Utilization of lignocellulosic biomass: A practical journey towards the development of emulsifying agent

Muhammad Taqi-uddeen Safian[1], Asim Ali Yaqoob[1], Albert Serrà[2, 3], Siti Hajar Sekeri[1*], Mohd Dzahir Jamudin[4], Mohamad Nasir Mohamad Ibrahim[1*],

[1]Materials Technology Research Group (MaTRec), School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia.

[2] Grup d'Electrodeposició de Capes Primes i Nanoestructures (GE-CPN), Departament de Ciència de Materials i Química Física, Universitat de Barcelona, Martí i Franquès, 1, E-08028, Barcelona, Catalonia, Spain.

[3] Institute of Nanoscience and Nanotechnology (IN^{2}UB), Universitat de Barcelona, Barcelona, Catalonia, Spain.

[4] Ekahala Resourses Sdn. Bhd., 52-1, Jalan Musytari AN U5/AN, Subang Pelangi, Seksyen U5, 40150 Shah Alam, Selangor, Malaysia.

***Correspondence**: hajarsekeri@gmail.com; mnm@usm.my; Tel.: +60-4653-3554.

***Correspondence postal address**: School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia

Abstract

With each passing year, the agriculture and wood processing industries generate increasingly high tonnages of biomass waste, which instead of being burned or left to accumulate should be utilized more sustainably. In parallel, advances in green technology have encouraged large companies and nations to begin using eco-friendly materials, including eco-friendly emulsifiers, which are used in various industries and in bio-based materials. The emulsion-conducive properties of lignocellulosic materials such as cellulose, hemicellulose, and lignin, the building blocks of plant and wood structures, have demonstrated a particular ability to alter the landscape of emulsion technology. Beyond that, the further modification of their structure may improve emulsion stability, which often determines the performance of emulsions. Considering those trends, this review examines the performance of lignocellulosic materials after modification according to their stability, droplet size, and distribution by size, all of which suggest their outstanding potential as materials for emulsifying agents.

Keywords: Lignin; Cellulose; Hemicellulose; Modification; Emulsion; Emulsifier; Stability.

List of Abbreviations

AFM	Atomic Force Microscopy
AL	Alkali lignin
BCN	Bacterial cellulose-based CNC
CCN	cotton-based CNC
ClaCN	Cladophora CNC
CMGGM	Carboxymethyl GGM
CML	Carboxymethylated lignin
CNC	Cellulose nanocrystals
CNC-H	Highly sulfonated CNC
CNC-M	Medium sulfonated CNC
CNC-S	Slightly sulfonated CNC
CNF	Cellulose nanofibrils
CTAB	Cetyltrimethylammonium bromide
DEAEMA	Diethylaminoethyl Methacrylate
EC	Ethylcellulose
FDA	Food and Drug Administration
GGM	Galactoglucomannan
HC	Hemicellulose
HLB	Hydrophilic-Lipophilic Balance
HPMC	Hydroxypropyl methylcellulose
KL	Kraft lignin
LCMs	Lignocellulosic materials
LCT	Longer-chain triglyceride
LG	Calcium-LS
L-PNIPAM	Lignin-poly (N-isopropyl acrylamide)
LS	Lignosulfonate
MCC	Microcrystalline cellulose
MCT	Medium-chain triglyceride
MFC	Micro-fibrilated cellulose

NPs	Nanoparticles
O/W	oil-in-water emulsion
O/W/O	Oil-in- water-in-oil emulsion
O-CNC	Phenyl grafted CNC
ORGL	Organosolv lignin
PDMAEMA	Poly[2-(dimethylamino)ethyl methacrylate]
PGPR	Polyglycerol Polyricinoleate
PHWE	Pressurized hot water extraction
PS	Polysaccharide
PSI	Pound per square inch
PSR	Polystyrene
SiO_2	Silica oxide
SL	Soda lignin
SMES	Sodium methyl ester sulfonate
SSL	Sodium-based-sulfite liquor
TS	Tristearin
W/O	water-in-oil emulsion
W/O/W	Water-in-oil-in-water emulsion
Wt%	Weight percentage

1. Introduction

Used extensively in diverse applications such as foods, personal care products, cosmetics, and medicines, emulsions are two immiscible liquids (e.g., oil and water) dispersed into a single liquid such that one is in the dispersed phase and the other in the continuous phase [1]. The two dominant emulsions with oil (O) and water (W) are O/W, with the oil droplets in the dispersed phase and water in the continuous phase, and W/O, with a vice-versa arrangement. In both types, the dispersed phase is encapsulated in the continuous phase. Although other types of complex emulsions exist, including water–oil–water emulsions and oil–water–oil emulsions, this review focuses only on O/W and W/O emulsions.

In any emulsion, stability, also called *emulsion stability*, is the primary factor of performance, achieved by maintaining a difference between the hydrophobic and hydrophilic content in oil and water to provide the force needed for stability. In particular, as droplets aggregate, ones bound to each other create more than enough mass for gravity to influence stability, and the longer that those gravitational forces take to separate them, the more stable the emulsion [2]. Unstable emulsions occur when the dispersed phase give rise to forms of physical instability such as creaming, sedimentation, flocculation, and/or coalescence.

Among the methods used to improve and maintain emulsions, emulsifiers are surface-active agents that can reduce the attractive forces at the oil–water interface, meaning the boundary connecting the two phases [3,4]. As such, emulsifiers are amphiphilic molecules with both hydrophilic and hydrophobic properties. To function correctly, emulsifiers need to exhibit surface activity at the interface of the dispersed and continuous phases [5]. Good emulsifiers can adsorb the droplets of the dispersed phase during integration, which serves to protect them from interacting with other droplets and thereby halts their aggregation. Because good emulsifiers thus lower interfacial tension, they help to make emulsions more stable.

The size of droplets within emulsions plays a major role in their stability. Micro-emulsions have nanoscale droplets (i.e., 1 to 100 nm in diameter) and are thermodynamically stable compared to macro-emulsions, which, in containing droplets greater than 0.1 mm in diameter, tend to coalesce and thus become thermodynamically unstable [6]. To overcome the reduction in interfacial energies in macro-emulsions, the coalescence rate can be measured as an indication of whether neighboring droplets are merging based on the potential energy barrier versus the thermal energy. According to the coalescence rate, if the energy barrier exceeds the thermal energy, then the emulsion is stable. Manipulating the phase inversion temperature has also been used to create stable macro-emulsions [7], in which the higher the phase inversion temperature, the more stable the macro-emulsion at ambient temperature.

In recent years, industries have shown high demand for natural plant-based emulsifiers instead of animal-based or synthetic emulsifiers [8]. Such demand is also correlated with the introduction of policies for utilizing biomass in industries in numerous developing countries [9]. Generally, the term *biomass* refers to all agricultural waste, including from chopped tree trunks, discarded husks, and seeds, as well as waste generated from animals, including manure, shells, and decaying carcasses [10]. The primary goal of the shift to natural plant-based emulsifiers is to utilize the agricultural waste that accumulates with each passing year and can be expected to continue doing so given the food industry's dependence on agriculture. In fact, agricultural waste from by-products is estimated to increase by 7–10% annually [11]. To that goal, modifying the structure of lignocellulosic materials (LCM) can allow tailoring emulsifiers to suit certain applications and has thus attracted the interest of many researchers, especially ones interested in utilizing LCM as nanostructures. Figure 1 illustrates the recent spike in published articles highlighting LCMs as emulsifiers.

This review focuses on biomass containing LCMs (e.g., cellulose, hemicellulose, and lignin), all commonly found in plants, and other small amounts of extractives [12]. Along with agricultural waste, waste generated from forest-based industries such as wood processing, pulp industries, and paper mills contributes significantly to the worldwide abundance of lignocellulosic biomass. For that reason, the utilization and application of bio-based materials have gained significant traction in the movement toward creating more sustainable, eco-friendly products. To that same end, LCMs have been studied for years as alternative materials for emulsifiers, and research has shown that LCMs, primarily cellulose and lignin, are equipped with surface-active functional groups that benefit the oil–water interface [13]. This review highlights the utilization of LCMs by showcasing the techniques used to modify them and thereby enhance the performance of O/W and W/O emulsions in terms of their stability, droplet size, and size distribution.

2. Emulsion stability and its mechanisms

At the interface in emulsions, the two phases tend to bind with their kind, and those natural forces hinder the droplets in the dispersed phase from separating into much smaller droplets and thereby separating the two phases. The accumulation of those forces separating the two phases is known as *interfacial tension*. Emulsion stability can be achieved once the interfacial tension is reduced, which is usually accomplished by reducing the viscosity of the medium or using an emulsifier. As suggested earlier, emulsifiers work by allowing droplets in the dispersed phase to produce smaller droplets and, in turn, preventing them from coalescing [5]. Given their hydrophobic and hydrophilic tendencies, emulsifiers align themselves so that both tendencies are embedded in their appropriate phase.

Among the physical properties that can be monitored to study emulsion stability, including droplet size, size distribution, viscosity, creaming level, and stability, droplet size is a critical factor of emulsion quality. Due to their difference in density, the oil and water phases separate under the influence of gravity. Therein, the behavior of all particles follows Brownian motion, which more heavily influences macro-sized droplets than nano-sized ones, thereby resulting in aggregation. Altogether, reducing the droplet size helps to maintain stability, for emulsification adheres to the equation for change in Gibbs free energy shown in Equation 1 [6]:

$$\Delta G = \Delta H - T\Delta S \qquad \text{Eq. (1)}$$

in which ΔG is the change in free energy, ΔH is the enthalpy energy, ΔS is the conformational entropy change, and T is the temperature. In an emulsion, $T\Delta S$ thus represents the entropy that correlates with the dispersion of the droplets, such that the more droplets that are dispersed, the higher the (positive) value. Meanwhile, because ΔH embodies the energy required to expand the interface during emulsification and a lower ΔH value indicates more emulsion stability, a value of $T\Delta S$ that exceeds ΔH means that emulsification is spontaneous, as exemplified in Figure 2a. Thus, macro-emulsions struggle to achieve stability because $\Delta G > 0$ (i.e., $\Delta H > T\Delta S$).

By contrast, a positive ΔG often indicates that the emulsification process is not spontaneous, as indicated in Figure 2b, hence the need for energy to achieve emulsion stability. Studies have shown that most emulsification processes use external energy input from the shear force of high-shear mixers [7], which helps to reduce the size of droplets. In that mechanism, liquid mixtures are forced into the narrow gaps between the cycling blades until they separate the droplets into much smaller droplets. In fact, a nano-emulsion can be achieved using an ultrasonic device or high-pressure homogenizer with forces equaling 10,000 PSI [9]. Even then, however, the smaller droplets often coalescence over time due to their thermodynamic instability. For that reason, shelf life is another physical property used to study the performance of emulsions. To that end, using emulsifiers helps tremendously to prevent coalescence by making the droplets mutually repulsive via static charges [14]. Achieving nano-emulsions affords significant advantages because the ΔH is near zero, which results in a negative ΔG value and, in turn, thermodynamic stability.

3. Types of emulsions

As indicated, emulsions are labeled based on their dispersed phase. W/O emulsions occur when water is in the dispersed phase, whereas O/W emulsions occur when oil is in that phase, as shown in Figure 3. Other emulsions comprised of tiny droplets dispersed in larger droplets while suspended in another phase are known as *complex emulsions*—for example, oil–water–oil or water–oil–water emulsions. Generally speaking, the dispersed phase is a suspended phase that contributes to its having a smaller percentage than the other phase. For example, a W/O emulsion has a small volume of water droplets scattered inside a far larger volume of oil. However, when both oil and water phases are equal in volume, other factors determine the type of emulsion, including temperature or other interfacial properties [15]. W/O and O/W emulsions can also be differentiated, for example, by measuring their electrical conductivity, in which a conductive reading indicates an O/W emulsion, whereas a non-conductive reading indicates a W/O emulsion [16].

Because oil and water are generally unmixable, emulsifiers can be added to help the two phases to mix by establishing a barrier that protects the dispersed phase from separating. In emulsion technology, the key in any application is *emulsion stability* [17], defined as the time taken for the two phases to separate, in which greater stability equals a longer time taken. Stabilization against demulsification can be accomplished by including a polar emulsifier for either W/O or O/W emulsions. The emulsifier adsorbs the interfacial tension between the phases because its concentration influences the value of interfacial tension based on the Gibbs isotherm, shown in Equation 2:

$$\Gamma = -\frac{1}{RT}\frac{\partial \gamma}{\partial \ln C} \qquad \text{Eq. (2)}$$

in which Γ is the excess interfacial concentration of the emulsifier (mmol/m^2) measured from the interfacial tension, γ (mN/m), against emulsifier concentration, C. Thus, increasing the concentration of the emulsifier also increases the surface pressure. In that way, an emulsifier's effectiveness can be determined by measuring the maximum surface pressure achieved at saturation, for good emulsifiers reduce the surface pressure [18].

Using an emulsifier can promote high emulsion stability. However, stabilization versus Ostwald ripening required other additives. Ostwald ripening relates to the movement and changes in the size of small droplets, which tend to settle onto far larger droplets due to the curvature effect as the droplets are scattered. The solubility of the smaller droplets, as long as they are not negligible, is higher and thus forces the formation of larger droplets and unites the remaining small droplets into a bulk [19]. Thus, W/O emulsions are easier to stabilize than O/W emulsions, because the latter requires more than one emulsifier for stabilization [20]. Because any emulsifier that can achieve high stability has excellent value on the open market, this review discusses types of emulsifiers need to achieve high stability.

3.1. W/O emulsions

W/O emulsions involve a water phase suspended in small droplets in a larger amount of a continuous oil phase. Owing to the high mobility of water droplets, W/O emulsions are often unstable and produce sedimentation relative to the difference in density between the two phases and flocculation due to the grouping of the suspended phase, as shown in Figure 4a [21]. Because W/O emulsions are heavily used in the pharmaceutical, cosmetic, agricultural, food, and oil and gas industries, the need for better, stabler emulsions is at an all-time high [22–24]. In addition, oil's low conductivity yields mixtures with low conductivity, which precludes using forces other than steric force to improve the emulsions [25]. Briefly, steric stabilization is the process of barrier formation around the suspended phase performed to prevent coalescence. Polymers with high molecular weights can provide steric force by covering the particles of droplets with a polymer absorption layer, thereby separating the droplets from cohering, as shown in Figure 4b [26].

Because the process of emulsification has to occur before droplets begin to coalesce, the efficiency of emulsifiers plays a major role in adsorbing the kinetics of droplet generation by reducing interfacial tension and thus stabilizing the emulsion. The polar and nonpolar parts of emulsifiers reside in the aqueous and organic phases, respectively [27]. However, emulsifiers for W/O need to have a low hydrophilic–lipophilic balance (HLB), typically from 3 to 6 [28]. In response, polyglycerol polyricinoleate (PGPR), an oligomeric, non-ionic compound, has been used in W/O emulsions due to its low-HLB and a long hydrophilic polyglycerol chain that helps to bind in water. PGPR is also edible, which makes it a suitable ingredient in butter, chocolate, and salad dressing in the food industry [29]. Marquez et al. have studied how the concentration of PGPR affects the stability of W/O emulsions by mixing it with sunflower oil for the continuous phase and using an aqueous phase with various concentrations of calcium chloride added later [25]. They observed that calcium chloride offered nutritional value while also interacting with the emulsifier for better stability and that the concentrations of both PGPR and calcium chloride increased stability. They attributed that dynamic to the calcium salt’s ability to reduce the size of water droplets, which improves resistance to coalescence. Although PGPR is an excellent emulsifier, it struggles to keep emulsions stable long enough for sufficient food storage.

In another study, Garti et al. studied various emulsifiers, including PGPR, to better understand W/O emulsions in fat particles. After constructing α-form crystals of hydrogenated fat from flash-cooling in the oil phase, they added triestarin (TS) with PGPR, thereby forming ideal stable fluid emulsions with stability lasting approximately 6–8 weeks [29]. A higher concentration of PGPR affected the size distribution and dispersion of the droplets in the W/O emulsions, whereas adding TS prolonged stability and shelf life. However, a threshold of PGPR emerged at approximately 2 wt% such that higher concentrations affected only the fluid's viscosity.

In both studies, the size distribution of the water droplets affected the stability of the W/O emulsions. Because fine water droplets disperse better in the organic phase, W/O emulsions are often designed to obtain the smallest droplet size possible [15]. Droplets can be modified using a disruptive apparatus that employs any of three mechanisms: laminar shear forces, turbulent shear forces, or turbulent inertial forces [30]. Droplets can also be either micro-sized or nano-sized, with the latter being the thermodynamically stabler version of the two [31]. Kolmogoroff has theorized that the size of droplets in turbulent flows is balanced by the tensions present in the turbulence, whether inertial or viscous [32]. In the inertial subrange, the droplets are balanced by inertial stresses independent of the viscosity of the continuous phase, and those stresses are considered to be more significant than viscous stresses at that point. While in the viscous subrange, the viscous stresses overshadow inertial stresses, thereby making the droplets dependent on viscous stress [14].

Lecithin is another food-grade emulsifier used as an alternative to PGPR. Although PGPR is edible, the U.S. Food and Drug Administration has set a maximum daily dosage for PGPR intake. Another factor is that PGPR is a semisynthetic emulsifier that deters consumers seeking to practice healthier lifestyles. Balcaen et al. used lecithin as an emulsifier to produce stable W/O emulsions in medium-chain triglyceride (MCT) oil, because the length of the fatty acid chain influences the aggregative tendency of water droplets. They found after comparing W/O emulsions with lecithin containing various lengths of triglyceride oil that large-chain triglyceride (LCT) appeared more aggregation than the spherical shape in the MCT [33]. Along similar lines, Knoth et al. found that water droplets were primarily held as a lump of spherical particles and an aggregated structure in MCT-based W/O emulsions. In particular, they observed that lecithin achieved stabilization comparably to PGPR albeit with greater viscosity. [34]. Because interfacial pressure correlates with an emulsion's specific surface area, higher viscosities of the continuous phase equal the high specific surface area. Therefore, higher viscosities can reduce the effect of coalescence in emulsions.

3.2. O/W emulsions

O/W emulsions occur when oil acts as the dispersed phase and water as the continuous phase, as shown in Figure 3. In O/W emulsions, flocculation indeed often occurs, although stabler O/W emulsions have shown diminished flocculation. Apart from variables of droplet size, other variables such as temperature, pH, ionic content, and the oil volume fraction can be manipulated for better stabilization in O/W emulsions [35,36], and stabilizers such as emulsifiers and surfactants can be used to the same end. As such, O/W emulsions are utilized in drilling in the oil and gas industry, where emulsion-based muds are used for their excellent performance in lubricants, wellbore stabilizers, filtration, and stabilizers for solids, salts, and acid contamination. The low density of O/W fluids can affect underbalanced drilling operations [37], and mineral oils such as diesel are typically used to their low viscosity profile and low flammability.

In work utilizing emulsifiers to boost emulsion stability, Paswan et al. used sodium methyl ester sulfonate (SMES)as an emulsifier for O/W drilling fluids, one synthesized from sunflower oil mixed with xanthan gum, which improved stability in correlation to increased concentration based on the negative zeta potential [38]. Zeta potentials values as high as –120 mV were recorded when both concentrations were increased, with SMES demonstrating the primary effect. O/W emulsions have also been employed in the recovery of trapped oil, in which case emulsified oil droplets were mobilized downstream to the reservoir rocks. That method enhanced the recovery of the entrapped crude oil by efficiently improving the primary and secondary extraction techniques. The water injected into the oil reservoir to displace the oil did not penetrate the area with high permeability and thus circumvented most of the oil trapped here [39]. The emulsified oil droplets mobilized before were entrapped in pores with high permeability, thus forcing the flow of water through them. The emulsifier enabled that process by actively reducing the trapped oil’s interfacial tension and stabilizing it from coalescence [40].

By extension, Onaizi et al. used rhamnolipid as the stabilizer for O/W emulsions to enhance the recovery of crude oil. They highlighted three methods of enhancing stability. The first involves using a bioemulsifier instead of a chemical emulsifier, the former of which had a critical micelle concentration 40 times less than the latter [41]. The second entails using a nano-sized rhamnolipid to enhance the process of stabilization. As reported in other research, nanoparticles (NP) perform better than other oprtions as emulsifiers due to their strong tendency to promote interface adsorption [42–44]. Again, droplet size played an essential role in emulsion stability, and a smaller droplet size was achieved by manipulating the concentration of NPs top have a concentration equal to smaller droplets. The third method involves harnessing the pH effect, in which the pH value stimulates the emulsion. Depending on the NPs used as stabilizers, changes in pH value may force the stabilizers to aggregate into larger molecules, thereby lessening the effect of NPs and weakening their stabilizing ability. As a result, that dynamic prompts flocculation and, in turn, demulsification. That effect can be a boon in the oil and gas industry, whose technologies heavily depend upon the separation of oil and water.

4. LCMs as emulsifiers

LCMs such as cellulose, hemicellulose, and lignin are biopolymers with tremendous potential in producing bioproducts such as biofuels, biochemicals, and biogas. LCMs in wood biomass vary depending on the plant species, growth conditions, age, and season. For example, hardwood comprises 40–50% cellulose, 20–25% hemicellulose, and 20–25% lignin, whereas softwood comprises 35–40% cellulose, 25–30% hemicellulose, and 27–30% lignin, as illustrated in Figure 5 [45]. In plant cells, cellulose, hemicellulose, and lignin are sticky and associated with each other; thus, separating them has to be done in a pretreatment process before utilizing each component individually, as also illustrated in Figure 5.

4.1. Lignin

Derived from the Latin word *lignum*, lignin was discovered by French chemist Anselme Payen in 1838 [46], who also discovered another insoluble residue, cellulose, after treating wood with acid [47]. Lignin is the component that forms the cell wall in plants. Lignin's rigidity derives from its complex chemical structure consisting of high molecular weight, polydispersity, and heterogeneous compounds, all of which result in many intermolecular bonds within the structure, as shown in Figure 6 [48]. Lignin is built on an amorphous polyphenol that emerges from the polymerization of enzyme-mediated dehydrogenates made up of three primary phenylpropanoid monomers: p-coumaryl such as H-lignin (i.e., without methoxy groups on the aromatic ring), coniferyl such as G-lignin (i.e., with one methoxy group on the aromatic ring), and sinapyl alcohol such as S-lignin (i.e., with two methoxy groups on the aromatic ring), as shown in Figure 7 [49,50]. Harley et al. have reported that softwood lignin contains mostly G-lignin monomers with traces of H-lignin monomers. By contrast, hardwood lignin contains mostly G- and S-lignin monomers and a low amount of H-lignin monomers [51]. The G-lignin unit of monolignol, in forming a radical structure, prefers to couple in β-positions, primarily β-O-4, β-β, β-5, and less common linkages such as 5-5, 5-O-4, and β-1 [52]. Unlike other LCMs, lignin cannot break down into sugar, which makes it less popular as an emulsifier [53].

As an emulsifier, lignin utilizes the polar and nonpolar affinity of the hydrophilic phenolic/aliphatic hydroxyl groups and lipophilic carbon backbone [54]. The structure of polyphenolic lignin reduces the interfacial tension between oil and water [55,56] and stabilizes liquid–liquid mixtures in a dispersant for solid–liquid mixtures [57]. The substitution pattern of the aromatic ring of the monomer is essential, because each type of interlinkage has a frequency that changes according to the pattern. Briefly explained, in any reaction involving free radicals, the ability of an unpaired electron to delocalize is influenced by the electronic properties of the conjugated substituent groups. Consequently, the reactivity of monolignols changes according to the number of methoxyl groups modifying the chemical structure of the final polymer [58]. Those ionizable groups tend to stimulate adsorption at dispersion interfaces.

The means of extracting lignin from biomass may affect the type and abundance of inter-monolignol linkages of lignin's structure. For example, a long pulping process may induce repolymerization in the structure due to condensation reactions [59]. Two types of lignin are heavily utilized—Kraft lignin (KL) and lgignosulfonate (LS)—that differ according to the ionizable groups attached. The alkaline pulping process produces KL, whereas LS is produced by the sulfite pulping process; KL contains phenolic hydroxyl groups, whereas LS contains sulfur functional groups [60]. KL is also insoluble in water, for it tends to aggregate when mixed with water, whereas LS is soluble in water. Although both are surface-active components due to polyelectrolytic expansion and sulfonation, LS has a higher degree of sulfonation than KL, thereby making it inferior in surface activity. Table 1 lists types of lignin used as emulsifiers.

In research on the topic, Gunderson et al. have studied the surface and interface properties between KL and LS and found that the ionization of the sulfonate and carboxyl groups suppressed the surface activity of the lignin [61]. In other work, lignin's performance as an emulsifier has been shown to not be tied with that surface activity, for both LS and KL can enable both steric and electrokinetic stabilization [62]. Solubilized LS tends to have an ellipsoidal shape and agglomerates; temperature and pH can enhance its hydrophobic interactions, thereby causing it to form a far larger agglomeration [63]. Mixing LS with an anionic emulsifier can help to increase the surface activity, whereas mixing LS with a cationic emulsifier is ineffective. Ruwoldt et al. observed that emulsions with low LS hydrophobicity showed larger droplets and greater droplet coalescence; however, such coalescence was significantly less noticeable with highly hydrophobic LS [59]. That significant difference derived from total separation time, such that hydrophobic LS exhibited maintained some emulsions even after 10 d compared with only 1 h of hydrophilic LS [6].

Although both LS and KL can perform well as emulsifying agents, KL has more hydrophobic groups on its surface than LS, which generate enough interfacial activity even at low concentrations. Because LS's high sulfur content makes it more hydrophilic than KL, LS shows a greater tendency to adsorb at the interface instead of in the interface due to the lower number of hydrophobic groups. From that dynamic, two conclusions can be drawn: One, LS requires a relatively high concentration for stable emulsions, and two, mixing LS with another emulsifier can help to increase the surface activity.

Table 1: Types of lignin used as emulsifiers.

Type of lignin	**Sources**	**Type of emulsion**	**Particle size**	**Droplet size**	**Function**	**Remarks**	**Ref**

KL	Lignin (supplied)	O/W	100 nm,	19-49 µm	Pickering emulsions.	Stabilized the emulsion for months and lowered the interfacial tension to as low as 19.2 mN/m in a 0.1% concentration of modified lignin	[64]
AL and ORGL	Sugarcane bagasse	W/O	115-680 nm	-	Pickering emulsions for pharmaceutical medicine	Stabilized the emulsion for 4 d	[65]
SL	Oil palm empty fruit bunch	W/O	< 100 nm,	-	Emulsifier for food emulsifier	Stabilized the emulsion for 90 d and lowered the interfacial tension to as low as 1.33 mN/m at a concentration 2% of modified lignin	[7]
AL	Lignin (supplied)	O/W	~ 129 - 152 nm	-	Pickering emulsions for biomedicine	Stabilized the emulsion (50%) for 50 h at a concentration 0.1 wt% of modified lignin	[66]
KL	Lignin (supplied)	O/W	533-750 nm	> 20 µm	Pickering emulsions for cosmetics, pharmaceutic	Stabilized the emulsion for up to 5 h at a concentration	[67]

					al or emulsion polymerizations	0.25% of modified lignin	
KL	Pine	O/W	-	-	Surfactant agent for bio-based product	Improved the stability of the emulsion for less than 24 h at concentrations higher than 1%	[68]
KL	Lignin (supplied)	O/W	100-500 nm	1−100 μm	Bio-based stabilizer	Stabilized the emulsion by lowering the interfacial tension between oil and water up to 9 h at a concentration of 1.5% of modified lignin	[69]

4.2. Cellulose

Cellulose, a homopolymer found in the cell walls of plants, is highly representative in plants due to endless photosynthetic cycles that yield tons of cellulose in a relatively pure form. The strength of cellulose in cell walls lies in its preserved structure–aggregation state and its capacity to not dissolve in aqueous environments. Its hydrophilic nature stems from reactive hydroxyl groups structured at C-2, C-3, and C-6 in the linear polymer chain of glucose monomer units connected via ß-1,4 linkages, as shown in Figure 8 [70]. The strength of cellulose derives from the weaving of intermolecular and intramolecular H-bonding monomer units that make the structure dense and robust [71]. Among other LCMs, cellulose is by far the most commonly used, primarily in paper, cellophane, and rayon, and is also extracted to produce biogas and biochemicals such as ethanol, ethers, methane, and others [72], usually from biomass such as wood pulp and cotton crops.

For emulsions, cellulose has garnered attention due to its biocompatibility, nontoxicity, renewability, and low cost [73], all of which enable its use in applications that require strict regulations, including in the food, medical, and cosmetics industries. Cellulose has also long been popular in Pickering emulsions, which derives from an emulsification process stabilized by solid particles that adsorb onto the boundary of two phases. That process utilizes tightly packed layers from the oil–water interface to prevent coalescence and Ostwald ripening emulsions. Thus, cellulose presents greater advantages than other species due to its excellent permeability, good elastic response, and excellent capacity to inhibit coalescence [74].

However,, cellulose's structure needs to be modified before cellulose can be effective as an emulsifier. Primarily breaking cellulose's structure into individualized micro- or nanostructures with high crystallinity, that modification also reduces the amount of amorphous material present in raw cellulose. Many terms for those structures of micro- and nano-cellulose have been coined, including *cellulose nanofibers* (CNF), *cellulose nanocrystals* (CNC), and *microcrystalline cellulose* (MCC). Cellulose in those forms possesses wettability, the primary parameter in emulsion stability that can be measured based on the three-phase contact angle upon the partial wetting of two phases (θ), as expressed in Equation 3 [75]:

$$\Delta E = \gamma_{ow} \pi b^2 (1 - \cos\theta)^2 \left[1 + \frac{4\left({}^{a}/_{b} - 1\right)(\sin\theta - \theta\cos\theta)}{\pi(1 - \cos\theta)^2}\right] + 4\gamma_{ow} \pi b^2 \cos\theta \left(\frac{a}{b}\right) \qquad \text{Eq. (3)}$$

in which ΔE is the desorption energy required for emulsion stabilization, γ is the oil–water tension, a is the dimension of long semi-axes, and b is the dimension of short semi-axes. Rod-like cellulose nanocrystal possesses θ between 90° to 180°, which suggests its better physical connection to the liquid phase than other spherical entities, whose spherical contact angle would be between 0° and 180° [75].

When Yuan et al. studied the effect of the different morphologies of cellulose on emulsion stability, they found that nano-sized particles were critical in producing a stabilized phase by reducing the surface tension and the coalescence effect at the interface of the droplets. Compared with its basic structure, nano-sized cellulose exhibits high viscosity, a high elastic modulus, and high anti-deformation [76]. The differences in their performance are due to the nano-sized version's having a long, flexible, tightly linked fiber forming a stabilized droplet–fiber network structure. Dong et al. used spherical CNCs to stabilize an emulsion, which achieved high stability in pH, ionic strength, and temperature [77]. Furthermore, the loading amount required to stabilize the emulsion was far less than the amount generally required by other commercial emulsifiers. Meanwhile, Nabata et al. found that micro-sized cellulose with nanofiber walls improved the stability of an emulsifier. In contrast to past studies, they observed that smaller cellulose could be achieved by mixing the emulsion with a decane containing sorbitan monooleate with intense stirring [78].

Many applications involving O/W emulsions use cellulose emulsion in which numerous kinds of cellulose are modified by breaking down their structure, as shown in Table 2. Another route of modifying cellulose is etherification. Cellulose ethers often used in drug delivery applications can be obtained by substituting the hydroxyl groups in the cellulose with ethoxyl groups—for example, using a sodium hydroxide aqueous solution—to degrade their structure [79]. On that topic, Melzer et al. found that cellulose stabilized ether emulsions by forming a colloidal precipitate, as also occurs at the oil–water interface [80].

As those studies indicate, cellulose modified to have certain structures can be an excellent emulsifying agent. Modifying cellulose's structure is essential to improving emulsion stability because it increases the surface area. Depending on the method of modification used, breaking down cellulose also induces different charge densities in its structure, which further facilitates emulsion stability as well as solubility in water. Moreover, the orientation of any micro- or nanoparticles involved becomes more impactful, to a degree that either improves contact with the liquid phase or distorts the oil–water interface, as shown in Figure 9. Such a distorted interface yields more clusters, which affect the particle-packing efficiency and consequently enlarge droplets. The mentioned chemical method can also be used to modify cellulose’s structure, which necessarily generates other cellulose derivatives that are also soluble in water. Because modified cellulose tends to have both a hydrophilic and hydrophobic side, it can self-assemble at the interface.

Table 2: Types of cellulose used as emulsifiers.

Type of cellulose	**Source**	**Type**	**Particle Size**	**Droplet size**	**Remarks**	**Ref.**
CNF	Cellulose maple and birch	O/W	D= 0.12 µm L= 9.93 µm	50 – 100 µm	The creaming index is less than the sedimentation ratio.	[76]
Spherical-CNC	Cellulose (supplied)	O/W	D= 30 – 60 nm	2.5 µm	It has high stability in pH and ionic strength.	[77]
CNC	Ginkgo seeds	O/W	D= 310 nm	1 – 10 µm	Cellulose length influences the release of free fatty acids.	[81]
CNF	Cellery pomace	O/W	H= 6-14 nm L= 0.8-1.5 nm	9 – 10 µm	It has excellent storage stability after 7 d.	[82]
Magnetic-CNC	Cellulose (supplied)	O/W	D= 6 -26 nm	1.14 µm	Magnetic cellulose nanocrystals (CNC)	[70]

			L= 50 – 450 nm		provide a robust electrostatic repulsion among droplets that prevents coalescence.	
Magnetic-CNC	Cotton cellulose	O/W	L= 165 nm H= 8 nm	2 – 3 µm	The magnetic index surface has a surface charge close to zero and good adsorption.	[83]
SC membrane	Cattail plant	O/W	L= ~100 µm D= 1 – 5 µm	< 20 µm	Droplets completely disperse on the membrane due to superoleophilicity and superhydrophilicity.	[72]
CNC/CNF	Lemon seeds	O/W	L= 155 nm D= 14 nm	65 – 70 µm	Shorter CNCs promote individual droplets, and cellulose nanofibers (CNF) stabilize at low ionic strength.	[73]
CNC/MPEG	Alfa fibers	Polymer	L= 250 nm D= 10 nm	350 – 400 µm	Methoxy poly(ethylene glycol) (mPEG) helps CNCs to stabilize in emulsion polymerization.	[74]
CNC/PS	Cellulose (supplied)	O/W	D= 35 nm	14 µm	Longer reactions induce longer polystyrene (PS) chains grafted to CNCs. It has	[84]

					a high PS concentration and smaller droplets.	
CNC/CAS	Cellulose (supplied)	O/W	-	3 – 36 µm	Low CNC loading is enough to stabilize emulsions, while high sodium caseinate (CAS) loading forms smaller droplets.	[85]
CNF	Cellulose (supplied)	O/W	D= 28.1 nm L= 4.9 µm	0.8 µm	Increasing the concentration of CNFs enlarges droplets and reduces their protection.	[86]
PLA/CNC	Wood pulp	-	D= 20 – 40 nm	-	The cellulose’s large aspect ratio prompts the formation of a network structure.	[87]
CNC	Cellulose (supplied)	Oleogel/w	L= 40 – 180 nm H= 2 – 9 nm	5 – 10 µm	Increasing CNC loading increases the viscosity and gel strength.	[88]
CNC/SPI	Cellulose (supplied)	O/W	L= 129 nm	10 µm	CNCs with amphiphilic functional groups lead to stable Pickering emulsions.	[89]
CTAB/CNC	Cellulose (supplied)	O/W	D= 20 – 50 nm	5 µm	Increasing Cetrimonium bromide	[90]

(CTAB) loading reduces their interfacial tension with CNCs.

4.3. Hemicellulose

The most abundant LCM after cellulose, hemicellulose is a heteropolymer consisting of fewer glucose molecules than cellulose. Figure 10 shows the functional groups present in the hemicellulose chain, namely pentoses (e.g., arabinose and xylose), hexoses (e.g., glucose, mannose, and galactose), hexuronic acids (e.g., glucuronic acid), acetyl groups, and small amounts of rhamnose [91]. Mannose is an essential hemicellulose monomer, followed in importance by xylose, glucose, galactose, and arabinose. Because building monomers can involve various feedstock sources, hemicellulose can be categorized based on primary sugar residues, the most common of which are xylans and glucomannans. For example, O-acetyl-galactoglucomannan (GGM) consists of mannose, glucose, and galactose, with mannose four times more present than other monomers. Some mannoses are acetylated at the C_2 or C_3 positions with an average of one substitute group for every four hexose units. GGM is therefore easily depolymerized by acids and alkalis, for the acetyl groups tend to be cleaved in acidic and alkaline reactions. Hemicellulose is also shapeless, lacks the crystalline structure of cellulose, and is more prone to dissolve in water at temperatures exceeding 180 °C. As such, hemicellulose can be extracted using hydrothermal techniques and hydrolysis [92], as well as easily converted to sugar oligomers in large yields. For instance, Krogell et al. extracted hemicellulose from spruce wood using a hydrothermal autoclave reactor at 170 °C, and their results revealed that they extracted the maximum amount of the LCM [93]. Given the weak water solubility of some hemicelluloses, the methods most used for extraction are alkaline-based extractions involving either sodium hydroxide or hydrogen peroxide at high operating temperatures.

The structure of hemicellulose is more complex than that of cellulose. Although with gummy-like properties similar to those of polymers and with emulsifying properties similar to cellulose's, the structure of hemicellulose is distinguished by monomers grafted as a backbone. As an emulsifier, hemicellulose has a branching degree that plays a crucial role in its emulsifying performance. Higher molecular weights and more complex branches of hemicellulose tend to pose more PSs, which increases steric interference and charge repulsion [94]. Such PSs have lipophilic groups that can absorb oil on their surface and, in turn, create emulsion effects. For example, phenolic residues in GGM can act as a hydrophobic anchor able to induce steric-stabilized emulsion [95]. Added to that, emulsion stability can be enhanced by introducing an amphiphilic residual protein fraction, because the physical and chemical interaction between proteins and PSs increases the steric repulsion of the emulsion. Taken together, hemicellulose's degree of branching, molecular weight, grafted functional groups, and protein content all contribute significantly to its emulsion performance, typically in macro-emulsions due to the number of PSs involved.

Table 3: Types of hemicellulose used as emulsifiers.

Type of hemicellulose	**Source**	**PS/Oil ratio**	**Droplet Size**	**Application**	**Remarks**	**Ref.**
Spruce-GGM	Spruce saw dust	0.8/1.5	1 – 10 µm	Beverage	Stability of emulsion maintained for 7 d.	[98]
Spruce Gum-GGM	Spruce saw meal	2/0.4	0.3 – 0.9 µm	Food	Macromolecular PS help with obtaining desired interfacial saturation.	[95]

Spruce-GGM	Pulp mill	0.1/1	-	Beverage	Galactoglucomannan (GGM) increases the turbidity of the emulsion.	[100]
Spruce-GGM	Pulp mill	1/5	0.4 µm	Food	More GGM leads to greater functionality and anchoring at the interface.	[96]
CMGGM	Pulp mill	1/5	0.1 – 1 µm	Food	Carboxymethyl at the C6 position is abundant in the aqueous phase but more often at the C3 position in the droplet phase.	[101]
CMGGM	Pulp mill	1/5	>1 µm	Food	Carboxymethyl decelerates the oxidation and lowers the amount of hydroperoxides after 8 d.	[102]
Glucuroxylans-GGM	Pulp mill	0.8/4	1 – 10 µm	Paint	Wood species determine the hemicellulose’s emulsion-conducive properties, phenolic residues, and carbohydrate content.	[103]

5. Modification of LCMs

In fabricating LCM-based emulsifiers, modifying their structure can improve their surface activity or composition in functional groups via the chemical and/or physical modification of particle size, ionic strength, temperature, solvent, concentration, or pH [104].

Chemical modification (e.g., alkylation, esterification, and cross-linking) occurs when additional functional groups are attached chemically to the LCM structure and thus enhance its emulsion-conducive properties [105]. By contrast, physical modification occurs when the LCM structure is modified mechanically by shear force, which forcefully breaks it into smaller structures.

5.1. Surface modification

Although the chemistry of plant sources generally defines the properties of their LCMs, those properties can be changed via chemical modification, as has been done for many applications, sometimes at the surface. As an example of surface modification, acetylation significantly enhances resistivity to biological attack, while esterification enhances the fire-retardant properties of fibers [106]. For emulsifiers, surface modification seeks to improve the affinity to specific polar and nonpolar molecules.

In other cases, modification seeks to link a functional group to the surface of the LCM in order to enhance reactivity (e.g., pH reactivity and thermo-reactivity). Ultimately, the modification can improve the performance of LCMs in emulsions by providing them with better stability. CNCs can be further modified with hydrophobic alkyl groups to increase the stability of Pickering emulsions, namely by helping to create small droplets (< 250 nm). CNCs can be modified due to their perfectly solid particles with well-defined planar structure. The hydrophilic crystalline groups, located at the end of CNCs, act as a minimal force for stabilization at the interface, and the surface is primarily flat, with repeated –CH groups of glucosyl moieties but without hydroxyl functions [107]. Thus, CNCs can absorb functional groups by way of covalent and non-covalent surface modification.

In Saidane et al.'s study on how charge densities affect modified CNCs in Pickering emulsions, three samples with an average length of 156 nm and width of 16 nm labeled CNC-

S, CNC-M, and CNC-H were prepared with various hydrolysis parameters and different charge densities: 0.08, 0.16, and 0.64 e nm^{-2}, respectively [108]. Their results showed that the repulsion between the charged CNCs limited the adequate surface density around the droplets, thereby leading to unstable O/W emulsions. In all samples, droplet size decreased as the concentration of emulsifier increased. Overall, the charge densities posed limitations, for they required critical concentrations due to limited flexibility and thus required more curvature to cover the droplets. Those results explain the CNCs' low capacity for adsorbing surface charges at the interface. In other work, Gong et al. suggested that inserting functional groups onto the surface of CNCs could increase the surface charge densities [109]. In their study, wood-based cellulose was oxidized with phenyltrimethylammonium chloride, which yielded phenyl groups with hydrophobic tendencies grafted around the CNCs (i.e., O-CNCs). Compared with unmodified CNCs, the flexibility of the O-CNCs indicated their alignment on the surface of droplets to a degree suggesting that some deformation had occurred. The phenyl groups' relatively high phenyl groups content also indicates improved hydrophobic interaction and electrostatic repulsion, both of which can influence the contact angle and enhance wettability. Therefore, the surface modification of CNCs can make their emulsion stability better than that of pristine CNCs, as shown in Figure 11.

Unlike other LCMs, hemicellulose's has to be surface-modified for emulsification, which can be accomplished by esterification, acetylation, cross-linking, and grafting [110]. Because hemicellulose is a heteropolymer, it can be both soluble and insoluble; therefore, its purification usually concentrates on the four major sugar compositions: xylans, mannans, xylogalactans, and xyloglucans. GGM, a small, linear chain of PSs in the group of mannans that adsorb at the dispersed interface, has shown promising results in fatty acid delivery and is suitable as an emulsifier [98]. However, modified GGM with carboxymethyl has been shown to enhance the accessibility of GGM's structure such that the structure can be revamped and the amount of anionic PSs increased [111]. That enhancement results in more hydroxyl activity due to the increased accessibility of the carboxymethylated cellulose and, in turn, more stable emulsions.

Natural surface activity (i.e., without chemical derivatization) can be achieved using hemicellulose-rich aqueous extracts [112]. Xu et al. have reported that pure GGM, given its molar mass, can be used to stabilize wood resin via steric stabilization as a means to reduce their tendency toward deposition in the system [113]. Nevertheless, with lignin or cellulose as phenolic materials, GGM's capability to stabilize emulsion increases. Lehtonen et al. have suggested that applying GGM with additional lignin-derived phenolic residue as a stabilizer can improve emulsion stability for months without any additional stabilizer or antioxidants [96]. Such stability derived from the lignin's phenolic compounds associated or covalently bound to hemicellulose (i.e., a sugar unit) via ester, ether, or glycosidic bonds that provide steric stabilization (i.e., repulsion) at the oil–water interface. Similarly, Lahtinen et al. found that pressurized hot water extraction (PHWE) hemicellulose with additional phenolic-rich lignin also extended the physical and oxidative properties of emulsions [114]. Table 4 details the performance of LCMs after surface modification.

Surface modification alters the inherently hydroxy-rich macrostructure of LCMs, which makes them less hydrophilic. The effect of charged densities also applies in that type of modification, which affords better hydrophobic interaction and alignment with the contact angle at the interface. Research has also shown that the method improved the interfacial activity of emulsions, enhanced the flow resistance, and increased the surface area of the particles.

Table 4: Lignocellulosic materials with surface modification and their performance.

Type of LCMs	**Sources**	**Type of emulsion**	**Modification**	**Mechanism of stability**	**Remarks**	**Ref**

KL	Lignin (supplied)	W/O	Modified with tetraethylene pentamine and formaldehyde	Improved the viscous flow resistance of the emulsion.	Stabilized the emulsion.	[115]
AL	Pine	O/W	Modified by quaternary ammonium and SiO_2 NPs via electrostatic adsorption	Improved the interfacial activity of the emulsion.	Stabilized the emulsion.	[116]
KL	Furfural residues	O/W	Coated with PSR microparticle via free radical polymerization	Improved the interfacial activity of emulsion.	Produced a reusable emulsifier and stabilized the emulsion.	[117]
KL	Pine	O/W	Modified via carboxymethylation with chloro- acetic acid, acetic acid, and sodium hydroxide	Lowered the surface activity of emulsion	Stabilized the emulsion for over 30 d.	[118]
SL	Oil palm empty fruit bunch	W/O	Modified with high sheer homogenizer	Increased the surface area of the particles and improved their stability.	Stabilized the emulsion for 30 d.	[119]
Cellulose	Cellulose (supplied)	O/W	Modified with acetoacetate	Formed a mechanical barrier and adsorbed the emulsion via the	Reduced and retained droplet size (i.e., 3–5 μm) for at least 7 d.	[120]

				amphiphilicity of modified cellulose.		
CNC and CNF	Lemon seeds	O/W	CNC modified with CNF concentration	Improved the viscosity of the emulsion.	Reduced and retained the droplet size, (i.e., 3–5 μm) for at least 15 d.	[73]
CNF	Miscanthus floridulus straw	O/W	Modified with high-pressure homogenizer	Increased the particle surface activity and created the irreversible adsorption of the interface.	Reduced and retained the droplet size (i.e., 10 μm) for 14 d.	[121]
GGM, hemicellulose	Pulp mill	O/W	CMGGM	PS adsorbed the interface of the emulsion.	Reduced droplet size to 400 nm and stabilized the emulsion against coalescence for more than 14 d.	[101]
GGM, Hemicellulose	Pulp mill	Lipid-water	Extracted with SSL (high lignin content)	Improved colloidal stability.	Stabilized monoolein-based system for at least 42 d.	[122]

5.2. Particle size

In emulsions, *particle size* often refers to the size of droplets of the emulsion. Pickering emulsions occur when solid molecules are used as emulsifiers and thus depend on the emulsifiers' size and shape. Modifying particle size in LCMs can involve either reducing the size to the micro- (i.e., 1 µm–100 nm) or nanoscale (i.e., <100 nm) or inserting another NPs component onto the LCMs. A small particle size in emulsifiers creates a large interfacial area between the two phases in emulsions [123]. Micro-sized emulsifiers have an excellent affinity for absorbing the water–oil interface due to their large surface area. Furthermore, the gravitational force is less of an effect for micro- and nano-sized colloids. Because micro-sized particles often promote wettability depending on the contact angle, the shape of the particles will influence the interface's coverage and stability, as shown in Table 5. Although various shapes can influence the stability of emulsions, plant-based materials typically have rod or spherical shapes. The rod-like structure possesses a contact angle between 90° and 180°, meaning that the surface of particles is evenly wetted in both [75]. Compared with the spherical structure, the rod-like structure provides a better surface ratio to form bridge structures with both phases.

Kalashnikova et al. found that even in CNCs with an elongated shape, a short aspect ratio affords better coverage. In their study, short rod-like CNCs afforded better network stability than longer ones [124] when three CNCs—CCN, bacterial cellulose-based CNC (BNC), and Cladophora CNC (ClaCN)—with respective aspect ratios of 13%, 47%, and 160% were compared. Interestingly, the CCN exhibited a significant coverage ratio (i.e., amount of CNCs involved in an emulsion, or *packing density*) of 84%, with the smallest aspect ratio of 13%, compared to only 44% for ClaCN with an aspect ratio of 160%. The difference in length and flexibility allowed the small aspect ratio to form a denser network structure than the high aspect ratios. Because similar nanocrystals exhibited the same flexibility and bending capacity, it was concluded that longer rod-shaped CNCs have a higher steric hindrance that reduces the density but also produces a multilayered profile. Along the same lines, Wang et al. found that shorter CNCs formed connections easier with the interface layer—the CNCs used ranged from 178.2 to 261.8 nm, with 72.4–77.2% crystallinity—and thus afforded better emulsion stability [125]. In their study, the length of the CNCs was controlled by increasing the duration of hydrolysis (>2.5 h), which resulted in cellulose particles shaped similarly to needles, as a shown in Figure 12. The needle-like shape stemmed from the purging of amorphous cellulose, and that final formation was reduced in length from 261.8 nm to 180.7 nm and 10 nm in diameter. Those changes improved emulsion stability because shorter CNCs formed better side-by-side alignment with each other by way of attractive force.

In contrast to cellulose, lignin is typically irregular in shape as a dried powder despite its origin. Morphologically, that irregular shape is considered to be unsuitable in Pickering emulsions due to the need for more energy in surface activities, especially packing density [126]. Further investigation showed that spherical particles had a maximum packing density of 0.74, which was less than the rod-like structure's packing density of 0.91 [127]. Given the lower packing density of spherical structures, cellulose-based emulsifiers are more popular in Pickering emulsions. However, the chemical modifications required to shape the lignin colloids can also enhance the lignin's surface activity. For example, Dai et al. used self-assembled Lignin-poly (N-isopropyl acrylamide) (L-PNIPAM) as a colloidal emulsifier in Pickering emulsions, in which radical polymerization retained L-PNIPAM's spherical form due to the minimization of surface energy [66]. In addition, L-PNIPAM was thermo-responsive, as shown by the change in diameter of the spherical particles. Upon being heated to 45 °C, the diameter shrank from 186.8 nm to 126.4 nm, as shown in Figure 13. As such, the center-to-center distance between the L-PNIPAM particles reduced and could not expand laterally, which proved to be stable against coalescence.

Bertolo et al. have reported that lignin macromolecules are rarely exploited due to their low solubility in aqueous media and natural heterogeneity but for those same reasons are primarily used as emulsion stabilizers [65]. Emulsion stability can be predicted by referring to the contact angle of particles in order to explore particle reactions at the interface. In O/W emulsions in their study, the adsorbent layer bent toward oil droplets as the aqueous phase wetted the hydrophilic region, which resulted in an angle range of $15° < \theta < 90°$. Meanwhile, in W/O emulsions, the hydrophobic particles were bent at a range of $90° < \theta < 165°$. In view of those results, Bertolo et al. proposed that NPs increased the surface area and hydrophilic activity such that water could spread more on the surface and lower the contact angle [65].

Ultimately, particle size is essential in LCM emulsifiers, and tailoring it can alter the wettability of particles. As shown in Equation 3, the energy required to remove a particle in the interface is directly influenced by the particle's radius and the contact angle. Thus, the smaller the particles, the greater the energy required for detachment. Therefore, the required energy is larger than the thermal energy, which renders the absorption process irreversible or stable. Modifying the structure of XXX also enables better packing conditions around the interface, which is especially true for cellulose given large numbers of hydroxyl groups that create the macromolecular structure responsible for its stiffness. Thus, the packing and stacking of cellulose without reducing the size of its particles enlarges droplets.

Table 5: Lignocellulosic materials with modified particle sizes and their performance as emulsifiers.

Type of LCMs	Sources	Particle size	Particle shape	Mechanism of stabilization	Details	Ref
Lignin-DEAEMA	Lignin (supplied)	237–404 nm	-	Formed a boundary at the oil phase	Stabilized the emulsion for 30 d	[128]

AL and ORGL	Sugarcane bagasse	105-130 nm	Spherical	Generated good particle stability and formed an adsorbent at the interface	Good encapsulating agent for bioactive compounds	[65]
AL	Lignin (supplied)	70-200 nm	Non-spherical	Facilitated self-assembly due to good particle stability while droplet size remained unchanged	Stabilized the emulsion for 60 d	[129]
SL	Oil palm empty fruit bunch	~100 nm	Non-spherical	Lowered the interfacial tension and creaming index of the emulsion	Stabilized the emulsion for 30 d	[119]
CNC	Asparagus	178-262 nm	Rodlike	Increased the adsorption of the interface and viscosity	Stabilized the emsulsion with droplets 1-10 μm in diamteter	[125]
Cellulose	Ginkgo seed shells	300 nm	Rodlike	Increased the adsorption of interface and the viscoelastic interfacial film	Improved emulsifying ability and stabilized the emulsion for 10 d	[130]
CNF	Miscanthus floridulus straw	33-49 nm	Rodlike	Increased the activity of particles and made adsorption	Imporced the emulsion stability due to small particles	[121]

at the interface
irreversible

5.3. pH

Emulsion systems behave differently depending on the pH. In particular, a specific pH can secure emulsion stability but creates instability when it differs by being either more acidic or alkaline. Such instability is due to the sensitivity of proteins or surface-active emulsifiers to changes in pH that affect electrostatic interactions [131]. Moreover, pH influences droplet size and the surface area of emulsions because ionic strength impacts the activity of the surface charge of particles in absorbing the oil/water at the interface [73]. Juttulapa et al. found that emulsions prepared at lower pH resulted in smaller droplets, higher viscosity, and longer stability [132]. They also found that increasing the pH affected the emulsifiers by generating negative charges that lessened the number of stable emulsions. Depending on the type of emulsion and the emulsifiers, an oppositely charged emulsifier can form electrostatic complexes that increase the stability of the emulsion. Equation 4 shows the Henderson–Hasselbach equation that describes the relationship between the emulsion system and pH:

$$\text{pH-p}K_a = \log[(1-\alpha)/\alpha] \qquad \text{Eq. (4)}$$

in which α is the degree of ionization and hinges on the difference of pH – pK_a [133]. Therefore, emulsion stability changes drastically if the pH and pK_a values are nearly identical, for they influence the wettability of the particles. Some structures are cationic at low pH but anionic at high pH depending on the ionization of the functional groups attached, as shown in Fig 14. When both phases are oppositely charged, the droplets are electrostatically attracted to surface-forming complexes, which may induce a far more viscous solution as a result.

LCMs also have an affinity toward pH that influences the performance of the emulsion system by changing the zeta potential, as shown in Table 6. For lignin, LS is more prone to ionize at acidic solutions, whereas KL is prone to ionize in alkaline solutions. Because lignin generally contains hydrophobic and hydrophilic functional groups with phenyl monomers and carboxyl groups, respectively, the different phases of pH heavily influence its performance as an emulsifier. Li et al. studied the phase behavior of KL in O/W emulsions and found that KL had the best affinity with water at a pH of 9 [118]. The distribution curve of the size of the oil droplets increased from 1.6 mm to 2.0 mm at pH values of 5 and 9, respectively. Although small droplets play a significant role in emulsion stability, slightly bigger droplets indicates that oil droplets have merged and thus reduced the interfacial area for more dynamic equilibrium. KL cannot reduce interfacial tension at lower pH values and produced less stable emulsions due to having less hydrophilicity and water solubility. Meanwhile, Rojas et al. found that KL emulsions at pH values greater than 7 can be described as Winsor type I, in which the emulsifier forms a micro-emulsion in the aqueous phase of an O/W emulsion [53]. However, similar results for solubility in relation to low pH were obtained as well. Thus, those authors proposed that modification via alkylation can increase the oleic phase's affinity to create a more hydrophobic structure. Even then, the partition between those two phases is apparent when using extreme pH values. That separation can be reduced by balancing the salt concentration, which determines electrostatic interactions and wettability.

Other than alkylation, modifying lignin's structure with hydrophilic NPs can improve emulsion stability. That modification is primarily done in emulsification through electrostatic interaction. However, the adsorption of NPs into lignin can be difficult due to the large number of hydroxyl groups on the surface of the interface. Wei et al. studied Pickering emulsions using alkaline lignin with polystyrene (PSR) NPs and found that the PSR could absorb and capsulate lignin by changing the pH value via π–π interaction/hydrogen bonding [117]. They also found that a pH of 2 stabilized the emulsion while pH values greater than 2 resulted in flocculation. Similar results were obtained by Lu et al. in Pickering emulsions using amphoteric lignin and SiO_2 NPs [116]. The pH-responsive effect to the ionic properties caused the quaternary ammonium groups to exhibit strong cationic properties at lower pH. At the same time, the carboxyl and phenolic hydroxyl groups exhibited strong anionic properties at higher pH. Thus, lignin and NPs could absorb each other at opposite charges at a specific pH. According to those results, pH-responsive emulsion is an excellent way to control emulsification and demulsification.

Modified cellulose can be heavily affected by changes in pH. For example, Punitha et al. found that the velocity value of hydroxypropyl methylcellulose (HPMC) changed at pH values between 4 to 7 [134]. In particular, the viscosity of HPMC decreased at lower pH and increased at higher pH. That variation in viscosity was due to the coiling nature of HPMC as ionic strength increased. Therefore, the number of hydrogen bonds in an emulsion differs with pH, such that low pH values mean a high number of hydrogen bonds. That dynamic simultaneously affects the interaction between cellulose and the continuous phase, as shown in Figure 15. The ability of cellulose-based emulsions to be stored is excellent regardless of changes in pH but affects the zeta potential. Li et al. investigated the activity of CNFs in relation to pH changes in Pickering emulsions and found that the CNFs were dispersed better at a pH values between 4 and 7 [121]. The distribution size of the droplets at or near that pH value was slightly bigger than at other pH values. However, the zeta potential indicated that the emulsion was stabler in that phase than in others. That phenomenon indicates that the droplets coalesced to reduce the interfacial area as similar to what occurs with lignin. In addition, the emulsion performed remarkably in terms of storage stability and showed generally excellent stability. Cellulose also can be used in pH-responsive emulsions due to its reaction to changes in pH. When Tang et al. modified CNCs with poly[2-(dimethylamino)ethyl methacrylate]

(PDMAEMA) as a pH-responsive emulsifier, they observed that the emulsion was cloudy (i.e., 8% transmittance) when the pH less than pK_a resulted in the positive charge of PDMAEMA and the negative charge of CNCs, which produced aggregation [135]. Because pH exceeded pK_a, the complete deprotonation of the amino groups resulted in only the negative charge of remaining CNCs. The PDMAEMA chain was sterically combined with the CNCs, thereby lowering the zeta potential.

Hemicellulose can be soluble or insoluble in water depending on which components are in the chain. Modified hemicellulose has been used in pH-responsive emulsions, especially in drug delivery. In addition to adding pH-responsive edges, most hemicellulose modifications focus on enriching certain PS groups to enhance their properties. For example, Sun et al. focused on isolating xylan in hemicellulose due to its antiphlogistic effects and immune function [136]. Xylan was modified with hydrogel owing to its sensitivity to changes in pH. As a result, the composite showed excellent biodegradability and sensitivity to pH suitable for oral drugs.

In any emulsion, the pH can be altered to influence stability by affecting the surface charges. Unlike other modifications, however, modifying pH only reveals its effectiveness in terms of stability in a certain pH range. In that range, the emulsifier and interface are oppositely charged and thus stabilize via electrostatic forces. Because the wettability of a particle depends on the pH, altering the pH alters the zeta potential. Some LCM derivatives have shown an excellent response to pH relative to others due to the amount of hydrophobic and hydrophilic groups in the structure. Moreover, such excellent affinity to pH is exploited in carrier applications, especially in drug delivery, because each human body has a different pH. Beyond that, the degree of ionization can be enhanced by using salt in the solution.

Table 6: Lignocellulosic materials with modified pH and their performance as emulsifiers.

Type of LCMs	**Sources**	**Type of emulsion**	**pH**	**Mechanism of stability**	**Details**	**Ref**
KL	Lignin (supplied)	O/W	3-10	Increased particle stability and reduced interfacial tension	Stabilized the emulsion at pH 3 and 5 and unstable at pH 7 and 10 for 18 h	[69]
KL	Furfural residues	O/W	3-9	Improved the adsorption layer of the emulsion	Stabilized the emulsion at pH 3-4 and unstable at pH 5-9 for 6 months	[117]
Modified lignin, amphoteric lignin, and SiO_2 NP.	Pine	O/W	2-11	Improved the adsorption layer and increased the viscosity of the emsulsion	Stabilized the emulsion at pH 3-4. Emulsion unstable at pH 5-11	[116]
CNF	Miscanthus floridulus straw	O/W	3–11	Increased particle stability and reduced droplet size	Stabilized the emulsion at pH 4.5–7.0. Emulsion unstable at pH 9.5-11.0	[121]
Modify bacterial cellulose	Cellulose (supplied)	O/W	2- 9	Improved the adsorption layer of the emsulsion, increased the viscosity, and reduced droplet size	Stabilized the emulsion at pH 4–5. Emulsion unstable at pH 9 for 14 d	[137]

5.4. Concentration

The concentration of emulsifiers can also contribute to emulsion stability. Because emulsifiers need to surround particles in the dispersed phase and prevent them from coalescing, having more emulsifiers present results in the complete coverage of said dispersed particles. The finer the droplet size, the greater the surface area that needs to be covered, and droplets merge until the emulsifier reaches full coverage. However, at a certain threshold value, the effect of increasing the concentration is maintained. Fox et al. found that the droplet size of dispersed oil decreased with the concentration of the emulsifier until the emulsifier volume reached 1.2 wt% while droplet size remained unchanged [138]. The type of emulsifier affects the total amount needed to reach such a threshold, for 2 or 3 times the amount of emulsifier may be needed to cover the surface area. LCMs also demonstrate a similar trend regarding emulsification, as shown in Table 7. Czaikoski et al. have suggested that increasing lignin's concentration promotes interaction with the interface of the droplet [60]. The presence of aromatic hydrophobic and hydrophilic fragments in lignin's structure also leads to self-aggregation and self-organization. As a result, dense-packing lignin forms a robust solid-film capsule around the interface. By comparison, a high dosage of emulsifier exceeding the threshold results in bubbles, which also implies the rupture of the film [139].

Li et al. have reported that the concentration of CNFs influences the rheological behavior of emulsions [121], which stabilized when the concentration of CNFs increased from 0.1% to 0.2% and thus contributed to compounding cross-linking in the network structure. The viscosity of the emulsions also increased, likely due to attractive forces, which also affected the shear rate rheology. Such rheological changes emerged because the surface of the emulsions were covered with CNFs. Modifying cellulose can also impact its wettability. For example, micro-fibrillated celluloses (MFCs) can give out low hydrophobicity, which confers a low degree of wettability owing to the high amount of carbon on the surface of cellulose fibrils bound to the oxygen during modification [140]. Increasing the concentration of the MFCs can afford enough of a network to reduce the interfacial region and therefore stabilize the emulsion. In the case of hemicellulose, GGM is considered to be a strong stabilizer in emulsions. A high concentration of GGM can drive steric repulsion, adsorb oil/water droplets, and consequently stabilize emulsions, as shown in Figure 16. GGM's adsorption of the dispersed phase also increases viscosity, especially in Pickering emulsions [96]. Knowing that emulsion stability can be monitored by the increasing viscosity of the continuous phase, Lehtonen et al. found that using GGM as an emulsifier gave the continuous phase more viscosity than the known surfactant (i.e., Tween20). Its performance also contributed to GGM's high-volume fraction [96].

Table 7: Lignocellulosic materials with different concentrations and their performance as emulsifiers.

Type of LCMs	**Sources**	**Type of emulsion**	**Concentration**	**Mechanism of stability**	**Details**	**Ref**
KL	Pine	O/W	0.25, 0.5, and 1 %	Higher concentration increased the adsorption at the xylene/water interface.	Stabilized the emulsion for less than 24 h	[68]
KL and LG	Lignin (supplied)	O/W	0.005, 0.05 and 0.5%	Higher concentration, 0.5% improved particle stability and increased the viscosity of the emulsion.	Reduced the emulsion droplet size and stabilized the emulsion for 28 d	[60]

SL	Oil palm empty fruit bunch	W/O	1, 1.5 and 2 %	Higher concentration, 2% improved the creaming index of emulsion.	Stabilized the emulsion for 90 d	[7]
CNC and CNF	Lemon seeds	O/W	Fixed concentration of CNC (0.5%) but varied CNF concentration, 0 % ~ 1 %	Higher concentration, > 0.3 % increased the emulsion viscosity	Reduced the droplet size and stabilized the emulsion for less than 15 d	[73]
CNF	Miscanthus floridulus straw	O/W	0.05–0.20 %	Resulted a good creaming index of the emulsion.	Reduced the droplet size (i.e., 10 μm) and stabilized the emulsion for 14 d	[121]
CMGGM	Pulp mill	O/W	0.01-1% (PS)	PS adsorbed the interface	Reduced the emulsion droplet <1 μm.	[101]
GGM, hemicellulose	Spruce and birch	O/W	8 and 12 %	Produced high viscosity and lower the surface tension of the emulsion.	Stabilized the emulsion for several months.	[112]

6. Application of LCMs as emulsifiers

Bio-based emulsions are currently heavily utilized due to green movements launched worldwide. LCMs are considered to be bio-based as well, and given their abundance, they have become the ultimate renewable resource. Furthermore, their use can reduce greenhouse effects and global warming. Table 8 lists LCMs used as emulsifiers and their applications. Yuliestyan et al. produced modified KL in an alkaline medium in the presence of tetraethylenepentamine and formaldehyde and used LCMs in fabricating cationic bitumen emulsions with up to 70 wt% bitumen content [115]. Meanwhile, Li et al. used carboxymethylated KL to stabilize kerosene-in-water emulsions, which have the potential for alternative use in fuel emulsions [118].

The food industry strongly advocates green emulsion technology because many food products depend on such technology, including sauces, creams, beverages, and dressings. The recent rapid growth in veganism and consumers seeking natural products amid heightened awareness of healthy lifestyles has forced major food companies to consider the side effects of the ingredients used, including emulsifiers. In particular, manufacturers often want to make new products entirely from natural ingredients so that they can make "all-natural" claims on their labels [141]. Alternative bio-based food emulsifiers have thus gained considerable attention from researchers, including Sekeri et al. [7], Wang et al. [125], Dai et al. [73], Lehtonen et al. [96], and Mikkonen et al. [112,101], who have focused on using LCMs as food emulsifiers. Such research approaches have involved types of reformulation to replace synthetic or animal-based byproducts with more label-friendly natural alternatives [142]. In pharmacological applications, lignin plays a protective role against the development of different diseases and thus improves human health [143]. In that field, Mikkonen et al. [101] and Lehtonen et al. [96] have used GGM, a hemicellulose, as a stabilizer for drug delivery applications, cosmetics, pharmaceutical products, paint, coatings, and medicine.

Table 8: Applications of lignocellulosic materials as emulsifiers.

Type of LCMs	**Sources**	**Type of emulsion**	**Modification**	**Stabilization mechanism**	**Application**	**Ref**
KL	Lignin (supplied)	O/W	Cationic modified lignin	Chipping surface dressing and mixed the asphalt	Bitumen emulsion, Road paving	[115]

SL	Oil palm empty fruit bunch	W/O	-	Increased the viscosity of the emulsion and lowered the surface tension.	Food emulsifier	[7]
KL	Pine	O/W	CML	Reduced droplet size and increased viscosity of the emulsion	Fuel emulsion	[118]
CNC	Asparagus	O/W	-	Increased the viscosity and adsorption of the emulsion	Food emulsifier	[125]
CNC and CNF	Lemon seeds	O/W	Varied the CNF concentration, 0 % ~ 1 %.	Increased the viscosity of the emulsion and reduced the droplet size	Food emulsifier	[73]
GGM, hemicellulose	Pulp mill	O/W	Extracted with lignin phenolic-rich	GGM covered the surface of the NPs without affecting the internal structure in water	Drug delivery system	[101]
GGM, hemicellulose	Pulp mill	O/W	Extracted with lignin phenolic-rich	Decreased the interface of the PHWE emulsion and provided stability for 8 months	Food emulsifier and pharmaceutical	[96]
GGM, hemicellulose	Spruce and birch	O/W	Extracted with lignin phenolic-rich	Increased the viscosity of emulsion and	Food, cosmetics, pharmaceutics, paint, and	[112]

				lowered the surface tension	coating industries	
GGM, hemicellulose	Pulp mill	O/W	Modified with carboxymethyl derivatives	Improved the interface adsorption of the emulsion	Food emulsifier	[101]

7. Conclusion

LCMs (e.g., cellulose, hemicellulose, and lignin) can be recovered from agricultural waste and industrial processes to produce bio-based emulsifiers. The amphiphilic properties of cellulose and lignin equipped with surface-active functional groups can reduce the tension of the oil–water interface. Modified lignin often transforms to self-assemble and thereby reduce the emulsion surface tension, whereas the amphiphilic tendency of modified cellulose forms a mechanical barrier and adsorbs the emulsion interface. The properties of GGM-rich hemicellulose differ slightly from those of lignin and cellulose, for GGM is extracted with phenolic and PS to increase the adsorptive tendency of the emulsion interface. In formulating bio-based emulsifiers, other factors affected their surface activity or composition in the functional group, including in chemical and physical surface modification, particle size, pH, and concentration, to improve their functionality. Lowering the particle size can increase the surface area and form a better wall construction surrounding the droplets, hence smaller droplets. A certain pH can increase the degree of ionization on the surface of LCMs, which effects a charge opposite to the charge at the interface. A small droplet size is a good indicator of emulsion stability, which also means a large droplet surface area. Increasing the concentration of the emulsifier can ensure that all of those surface areas are covered. Given the diversity of approaches, LCMs can indeed be used as emulsifiers and may even be the future of such materials. Although many improvements that can be made, especially in emulsion stability, the knowledge provided here can help to advance emulsion technology.

Credit Author Statement

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] M.M. Robins, A.D. Watson, P.J. Wilde, Emulsions - Creaming and rheology, Current Opinion in Colloid and Interface Science. 7 (2002) 419–425. https://doi.org/10.1016/S1359-0294(02)00089-4.

[2] S. Ogawa, E.A. Decker, D.J. McClements, Production and characterization of O/W emulsions containing cationic droplets stabilized by lecithin - Chitosan membranes, Journal of Agricultural and Food Chemistry. 51 (2003) 2806–2812. https://doi.org/10.1021/jf020590f.

[3] C. Nunez, R. Dabirian, I. Gavrielatos, R.S. Mohan, O. Shoham, Emulsion stability with nanoparticles and utilization of demulsifiers for break-up, Powder Technology. 357 (2019) 248–261. https://doi.org/10.1016/j.powtec.2019.08.076.

[4] S.N. Kale, S.L. Deore, Emulsion micro emulsion and nano emulsion: A review, Systematic Reviews in Pharmacy. 8 (2016) 39–47. https://doi.org/10.5530/srp.2017.1.8.

[5] R. Pal, Effect of Droplet Size on the Rheology of Emulsions, AlChE Journal. 42 (1996) 3181–3190.

[6] N. Querol, C. Barreneche, L.F. Cabeza, Method for controlling mean droplet size in the manufacture of phase inversion bituminous emulsions, Colloids and Surfaces A: Physicochemical and Engineering Aspects. 527 (2017) 49–54. https://doi.org/10.1016/j.colsurfa.2017.05.018.

[7] S.H. Sekeri, M.N.M. Ibrahim, K. Umar, A.A. Yaqoob, M.N. Azmi, M.H. Hussin, M.B.H. Othman, M.F.I.A. Malik, Preparation and characterization of nanosized lignin from oil palm (Elaeis guineensis) biomass as a novel emulsifying agent, International Journal of Biological Macromolecules. 164 (2020) 3114–3124. https://doi.org/10.1016/j.ijbiomac.2020.08.181.

[8] T.G. Burger, Y. Zhang, Recent progress in the utilization of pea protein as an emulsifier for food applications, Trends in Food Science and Technology. 86 (2019) 25–33. https://doi.org/10.1016/j.tifs.2019.02.007.

[9] J. Peng, W.J. Dong, L. Li, J.M. Xu, D.J. Jin, X.J. Xia, Y.L. Liu, Effect of high-pressure homogenization preparation on mean globule size and large-diameter tail of oil-in-water injectable emulsions, Journal of Food and Drug Analysis. 23 (2015) 828–835. https://doi.org/10.1016/j.jfda.2015.04.004.

[10] S. V Vassilev, D. Baxter, L.K. Andersen, C.G. Vassileva, An overview of the chemical composition of biomass, Fuel. 89 (2010) 913–933. https://doi.org/10.1016/j.fuel.2009.10.022.

[11] H. yuan Wang, S. Liu, L. mei Zhai, J. zong Zhang, T. zhi Ren, B. quan Fan, H. bin Liu, Preparation and utilization of phosphate biofertilizers using agricultural waste, Journal of Integrative Agriculture. 14 (2015) 158–167. https://doi.org/10.1016/S2095-3119(14)60760-7.

[12] Z. Peter, Order in cellulosics: Historical review of crystal structure research on cellulose, Carbohydrate Polymers. 254 (2021) 117417. https://doi.org/10.1016/j.carbpol.2020.117417.

[13] L. Bai, L.G. Greca, W. Xiang, J. Lehtonen, S. Huan, R.W.N. Nugroho, B.L. Tardy, O.J. Rojas, Adsorption and Assembly of Cellulosic and Lignin Colloids at Oil/Water Interfaces, Langmuir. 35 (2019) 571–588. https://doi.org/10.1021/acs.langmuir.8b01288.

[14] J.A. Boxall, C.A. Koh, E.D. Sloan, A.K. Sum, D.T. Wu, Droplet size scaling of water-in-oil emulsions under turbulent flow, Langmuir. 28 (2012) 104–110. https://doi.org/10.1021/la202293t.

[15] F. Goodarzi, S. Zendehboudi, A comprehensive review on emulsions and emulsion stability in chemical and energy industries, Canadian Journal of Chemical Engineering. 97 (2019) 281–309. https://doi.org/10.1002/cjce.23336.

[16] C. Tan, P. Li, W. Dai, F. Dong, Characterization of oil – water two-phase pipe fl ow with a combined conductivity / capacitance sensor and wavelet analysis, Chemical Engineering Science. 134 (2015) 153–168. https://doi.org/10.1016/j.ces.2015.04.046.

[17] D. Arab, A. Kantzas, S.L. Bryant, Nanoparticle stabilized oil in water emulsions : A critical review, Journal of Petroleum Science and Engineering. 163 (2018) 217–242. https://doi.org/10.1016/j.petrol.2017.12.091.

[18] D.J. McClements, S.M. Jafari, Improving emulsion formation, stability and performance using mixed emulsifiers: A review, Advances in Colloid and Interface Science. 251 (2018) 55–79. https://doi.org/10.1016/j.cis.2017.12.001.

[19] F. Ravera, K. Dziza, E. Santini, L. Cristofolini, L. Liggieri, Emulsification and emulsion stability: The role of the interfacial properties, Advances in Colloid and Interface Science. 288 (2021) 102344. https://doi.org/10.1016/j.cis.2020.102344.

[20] P.J. García-moreno, J. Yang, S. Gregersen, N.C. Jones, C. Claire, L.M.C. Sagis, S. V Hoffmann, P. Marcatili, T. Michael, E.B. Hansen, C. Jacobsen, The structure, viscoelasticity and charge of potato peptides adsorbed at the oil-water interface determine the physicochemical stability of fish oil-in-water emulsions, Food Hydrocolloids. (2021) 106605. https://doi.org/10.1016/j.foodhyd.2021.106605.

[21] F.Y. Ushikubo, R.L. Cunha, Stability mechanisms of liquid water-in-oil emulsions, Food Hydrocolloids. 34 (2014) 145–153. https://doi.org/10.1016/j.foodhyd.2012.11.016.

[22] D. Wang, D. Yang, C. Huang, Y. Huang, D. Yang, H. Zhang, Q. Liu, T. Tang, M. Gamal El-Din, T. Kemppi, B. Perdicakis, H. Zeng, Stabilization mechanism and chemical demulsification of water-in-oil and oil-in-water emulsions in petroleum industry: A review, Fuel. 286 (2021) 119390. https://doi.org/10.1016/j.fuel.2020.119390.

[23] M. Tabibiazar, H. Hamishehkar, Formulation of a food grade water-in-oil nanoemulsion: Factors affecting on stability, Pharmaceutical Sciences. 21 (2015) 220–224. https://doi.org/10.15171/PS.2015.40.

[24] C.I. Park, W.G. Cho, S.J. Lee, Emulsion stability of cosmetic creams based on water-in-oil high internal phase emulsions, Korea Australia Rheology Journal. 15 (2003) 125–130.

[25] A.L. Márquez, A. Medrano, L.A. Panizzolo, J.R. Wagner, Effect of calcium salts and surfactant concentration on the stability of water-in-oil (w/o) emulsions prepared with polyglycerol polyricinoleate, Journal of Colloid and Interface Science. 341 (2010) 101–108. https://doi.org/10.1016/j.jcis.2009.09.020.

[26] G. Gotchev, T. Kolarov, K. Khristov, D. Exerowa, Electrostatic and steric interactions in oil-in-water emulsion films from Pluronic surfactants, Advances in Colloid and Interface Science. 168 (2011) 79–84. https://doi.org/10.1016/j.cis.2011.05.001.

[27] M. Fingas, B. Fieldhouse, A review of knowledge on water-in-oil emulsions, Environment Canada Arctic and Marine Oil Spill Program Technical Seminar (AMOP) Proceedings. 1 (2006) 1–56.

[28] G. Lv, F. Wang, W. Cai, H. Li, X. Zhang, Influences of addition of hydrophilic surfactants on the W/O emulsions stabilized by lipophilic surfactants, Colloids and Surfaces A: Physicochemical and Engineering Aspects. 457 (2014) 441–448. https://doi.org/10.1016/j.colsurfa.2014.06.031.

[29] N. Garti, H. Binyamin, A. Aserin, Stabilization of Water-in-Oil Emulsions by Submicrocrystalline α -Form Fat Particles, Journal of American Oil Chemists Society. 75 (1998) 1825–1831.

[30] I. Scherze, A. Knoth, G. Muschiolik, Effect of emulsification method on the properties of lecithin- and PGPR-stabilized water-in-oil-emulsions, Journal of Dispersion Science and Technology. 27 (2006) 427–434. https://doi.org/10.1080/01932690500357081.

[31] A. Dukhin, P. Goetz, Evolution of water-in-oil emulsion controlled by droplet-bulk ion exchange: Acoustic, electroacoustic, conductivity and image analysis, Colloids and Surfaces A: Physicochemical and Engineering Aspects. 253 (2005) 51–64. https://doi.org/10.1016/j.colsurfa.2004.10.125.

[32] M.M. Clark, Drop breakup in a turbulent flow-I. Conceptual and modeling considerations, Chemical Engineering Science. 43 (1988) 671–679. https://doi.org/10.1016/0009-2509(88)87025-8.

[33] M. Balcaen, J. Steyls, A. Schoeppe, V. Nelis, P. Van der Meeren, Phosphatidylcholine-depleted lecithin: A clean-label low-HLB emulsifier to replace PGPR in w/o and w/o/w emulsions, Journal of Colloid and Interface Science. 581 (2021) 836–846. https://doi.org/10.1016/j.jcis.2020.07.149.

[34] A. Knoth, I. Scherze, G. Muschiolik, Effect of lipid type on water-in-oil-emulsions stabilized by phosphatidylcholine-depleted lecithin and polyglycerol polyricinoleate, European Journal of Lipid Science and Technology. 107 (2005) 857–863. https://doi.org/10.1002/ejlt.200501205.

[35] X. Zhang, B. Qi, F. Xie, M. Hu, Y. Sun, L. Han, L. Li, S. Zhang, Y. Li, Emulsion stability and dilatational rheological properties of soy/ whey protein isolate complexes at the oil-water interface : Influence of pH, Food Hydrocolloids. 113 (2021) 106391. https://doi.org/10.1016/j.foodhyd.2020.106391.

[36] A.M. Howe, A.R. Pitt, Rheology and stability of oil-in-water nanoemulsions stabilised by anionic surfactant and gelatin 2) addition of homologous series of sugar-based co-surfactants, Advances in Colloid and Interface Science. 144 (2008) 30–37. https://doi.org/10.1016/j.cis.2008.08.004.

[37] D. Eckhout, S. Dolan, R. Gogan, H. Ledgister, C. Mowat, D. Williams, Development process and field applications of a new ester-based mud system for ERD wells on Australia's northwest shelf, in: IADC/SPE Asia Pacific Drilling Technology, Elsevier B.V., 2000: p. SPE-62781-MS. https://doi.org/10.2118/62791-MS.

[38] B.K. Paswan, V. Mahto, Development of environment-friendly oil-in-water emulsion based drilling fluid for shale gas formation using sunflower oil, Journal of Petroleum Science and Engineering. 191 (2020) 107129. https://doi.org/10.1016/j.petrol.2020.107129.

[39] B. Shibulal, S.N. Al-Bahry, Y.M. Al-Wahaibi, A.E. Elshafie, A.S. Al-Bemani, S.J. Joshi, Microbial enhanced heavy oil recovery by the aid of inhabitant spore-forming bacteria: An insight review, The Scientific World Journal. 2014 (2014). https://doi.org/10.1155/2014/309159.

[40] A. Mandal, A. Samanta, A. Bera, K. Ojha, Role of oil-water emulsion in enhanced oil recovery, in: ICCCE 2010 - 2010 International Conference on Chemistry and Chemical Engineering, Proceedings, 2010: pp. 190–194. https://doi.org/10.1109/ICCCENG.2010.5560393.

[41] S.A. Onaizi, M. Alsulaimani, M.K. Al-Sakkaf, S.A. Bahadi, M. Mahmoud, A. Alshami, Crude oil/water nanoemulsions stabilized by biosurfactant: Stability and pH-Switchability, Journal of Petroleum Science and Engineering. 198 (2021) 108173. https://doi.org/10.1016/j.petrol.2020.108173.

[42] M. Lestari, A. Taufiq, A. Hidayat, Green synthesis of CrFe2O4 nanoparticles using Cucumis sativus as a natural surfactant, Materials Today: Proceedings. (2020) 3–6. https://doi.org/10.1016/j.matpr.2020.11.442.

[43] B.P. Binks, W. Liu, J.A. Rodrigues, Novel stabilization of emulsions via the heteroaggregation of nanoparticles, Langmuir. 24 (2008) 4443–4446. https://doi.org/10.1021/la800084d.

[44] B.P. Binks, Particle as surfactants - similaritites and differences, Current Opinion in Colloid and Interface Science. 7 (2002) 21–41. https://doi.org/10.1016/S1359-0294(02)00008-0.

[45] M.M. Sarr, H. Inoue, T. Kosaka, Study on the improvement of interfacial strength between glass fiber and matrix resin by grafting cellulose nanofibers, Composites Science and Technology. 211 (2021) 108853. https://doi.org/10.1016/j.compscitech.2021.108853.

[46] F.G. Calvo-Flores, J.A. Dobado, Lignin as renewable raw material, ChemSusChem. 3 (2010) 1227–1235. https://doi.org/10.1002/cssc.201000157.

[47] J.L. McCarthy, A. Islam, Lignin Chemistry, Technology, and Utilization: A Brief History, in: Lignin: Historical, Biological, and Materials Perspectives, 1999: pp. 2–99. https://doi.org/10.1021/bk-2000-0742.ch001.

[48] T. Rashid, N. Gnanasundaram, A. Appusamy, C.F. Kait, M. Thanabalan, Enhanced lignin extraction from different species of oil palm biomass: Kinetics and optimization of extraction conditions, Industrial Crops and Products. 116 (2018) 122–136. https://doi.org/10.1016/j.indcrop.2018.02.056.

[49] M.N.M. Ibrahim, S.B. Chuah, W.D.W. Rosli, Characterization of Lignin Precipitated From The Soda Black Liquor Of Oil Palm Empty Fruit Bunch Fibers By Various Mineral Acids, ASEAN Journal on Science and Technology for Development. 21 (2004) 57–67.

[50] N.A. Rozuli, S.B. Yusoff, F. Gambier, N. Brosse, Production of oil palm (Elaeis guineensis) fronds lignin-derived non-toxic aldehyde for eco-friendly wood adhesive, Biological Macromolecules. (2018). https://doi.org/10.1016/j.ijbiomac.2018.03.048.

[51] H.E. Stewart, Development of Food-grade Microparticles from Lignin, 2015.

[52] G. Maniet, Q. Schmetz, N. Jacquet, M. Temmerman, S. Gofflot, A. Richel, Effect of steam explosion treatment on chemical composition and characteristic of organosolv fescue lignin, Industrial Crops and Products. 99 (2017) 79–85. https://doi.org/10.1016/j.indcrop.2017.01.015.

[53] O.J. Rojas, J. Bullón, F. Ysambertt, A. Forgiarini, J.L. Salager, D.S. Argyropoulos, Lignins as emulsion stabilizers, in: Materials, Chemicals, and Energy from Forest Biomass, 2007: pp. 182–199. https://doi.org/10.1021/bk-2007-0954.ch012.

[54] Z. Zhang, Y. Zhang, Z. Lin, A. Mulyadi, W. Mu, Y. Deng, Butyric anhydride modified lignin and its oil-water interfacial properties, Chemical Engineering Science. 165 (2017) 55–64. https://doi.org/10.1016/j.ces.2017.02.025.

[55] W.T. Hay, G.F. Fanta, F.C. Felker, S.C. Peterson, C.D. Skory, M.P. Hojilla-evangelista, G. Biresaw, W. Gordon, Emulsification properties of amylose-fatty sodium salt inclusion complexes, Food Hydrocolloids. 90 (2019) 490–499. https://doi.org/10.1016/j.foodhyd.2018.12.038.

[56] D.J. McClements, J. Rao, Food-Grade nanoemulsions: Formulation, fabrication, properties, performance, Biological fate, and Potential Toxicity, Critical Reviews in Food Science and Nutrition. 51 (2011) 285–330. https://doi.org/10.1080/10408398.2011.559558.

[57] G. Chen, D. Tao, An experimental study of stability of oil-water emulsion, Fuel Processing Technology. 86 (2005) 499–508. https://doi.org/10.1016/j.fuproc.2004.03.010.

[58] B. Cathala, L.T. Lee, V. Aguié-Béghin, R. Douillard, B. Monties, Organization behavior of guaiacyl and guaiacyl/syringyl dehydrogenation polymers (lignin model compounds) at the air/water interface, Langmuir. 16 (2000) 10444–10448. https://doi.org/10.1021/la000939y.

[59] J. Ruwoldt, A critical review of the physicochemical properties of lignosulfonates: Chemical structure and behavior in aqueous solution, at surfaces and interfaces, Surfaces. 3 (2020) 622–648. https://doi.org/10.3390/surfaces3040042.

[60] A. Czaikoski, A. Gomes, K.C. Kaufmann, R.B. Liszbinski, M.B. de Jesus, R.L. da Cunha, Lignin derivatives stabilizing oil-in-water emulsions: Technological aspects, interfacial rheology and cytotoxicity, Industrial Crops and Products. 154 (2020) 112762. https://doi.org/10.1016/j.indcrop.2020.112762.

[61] S.A. Gundersen, M.H. Ese, J. Sjöblom, Langmuir surface and interface films of lignosulfonates and Kraft lignins in the presence of electrolyte and asphaltenes: Correlation to emulsion stability, Colloids and Surfaces A: Physicochemical and Engineering Aspects. 182 (2001) 199–218. https://doi.org/10.1016/S0927-7757(00)00739-1.

[62] K.S. Mikkonen, Strategies for structuring diverse emulsion systems by using wood lignocellulose-derived stabilizers, Green Chemistry. 22 (2020) 1019–1037. https://doi.org/10.1039/c9gc04457d.

[63] Y. Qian, Y. Deng, X. Qiu, J. Huang, D. Yang, Aggregation of sodium lignosulfonate above a critical temperature, Holzforschung. 68 (2014) 641–647. https://doi.org/10.1515/hf-2013-0167.

[64] K.S. Silmore, C. Gupta, N.R. Washburn, Tunable Pickering emulsions with polymer-grafted lignin nanoparticles (PGLNs), Journal of Colloid and Interface Science. 466 (2016) 91–100. https://doi.org/10.1016/j.jcis.2015.11.042.

[65] M.R. v. Bertolo, L.B.B. de Paiva, V.M. Nascimento, C.A. Gandin, M.O. Neto, C.E. Driemeier, S.C. Rabelo, Lignins from sugarcane bagasse : Renewable source of nanoparticles as Pickering emulsions stabilizers for bioactive compounds encapsulation, Industrial Crops & Products. 140 (2019) 111591. https://doi.org/10.1016/j.indcrop.2019.111591.

[66] L. Dai, Y. Li, F. Kong, K. Liu, C. Si, Y. Ni, Lignin-Based Nanoparticles Stabilized Pickering Emulsion for Stability Improvement and Thermal-Controlled Release of trans-Resveratrol, ACS Sustainable Chemistry & Engineering. 7 (15), 13 (2019) 13497–13504. https://doi.org/10.1021/acssuschemeng.9b02966.

[67] N. Ghavidel, P. Fatehi, Pickering/non-Pickering Emulsions of Nanostructured Sulfonated Lignin Derivatives, ChemSusChem. 13 (2020) 4567–4578. https://doi.org/10.1002/cssc.202000965.

[68] N. Delgado, F. Ysambertt, G. Chávez, B. Bravo, D.E. García, J. Santos, Valorization of Kraft Lignin of Different Molecular Weights as Surfactant Agent for the Oil Industry, Waste and Biomass Valorization. 10 (2019) 3383–3395. https://doi.org/10.1007/s12649-018-0352-4.

[69] S. Gharehkhani, N. Ghavidel, P. Fatehi, Kraft Lignin–Tannic Acid as a Green Stabilizer for Oil/Water Emulsion, ACS Sustainable Chemistry & Engineering. 7 (2019) 2370–2379. https://doi.org/10.1021/acssuschemeng.8b05193.

[70] X. Hu, S. Zhu, T. Ma, S. Lu, J. Zhao, X. Hu, Y. Song, X. Liao, Magnetic modified cellulose nanocrystals fabricated using ultrasound-coprecipitation: Characterization and application as pickering emulsion stabilizers, Lwt. 148 (2021) 111680. https://doi.org/10.1016/j.lwt.2021.111680.

[71] V.I. Mikhaylov, M.A. Torlopov, I.N. Vaseneva, P.A. Sitnikov, Magnetically controlled liquid paraffin oil-in-water Pickering emulsion stabilized by magnetite/cellulose nanocrystals: Formation and Cr(VI) adsorption, Colloids and Surfaces A: Physicochemical and Engineering Aspects. 622 (2021) 126634. https://doi.org/10.1016/j.colsurfa.2021.126634.

[72] Z. Li, F. Qiu, X. Yue, Q. Tian, D. Yang, T. Zhang, Eco-friendly self-crosslinking cellulose membrane with high mechanical properties from renewable resources for oil/water emulsion separation, Journal of Environmental Chemical Engineering. 9 (2021) 105857. https://doi.org/10.1016/j.jece.2021.105857.

[73] H. Dai, H. Zhang, Y. Chen, L. Ma, J. Wu, Y. Zhang, Co-stabilization and properties regulation of Pickering emulsions by cellulose nanocrystals and nanofibrils from lemon seeds, Food Hydrocolloids. 120 (2021) 106884. https://doi.org/10.1016/j.foodhyd.2021.106884.

[74] A. Ben Mabrouk, A. Dufresne, S. Boufi, Cellulose nanocrystal as ecofriendly stabilizer for emulsion polymerization and its application for waterborne adhesive, Carbohydrate Polymers. 229 (2020). https://doi.org/10.1016/j.carbpol.2019.115504.

[75] A. Sarkar, E. Dickinson, Sustainable food-grade Pickering emulsions stabilized by plant-based particles, Current Opinion in Colloid and Interface Science. 49 (2020) 69–81. https://doi.org/10.1016/j.cocis.2020.04.004.

[76] T. Yuan, J. Zeng, B. Wang, Z. Cheng, K. Chen, Pickering emulsion stabilized by cellulosic fibers: Morphological properties-interfacial stabilization-rheological behavior relationships, Carbohydrate Polymers. 269 (2021) 118339. https://doi.org/10.1016/j.carbpol.2021.118339.

[77] H. Dong, Q. Ding, Y. Jiang, X. Li, W. Han, Pickering emulsions stabilized by spherical cellulose nanocrystals, Carbohydrate Polymers. 265 (2021) 118101. https://doi.org/10.1016/j.carbpol.2021.118101.

[78] R. Nabata, M. Tsudome, S. Deguchi, Preparation of cellulose microparticles having hierarchical internal structures from multiple emulsion templates, Colloids and Surfaces A: Physicochemical and Engineering Aspects. 622 (2021) 126718. https://doi.org/10.1016/j.colsurfa.2021.126718.

[79] K. Wasilewska, K. Winnicka, Ethylcellulose-a pharmaceutical excipient with multidirectional application in drug dosage forms development, Materials. 12 (2019). https://doi.org/10.3390/ma12203386.

[80] E. Melzer, J. Kreuter, R. Daniels, Ethylcellulose: A new type of emulsion stabilizer, European Journal of Pharmaceutics and Biopharmaceutics. 56 (2003) 23–27. https://doi.org/10.1016/S0939-6411(03)00025-0.

[81] Y. Ni, Q. Gu, J. Li, L. Fan, Modulating in vitro gastrointestinal digestion of nanocellulose-stabilized pickering emulsions by altering cellulose lengths, Food Hydrocolloids. 118 (2021). https://doi.org/10.1016/j.foodhyd.2021.106738.

[82] J. Luo, K. Huang, X. Zhou, Y. Xu, Elucidation of oil-in-water emulsions stabilized with celery cellulose, Fuel. 291 (2021) 120210. https://doi.org/10.1016/j.fuel.2021.120210.

[83] V.I. Mikhaylov, M.A. Torlopov, I.N. Vaseneva, P.A. Sitnikov, Magnetically controlled liquid paraffin oil-in-water Pickering emulsion stabilized by magnetite/cellulose nanocrystals: Formation and Cr(VI) adsorption, Colloids and Surfaces A: Physicochemical and Engineering Aspects. 622 (2021) 126634. https://doi.org/10.1016/j.colsurfa.2021.126634.

[84] C. Tang, S. Spinney, Z. Shi, J. Tang, B. Peng, J. Luo, K.C. Tam, Amphiphilic Cellulose Nanocrystals for Enhanced Pickering Emulsion Stabilization, Langmuir. 34 (2018) 12897–12905. https://doi.org/10.1021/acs.langmuir.8b02437.

[85] L. Urbánková, T. Sedláček, V. Kašpárková, R. Bordes, Formation of oleogels based on emulsions stabilized with cellulose nanocrystals and sodium caseinate, Journal of Colloid and Interface Science. 596 (2021) 245–256. https://doi.org/10.1016/j.jcis.2021.02.104.

[86] F. Arancibia, E. Izquierdo, M. Pereira, Stabilization of the emulsion of Alkenyl Succinic Anhydride (ASA) in water using cellulose nanofibrils, Chemical Engineering Science. 233 (2021) 116407. https://doi.org/10.1016/j.ces.2020.116407.

[87] L. Cui, L. Yi, Y. Wang, Y. Zhang, P. Polyák, X. Sui, B. Pukánszky, Rheology of PLA/regenerated cellulose nanocomposites prepared by the pickering emulsion process: Network formation and modeling, Materials and Design. 206 (2021) 109774. https://doi.org/10.1016/j.matdes.2021.109774.

[88] W. Qi, T. Li, Z. Zhang, T. Wu, Preparation and characterization of oleogel-in-water pickering emulsions stabilized by cellulose nanocrystals, Food Hydrocolloids. 110 (2021) 106206. https://doi.org/10.1016/j.foodhyd.2020.106206.

[89] S.K. Wong, J. Supramaniam, T.W. Wong, A. Soottitantawat, U.R. Ruktanonchai, B.T. Tey, S.Y. Tang, Synthesis of bio-inspired cellulose nanocrystals-soy protein isolate nanoconjugate for stabilization of oil-in-water Pickering emulsions, Carbohydrate Research. 504 (2021) 108336. https://doi.org/10.1016/j.carres.2021.108336.

[90] C. Bao, X. Chen, C. Liu, Y. Liao, Y. Huang, L. Hao, H. Yan, Q. Lin, Extraction of cellulose nanocrystals from microcrystalline cellulose for the stabilization of cetyltrimethylammonium bromide-enhanced Pickering emulsions, Colloids and Surfaces A: Physicochemical and Engineering Aspects. 608 (2021) 125442. https://doi.org/10.1016/j.colsurfa.2020.125442.

[91] O.M. Terrett, P. Dupree, Covalent interactions between lignin and hemicelluloses in plant secondary cell walls, Current Opinion in Biotechnology. 56 (2019) 97–104. https://doi.org/10.1016/j.copbio.2018.10.010.

[92] F.M. Gírio, C. Fonseca, F. Carvalheiro, L.C. Duarte, S. Marques, R. Bogel-Łukasik, Hemicelluloses for fuel ethanol: A review, Bioresource Technology. 101 (2010) 4775–4800. https://doi.org/10.1016/j.biortech.2010.01.088.

[93] J. Krogell, E. Korotkova, K. Eränen, A. Pranovich, T. Salmi, D. Murzin, S. Willför, Intensification of hemicellulose hot-water extraction from spruce wood in a batch extractor - Effects of wood particle size, Bioresource Technology. 143 (2013) 212–220. https://doi.org/10.1016/j.biortech.2013.05.110.

[94] S.P. Nie, C. Wang, S.W. Cui, Q. Wang, M.Y. Xie, G.O. Phillips, A further amendment to the classical core structure of gum arabic (Acacia senegal), Food Hydrocolloids. 31 (2013) 42–48. https://doi.org/10.1016/j.foodhyd.2012.09.014.

[95] M. Bhattarai, L. Pitkänen, V. Kitunen, R. Korpinen, H. Ilvesniemi, P.O. Kilpeläinen, M. Lehtonen, K.S. Mikkonen, Functionality of spruce galactoglucomannans in oil-in-water

emulsions, Food Hydrocolloids. 86 (2019) 154–161. https://doi.org/10.1016/j.foodhyd.2018.03.020.

[96] M. Lehtonen, M. Merinen, P.O. Kilpeläinen, C. Xu, S.M. Willför, K.S. Mikkonen, Phenolic residues in spruce galactoglucomannans improve stabilization of oil-in-water emulsions, Journal of Colloid and Interface Science. 512 (2018) 536–547. https://doi.org/10.1016/j.jcis.2017.10.097.

[97] Y.F. Li, P.P. Yue, X. Hao, J. Bian, J.L. Ren, F. Peng, R.C. Sun, Comparison of emulsifying capacity of two hemicelluloses from moso bamboo in soy oil-in-water emulsions, RSC Advances. 10 (2020) 4657–4663. https://doi.org/10.1039/c9ra08636f.

[98] F. Valoppi, N. Maina, M. Allén, R. Miglioli, P.O. Kilpeläinen, K.S. Mikkonen, Spruce galactoglucomannan-stabilized emulsions as essential fatty acid delivery systems for functionalized drinkable yogurt and oat-based beverage, European Food Research and Technology. 245 (2019) 1387–1398. https://doi.org/10.1007/s00217-019-03273-5.

[99] N.M.L. Hansen, D. Plackett, Sustainable films and coatings from hemicelluloses: A review, Biomacromolecules. 9 (2008) 1493–1505. https://doi.org/10.1021/bm800053z.

[100] K.S. Mikkonen, M. Tenkanen, P. Cooke, C. Xu, H. Rita, S. Willför, B. Holmbom, K.B. Hicks, M.P. Yadav, Mannans as stabilizers of oil-in-water beverage emulsions, LWT - Food Science and Technology. 42 (2009) 849–855. https://doi.org/10.1016/j.lwt.2008.11.010.

[101] K.S. Mikkonen, C. Xu, C. Berton-Carabin, K. Schroën, Spruce galactoglucomannans in rapeseed oil-in-water emulsions: Efficient stabilization performance and structural partitioning, Food Hydrocolloids. 52 (2016) 615–624. https://doi.org/10.1016/j.foodhyd.2015.08.009.

[102] M. Lehtonen, S. Teräslahti, C. Xu, M.P. Yadav, A.M. Lampi, K.S. Mikkonen, Spruce galactoglucomannans inhibit lipid oxidation in rapeseed oil-in-water emulsions, Food Hydrocolloids. 58 (2016) 255–266. https://doi.org/10.1016/j.foodhyd.2016.03.006.

[103] K.S. Mikkonen, S. Kirjoranta, C. Xu, J. Hemming, A. Pranovich, M. Bhattarai, L. Peltonen, P. Kilpeläinen, N. Maina, M. Tenkanen, M. Lehtonen, S. Willför, Environmentally-compatible alkyd paints stabilized by wood hemicelluloses, Industrial Crops and Products. 133 (2019) 212–220. https://doi.org/10.1016/j.indcrop.2019.03.017.

[104] D.R. Ratnaweera, D. Saha, S.V. Pingali, N. Labbé, A.K. Naskar, M. Dadmun, The impact of lignin source on its self-assembly in solution, RSC Advances. 5 (2015) 67258–67266. https://doi.org/10.1039/c5ra13485d.

[105] C. Onyango, G. Unbehend, M.G. Lindhauer, Effect of cellulose-derivatives and emulsifiers on creep-recovery and crumb properties of gluten-free bread prepared from sorghum and gelatinised cassava starch, Food Research International. 42 (2009) 949–955. https://doi.org/10.1016/j.foodres.2009.04.011.

[106] R.M. Rowell, B.A. Cleary, J.S. Rowell, C. Clemons, R.A. Young, Results of chemical modification of lignocellulosic fibers for use in composites, Wood–Fiber/Polymer Composites: Fundamental Concepts, Processes and Material Options. (1993) 121–127.

[107] I. Kalashnikova, H. Bizot, B. Cathala, I. Capron, Modulation of cellulose nanocrystals amphiphilic properties to stabilize oil/water interface, Biomacromolecules. 13 (2012) 267–275. https://doi.org/10.1021/bm201599j.

[108] D. Saidane, E. Perrin, F. Cherhal, F. Guellec, I. Capron, Some modification of cellulose nanocrystals for functional Pickering emulsions, Philosophical Transactions of the

Royal Society A: Mathematical, Physical and Engineering Sciences. 374 (2016). https://doi.org/10.1098/rsta.2015.0139.

[109] X. Gong, Y. Wang, L. Chen, Enhanced emulsifying properties of wood-based cellulose nanocrystals as Pickering emulsion stabilizer, Carbohydrate Polymers. 169 (2017) 295–303. https://doi.org/10.1016/j.carbpol.2017.04.024.

[110] E.O. Olorunsola, E.I. Akpabio, M.O. Adedokun, D.O. Ajibola, Emulsifying Properties of Hemicelluloses, Science and Technology Behind Nanoemulsions. (2018). https://doi.org/10.5772/intechopen.74473.

[111] C. Xu, C. Eckerman, A. Smeds, M. Reunanen, P.C. Eklund, R. Sjöholm, S. Willför, Carboxymethylated spruce galactoglucomannans: Preparation, characterisation, dispersion stability, water-in-oil emulsion stability, and sorption on cellulose surface, Nordic Pulp and Paper Research Journal. 26 (2011) 167–178. https://doi.org/10.3183/npprj-2011-26-02-p167-178.

[112] K.S. Mikkonen, D. Merger, P. Kilpeläinen, L. Murtomäki, U.S. Schmidt, M. Wilhelm, Determination of physical emulsion stabilization mechanisms of wood hemicelluloses: Via rheological and interfacial characterization, Soft Matter. 12 (2016) 8690–8700. https://doi.org/10.1039/c6sm01557c.

[113] C. Xu, A.I. Smeds, M. Reunanen, P.C. Eklund, Carboxymethylated spruce galactoglucomannans : preparation , characterisation , dispersion stability , water-in-oil emulsion stability , and sorption on cellulose surface, Nordic Pulp and Paper Research Journal. 26 (2011) 167–179.

[114] M.H. Lahtinen, F. Valoppi, V. Juntti, S. Heikkinen, Lignin-Rich PHWE Hemicellulose Extracts Responsible for Extended Emulsion Stabilization, Frontiers in Chemistry. 7 (2019) 1–18. https://doi.org/10.3389/fchem.2019.00871.

[115] A. Yuliestyan, M. García-morales, E. Moreno, V. Carrera, P. Partal, Assessment of modified lignin cationic emulsifier for bitumen emulsions used in road paving, Materials & Design. 131 (2017) 242–251. https://doi.org/10.1016/j.matdes.2017.06.024.

[116] S. Lu, D. Yang, M. Wang, M. Yan, Y. Qian, D. Zheng, X. Qiu, Pickering Emulsions Synergistic-Stabilized by Amphoteric Lignin and SiO2 Nanoparticles: Stability and pH-responsive Mechanism, Colloids and Surfaces A: Physicochemical and Engineering Aspects. (2019) 1–30. https://doi.org/10.1016/j.colsurfa.2019.124158.

[117] Z. Wei, Y. Yang, R. Yang, C. Wang, Alkaline lignin extracted from furfural residues for pH-responsive Pickering emulsions and their recyclable polymerization, Green Chemistry. 14 (2012) 3230–3236. https://doi.org/10.1039/c2gc36278c.

[118] S. Li, J.A. Willoughby, O.J. Rojas, Oil-in-Water Emulsions Stabilized by Carboxymethylated Lignins: Properties and Energy Prospects, ChemSusChem. 9 (2016) 2460–2469. https://doi.org/10.1002/cssc.201600704.

[119] A.A. Yaqoob, S.H. Sekeri, M.B.H. Othman, M.N.M. Ibrahim, Z.H. Feizi, Thermal degradation and kinetics stability studies of oil palm (Elaeis Guineensis) biomass-derived lignin nanoparticle and its application as an emulsifying agent, Arabian Journal of Chemistry. 14 (2021) 103182. https://doi.org/10.1016/j.arabjc.2021.103182.

[120] L. Rong, X. Shen, B. Wang, Z. Mao, X. Feng, X. Sui, Antibacterial thyme oil-loaded organo-hydrogels utilizing cellulose acetoacetate as reactive polymer emulsifier, International Journal of Biological Macromolecules. 147 (2020) 18–23. https://doi.org/10.1016/j.ijbiomac.2020.01.052.

[121] Q. Li, B. Xie, Y. Wang, Y. Wang, L. Peng, Y. Li, B. Li, S. Liu, Cellulose nanofibrils from Miscanthus floridulus straw as green particle emulsifier for O/W Pickering

emulsion, Food Hydrocolloids. 97 (2019). https://doi.org/10.1016/j.foodhyd.2019.105214.

[122] P. Naidjonoka, M. Fornasier, D. Pålsson, G. Rudolph, B. Al-Rudainy, S. Murgia, T. Nylander, Bicontinuous cubic liquid crystalline phase nanoparticles stabilized by softwood hemicellulose, Colloids and Surfaces B: Biointerfaces. 203 (2021) 111753. https://doi.org/10.1016/j.colsurfb.2021.111753.

[123] S. Moradi, K. Shayesteh, G. Behbudi, Preparation and characterization of biodegradable lignin-sulfonate nanoparticles using the microemulsion method to enhance the acetylation efficiency of lignin-sulfonate, International Journal of Biological Macromolecules. 160 (2020) 632–641. https://doi.org/10.1016/j.ijbiomac.2020.05.157.

[124] I. Kalashnikova, H. Bizot, P. Bertoncini, B. Cathala, I. Capron, Cellulosic nanorods of various aspect ratios for oil in water Pickering emulsions, Soft Matter. 9 (2013) 952–959. https://doi.org/10.1039/c2sm26472b.

[125] W. Wang, G. Du, C. Li, H. Zhang, Y. Long, Y. Ni, Preparation of cellulose nanocrystals from asparagus (Asparagus officinalis L.) and their applications to palm oil/water Pickering emulsion, Carbohydrate Polymers. 151 (2016) 1–8. https://doi.org/10.1016/j.carbpol.2016.05.052.

[126] M. Österberg, M.H. Sipponen, B.D. Mattos, O.J. Rojas, Spherical lignin particles: A review on their sustainability and applications, Green Chemistry. 22 (2020) 2712–2733. https://doi.org/10.1039/d0gc00096e.

[127] S.X. Li, J. Zhao, P. Lu, Y. Xie, Maximum packing densities of basic 3D objects, Chinese Science Bulletin. 55 (2010) 114–119. https://doi.org/10.1007/s11434-009-0650-0.

[128] Y. Qian, Q. Zhang, X. Qiu, S. Zhu, CO2-responsive diethylaminoethyl-modified lignin nanoparticles and their application as surfactants for CO2/N2-switchable Pickering emulsions, Green Chemistry. 16 (2014) 4963–4968. https://doi.org/10.1039/c4gc01242a.

[129] Y. Pang, S. Wang, X. Qiu, Y. Luo, H. Lou, J. Huang, Preparation of Lignin/Sodium Dodecyl Sulfate Composite Nanoparticles and Their Application in Pickering Emulsion Template-Based Microencapsulation, Journal of Agricultural and Food Chemistry. 65 (2017) 11011–11019. https://doi.org/10.1021/acs.jafc.7b03784.

[130] Y. Ni, J. Li, L. Fan, Effects of ultrasonic conditions on the interfacial property and emulsifying property of cellulose nanoparticles from ginkgo seed shells, Ultrasonics Sonochemistry. 70 (2021) 105335. https://doi.org/10.1016/j.ultsonch.2020.105335.

[131] T.F. Tadros, Emulsion Formation and Stability, in: Emulsion Formation and Stability, 2013: pp. 1–72. https://doi.org/10.1002/9783527647941.

[132] M. Juttulapa, S. Piriyaprasarth, P. Sriamornsak, Effect of ph on stability of oil-in-water emulsions stabilized by pectin-zein complexes, Advanced Materials Research. 747 (2013) 127–130. https://doi.org/10.4028/www.scientific.net/AMR.747.127.

[133] B.P. Binks, R. Murakami, S.P. Armes, S. Fujii, Effects of pH and salt concentration on oil-in-water emulsions stabilized solely by nanocomposite microgel particles, Langmuir. 22 (2006) 2050–2057. https://doi.org/10.1021/la053017+.

[134] S. Punitha, R. Uvarani, A. Panneerselvam, Effect of pH in aqueous (Hydroxy Propyl Methyl Cellulose) polymer solution, Results in Materials. 7 (2020) 100120. https://doi.org/10.1016/j.rinma.2020.100120.

[135] J. Tang, M.F.X. Lee, W. Zhang, B. Zhao, R.M. Berry, K.C. Tam, Dual responsive pickering emulsion stabilized by poly[2-(dimethylamino) ethyl methacrylate] grafted cellulose nanocrystals, Biomacromolecules. 15 (2014) 3052–3060. https://doi.org/10.1021/bm500663w.

[136] X.F. Sun, H.H. Wang, Z.X. Jing, R. Mohanathas, Hemicellulose-based pH-sensitive and biodegradable hydrogel for controlled drug delivery, Carbohydrate Polymers. 92 (2013) 1357–1366. https://doi.org/10.1016/j.carbpol.2012.10.032.

[137] X. Zhang, Y. Lei, X. Luo, Y. Wang, Y. Li, B. Li, S. Liu, Impact of pH on the interaction between soybean protein isolate and oxidized bacterial cellulose at oil-water interface: Dilatational rheological and emulsifying properties, Food Hydrocolloids. 115 (2021) 106609. https://doi.org/10.1016/j.foodhyd.2021.106609.

[138] C.B. Fox, S. Lin, S.J. Sivananthan, T.S. Dutill, K.T. Forseth, S.G. Reed, T.S. Vedvick, Effects of emulsifier concentration, composition, and order of addition in squalene-phosphatidylcholine oil-in-water emulsions, Pharmaceutical Development and Technology. 16 (2011) 511–519. https://doi.org/10.3109/10837450.2010.495397.

[139] W. Liu, J. Zhang, Q. Liu, J. Pei, C. Zhu, P. Liu, Effects of Emulsifier Dosage and Curing Time on Self-Healing Microcapsules Containing Rejuvenator and Optimal Dosage in Asphalt Binders, Journal of Nanoscience and Nanotechnology. 19 (2018) 57–65. https://doi.org/10.1166/jnn.2019.16466.

[140] K. Xhanari, K. Syverud, P. Stenius, Emulsions stabilized by microfibrillated cellulose: The effect of Hydrophobization, concentration and O/W ratio, Journal of Dispersion Science and Technology. 32 (2011) 447–452. https://doi.org/10.1080/01932691003658942.

[141] C.E. Gumus, Plant-based proteins: An alternative to synthetic emulsifiers, International News on Fats, Oils and Related Materials. 29 (2018) 14–16. https://doi.org/10.21748/inform.05.2018.14.

[142] A. Can Karaca, N.H. Low, M.T. Nickerson, Potential use of plant proteins in the microencapsulation of lipophilic materials in foods, Trends in Food Science and Technology. 42 (2015) 5–12. https://doi.org/10.1016/j.tifs.2014.11.002.

[143] M.P. Vinardell, M. Mitjans, Lignins and their derivatives with beneficial effects on human health, International Journal of Molecular Sciences. 18 (2017) 1219. https://doi.org/10.3390/ijms18061219.

[144] C. Solans, D. Morales, M. Homs, Spontaneous emulsification, Current Opinion in Colloid and Interface Science. 22 (2016) 88–93. https://doi.org/10.1016/j.cocis.2016.03.002.

[145] J. Zakzeski, P.C.A. Bruijnincx, A.L. Jongerius, B.M. Weckhuysen, The catalytic valorization of lignin for the production of renewable chemicals, Chemical Reviews. 110 (2010) 3552–3599. https://doi.org/10.1021/cr900354u.

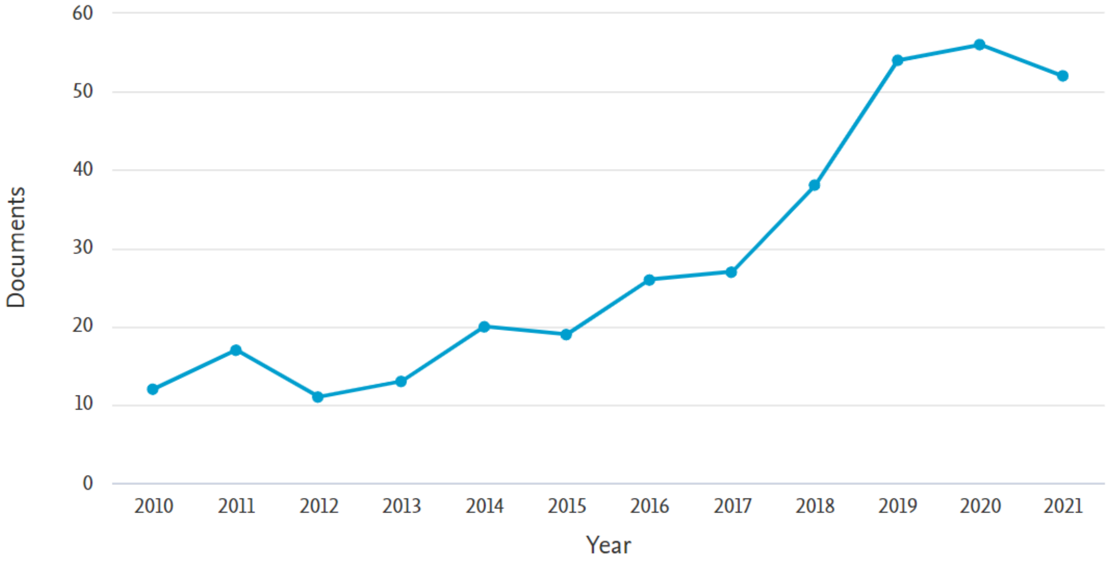
[146] Y. Zhao, H. Sun, B. Yang, Y. Weng, Hemicellulose-based film: Potential green films for food packaging, Polymers. 12 (2020) 1–14. https://doi.org/10.3390/polym12081775.

[147] W. Du, J. Guo, H. Li, Y. Gao, Heterogeneously Modified Cellulose Nanocrystals-Stabilized Pickering Emulsion: Preparation and Their Template Application for the Creation of PS Microspheres with Amino-Rich Surfaces, ACS Sustainable Chemistry and Engineering. 5 (2017) 7514–7523. https://doi.org/10.1021/acssuschemeng.7b00375.

[148] S. Varanasi, L. Henzel, L. Mendoza, R. Prathapan, W. Batchelor, R. Tabor, G. Garnier, Pickering Emulsions Electrostatically Stabilized by Cellulose Nanocrystals, Frontiers in Chemistry. 6 (2018) 1–9. https://doi.org/10.3389/fchem.2018.00409.

[149] X. Wu, L. Zhang, X. Zhang, Y. Zhu, Y. Wu, Y. Li, B. Li, S. Liu, J. Zhao, Z. Ma, Ethyl cellulose nanodispersions as stabilizers for oil in water Pickering emulsions, Scientific Reports. 7 (2017) 1–10. https://doi.org/10.1038/s41598-017-12386-4.

a) Articles published on LCM as emulsifier



b) Articles published on Modification of LCM

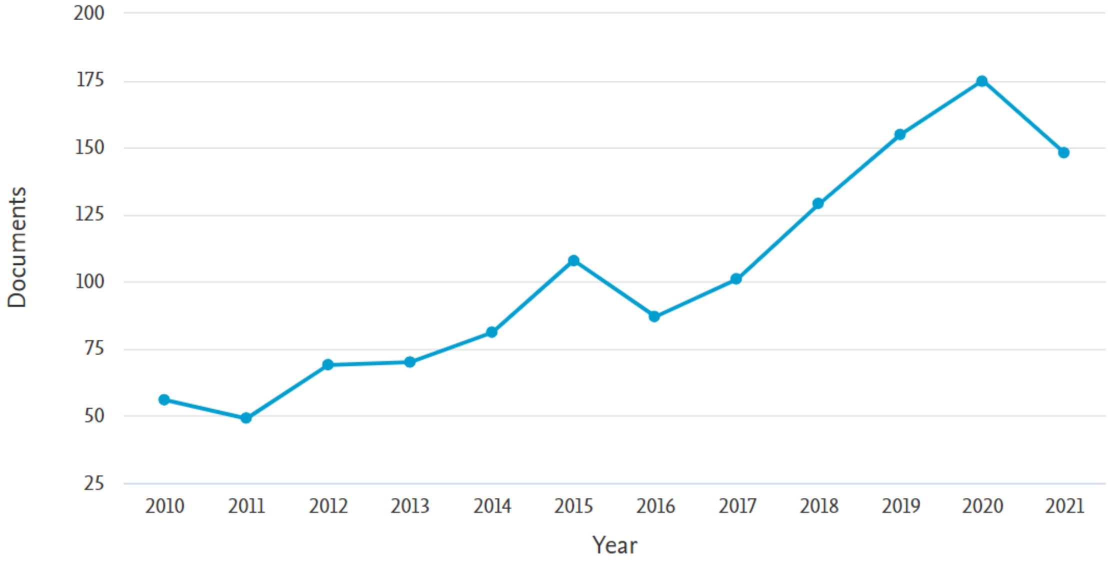
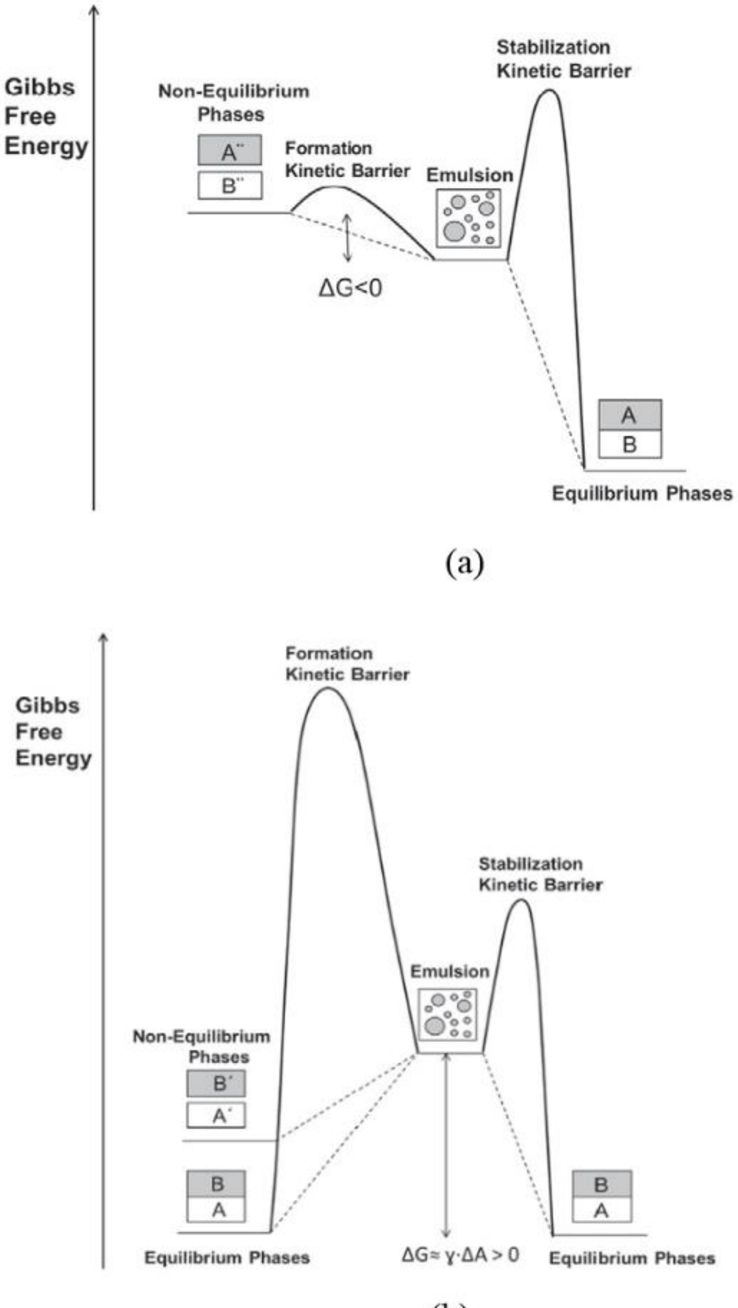


Figure 1. Number of articles published from 2010 to 2021 addressing (a) lignocellulosic materials (LCM) used as emulsifiers and (b) the modification of the structure of LCMs. Data source: SCOPUS [11].



(a)

(b)

Figure 2. Gibbs free energy of emulsification produced (a) spontaneously (b) unspontaneous [144].

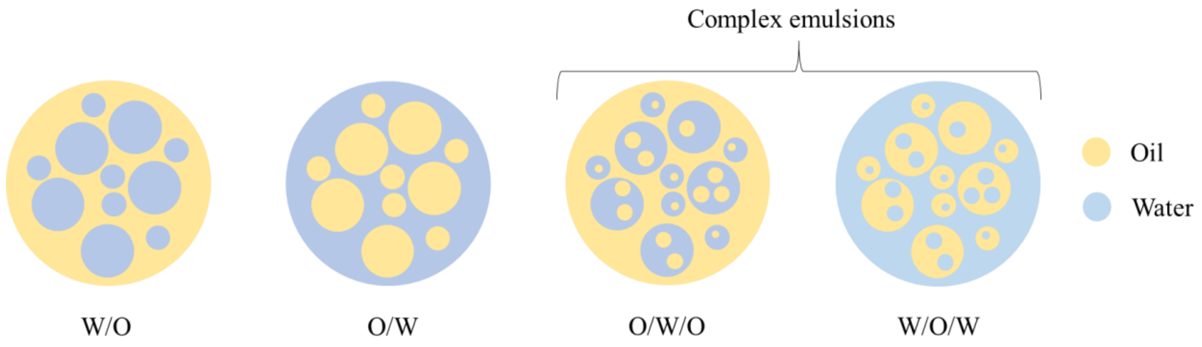


Figure 3. Type of emulsions.

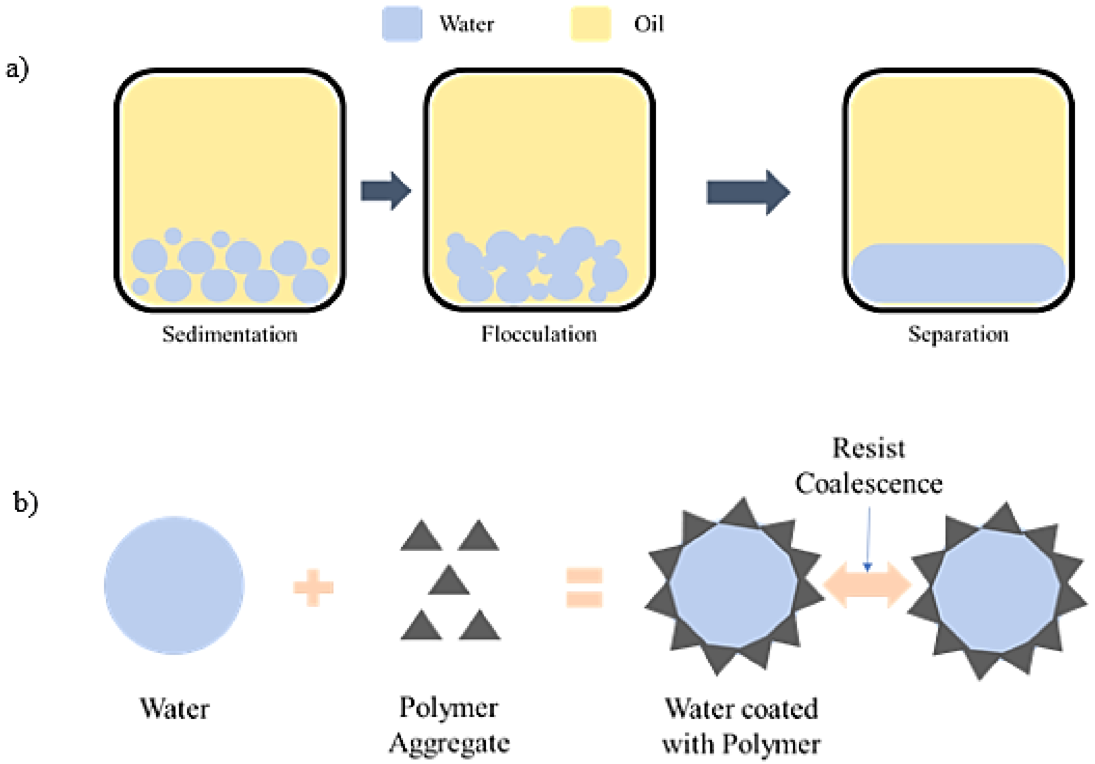


Figure 4. (a) Demulsification of W/O emulsions and (b) W/O emulsion with steric stabilization due to polymer adsorption.

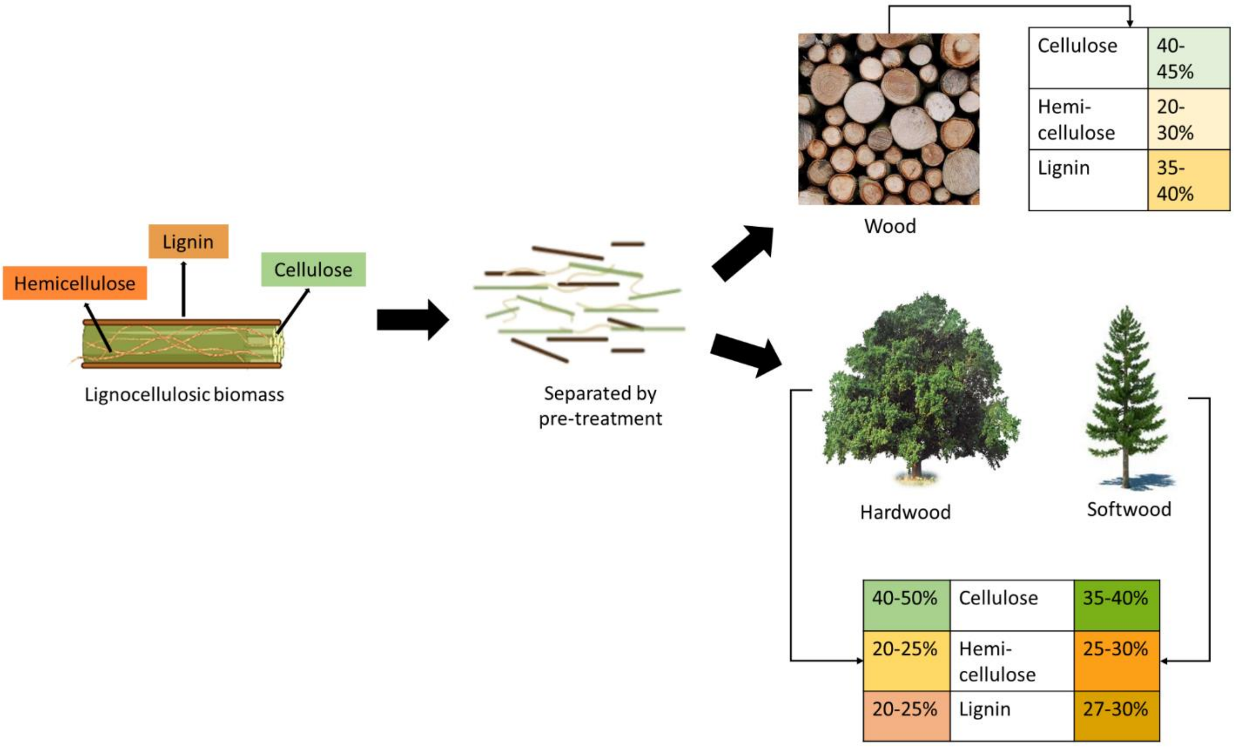


Figure 5. The percentage of LCMs in hardwood and softwood.

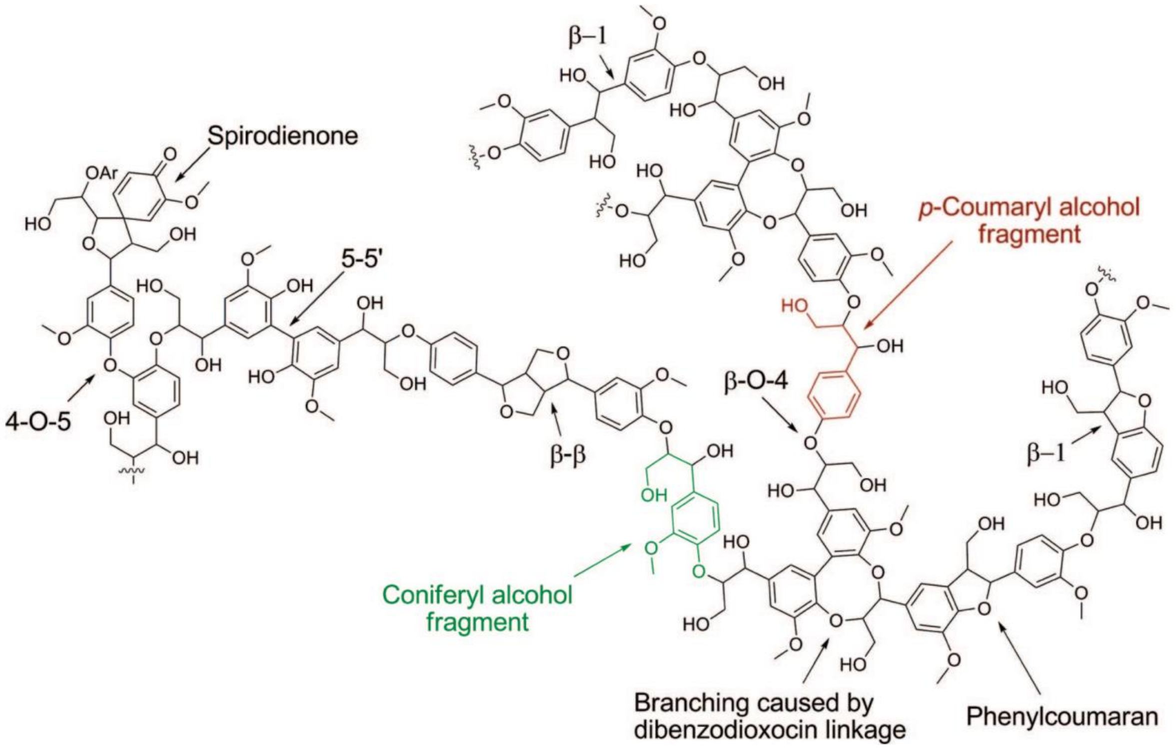


Figure 6. Proposed lignin structure. Reprinted (adapted) with permission from [145]. Copyright 2010 American Chemical Society.

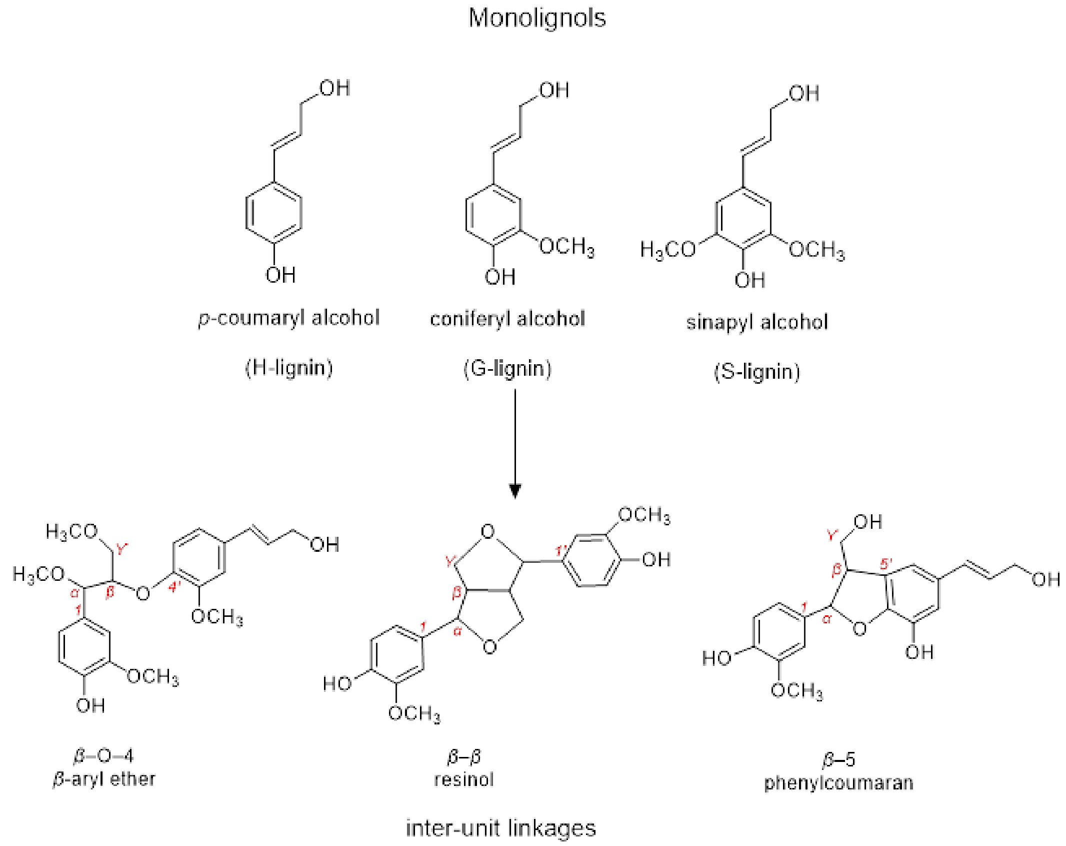


Figure 7. The major phenylpropanoid monomers and the most common inter-unit linkage of lignin.

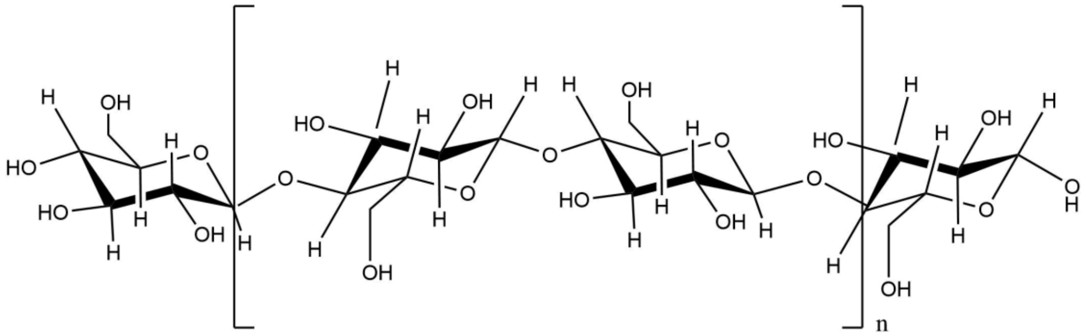


Figure 8. The structure of cellulose.

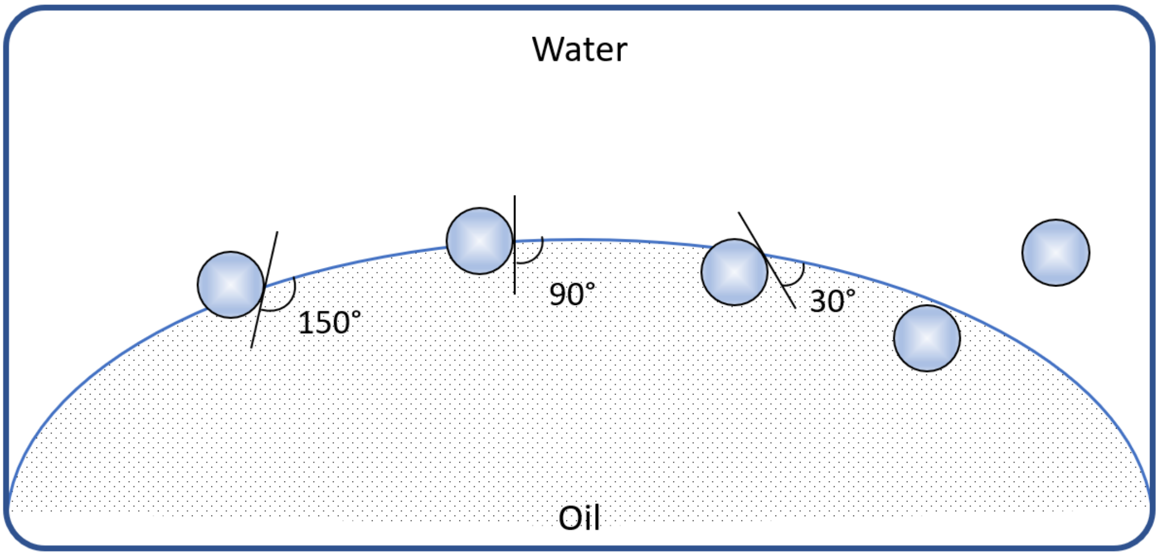


Figure 9. Illustration of particle and the contact angle in the interface.

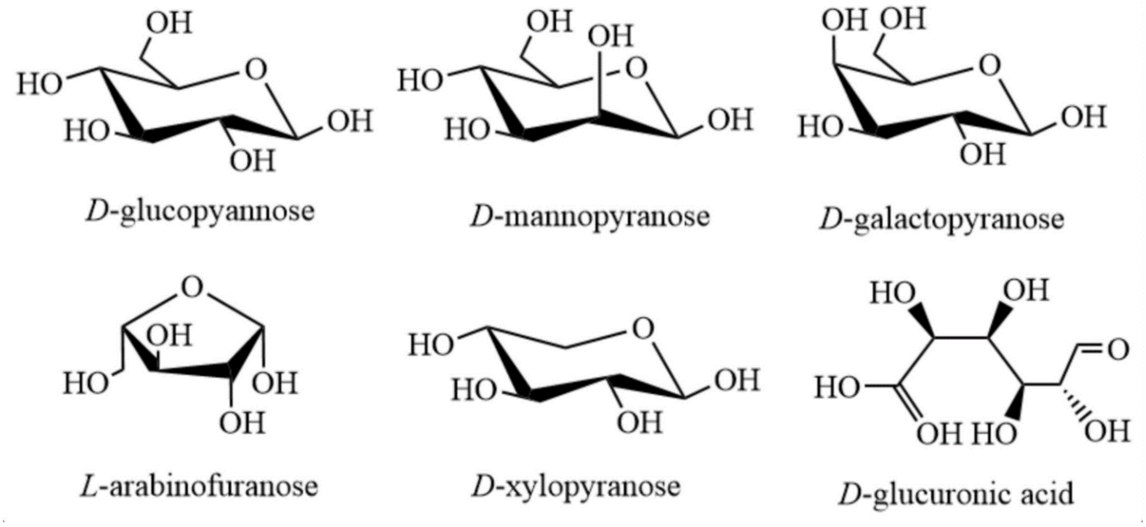


Figure 10. Functional groups in hemicellulose [146].

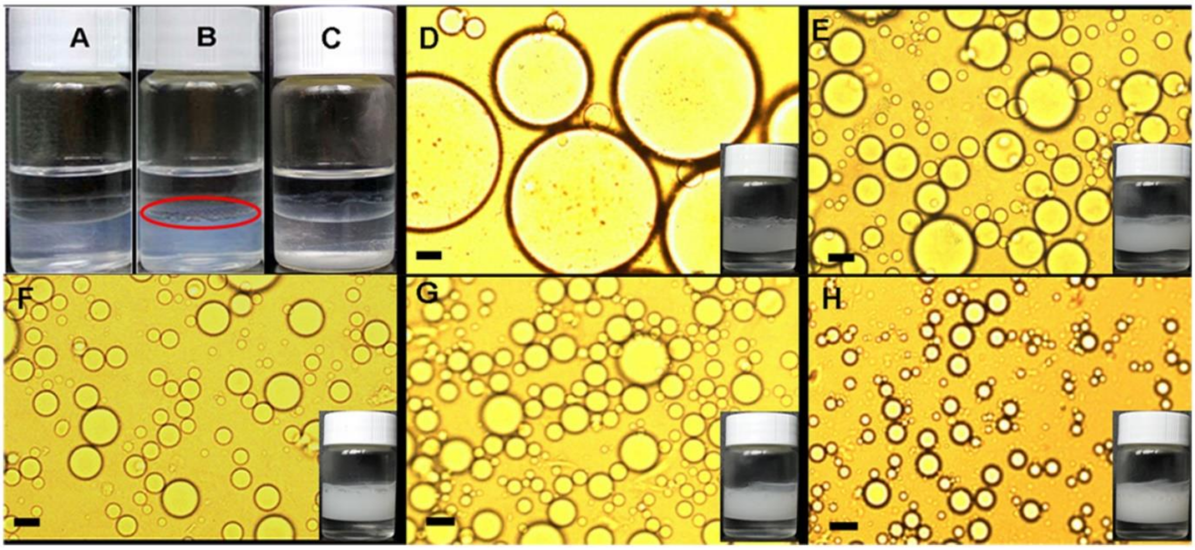


Figure 11. The difference between pristine-CNCs with various concentration of a) 0.05 wt%, and b) 0.5 wt%, versus modified PSR-CNCs with various concentration of c) 0.2 wt%. The optical micrographs showed the droplets size with various PSR-CNCs, d) 0.05 wt%, e) 0.15 wt%, f) 0.2 wt%, g) 0.25 wt%, h) 0.3 wt%. Reprinted (adapted) with permission from [147]. Copyright 2017 American Chemical Society.

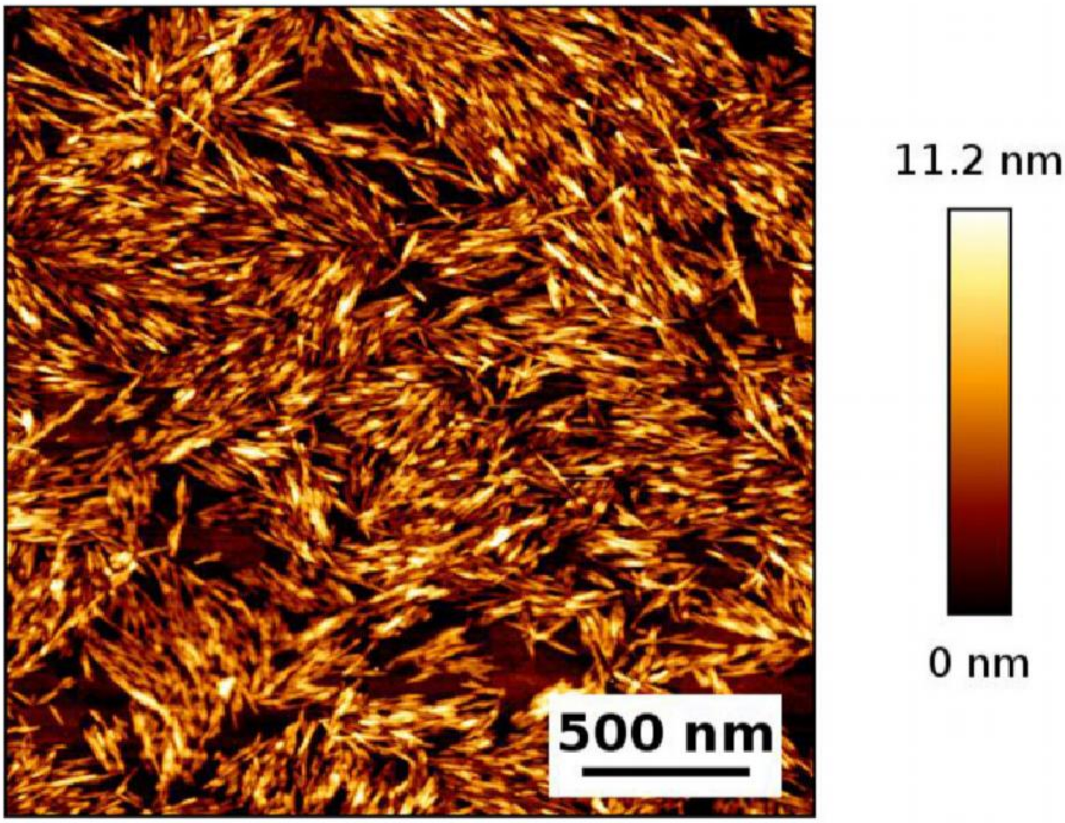


Figure 12. AFM image of CNC showed a rod-like structure [148].

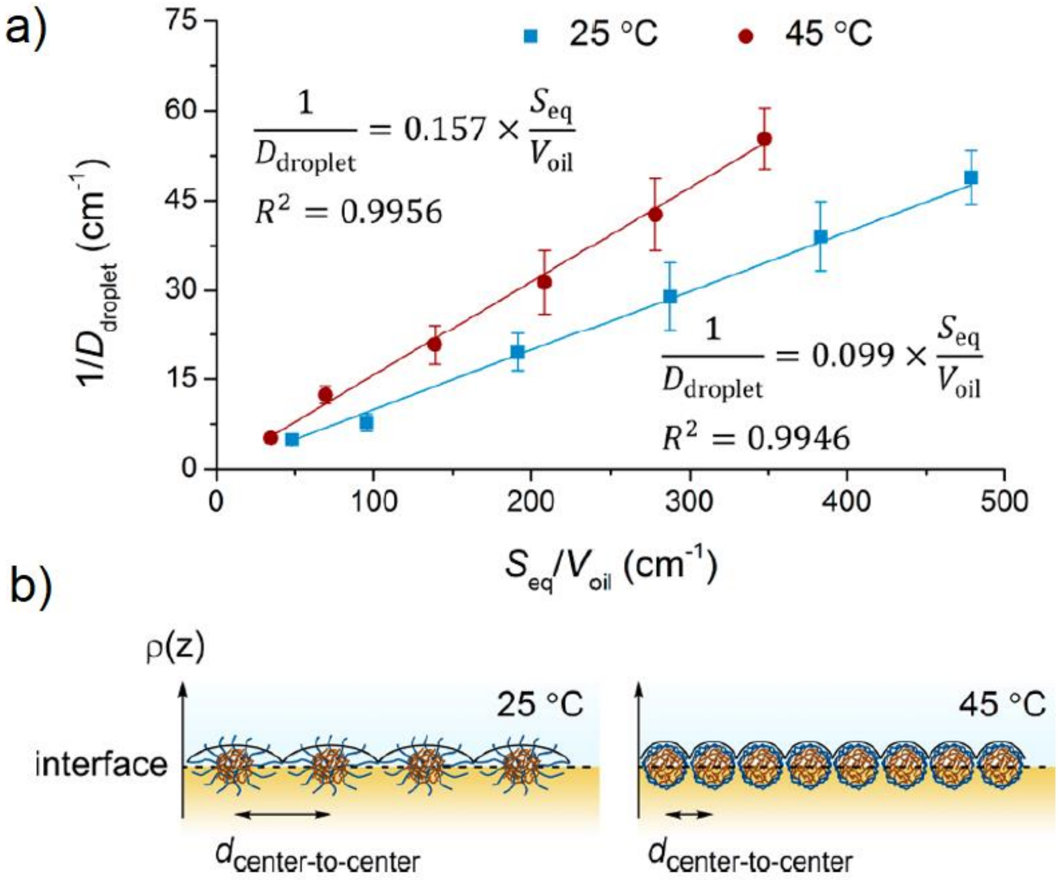
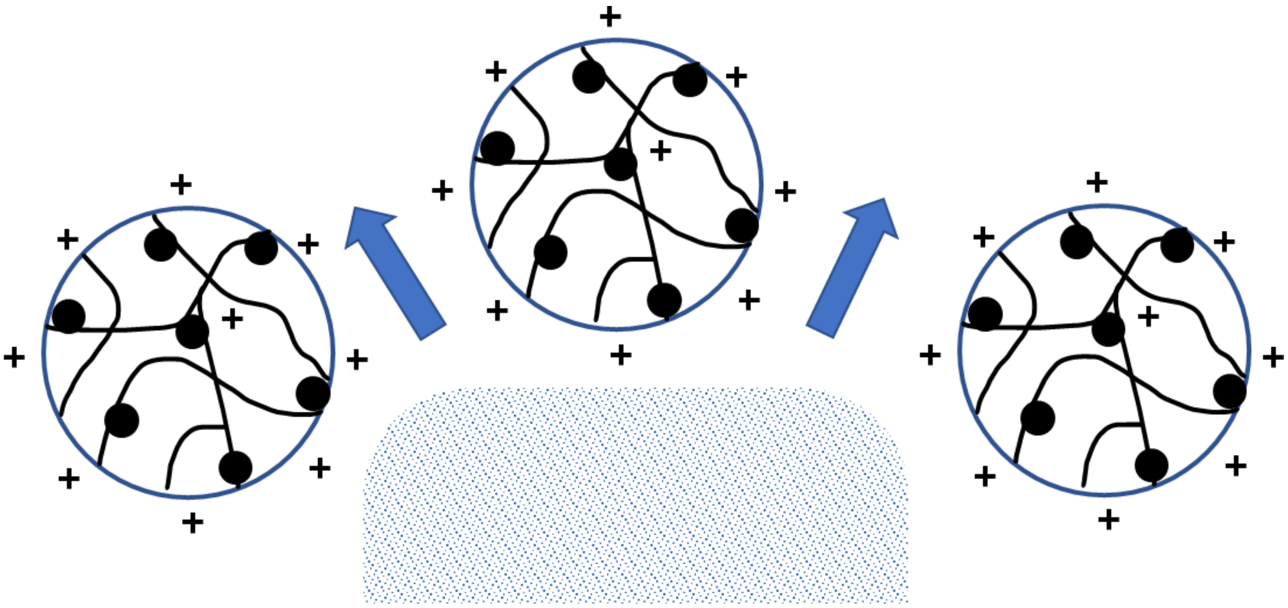
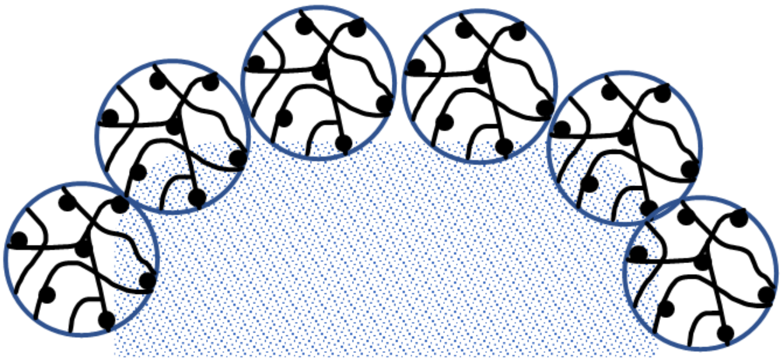


Figure 13. (a) The influence of L-PNIPAM on droplet size in Pickering emulsions at 25 °C and 45 °C and (b) illustration of the L-PNIPAM adsorbed at the interface at different temperatures. Reprinted (adapted) with permission from [66]. Copyright 2019 American Chemical Society.



Cationic at low pH



Anionic at high pH

Figure 14. Illustration of how the difference in ionization affects the stability of coalescence between the two phases.

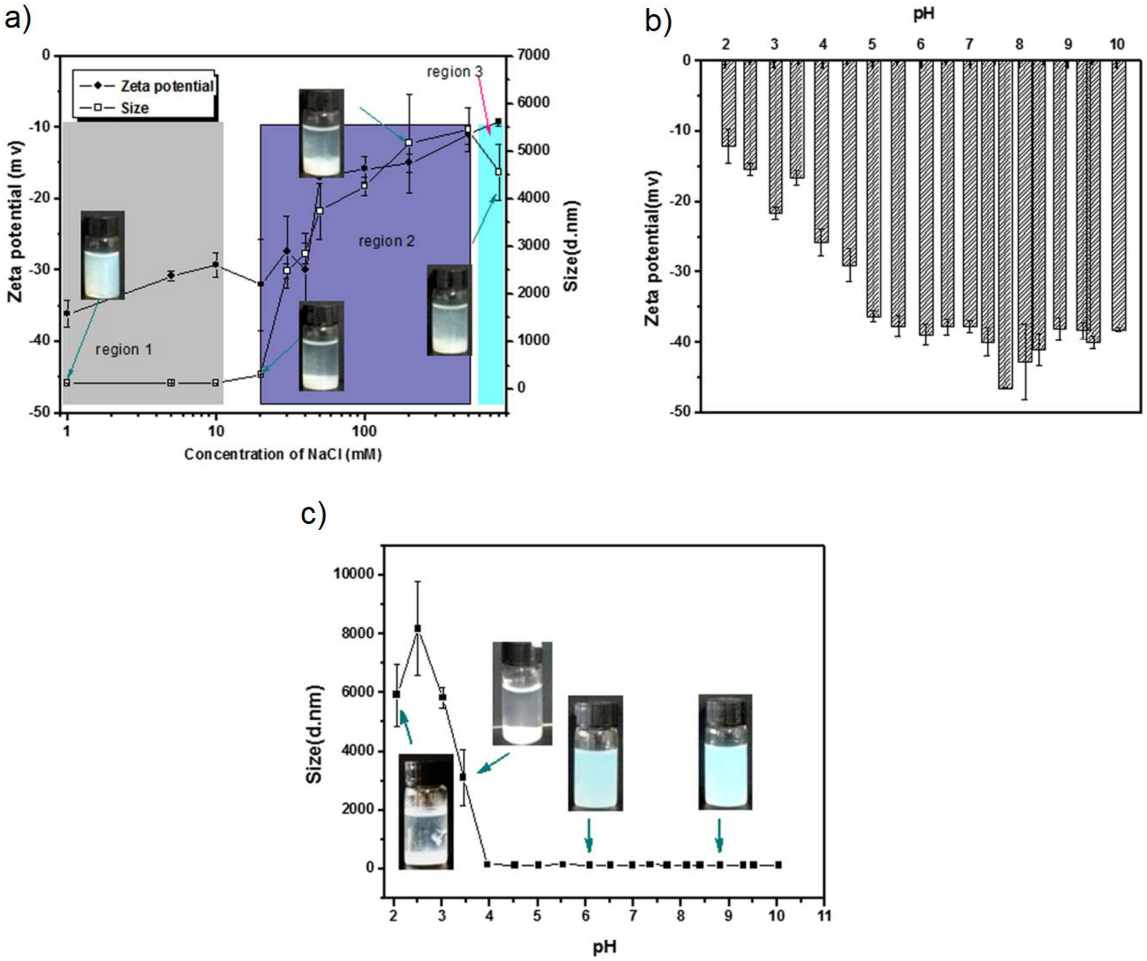


Figure 15. The influence of (a) ionic strength and the particle size of cellulose ethers on the zeta potential, (b) pH on the zeta potential, and (c) the particle size of cellulose ethers on EC [149].

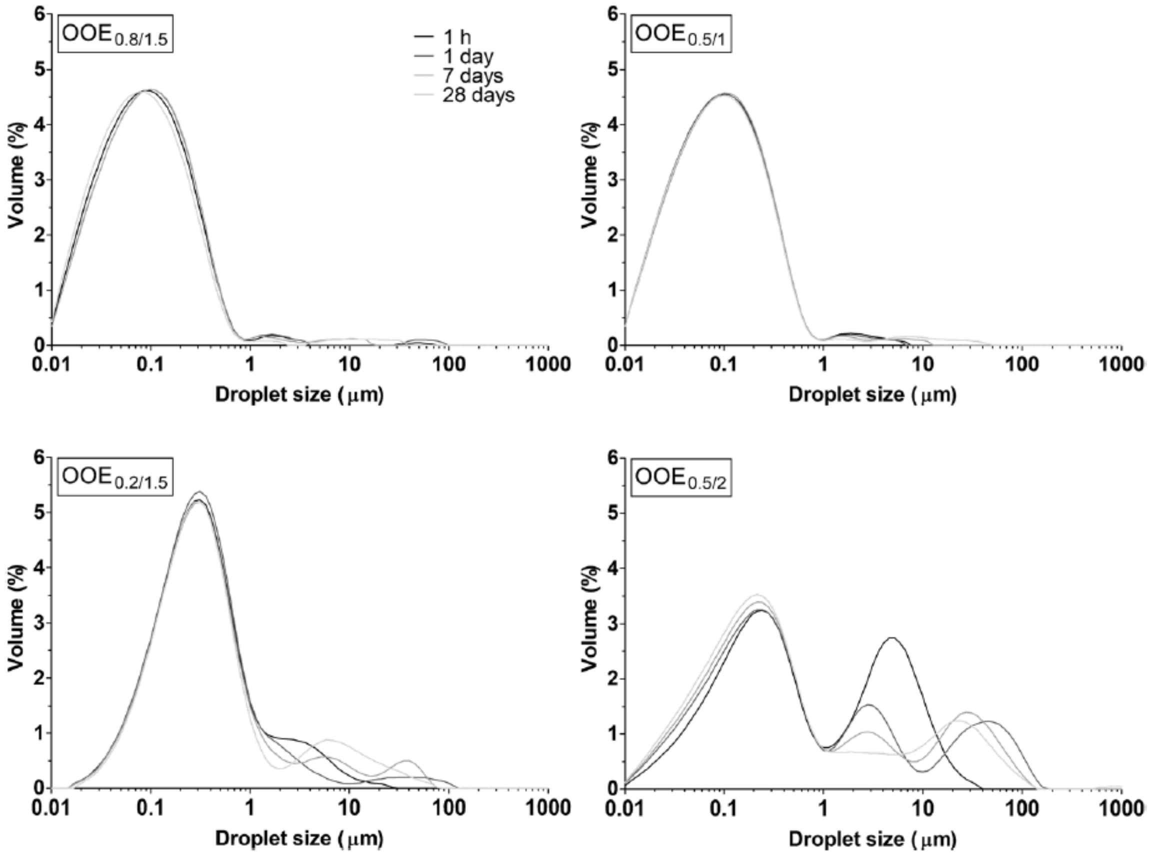


Figure 16. Distribution of droplet size between various galactoglucomannan (GGM)-to-oil ratios, showing that high concentrations of GGM retained small droplets even after 28 d [98].

Graphical Abstract