaches for prediction of antioxidant peptides. The AnOxPePred tool was published in 2020 [318] and predicts the antioxidant activity of peptides using a convolutional neural network. It is an open source and can be accessed via its web server (https://services.healthtech.dtu.dk/services/AnOxPePred-1.0/). The developed model was trained on a curated dataset consisting of experimentally tested antioxidant and non-antioxidant peptides and uses deep learning for the prediction. The AnOxPePred tool can be used by submitting proteins or peptides in a single sequence or several sequences at once. The results are obtained as prediction scores indicating the radical scavenging and metal chelating activities. After testing the functional properties of selected peptides from the prediction list, bottom-up proteomics is applied to obtain antioxidant peptides from the protein source of interest. The proteomics workflow allows the design of downstream processing by targeted enzymatic hydrolysis by the release of identified abundant antioxidant peptides derived from various protein sources.

In a recent study, antioxidant peptides derived from potato, seaweed, microbial, and spinach proteins were identified based on the above-mentioned novel approach [319]. Peptides that scored the highest based on their radical scavenging activity were screened using in vitro DPPH radical scavenging activity (IC50 $\leq$ 16 mg/mL) and a set of peptides was selected based on their prediction scores, in vitro DPPH radical scavenging activity, their relative abundance in their parent proteins and their potential to be released by enzymatic hydrolysis using trypsin for further evaluation of their activity in a model O/W emulsion stabilized with Tween 20. A similar approach was also followed for metal chelator peptides by using the ferrozine assay instead of the DPPH radical scavenging assay [319]. However, the results showed inhibition factors lower than 30% and were inconsistent and not replicable. This

study highlighted the lack of reliable screening techniques for testing the metal chelation of synthetic peptides and the need for new advanced techniques. On the other hand, other important parameters for metal chelating activity were considered such as isoelectric point and net charge at pH 7.0 for the selection of metal chelating peptides. Results showed that all the peptides provided better or similar oxidative stability compared to the control emulsion without antioxidants and thus prevented lipid oxidation in a model emulsion system. Particularly, charged peptides performed better than neutral ones, and active peptides' lengths ranged between 6 and 14 amino acids. This study demonstrated the potential of bioinformatics and proteomics for identifying natural, sustainable antioxidant peptides abundant in parent proteins. The methodology enables precise peptide targeting through designed enzymatic hydrolysis, using protease specificity and bioinformatics sequence analysis.

The antioxidant effect of the selected peptides was also evaluated in both low-fat emulsion at pH 4.0 and in mayonnaise [320]. Even though the antioxidant activity of peptides was different in both systems, the performance of peptides highlighted the importance of concentration, composition, and structure (e.g., pI and charge) for emulsion stabilization. Notably, peptide net charge significantly influenced metal chelation. Anionic peptides in the aqueous phase of pH 4.0-emulsions and mayonnaises enhanced their oxidative stability. These results emphasize that peptide potential cannot be extrapolated between matrices due to the complexity of real food systems and the breadth of influencing factors. Overall, the prediction scores did not fully correlate with the experimental results; however, the scoring of the peptides by the AnOXPePred model may help to eliminate peptides without antioxidant activity and target the high-potential ones. Therefore, more research is still needed to fully understand the relationship between the molecular structure of peptides and their antioxidant efficacy in food emulsions.

Peptidomics offers insights into targeted hydrolysis by identifying enzymes with specific cleavage sites. The use of in silico proteolysis can enable the identification of the most efficient enzymes for the production of antioxidant protein hydrolysates. This approach has also been used for obtaining emulsifier peptides as reported in the review by García-Moreno et al. [321]. Although the approach described above relied on the AnOXPePred model for the prediction of both radical scavenging and metal chelation activities, there are also other prediction tools available. For example, the hard and soft acid and base theory (HSAB) [322] has been used to predict peptide-metal ion interactions. The hard/soft acid distinction can be used to explain the metal ion behavior in the presence of a peptide. The HSAB theory states that in order to form a bond between two atoms, one atom behaves like a Lewis acid whereas the other one behaves like a Lewis base. Metal ions are electron pair acceptors, and are thus Lewis acids, whereas peptides are electron pair donors, and thus are Lewis bases. Stable complexes are formed between Lewis acid and Lewis base having the same character, namely hard acid with hard base, and soft acid with soft base. Metal ions can be classified as hard acids (e.g., Fe(III), Ca(II) and Mg(II), or soft Lewis acids (e.g., Cu(I)), whereas Cu(II), Ni(II), Fe(II) have properties in between. Based on the amino acid composition, the amino acid-metal ion interaction can thus be predicted.

5.2.3. Screening of metal chelating peptides

Due to the presence of trace metals in most food systems, the metal chelating activity of antioxidants is often required for an antioxidant to be efficient in a food system. Therefore, metal chelation activity is an important property to screen for when evaluating the potential of antioxidant peptides. However, as evoked above, the ferrozine assay has limitations as a screening tool for peptides and in fact, also for many other antioxidants.

Therefore, recent research has looked into more advanced, alternative tools to evaluate the metal binding properties of peptides such as surface plasmon resonance (SPR), electrically switchable nanolever technology (switchSENSE®) and immobilized metal ion affinity chromatography (IMAC). The SPR technology is an optical technique for the determination of dissociation constants (K_D) in ligand-analyte interactions. The ligand is immobilized, and the analyte forms a complex with the immobilized ligand according to its related affinity. The switchSENSE® technology is based on electro-switchable DNA nanolevers and is used to study biomolecule interactions in real time between proteins immobilized on the nanolevers and analytes such as proteins, nucleic acids, or small molecules. IMAC is mainly based on the interactions between the immobilized metal ions and the electron donor groups of molecules that flow in a mobile phase, thus it can be used to separate peptides according to their metal binding properties. The reader is referred to [323] for more details on these techniques. SPR and switchSENSE® have been used to screen hydrolysates for the presence of metal chelating peptides [324,325] and for investigating the affinity of synthetic peptides for immobilized Ni^{2+}. IMAC has, for example, been used to fractionate pollock skin collagen-derived mineral chelating peptides [326] or to purify metal chelating peptides from oyster protein hydrolysate [327] and rapeseed protein hydrolysate [328].

However, it remains to be investigated to which extent there is a good correlation between the ranking of the metal chelating properties of hydrolysates and/or peptides obtained with these tools and the antioxidant efficiency obtained in real food systems.

5.3. Antioxidant-loaded Pickering particles: purposely designed particles (bottom-up) vs natural structures (top-down)

In addition to identifying and/or generating new antioxidant molecules, as in the aforementioned examples, another route to improve the protection of emulsified lipids against oxidation is to increase the efficiency of well-known antioxidants by controlling their localization in emulsions, and in particular, by anchoring them at the oil-water interface. A pathway to do so can be to entrap antioxidants in Pickering particles, of which the emulsion stabilization principle was explained in section 3.2.2. As exemplified in this earlier part, although antioxidant-free Pickering particles do not have obvious intrinsic potential at protecting oil droplets against oxidation through a physical barrier effect, it is still feasible to functionalize such particles to mitigate lipid oxidation by assigning them an additional role as an antioxidant reservoir. This concept was patented and published by Schröder et al. [329,330]. This work demonstrated that encapsulating antioxidants such as α-tocopherol or carnosic acid within colloidal solid lipid particles (CLPs) used as Pickering stabilizers for O/W emulsions greatly improved oxidative stability compared to a control Pickering emulsion with a similar overall composition and structure, but where the antioxidant was initially dissolved in the liquid oil phase. In this innovative emulsion structure, the antioxidant was gradually released from the interfacial particles into the core of the liquid oil droplets, suggesting that CLPs act as a reservoir of antioxidants at the critical interfacial zone, thus extending their interfacial residency time. Interestingly, when antioxidant-loaded CLPs were introduced only in the continuous phase, there was no observable antioxidant-enhancing effect, underscoring the significance of their interfacial location [329]. This concept of antioxidant-loaded Pickering particles has also been applied to other combinations of carrier particles and antioxidants. Protein-based particles, such as zein or gliadins (i.e., hydrophobic prolamins from maize or gluten, respectively) combined with hydrophilic phenolics, have shown promise in forming composite particles through antisolvent precipitation. For instance, zein-tannic acid and gliadin-proanthocyanidin particles led to Pickering emulsions with significantly higher oxidative stability compared to bulk oil or control protein-stabilized emulsions [331,332]. In another study, emulsions stabilized by gliadin-proanthocyanidin composite particles exhibited superior protection against lipid oxidation compared to control emulsions stabilized by antioxidant-free particles [333], and similar protective effects were reported in high internal phase emulsions stabilized by epigallocatechin gallate-soy protein particles [334]. A recent development includes dendritic mesoporous silica nanospheres

(DMSNs), which function both as nanocarriers for hydrophilic or hydrophobic antioxidants (demonstrated for epigallocatechin gallate and resveratrol) and as Pickering stabilizers [335]. Although this system was only tested for stabilizing flavor oil (not PUFA-rich oil), the particles effectively retained the targeted antioxidant within their internal structure and significantly protected citral against oxidation. These advanced hierarchical designs for bi-functional Pickering particles have established the proof of concept for interfacial antioxidant reservoirs and offer promise for enhancing the effectiveness of natural antioxidants. However, a major drawback that may limit their widespread application is the complexity and cost of such a strategy, which may not align with the current trend towards natural, clean-label, and minimally processed food systems. An alternative approach, while still utilizing the concept of antioxidant-loaded Pickering particles, could involve leveraging the endogenous antioxidant content of naturally occurring particles (i.e., deploying a "top-down" approach rather than "bottom-up", as in the previous examples), such as food and biobased product side-streams. While the level of control over the composition and structure of such particles will be necessarily lower than that of tailor-made composite particles, they hold significant potential in terms of sustainability, naturalness, and interfacial retention of antioxidants [159]. One example of such a strategy involves Pickering emulsions stabilized with milled red rice particles containing anthocyanins [336]. This study showed that these polyphenol-rich particles provided better protection for emulsified oil droplets against oxidation compared to white rice starch-stabilized emulsions and bulk oil. Another recent study focusing on preparing Pickering emulsions using various plant-based particles, demonstrated that emulsions stabilized by matcha tea and spinach leaf particles were highly stable against lipid oxidation, in contrast to reference emulsions stabilized by conventional emulsifiers [337]. This protective effect is likely attributed to the presence of endogenous antioxidants in these fractions, such as free radical-scavenging phenolics and chelating organic acids, respectively. Using such natural particles appears to be a promising approach for physically and oxidatively stabilizing clean-label emulsions. Given the widespread presence and diversity of phenolic antioxidants in food-compatible plant materials, there are undoubtedly numerous prospective sources of Pickering particles to explore.

To be complete, there has been a notable shift in the usage of the term "Pickering emulsions," now encompassing various food emulsions formulated with a range of aggregates or supramolecular structures [16]. This deviates from the initial definition characterizing Pickering emulsions as solely stabilized by solid particles firmly attached to the oil-water interface. Most biobased particulate materials inherently exhibit greater complexity compared to the inorganic model particles employed in the early stages of Pickering research. In itself, this is not an issue as the 'Pickering era' can be seen as a spectacular entrance for exploring new biobased ingredients as antioxidant solutions, as exemplified in the next section (5.4). Nevertheless, in our opinion it is important to reserve the use of the term 'Pickering emulsions' to systems that truly meet the aforementioned physical definition.

5.4. Towards clean-label and multifunctional ingredients

Effective and food-grade antioxidants such as EDTA have been used for decades but have fallen out of grace by consumers due to their unnatural perception [338]. This has prompted research into natural, biobased alternatives. For plain vegetable oils, the use of natural plant extracts has been effective in retarding lipid oxidation [339] and these have also been proven effective in food emulsions [340]. Agro-food by-products have been proposed as promising potential sources of ingredients with antioxidant properties [341]. A range of natural and potentially clean-label ingredients have been shown to be effective as antioxidants in food emulsions, but the mechanisms of actions were typically assessed at the level of phenolic content only (Table 2). Most ingredients in Table 2 are extracts of natural products, some of them originating from waste- or side-streams. For most of the ingredients in Table 2, their antioxidant activity was attributed to presence of phenolics in the water phase of food emulsions, yet without establishing a clear causal mechanistic link.

Table 2
Overview of (potential) clean-label ingredients with antioxidant activity in O/W food emulsions.

Food emulsion	Biobased ingredient	Proposed antioxidant components/ mechanisms	Reference
Mayonnaise	Apple pomace	Phenolics	[342]
	Ginger powder	Not defined	[343]
	Grape seed extract	Radical scavenging by phenolics	[344]
	Grape, apple vinegar	Phenolics	[345]
	Balsamic vinegar	Melanoidins	[346]
	Apple peel extract	Phenolics	[347]
	Brown seaweed extracts	Phenolics	[348]
	Beet root	Phenolics, betalain	[349]
	Beet root peel	Phenolics, betalain	[350]
	Tomato by-product	Carotenoids	[351]
	Purple corn extracts	Anthocyanins	[352]
	Cucumis seed extracts	Phenolics	[353]
Vegan mayonnaise	Olive mill waste	Phenolics	[354]
	Fruit flour	Phenolics	[355]
	Olive vinegar	Phenolics	[356]
	Cumin cake extract	Phenolics, radical scavenging	[357]
Model O/W emulsion	Roasted coffee fractions	Partitioning of MRPs	[358]
	Olive leaf vinegar	Phenolics, oleuropin	[359]
	Rice bran extracts	Not specified	[360]

Note: Vegetable oils with high natural antioxidant content have not been listed.

In food emulsions, as detailed earlier, it has been proposed that the most effective antioxidants are likely to specifically act at the oil-water interface, since this is where oxidation is initiated. Maillard reaction products (MRPs) [361] have been put forward as surface-active antioxidants that specifically act at colloidal interfaces [362]. A proof-of-principle of using MRPs as antioxidants has recently been demonstrated for coffee brew fractions in model emulsions [358]. A specific antioxidant role was assigned to melanoidins, which are high molecular weight MRPs [363] that also have a strong tendency to adsorb and stabilize droplet interfaces. Melanoidins may also be responsible for the antioxidant activity of specific vinegars. The antioxidant effect of balsamic vinegar was already recognized at an early stage [346,364] and was followed up by studies testing the efficacy of vinegars manufactured from other sources [356,359]. The mechanism by which vinegars can act as antioxidants has often been ascribed to their low molecular weight phenolic content (Table 2), which, due to their polarity, are not likely to be directly active at the droplet surface. For balsamic vinegars, it has been established that they are a rich source of melanoidins [365–367], and their antioxidant activity in mayonnaise was proposed at an early stage [346]. Whether and how melanoidins present in vinegars can act as antioxidants in food emulsions remains, however, to be elucidated.

It is worth mentioning that regulatory aspects regarding the utilization of by-products in foods is a complex landscape, particularly evident within the European Union (EU) where stringent directives and legislation usually apply. In the EU, the valorization of food by-products encounters regulation through various legislative frameworks [368,369]. EC Regulation No. 178/2002 establishes general guidelines

ensuring food safety, encompassing by-products used as food ingredients. However, when these by-products function as natural additives, compliance with the Novel Food Regulation (EU Regulation No. 2015/2283) becomes mandatory. This regulation delineates novel food categories originating from plants, animals, microorganisms, and novel production technologies. These foods require authorization and indexing on the list of authorized novel foods managed by the European Food Safety Authority (EFSA) [368]. It should be pointed out that the lack of a clear definition of food waste and by-products poses a challenge, hampering accurate assessment and impeding measures to address food loss and waste. Therefore, clear definitions of these terms seem crucial for future research and business programs to promote innovation in a circular economy scheme [368,370]. Harmonizing policies, reducing administrative burdens, and establishing stable regulations are pivotal to foster investments and facilitate the transformation of waste into valuable resources. Furthermore, the Codex Alimentarius, an initiative by the Food and Agriculture Organization (FAO) and the World Health Organization (WHO), serves as a global reference for food safety, establishing international standards and guidelines [371]. These guidelines often include permissible limits for contaminants, additives, and nutrients, which are crucial to develop sound food safety regulations. Regulatory bodies such as the FDA (US) and EFSA determine acceptable daily intake (ADI) levels for additives to safeguard consumers from harmful substances. However, challenges persist in assessing by-products' suitability and safety due to the absence of specific legal limits. Therefore, reference values for evaluating by-products in that respect often rely on limits set for original materials or similar matrices, leading to complexity in interpreting results and ensuring consumer safety [370].

To wrap-up, while existing regulations provide a framework for valorizing by-products in foods, challenges remain in establishing comprehensive legislation, necessitating clear definitions and harmonization to promote innovation and ensure food safety in the utilization of by-products within the food industry.

6. Conclusions and perspective

In 2000, McClements and Decker [3] highlighted the complexity of the reactions at stake during the oxidation of O/W emulsions and the importance of the molecular environment. The present review highlights the progress that has been done over the past two decades towards a better understanding of this subject. The number of studies to elucidate lipid oxidation in O/W emulsions has exponentially increased, providing new insights into "the relationship between the molecular structure of lipids, antioxidants, and pro-oxidants; their partitioning between oil, aqueous, and interfacial regions", "the influence of droplet characteristics", and "the importance of interfacial characteristics […] to new strategies for retarding lipid oxidation", for which further research was identified as of pivotal importance 20 years ago [3]. This latter point is not only true when it comes to the surface of the oil droplets, but also when it comes to the interfacial areas from a more holistic perspective, i.e., including other colloidal structures in the oil and aqueous phases. Accordingly, the simplistic paradigm of solely considering emulsion droplets versus non-adsorbed emulsifiers must evolve. Embracing a nuanced perspective acknowledges the coexistence of multiple colloidal structures spanning various sizes, including lipid-bearing entities, within the colloidal landscape [24]. Understanding these diverse colloidal structures is paramount as they may significantly influence and govern lipid oxidation reactions.

On top of that, more effort has been done to not only consider lipid oxidation on its own, but also look at other reactions (e.g., protein oxidation, non-enzymatic browning reactions, surfactant oxidation) that could influence the multifaceted chemical pathways. Still, further investigation is needed to fully understand the complexity of lipid oxidation in real food emulsions, in particular in regard to the interactions between different factors and/or molecules. Next to state-of-the-art methodological advancements that are currently under active development, the establishment of standardized practices will be pivotal in addressing the complexity of lipid oxidation reactions [372]. This alignment in methodologies across research endeavors will not only enhance comparability but also facilitate a more holistic understanding of oxidation mechanisms. Simultaneously, the evolution of modelling techniques is emerging as a critical frontier. Refinement and development of these models will be indispensable in predicting and simulating the behavior of lipid oxidation within such systems, aiding in experimental design and unravelling complex interrelationships between the involved factors.

Therefore, the future trajectory of research on lipid oxidation in O/W emulsions requires an integrated approach. Combining methodological advancements, sophisticated modelling techniques, and a refined understanding of the intricate kinetic and colloidal aspects will unravel complexities inherent to this phenomenon. Such endeavors will pave the way for innovative strategies to control and mitigate oxidation reactions in food emulsions, ensuring enhanced product stability and quality within an evolving landscape of more sustainable, clean-label and mildly processed ingredients, which are often less pure and for which compositional information has been, so far, overlooked.

Funding sources

This work received funding from the Netherlands Organization for Scientific Research (NWO) in the framework of the Innovation Fund for Chemistry (grant number 731.017. 301) and from the Ministry of Economic Affairs in the framework of the "TKI/PPS-Toeslagregeling". The funders had no role in the study design, in the collection, analysis, or interpretation of data, in the writing of the manuscript, or in the decision to publish the article. CBC would like to acknowledge Nantes Métropole and Région Pays de la Loire (France) for support of her research through her "Connect Talent" grant (VESTA, 2021-2025).

CRediT authorship contribution statement

Marie Hennebelle: Conceptualization, Investigation, Project administration, Writing – original draft, Writing – review & editing. **Pierre Villeneuve:** Conceptualization, Investigation, Writing – original draft, Writing – review & editing. **Erwann Durand:** Conceptualization, Investigation, Writing – original draft, Writing – review & editing. **Jérôme Lecomte:** Conceptualization, Investigation, Writing – original draft, Writing – review & editing. **John van Duynhoven:** Conceptualization, Investigation, Writing – original draft, Writing – review & editing. **Anne Meynier:** Conceptualization, Investigation, Writing – original draft, Writing – review & editing. **Betül Yesiltas:** Conceptualization, Investigation, Writing – original draft, Writing – review & editing. **Charlotte Jacobsen:** Conceptualization, Investigation, Writing – original draft, Writing – review & editing. **Claire Berton-Carabin:** Conceptualization, Investigation, Project administration, Writing – original draft, Writing – review & editing.

Declaration of competing interest

JvD is employed by a company (Unilever) that manufactures and markets food emulsions.

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