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New Trends in Natural Emulsifiers and Emulsion Technology for the Food Industry

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Abstract

The food industry depends on using different additives, which increases the search for effective natural or natural-derived solutions, to the detriment of the synthetic counterparts, a priority in a biobased and circular economy scenario. In this context, different natural emulsifiers are being studied to create a new generation of emulsion-based products. Among them, phospholipids, saponins, proteins, polysaccharides, biosurfactants (e.g., compounds derived from microbial fermentation), and organic-based solid particles (Pickering stabilizers) are being used or start to gather interest from the food industry. This chapter includes the basic theoretical fundamentals of emulsions technology, stabilization mechanisms, and stability. The preparation of oil-in-water (O/W) and water-in-oil (W/O) emulsions, the potential of double emulsions, and the re-emerging Pickering emulsions are discussed. Moreover, the most relevant natural-derived emulsifier families (e.g., origin, stabilization mechanism, and applications) focusing food applications are presented. The document is grounded in a bibliographic review mainly centered on the last 10-years, and bibliometric data was rationalized and used to better establish the hot topics in the proposed thematic.

Keywords: natural emulsifiers, biosurfactants, emulsion technology, Pickering emulsions, food applications, market and product trends

1. Introduction

Food emulsions are produced from two immiscible liquids (usually oil and water), which in the presence of an emulsifier and by applying an emulsification method, can be dispersed one into another. Some typical examples include mayonnaise, salad dressings, sauces, milk, ice cream, and sausages. These systems can be used to encapsulate, protect, and deliver biocompounds, including vitamins, flavors, colorants, and nutraceuticals [1]. Emulsifiers are food additives acting by forming a physical barrier between the oil and water, enabling their compatibilization. Effective emulsifiers must be quickly adsorbed at the oil–water interfaces

leading to a rapid decrease in the interfacial tension, preventing droplets aggregation. Moreover, they must generate strong repulsive interactions promoting emulsion stability [2, 3].

Synthetic emulsifiers (e.g., Tweens and Spans) are well-known for their ability to form highly stable emulsions. However, consumers' preferences for healthy, sustainable and natural lifestyle habits have increased worldwide. Moreover, some studies have reported intestinal dysfunctions caused by synthetic emulsifiers [4, 5]. In this context, natural emulsifiers have emerged as great alternatives to replace their conventional counterparts, namely proteins [6], polysaccharides [7], phospholipids [8] and saponins [9]. Concerning protein-based natural emulsifiers, the most use ones come from animal sources (e.g., whey proteins, caseins, egg protein, gelatin) [10]. However, plant-based proteins have demonstrated to be good alternatives for their replacement in products with dietary restrictions (e.g., lactose-free) and in vegetarian and vegan foods. Moreover, plant-based proteins are more sustainable as they have a lower carbon footprint [11, 12]. Examples include pea [13, 14] and soy proteins [15], which have been reported for emulsions production.

Aligned with natural emulsifiers, Pickering stabilizers (in particular organic-based colloidal particles) are emerging as promising solutions. Pickering emulsions or particle-stabilized emulsions present high resistance to coalescence and Oswald ripening due to the tight fixation of the particles to the droplets surface [16]. Several food-grade particles have been studied, namely particles based on proteins [17], polysaccharides [18], and protein/polysaccharide complexes [19]. Furthermore, natural emulsifiers from microbial origin such as biosurfactants and bioemulsifiers are also potential alternatives to be explored in food emulsions [20, 21].

This chapter covers a bibliographic review focused on the last 10-years on natural emulsifiers and emulsion technology field. Research and market trends are also highlighted, showing the most relevant natural emulsifier families. Basic concepts concerning emulsion production, classification, and stabilization methods are introduced. A special emphasis is given to Pickering emulsions regarding novel trends in food emulsion systems.

1.1 Bibliometric and market trend analysis

According to the Research and Markets report, amidst the Covid-19 crisis, the global emulsifiers' market is projected to reach US\$ 6.1 Billion by 2027, growing at a Compound Annual Growth Rate (CAGR) of 4.8% over the forecast period (2020–2027). Particularly, natural emulsifiers' area is estimated to get US\$ 3.3 Billion, recording a 5.4% CAGR [22]. In agreement, the "Global Food Emulsifiers Market 2020-2027 report" from MarketResearch, foresees a high potential for the plant-based emulsifiers in the global food emulsifiers market [23].

Concurrently, scientific literature corroborates the global food emulsifiers report's projections. More than 8,000 documents were found using the terms "natural emulsifier*" OR "bioemulsifier*" OR "bio-emulsifier*" OR "biosurfactant*" OR "bio-surfactant*" OR "Pickering emulsion*" searched in title, abstract, keywords and Keywords plus sections using the Web of Science Core Collection (SCI-EXPANDED), in the 2010–2020 period. Excluding documents with early publication and applying the "Food Science and Technology" filter from WOS, 792 documents were found. By removing 4 documents from 2021 in a final manual screening, 788 documents were analyzed using Biblioshiny app from the Bibliometrix-R package (RStudio) [24] and VosViewer software [25]. The survey was performed on April 25th, 2021.

Table 1 presents some of the retrieved 788 documents concerning the application of natural emulsifiers or Pickering stabilizers in emulsion formation/stability,

Natural emulsifiers or Pickering stabilizers	Emulsification method	Main target	Reference
Zein-Chitosan complex particles	High-shear homogenization	Delivery system (Curcumin)	[26]
Mannoprotein	High-shear homogenization	Formation/Stability	[27]
Whey protein Gum arabic <i>Quillaja</i> saponin Lecithin	Dual-channel microfluidization	Formation/Stability	[28]
Gum arabic Beet pectin Corn fiber gum	High-shear homogenization Microfluidizer	Formation/Stability	[7]
Ginseng saponins	High-shear/ High-pressure homogenization	Delivery system (Astaxanthin)	[9]
Wheat gluten nanoparticles (WPN) WPN-xanthan gum nanoparticles	High-shear homogenization	Delivery system (β -carotene)	[29]
Pea protein microgel particles	High-pressure homogenization	Formation/Stability	[30]

Table 1.
Studies reporting the use of natural molecules and Pickering stabilizers selected from the retrieved 788 documents of the bibliometric search.

including their use in biocompound delivery systems. Some works regarding the production of bioemulsifiers or biosurfactants by microorganisms were also found [31, 32]. Several studies addressing Pickering emulsions and the use of high-pressure homogenization were identified.

Figure 1a shows the wordcloud from Author’s Keyword. The higher font size indicates an increased frequency of the keyword. **Figure 1b** also illustrates keyword co-occurrence network analysis; the terms distributed in the same cluster present the higher similarity, in comparison with the terms distributed in different clusters. “Pickering emulsions” is the most frequent keyword, followed by biosurfactant (**Figure 1**). Other keywords (e.g., whey protein, sodium caseinate, glycolipid, sophorolipids, rhamnolipids, *Quillaja* saponin) appeared in the wordcloud.

These findings substantiate the keyword co-occurrence analysis (**Figure 1**). 93 keywords (Author’s keywords) were organized in 9 clusters. The number of occurrences indicates the number of documents where the keyword appears. Each circle represents a keyword with at least 5 occurrences, being their areas proportional to the number of occurrences. The clusters are characterized by different colors and their words can be related.

Some clusters present words associated to recent trends in the area of natural emulsifiers. Clusters 1, 6, 8 and 9 refer to “Pickering emulsions” and other inter-related words, including nanoparticles, Pickering stabilization, and some commonly used Pickering stabilizers such as starch granules, cellulose nanocrystals and kafirin. Clusters 1 and 2 comprise terms related to the rheological properties of emulsions, an important parameter in food applications. The words included in clusters 4 and 5 are associated with microorganisms (e.g., *Pseudomonas aeruginosa*; *Starmerella bombicola*; *Bacillus subtilis*) and the biosurfactants they produce (e.g., rhamnolipids; surfactin; sophorolipids). *P. aeruginosa* is a food-borne pathogen and a source of rhamnolipids [33]. *Starmerella bombicola* is a non-pathogenic yeast

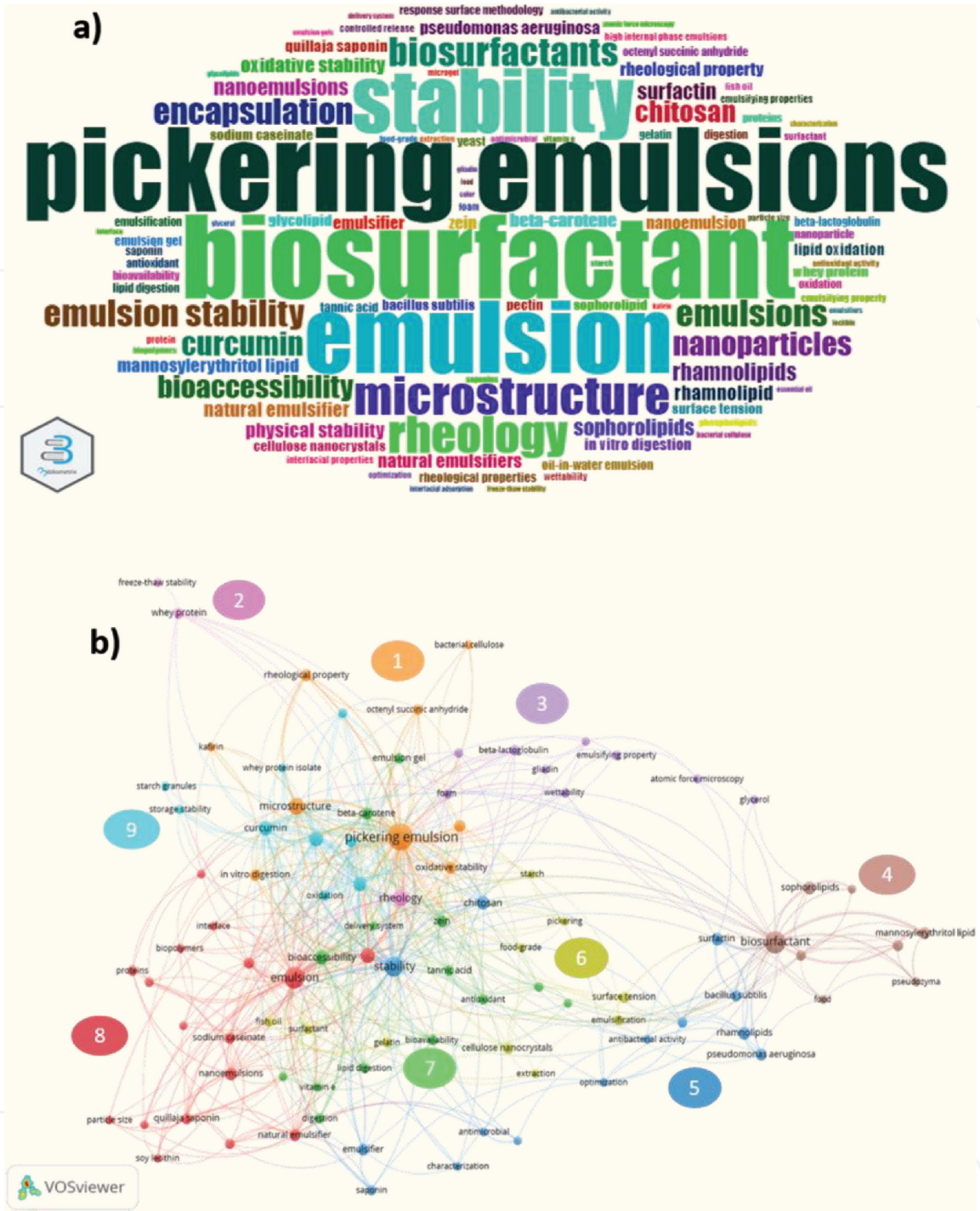


Figure 1. (a) Wordcloud from Author's keywords (100 keywords; minimum frequency of 5); (b) keyword co-occurrence network (9 clusters; Author's keywords; number of occurrences 5).

producing sophorolipids, whereas *B. subtilis* is a non-pathogenic bacteria yielding surfactin [31, 34]. Some of these biosurfactants have been applied in food emulsion systems (e.g., surfactin in O/W food emulsions [20]) due to their high ability to stabilize emulsions, and present antioxidant and antimicrobial properties. However, some aspects, especially safety, require attention as biosurfactants may be produced by pathogenic bacteria [35].

Cluster 7 and 9 are centered in words related to the biocompounds delivery systems, namely bioavailability/bioaccessibility, controlled release, encapsulation and examples of used biocompounds, such as beta-carotene, curcumin, and vitamin E. Clusters 8 and 9 refer to proteins, phospholipids, saponins and polysaccharides, such as whey protein isolate, soy lecithin, *Quillaja* saponin,

and pectin, respectively. Some of these natural emulsifiers also appeared in the wordcloud analysis, being the most used ones in the food science and technological fields.

In a general overview, the analysis showed the progressive interest in natural emulsifiers due to their relevance for the scientific and industrial communities, as well as for the global market. Moreover, Pickering emulsions are emerging as advanced emulsion technologies within future trends in the food industry.

2. Principal natural-based emulsifier groups

Natural emulsifiers belong to a broad range of chemical families and some main examples are shown in **Figure 2**. Within each family, aspects such as the used natural source or extraction method can lead to different properties. Therefore, the next sections summarize the most relevant families in the area of natural emulsifiers and their contextualization in the field of food applications.

2.1 Phospholipids

Phospholipids are amphiphilic molecules, and a main constituent of natural membranes. Their structure comprises a hydrophilic head holding a phosphoric acid (H_3PO_4), combined with a hydrophobic tail composed by one or two non-polar fatty acids. They comprise groups as glycerophospholipids or sphingolipids, with lecithins (glycerophospholipid) assuming an important role. Phospholipids can be obtained from diverse natural sources, including milk, vegetable oils (soybean, rapeseed or sunflower), egg yolk, meat and fish [36, 37]. Specifically, lecithins are known to be good stabilizers for food emulsions, for example the ones derived from soy or egg yolk are applied in mayonnaise, creams, or sauces [38]. Other phospholipid examples include phosphatidylcholine, phosphatidylglycerol, phosphatidylethanolamine, phosphatidylinositol, phosphatidylserine, phosphatidic acid, sphingomyelin. The amphiphilic character of these compounds supports their capacity to stabilize emulsions. Concurrently to their ability to stabilize emulsions

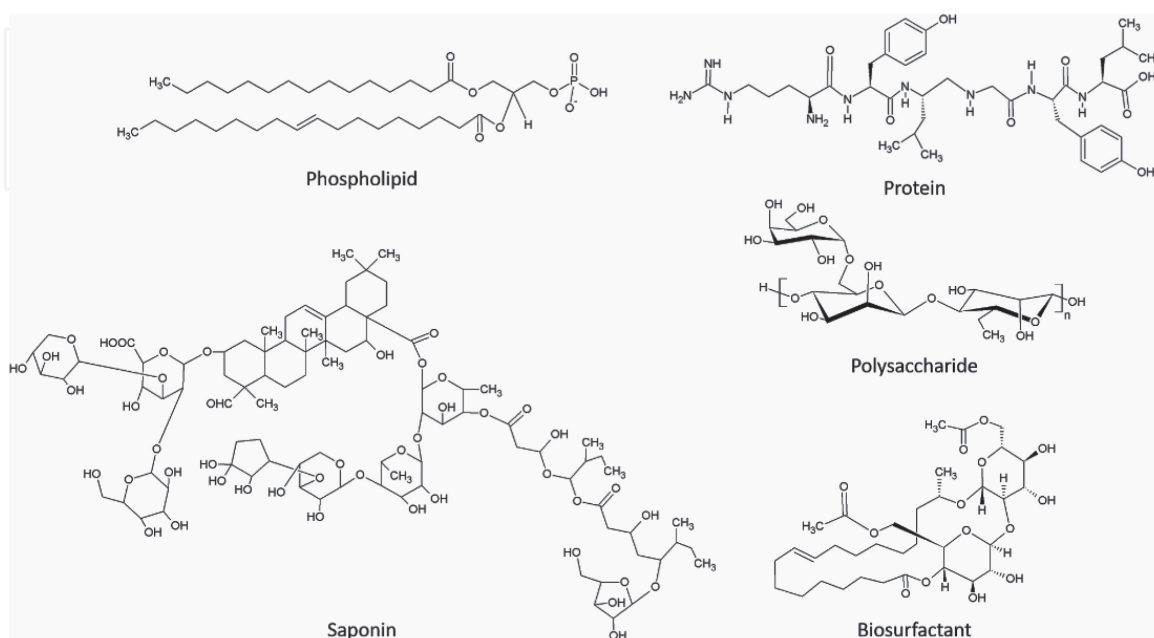


Figure 2.
 Representative chemical structures for each emulsifier family.

they can act as texturizing agents, thus influencing the organoleptic attributes of the final product [39].

2.2 Saponins

Saponins are a complex family derived from plants, constituted by triterpenes or steroid aglycones linked to glycosyl derived sugar structures [40]. Usually the aglycones involve pentacyclic triterpenoids with oleanolic acid and the sugars moieties comprise rhamnose, xylose, glucose or galactose [41]. Factors conditioning the composition of saponins are their botanical origin and extraction method. *Quillaja saponaria* Molina is the principal source of saponins, named *Quillaja* saponins, characterized by high contents of quillaic acid groups (hydrophobic) and rhamnose, galactose or glucuronic acids (hydrophylic) [42]. Saponins produce highly stable emulsions, including at the nanoscale, and at relatively low surfactant contents, with promising stability in terms of pH, ionic strength or temperature conditions [40]. Their promising properties avail their use in diverse applications, with examples of food-grade saponins applied in beverages added with flavors or bioactives such as vitamins [43]. More recently, the utilization of saponins was extended to the use of saponin-rich extracts obtained from plant sources [44], by-products and food wastes [40]. Besides the increased costs of using highly pure saponins, they provide weaker functional properties comparatively with extracts, due to the lack of additional bioactive compounds, e.g. polyphenols [45].

2.3 Proteins

Proteins are molecules resulting from the combination of 21 different amino acids, having diverse properties, including water solubility, which varies depending on their composition [46]. Structurally, the presence of both hydrophobic and hydrophilic amino acids confer an amphiphilic character, allowing them to be absorbed at oil/water interfaces, leading to emulsion stabilization [47]. However, proteins have low surface activity in comparison with conventional emulsifiers. This is attributed to the random distribution of the hydrophilic and hydrophobic groups within the peptide chains, limiting their adsorption. This effect is balanced by the protein film formation around the droplets, leading to stabilization through molecular interactions [48]. Diverse proteins (e.g., whey, casein, soy or faba bean proteins) have been tested in food applications, e.g., emulsions for the controlled release of lutein [49], w-3 oil [50], bioactive hydrophobic compounds [51], fish oil [52, 53] or β -carotene [54]. Their application in final products is still hindered by environmental conditions such as pH, temperature and ionic strength [48]. However, these drawbacks can be surpassed by using more complex formulations, namely by combining proteins with polysaccharides [48] or by chemically modifying the proteins through grafting with other compounds such as polyphenols [54].

2.4 Polysaccharides

Polysaccharides are biopolymers composed of monosaccharide units such as glucose, fructose, mannose or galactose, bonded by glycosidic bonds. Their structural rearrangement, i.e., type and number of monosaccharides, type of glycosidic bonds, molecular weight, electrical charge, branching degree, hydrophobicity and the presence of other groups (carboxylate, sulfate or phosphate), rule the polysaccharides functional properties such as solubility, rheology, and amphiphilic character, among others [10]. Their amphiphilicity depends on the presence of hydrophobic (glycolipids) and hydrophilic (hydroxyls) groups, being adsorbed

at the interface, forming a thick stabilizing layer (e.g., pectins, gum Arabic) [55]. Moreover, non-amphiphilic polysaccharides can contribute to emulsion stabilization due to their thickener role, increasing the viscosity and decreasing oil droplets' motion (e.g., alginates, carrageenan) [56]. Despite the high number of polysaccharides available in nature, only few are authorized as food emulsifiers in EU, namely alginic acid (E400), gum Arabic (E414), pectin (E440), cellulose and chemically modified celluloses (E460 to E469) [57]. Polysaccharides can be obtained from animal, vegetal, microbial fermentation or marine sources (algae), being their properties mostly dependent on the source and extraction process [10].

2.5 Natural based emulsifiers from microbial sources

Microbial synthetic routes are emerging as valuable sustainable and green alternatives to produce emulsifiers. They generate compounds with low ecotoxicity, biodegradability, stability (pH and salinity) and low critical micellar concentration (CMC), in addition to biological activity, biocompatibility and digestibility [58]. Emulsifiers produced by microorganisms are classified according to their molecular weight. Low molecular weight family includes glycolipids (e.g., rhamnolipids, sophorolipids, trehalose lipids) and lipopeptides (e.g., surfactin, iturin, fengycin) and are referred as biosurfactants. Polysaccharides, proteins, lipoproteins, and lipopolysaccharides belong to the high molecular weight family and are referred as bioemulsifiers [59, 60]. Glycolipids like rhamnolipids and trehalose lipids are mostly produced by bacterial strains like *Pseudomonas aeruginosa*, *Pseudomonas fluorescens*, *Rhodococcus erythropolis*, *Nocardia erythropolis*, *Arthrobacter sp.* or *Mycobacterium sp.* while sophorolipids are generally produced by yeasts (e.g. *Candida bombicola* or *Candida antartica*) or by filamentous fungi like *Aspergillus flavus* or *Rhizopus oryzae* [58, 61]. Lipopeptides can be produced by *Bacillus sp.*, *Serratia marcescens* and *P. fluorescens* [58]. Bioemulsifiers such as Emulsan/Biodispersan are commercially available products, being produced by *Acinetobacter spp.*, while mannoproteins are commonly obtained from the yeasts *Saccharomyces cerevisiae* or *Kluyveromyces marxianus* [61]. The excellent properties of both microbial derived biosurfactants and bioemulsifiers make them appealing as natural based emulsifiers for foods. Several studies reported the use of glycolipids for fat emulsions stabilization [62, 63], and glycolipids and lipopeptides as rheology modifiers in cookies and muffins dough [64–66]. Other works refer bioemulsifiers (e.g., exopolysaccharides, mannoproteins) as having high potential in aromas emulsification [67]. Nevertheless, the practical application in foods is still limited due to two main factors, their high production costs narrowing the commercial profit, together with the legal regulations that limit the use of compounds produced by microbial strains classified as pathogenic in food applications. Examples include the bacteria genera like *Pseudomonas* and *Bacillus*. In opposition, yeasts like *S. cerevisiae* and *Kluyveromyces lactis*, which are classified as GRAS organisms, are authorized for food applications [68].

3. Emulsion technology

Emulsions are colloidal systems constituted by two immiscible liquids (oil and water), formed in the presence of an emulsifier, and, usually, by applying an energy input. The emulsifier selection is therefore an important step to reach stability. They can be classified based on the hydrophilic region that correspond to ionic structures (anionic or cationic surfactants), change charge with pH (amphoteric surfactants) or present no charged centers (nonionic surfactants) [69]. Among them, nonionic surfactants are often used in food applications because

they are less toxic and less affected by pH and ionic strength changes [70, 71]. The choice of a nonionic surfactant can be based on the hydrophilic–lipophilic balance (HLB) index [72]. This scale (0–20), reflects the changing from hydrophobic to hydrophilic character, that is, a lower HLB value corresponds to a lipophilic surfactant being appropriate to stabilize water-in-oil (W/O) emulsions, whereas a high HLB indicates the ability to stabilize oil-in-water (O/W) emulsions, due to the strong hydrophilic balance [72].

3.1 Emulsion classification

Emulsions can be classified according to their typology and structure. The first refers to the relative distribution of the immiscible phases (oil and water), and the latter refers to the arrangement of the emulsified entities [73]. Considering the typology, they can be classified as simple (O/W and W/O) or double (oil-in-water-in-oil (O/W/O), and water-in-oil-in-water (W/O/W)) emulsions (**Figure 3**). Examples of O/W emulsions in food systems include products such as milk, sauces, beverages, yogurts, ice-creams, and mayonnaise [74]. W/O emulsions are not so frequent but can be found in butter and margarine [73, 75]. For double emulsions, W/O/W are the most used systems due to their ability to generate reduced-fat products, when compared to O/W emulsions. Moreover, they can serve as base systems to encapsulate and control the release of sensitive water-soluble compounds, such as flavors or bioactive ingredients [16, 75, 76].

Regarding structure, emulsions can be classified as macroemulsions (usually called emulsions), nanoemulsions, or microemulsions. These systems present specific physicochemical properties that influence their range of applications [71]. Emulsions and nanoemulsions are thermodynamically unstable systems because their free energy is higher than the one of the individual phases [74, 77]. Thus, considering that all systems tend to their lowest energy state, phase separation will occur. However, due to their kinetic stability, they may remain in a metastable state for a considerable period of time, delaying the phase separation phenomenon. The kinetic stability is governed by two mechanisms, namely the energy barriers between the two states (emulsified and separated phases) and mass transfer between the phases. Therefore, high energy barriers and slow mass transfer processes delay phase separation [78]. By contrast, microemulsions are

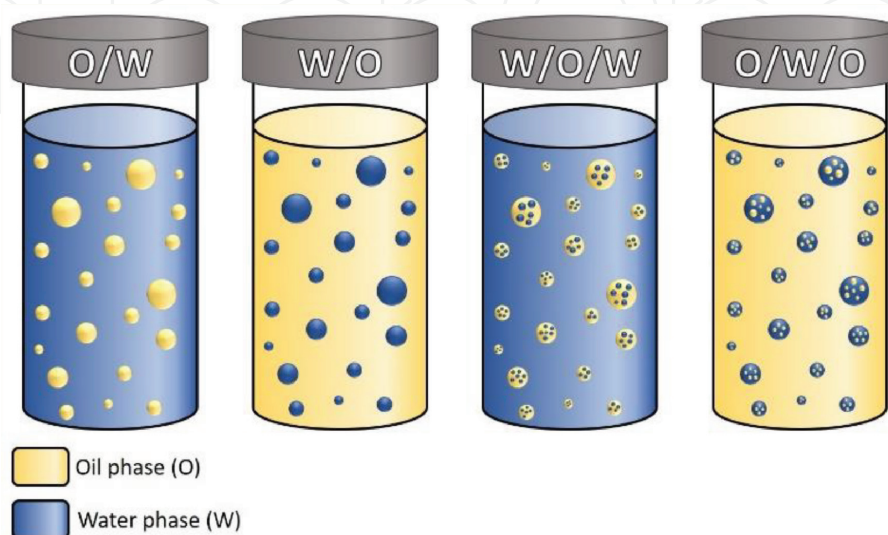


Figure 3.
Typology of simple and double emulsions.

thermodynamically stable systems because their free energy is lower than the one of separate phases. Thus, they can be formed spontaneously under particular compositions and temperature conditions. In practice, some energy input is needed due to the existence of kinetic energy barriers [71]. Regarding the droplet size, nanoemulsions and microemulsions present droplet sizes <200 nm, whereas emulsions hold sizes between 200 nm and 100 µm [16, 71].

Nanoemulsions and microemulsions are optically transparent or slightly turbid due to their small droplet size, being valuable for applications requiring transparency, such as soft drinks [79]. Comparatively with nanoemulsions, microemulsions require a higher emulsifier content, have a lower particle size, and droplets can assume a non-spherical shape, feature that can be used to differentiate the two systems. Emulsions are typically turbid to opaque and are used in creamy systems such as dairy products [80]. **Table 2** provides some application examples for each system addressing natural emulsifiers.

System	Type	Natural emulsifiers	Final applications	Reference
Emulsions	O/W	Whey protein	Ice-cream	[81]
	O/W	<i>Quillaja</i> saponin and soy lecithin	Coffee creamers	[82]
	W/O/W	Whey, rice and pumpkin seed proteins	Cheese	[83]
	O/W	Faba bean protein	Tofu and yogurts	[84]
	O/W	Pectin	Functional foods	[85]
	O/W	Rhamnolipid	Beverages	[86]
	O/W	Whey protein, locust bean gum, and iota-carrageenan	Mayonnaise, salad dressings, and sauces	[87]
	O/W	Modified starch	Dairy products	[88]
Nanoemulsions	O/W	Soy lecithin	Fruit juices	[89]
	O/W	<i>Quillaja</i> saponin, whey protein, and soy lecithin	Soft foods, creams, sauces, and salad dressings	[90]
	O/W	<i>Quillaja</i> saponin and soy lecithin	Functional foods and beverages	[91]
	O/W	Ginseng saponin		[9]
	O/W	Whey protein, gum Arabic, and soy lecithin		[92]
	O/W	Modified starch, whey and casein proteins		[93]
Microemulsions	W/O	Soy lecithin	Extraction of edible vegetable oils	[94]
	W/O	Soy lecithin	Functional foods and	[95]
	O/W	Soy lecithin	soft drinks	[96]
	O/W	<i>Quillaja</i> saponin, Rhamnolipid, and soy lecithin	Soft drinks and minced meat	[97]

Table 2.
Food applications of emulsions, nanoemulsions and microemulsions using natural emulsifiers.

3.2 Stabilization mechanisms

Emulsions are thermodynamically unstable mixtures, characterized by the presence of at least two immiscible phases and an emulsifier that, when provided with enough mixing energy, are able to maintain stability over time [98]. The role of the emulsifier is essential to assure stable long-term properties. In general, emulsifiers are active surface substances, enabling their positioning at the oil–water interface, reducing the interfacial tension, hindering (or delaying) aggregation phenomena [99]. Typically, the hydrophilic part of the emulsifier is located in the aqueous phase, while the hydrophobic tail remains enclosed in the oil phase [82, 100]. During emulsion formation, the surfactant molecules require time to move to the interface, forming a layer to reach the interfacial tension equilibrium, a phenomenon related with their adsorption kinetics [82]. This pattern is dependent on emulsifiers' nature, taking from minutes (e.g., some saponins) to hours (e.g., some proteins), besides being dependent on environmental conditions (e.g., pH, temperature) [82]. To note that, even emulsions are commonly stabilized by a monolayer structure around the droplets, multilayer structures can also be formed. The multilayer pattern favors the electrostatic and steric repulsion of the droplets, improving stability while providing additional protection to the internal phase [16].

The emulsion stabilization mechanism can differ depending on the nature of the used surfactant. In this context four principal stabilization mechanisms are known, namely electrostatic repulsion, steric repulsion, Marangoni-Gibbs effect, and thin film stabilization mechanisms [101]. The electrostatic repulsion is related to ionic emulsifiers and consists on the formation of an electrical double layer at the droplet's interface, hindering their approximation. Steric repulsion is characteristic of nonionic and/or polymeric emulsifiers, and droplet's distance is kept due to the adsorption of the hydrophobic segment by the oil phase [101]. The Marangoni-Gibbs effect preserve emulsions' structure through the deformation of adjacent droplet's surface, avoiding their outflow, whereas the thin film stabilization mechanism avail the stability of the emulsion by generating a rigid and viscoelastic film, preventing droplets from destabilization effects [101].

Other factors can condition emulsion's stabilization mechanism, including the emulsifier content, the oil to water ratio or the preparation conditions (pH or temperature). For example, some phospholipids can have no charge at neutral pH, turning into anionic at acidic media, promoting molecule's swelling at the interface [100]. Moreover, the surfactant concentration can have also impact, e.g., sunflower lecithin in O/W emulsions, at low contents, create a layer surrounding the oil droplets, while at higher concentrations, the stabilization mechanism changes, producing, concurrently, liposomes that might destabilize the emulsion [10]. Considering amphiphilic polymers, when they are used as emulsifiers, they become positioned at the interface, just like the small molecules, but their ability to create intermolecular interactions can provide additional stabilization effects. Their effect on viscosity can also provide a positive stabilization effect [102]. The high hydrophilicity of most polysaccharides can difficult their emulsifier role, if considering the importance of the emulsifiers' hydrophilic/lipophilic character to interact with both phases. This constraint can be overcome by either chemical or physical strategies [103]. Namely, the suitability of anchoring hydrophobic groups into the polysaccharide structure can equilibrate the hydrophilic/lipophilic balance, that is the hydrophobisation of emulsifier's surface. Otherwise, alternative approaches imply the mixture of the polysaccharides with other polymers (co-surfactants) to favor the hydrophilic/lipophilic equilibrium and stabilization role.

3.3 Production methods

Food emulsions can be produced using several methods, classified as low-energy and high-energy processes, as represented schematically in **Figure 4**. The selection of the most appropriate method and respective equipment is based on the volume to process, characteristics of the initial mixture, emulsion’s physicochemical properties, droplet size, and process costs [104]. In **Table 3** a survey of recent works dealing with emulsion production through different methods and using natural emulsifiers in their pure form or compounded with synthetic emulsifiers is presented. Moreover, their potential to encapsulate bioactives for food industry applications is also described.

Low-energy methods comprise, spontaneous emulsion, and emulsion phase inversion (e.g., phase inversion composition and phase inversion temperature), which occur due to environmental or composition changes namely temperature, pH, and ionic strength of the formulation [104]. Low-energy approaches are more cost effective than high-energy methods. However, they are limited to certain oils

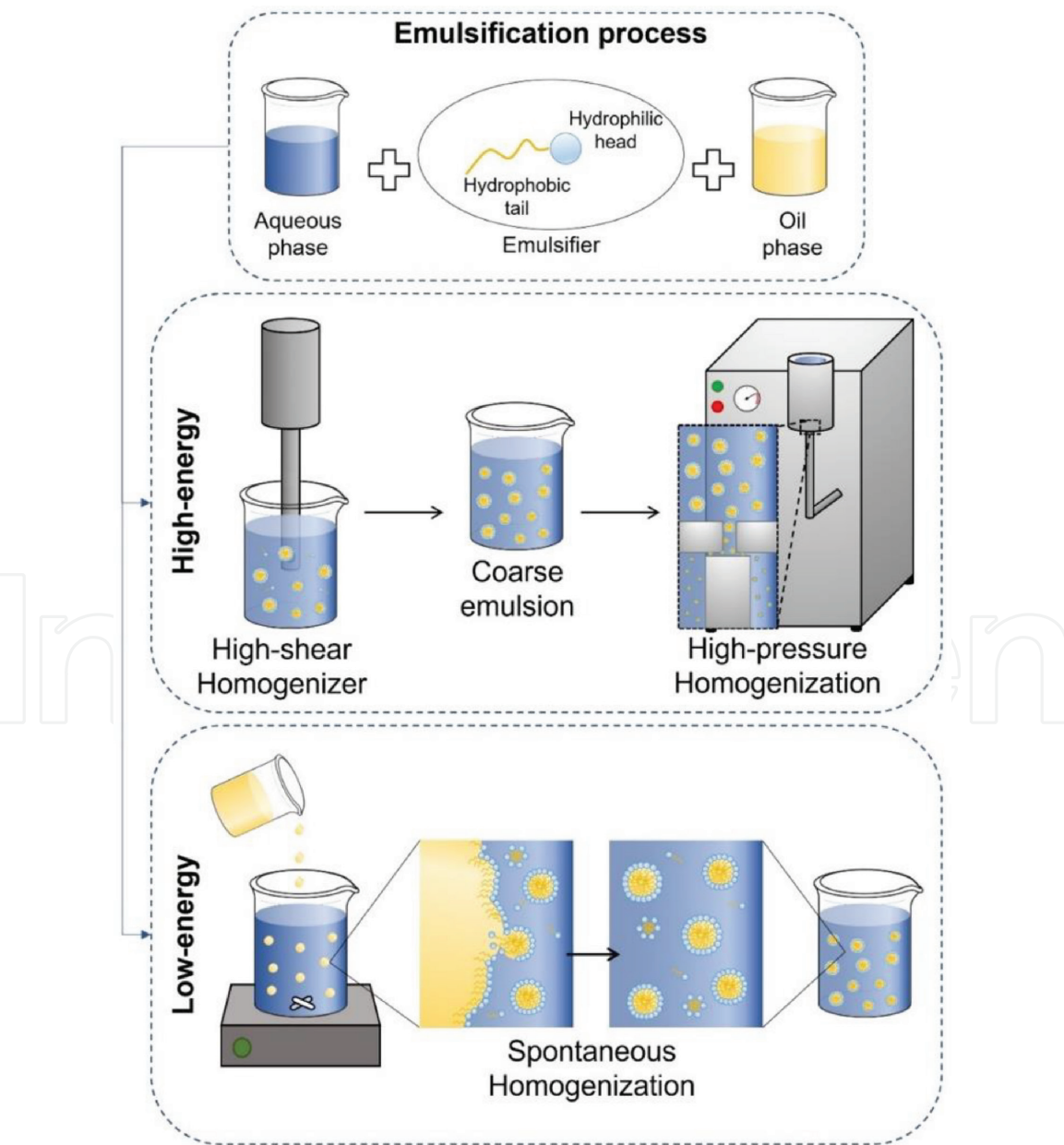


Figure 4.
Schematic representation of the emulsification process through high- and low-energy methodologies.

Productive method	Emulsion type	Oil phase	Particle diameter	Bioactive compound	Emulsifiers	Reference
<i>Low-energy methods</i>						
Spontaneous emulsification	O/W	MCT	> 10 µm	—	Sunflower phospholipids	[36]
Emulsion phase inversion	W/O	MCT and orange oil	> 10 µm	Vitamin E	WPI; SMP; Casein; <i>Quillaja saponin</i>	[105]
Phase inversion temperature	O/W	Peppermint oil	< 12 nm	Coenzyme Q10	Lecithin/Tween 20	[106]
<i>High-energy methods</i>						
High-pressure homogenization	O/W	Paprika oleoresin	<150 nm	—	Soy lecithin; WPC; Gum Arabic	[92]
Microfluidization	O/W	Fish oil	<150 nm	Omega-3 fatty acids	Sunflower phospholipids	[8]
Colloid mills	W/O	Rapeseed oil	4.8 µm	—	WPI; Pectin	[107]
Ultrasonic homogenizer	O/W	MCT; Palm oil; Soybean oil; Rapeseed oil	0.5–24.1 µm	—	Soy protein isolate	[6]
Membrane emulsification	W/O/W	Sunflower oil	35–320 µm	Magnesium	Starch; Pea protein isolate	[108]
Microchannel homogenizer	O/W	Soybean oil	35–47 µm	—	Sodium alginate; Pectin; Gum Arabic; Carboxymethyl cellulose	[109]
High-speed homogenization	O/W	Soybean oil	143.5 nm	β-carotene; Eugenol	Lecithin; WPI	[110]

WPI: Whey protein isolate; WPC: Whey protein concentrate; MCT: medium-chain triglycerides; SMP: Sucrose monopalmitate.

Table 3.

Studies applying different productive methods using natural emulsifiers or natural/synthetic blends to form emulsions and/or to encapsulate biocompounds for food industry applications.

and emulsifiers, requiring also large amounts of surfactants, which is not desirable for many food applications [71]. In the work reported by Komaiko et al. [36], spontaneous emulsification lead to emulsions with large droplet size ($>10\ \mu\text{m}$), comparatively with those produced by high-energy methods ($<10\ \mu\text{m}$). The authors concluded that natural emulsifiers can be used in SE emulsions for applications where fine droplets are not essential (**Table 3**). By contrast, Mayer et al. [105] concluded that it was not possible to produce nanoemulsions using natural emulsifiers by the emulsion phase inversion method. These limitations imply that even natural-based emulsions can be prepared through low-energy methods, high-energy approaches are needed when natural emulsifiers are used.

High-energy methods generate intensive forces promoting the water and oil phases disruption and their subsequent mixture. High-shear homogenizers are the most used equipment's for producing emulsions in the food industry. They consist on a rotor-stator or stirrer device able to mix the components at high speeds. Usually, large droplets are produced using this approach ($1\text{--}10\ \mu\text{m}$) in comparison to alternative high-energy methods. High-pressure homogenization is also widely used in the food industry, being more effective to reduce the droplet size of a pre-emulsion. Generally, this coarse pre-emulsion is produced by high-shear homogenizers, then subjected to the high-pressure homogenization process. The equipment consists of a high-pressure pump ($3\text{--}500\ \text{MPa}$) to pass the coarse emulsion through a narrow homogenizing valve, generating intensive disruptive forces (shear and cavitation), breaking down the droplets into smaller ones [80, 81].

Many studies have been conducted using two high-energy sequential methods (high-shear and -pressure homogenizers) to produce emulsions/nanoemulsions with natural emulsifiers [111–113]. Flores-Andrade and co-workers performed a study with soy lecithin, whey protein concentrate (WPC) and gum Arabic as natural emulsifiers, and paprika oleoresin as the oil phase. The coarse emulsion was produced by a high-speed homogenizer, then treated in a high-pressure homogenizer. O/W nanoemulsions were produced, being WPC more effective to form small droplets ($d < 150\ \text{nm}$) than the other tested emulsifiers [92].

Microfluidization is the most effective method for producing emulsions with fine droplets ($d < 100\ \text{nm}$). This approach is based on feeding the fluid into the homogenizer, which consists of a mixture chamber with two channels. Intensive disruptive forces are generated when these two fluid streams collide at high speed, breaking larger droplets and intermingling the fluids [3]. As the high-pressure homogenizers, microfluidizers were used after preparing a pre-emulsion by high-shear mixers [42, 114]. Ultrasound technique uses high-intense ultrasonic waves, generating intense shear and pressure gradients. The droplets are disrupted mainly by cavitation and turbulent effects [99, 115].

Currently, high-energy approaches are commonly used in the food industry due to their large-scale production capacity and the possibility to process a wide range of raw ingredients [71]. Although several high-energy emulsification devices are available, high-shear and pressure homogenizers, microfluidizers and ultrasound equipment's are the most used in the production of natural emulsifiers-based emulsions.

3.4 Emulsion stability

Emulsion stability is an important parameter indicating its ability to resist physicochemical changes over time [116]. For food emulsions, the required stability varies according to the intended final application. For example, short-term stability of minutes to hours, is enough for intermediate food emulsions such as cake batter and ice cream mixtures, while long-term stability is required for long shelf-life

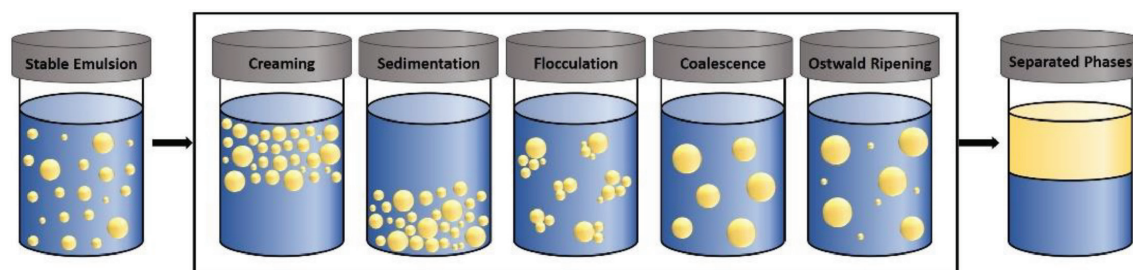


Figure 5.
Common types of instability phenomena in emulsions.

products, including mayonnaise and salad dressings [117]. For the latter ones, the development of effective strategies to retard emulsion destabilization implies the identification of the main mechanisms leading to this effect [73].

Emulsion instability can occur due to physical and/or chemical processes. The physical instability is responsible for modifying the emulsion droplets spatial distribution and structure, including gravitational separation (creaming/sedimentation), flocculation, coalescence, and Ostwald ripening phenomena (**Figure 5**). These effects depend on the emulsion composition and structure, besides the storage conditions, namely temperature variation and mechanical stirring [74, 116]. Moreover, the physical phenomena are interrelated and can influence each other during emulsion storage [77].

Gravitational separation is driven by density differences between the droplets and the continuous phase. The droplets are subjected to gravitational forces tending to accumulate in the top (creaming) or in the bottom (sedimentation) of the system. Most edible oils present densities lower than water, favoring creaming in O/W emulsions, whereas sedimentation is usually observed in W/O emulsions [116]. Considering the impact of gravitational forces in the large droplets, the separation usually occurs for emulsions with droplet sizes higher than 100 nm or in a final stage of a sequence of instability phenomena [116]. By contrast, for lower droplet sizes, e.g., nanoemulsions, Brownian motion dominates over gravitational forces. Thus, reducing the droplet size is a suitable strategy to retard gravitational separation, with the emulsifier playing an important role to effectively reduce droplets' size [2, 74]. Furthermore, the emulsifier' layers tend to minimize the density difference between the emulsion phases, thus reducing the velocity of gravitational separation. Other strategies include modifying the rheology of the continuous phase or increasing the concentration of the droplets [74, 116].

Ostwald Ripening consists of the increase of the droplets size due to the diffusion of small droplets into larger ones, effect driven by their solubility in the continuous phase. This effect is promoted when the droplet's size decreases [73], being also influenced by the emulsifiers' properties. Namely, Ostwald Ripening can be retarded by decreasing the interfacial tension of the phases, favored when small-molecule surfactants are used or when using emulsifiers able to form rigid shell around the droplets. By contrast, emulsifiers prone to solubilize the oil and water phases through the formation of colloidal structures (e.g., micelles) accelerate the Ostwald Ripening [2].

Flocculation and coalescence mechanisms are related to droplets aggregation, effect leading to droplet size increase [74]. In flocculation the association of at least two droplets in an aggregate occurs, whereas in the coalescence, the droplets merge into a larger one [77]. Both phenomena are highly dependent on the selected emulsifier [77, 116], namely their nature and colloidal interactions' capacity [2].

4. Pickering emulsions

Pickering emulsions are defined as systems stabilized by solid colloidal particles adsorbed at the oil–water interface in a practically irreversible process, creating a coating around the droplets, either in the form of a single or multiple layer, generating a strong steric barrier providing high stability [118]. In the context of Pickering emulsions, the search for natural-based particles is currently a hot topic to face market demands for novel clean label products (absent of emulsifiers) [119]. Pickering emulsions (**Figure 6**) are raising high interest in the recent years. They are characterized by a long-term stability and have green connotations due to the absence of conventional emulsifiers. These attributes comply with the recent trends of food industry towards the use of sustainable and healthy technologies [16]. The stability of Pickering emulsions is related with the intrinsic properties of the oil and water phases (e.g., type, oil/water ratio, pH, ionic strength) and of the particle stabilizers (e.g., wettability, particle morphology, size and concentration). Particles presenting a contact angle (θ) below 90° are generally suitable for preparing O/W emulsions, whereas θ values greater than 90° indicate good stabilizers for W/O emulsions. At 90° , the particle is immersed equally in both phases [120].

Regarding natural-based particles, three main typologies of stabilizers can be used, namely nanoparticles, microgels and fibrils. Examples include protein derived stabilizers, namely nanoparticles based on corn zein, and colloidal particles of kafirin and gliadin [118, 121–123]. Although many polysaccharides have high hydrophilic character, some can include hydrophobic side groups (e.g., beet pectin and modified starch) or even active proteins attached to the surface (e.g., gum Arabic) [120], offering potential to act as Pickering stabilizers. Other polysaccharides widely used to produce Pickering bionanoparticles include chitin, chitosan and cellulose. To overcome particle's limitations as Pickering stabilizers, the formation of complexes has been also proposed, namely complexes such as polysaccharide-polysaccharide, protein–protein, and polysaccharide-protein [124]. Examples include zein-xanthan [125], and tea water insoluble proteins/ κ -carrageenan complexes [126].

In the context of the recent trends in Pickering emulsions, research aiming at finding new biological particles, the use of high internal phase emulsions (HIPPE),

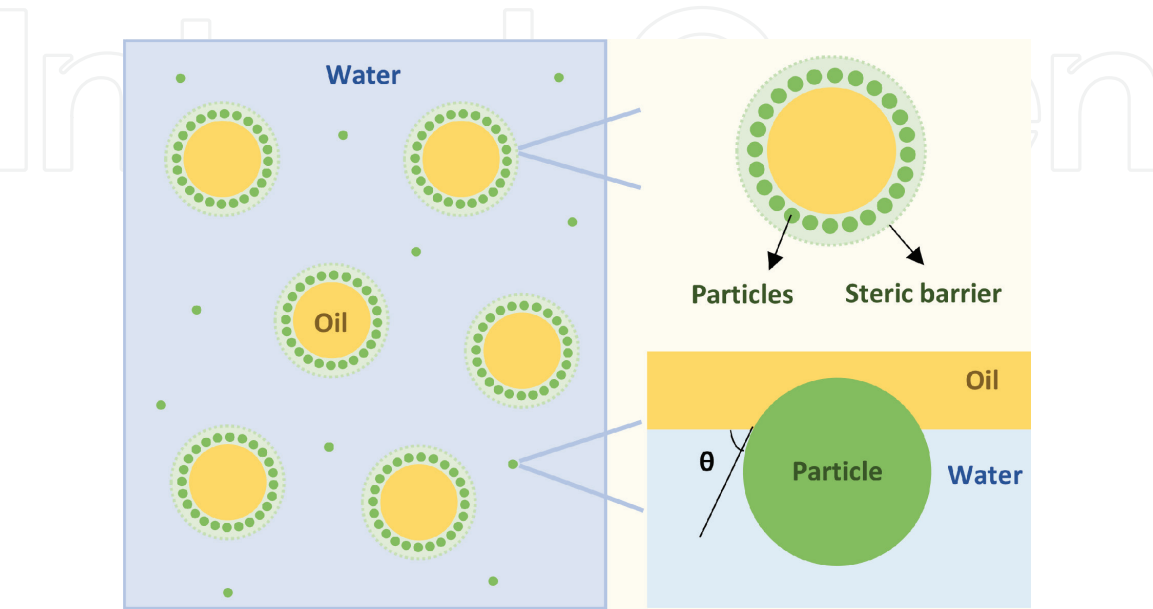


Figure 6.
Schematic representation of a Pickering emulsion putting in evidence the particle stabilizers where θ represent the contact angle.

and the development of bio-based films from Pickering emulsions are becoming topics of high interest for the development of novel food applications. **Table 4** presents an overview of recent works dealing with the preparation of Pickering emulsions based on novel biological particles together with the description of the main results envisaging potential food applications.

HIPPEs are characterized by having a high volume fraction of internal phase (generally higher than 74%), together with relatively low particles concentration resulting in an extremely compacted droplet's structure [140]. HIPPEs are becoming a novel approach of increasing interest in the food industry, since it combines

Particle materials	Main results	Reference
Apple pomace	Smaller particles led to emulsions with smaller droplet size, showing higher stability over time (30 days), in addition to improved physical properties (gel-like samples) and antioxidant activity.	[127]
Bamboo shoots dietary fiber	The emulsions were stable for 4 weeks avoiding coalescence against pH and ionic strength changes and pasteurization conditions.	[128]
Chitosan-sodium tripolyphosphate	The emulsions presented good thermal stability, showing potential to be applied as a food delivery system for essential oils.	[129]
Gliadin-pectin	The emulsion with higher particles content (2%) showed suitable physical stability for 30 days, elastic-solid characteristics and good thermal stability (20–80°C).	[130]
Hordein-chitosan	The emulsions exhibited good stability during storage (14 days, oil ratio = 0.5 and 0.6) and physical properties (elastic gel-like network).	[131]
Pea protein	The emulsions with higher particle content showed stability against coalescence over 3 months.	[30]
Sago starch nanocrystals	The emulsions were stable with no signs of creaming for over 2 months.	[132]
Soy protein isolate-anthocyanin	The emulsions were reached a cream index of 17%, presenting stability for 7 weeks. They presented improved oxidative stability and resistance to <i>in vitro</i> digestion conditions.	[133]
Soy protein isolate-chitosan	Cream index values were very low, and the emulsion presented good stability to a broad range of ionic strength and mild temperature conditions (4–60°C).	[134]
Tea protein	Emulsions with gel-like properties were produced, presenting no creaming over 50 days.	[135]
Zein-corn fiber gum	High oil concentrations (oil ratio = 0.5) led to higher stability and the formation of a gel-like structure.	[136]
Zein-gum arabic	The emulsion showed a high stability against coalescence and Ostwald ripening during 30 days of storage (oil ratio = 0.7).	[137]
Zein-pectin	The emulsions maintained excellent physical stability for 1 month. In addition, they demonstrated good performance as delivery systems of essential oils.	[138]
β-lactoglobulin-gum arabic	The particles provided stability against coalescence and Ostwald ripening for up to 12 weeks, in addition to improve chemical stability.	[139]

Table 4.
Examples of bionanoparticles as Pickering stabilizers. All the systems are of O/W type.

diverse advantages, namely a semi-solid texture with the ability to encapsulate high amounts of bioactive compounds [141]. HIPPEs allow to control the droplet size distribution, manipulate the morphology and rheological properties, generally presenting enhanced stability against physical, chemical and microbiological stresses [142]. They are positioned as extremely promising substitutes for foods such as margarine, mayonnaise or ice creams [143, 144]. For example, Liu et al. studied wheat gluten as stabilizer in a HIPPE to develop a novel mayonnaise substitute [145]. They obtained excellent results concerning texture and sensory attributes when compared with commercial products.

Bio-based films made from hydrophilic particles added with hydrophobic compounds is another emerging approach in the scope of new applications developed from Pickering emulsions [146]. These strategies provide the ability to improve the stability of the base materials (hydrophilic), in addition to facilitate the combination with hydrophobic materials (e.g., waxes, fatty oils and oils) leading to systems with enhanced moisture barrier properties [147].

5. New trends in food emulsion systems

The wide variety of emulsion-based systems using natural emulsifiers makes their applicability attractive for various products, particularly in the food industry. The nature and function of emulsifiers, and the formed emulsion type (e.g., nano/micro-scale, simple or double character) can tailor appearance, sensorial characteristics, and attractiveness of foods. Among their diverse functions, the increasing use of emulsions as functionality carriers should be highlighted. In fact, recent works have demonstrated their potential and versatility for the encapsulation of flavors, and to protect and deliver specific bioactives in foods or beverages, helping to strengthen nutritional balances, and enabling the production of reduced-fat products. A summary of examples addressing new trends of emulsion-based products with potential in the food industry are included in **Table 5**, with some highlights provided next.

Lopes Francisco et al. [149] reported an emulsifying system with encapsulation potential based on commercial pea and soy proteins. The work involved the encapsulation of an orange essential oil rich in d-limonene using a O/W emulsion followed by spray drying to obtain powder microparticles. It was demonstrated the ability of pea and soy proteins to act as emulsifiers in the encapsulation of orange essential oil, getting a slightly higher efficiency if using soy protein as the natural emulsifier. These promising results can help consolidate a platform aiming at developing new protective systems to encapsulate flavors for foods, complying with the increasing demand from this industrial sector for natural-based systems.

At the nanoscale, Flores-Andrade et al. [92] reported the preparation of O/W nanoemulsions by high-pressure homogenization, using amphiphilic biopolymers to stabilize paprika oleoresin, namely whey protein, gum Arabic, phospholipids, and soy lecithin. The results demonstrated the effective oil encapsulation, preserving carotenoids (e.g., lipophilic colorants) from chemical degradation, besides positioning this strategy as an attractive route to design new protective and delivery carriers for bioactive compounds aimed at food and/or beverage products.

The potential of double emulsions was also demonstrated by Cetinkaya et al. [152] that evidenced the reduction of the saturated fat content in O1/W/O2 emulsions prepared by fat crystallization according to a two-stage process. Firstly, the

Emulsion type	Oil phase	Emulsifier	Highlights	Reference
O/W	Vegetable oil	Orange pulp and peel powders	Base emulsions for food applications	[148]
O/W	Orange essential oil	Pea protein concentrate and soy protein isolate	Encapsulation of flavors for the food industry (powder form)	[149]
O/W	Sunflower, soybean, MCT, and orange oils	Crude saponins isolated from onion skin wastes	Food nanoemulsions (stable emulsions, except at acidic pH and high ionic strength)	[40]
O/W	Paprika oleoresin	Whey protein and gum Arabic, and soy lecithin	Food and beverage systems for the delivery of carotenoids	[92]
O/W	Hemp seed oil	<i>Aesculus hippocastanum</i> L. extract	Food nanoemulsions with enhanced nutritional properties	[150]
O/W	Almond, mustard, olive, and soyabean oils	Biosurfactants isolated from <i>Candida albicans</i> SC5314 and <i>Candida glabrata</i> CBS138 yeast strains	Food emulsions with improved antibacterial capacity	[151]
O/W	Corn and sunflower oils) /	Biosurfactant isolated from <i>Candida utilis</i>	Food emulsions with promising properties for salad dressings	[63]
O1/W/O2	O1 – Sunflower; O2 - palm oil	Primary emulsion - gelatin, xanthan gum; Secondary emulsion - solid fat crystals	Oil encapsulation systems for texturizing reduced-fat agents	[152]

Table 5.
Applications of natural-based emulsifiers in food industry.

primary O1/W emulsion was prepared using sunflower oil and xanthan gum and gelatin as emulsifiers, which was then stabilized in a second oil phase (palm oil), resulting in a structured O1/W/O2 system. Microstructure examination revealed that the accumulation of fat crystals at the interface contributed to stabilize the internal water phase containing the encapsulated sunflower phase. These complex structures showed potential to directly encapsulate hydrophobic oils and act as texturizing reduced-fat agents, which might be of particular interest for the edible oils industry.

6. Conclusions

This chapter presents an up-to-date overview of current trends in natural emulsifiers and their application in emulsion technology directed to food applications. For this purpose, first, the evolution of food emulsifiers’ scenario over the last 10 years was analyzed through the Bibliometrix-R package (RStudio) and VosViewer software. This analysis indicated a clear driving force towards using natural emulsifiers and the re-emerging importance of the Pickering emulsions. These facts are expected to impact the market growth following the prospectus of available market analysis. The six main identified families of natural emulsifiers

were phospholipids, saponins, proteins, polysaccharides, emulsifiers from microbial sources and Pickering stabilizers. Some of them already find extensive use in practical food applications. However, others, mainly natural-based emulsifiers from microbial sources and Pickering stabilizers, despite their high potential, are still needing research investment and regulation clarification (e.g., related to the use of nanoparticles and the use of microbial strains classified as pathogenic in foods). From a technological perspective, the main concepts related to the typology, production methods, stabilization mechanisms, and instability phenomena were presented. Highlighting the increasing interest in Pickering emulsions, a summary of the most recent applications of these systems, including the so-called HIPPEs and their advantages in reduced-fat products development, was provided. To conclude, an analysis of current trends in food emulsion-based products was discussed, putting in evidence the emulsions increasing role as delivery systems of bioactives to support innovative fortified foods advances and the increasing interest in systems based on double emulsions, which provide the opportunity to combine bioactives of different nature. Overall, the field of natural-based emulsifiers combined with the new trends in emulsion technology can, hopefully, be the basis of a new generation of healthy and nutritious food products.

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Conflict of interest

The authors declare no conflict of interest.

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