Strategies for structuring diverse emulsion systems by using wood lignocellulose-derived stabilizers

Kirsi S. Mikkonen

Wood biomass is an abundant renewable source of materials, but due to the accelerating depletion of natural resources, it is important to explore new ways to use it in a more sustainable manner. Modern technologies enable the recovery and valorization of the main components of wood—namely, cellulose, lignin, and hemicelluloses—contributing to sustainability. However, the method of isolation and resulting structure and purity of lignocellulosic materials determine their functionality and applicability. This review discusses the properties of all three main wood-based compounds that can stabilize emulsions, a class of industrial dispersions that are widely used in life science applications and chemicals. Due to the multi-billion-dollar annual market for hydrocolloids, the food, pharmaceutical, cosmetic, coating, and paint industries are actively seeking new sustainable emulsion stabilizers that fulfill the demanding requirements regarding safety and functionality. Wood-derived stabilizers facilitate various mechanisms involved in emulsion stabilization: (1) development of amphiphilic structures that decrease interfacial tension, (2) stabilization of interfaces by particles according to the Pickering theory, and (3) increase in the viscosity of emulsions’ continuous phase. This review presents pathways for treating cellulose, lignin, and hemicelluloses to achieve efficient stabilization and provides suggestions for their broad use in emulsions.

1. Introduction

On average, the Earth is covered by about 200 trees per ha, totaling an estimated 3.04 trillion. Forests are important, acting as a carbon sink and maintaining vital oxygen levels in the atmosphere via photosynthesis. In addition, forest ecosystems foster biological diversity and serve as sources of valuable commodities to meet the demands of modern society. When managed conservatively and used economically, forests can be viewed as a major renewable and sustainable resource.

The forest industry, which has a long tradition of exploiting and processing wood, is currently undergoing a transition from pulp and paper mills to biorefineries. These establishments provide new, diverse, and refined bio-based products to replace those that were typically derived from fossil fuels in addition to manufacturing more traditional fiber-based products. Within the circular (bio)economy vision, all material streams are fully utilized and recycled, reducing industrial waste and saving resources. However, the traditional forest industry was based on the refinement of cellulose—the main constituent of wood—and the other constituents, most importantly lignin and hemicelluloses, were partly lost with the process water, degraded, or burned for energy. To overcome this problem, extensive research and development have been performed within the past few decades, resulting in the invention and application of methods to upgrade wood-based compounds into various types of chemicals, precursors, particles, and fuel in addition to traditional cellulose fibers.
Cellulose, lignin, and hemicelluloses are distinguished by their chemical structures, physical attributes, methods for recovery from woody biomass, further derivatization treatments, and functional properties. Their unique characteristics are beneficial for specific applications. For example, regular-structured, high-molecular mass cellulose can form strong materials, and the complex polyphenolic composition of lignin enables multiple pathways for its modification into chemical reagents. Hemimcelluloses, on the other hand, are intermediate in size, which compromises their performance in materials for which high stiffness or strength is required. They may be hydrolyzed into monosaccharides and fermented to produce ethanol, or they may be converted into furfural.

The variation in their properties enables bio-based raw materials to play a large role in manufactured products, including emulsions, a class of industrial dispersions widely used in food and other life science products, paints, coatings, and adhesives. As there is currently a multi-billion-dollar annual market for hydrocolloids, industries are actively seeking new sustainable emulsion stabilizers that fulfill the demanding requirements regarding safety and functionality. For example, the global consumption of emulsion stabilizers for beverages alone was foreseen to surpass 210 000 MT in 2018, and it continues to grow annually by 4%. The global consumption of emulsion stabilizers for beverages alone was foreseen to surpass 210 000 MT in 2018, and it continues to grow annually by 4%. The global surfactant market for detergent formulations is more than 18 MT, which is worth 19 $ billion per year. The market value of food hydrocolloids is about 4.4 $ billion. Large quantities of surfactants are continuously released into the environment, where they may or may not be degraded, depending on their structure.

In contrast to starch, the production and utilization of wood-based stabilizers does not compete with food production. Wood-based stabilizers may replace non-renewable chemicals, provide clean-label alternatives to synthetic additives, and/or serve as non-toxic, biocompatible, and biodegradable structuring agents in dispersed systems. Various methods are used to convert wood or pulp into efficient stabilizers. For example, optimized aqueous extraction of hemicelluloses yields native functional emulsifiers. Cellulose may be disintegrated into nanoparticles or modified to become a water-soluble derivative, and lignin may be transformed into amphiphilic molecules via grafting with other building blocks. Subsequently, emulsion stability is achieved through interfacial activity of the amphiphilic surfactants, Pickering stabilization with insoluble particles, or an increase in the viscosity of the continuous phase. This review discusses these conversion methods and the functionality they achieve, emphasizing the design of new safe green materials.

2. Emulsions as diverse modern industrial systems

Emulsions are dispersions of at least two immiscible liquids, typically oil and water, in which one of the liquids forms the dispersed phase (i.e., droplets that are surrounded by the other liquid) and the other forms the continuous phase. Oil-in-water (o/w) emulsions feature oil droplets immersed in water, water-in-oil (w/o) emulsions consist of aqueous droplets immersed in oil, and oil-in-water-in-oil (w/o/w) or water-in-oil-in-water (w/o/w) compositions are multiple emulsions that can be applied in certain cases that require their good encapsulation and protection capacity. These morphologies result in a large interfacial area between the different phases, causing interfacial tension at the oil–water interface. Therefore, emulsion formation requires energy. During storage, emulsions seek to minimize the energy used by reducing the interfacial area, which is why emulsion structures tend to break down during time.

The energy required for emulsion formation can be reduced by using emulsifiers. Typically, these are relatively low-molar mass amphiphilic compounds that can be rapidly assembled at the interface at which droplets are formed during liquid flow in emulsion mixing. Surface-active emulsifiers lower the interfacial tension between the dispersed and continuous phases and thus decrease droplet size. In most cases, emulsifiers provide only short-term stability. Long-term kinetic stability is achieved by applying stabilizing agents, which may function by lowering interfacial tension, forming a mechanical barrier between the droplets and the continuous phase, or increasing viscosity of the continuous phase. A stabilizer may reinforce the interfacial layer between the emulsion phases, forming a film and causing steric hindrance, which separates droplets and prevents them from coalescing. Interfacial layers can be formed by amphiphilic molecules or insoluble particles. The sides of these molecules or particles exhibit different polarities, and the nonpolar side is drawn towards oil while the polar side is drawn towards water. Depending on the morphology and electrostatic properties of the interfacial layer, droplets can be protected against coalescence and flocculation. Furthermore, the mobility of droplets can be regulated by adjusting the viscosity of the continuous phase. In o/w emulsions, this can be done with macro-molecular hydrocolloids; entangling them in an aqueous environment entraps the droplets and prevents them from creaming/undergoing sedimentation and collision. Viscosity and droplet mobility in w/o emulsions are most influenced by the lipid structure and flow properties of the oil.

The physical stability of emulsions requires the maintenance of evenly dispersed droplets with constant size distribution. However, physical stabilization alone is not sufficient to preserve the quality of emulsions, especially those containing polyunsaturated lipids, as the double bonds in lipids are prone to oxidation through a radical chain mechanism. Lipid oxidation deteriorates life science products by decreasing the lipids’ nutritional or pharmacological value, leading to the development of rancid flavors and, possibly, the formation of toxic reaction products. Emulsification accelerates the oxidation rate by increasing the total surface area of oil droplets, which exposes them to reactions with oxygen. Consequently, there is considerable interest in the development of effective strategies for retarding the oxidation of unsaturated lipids in emulsions.
Emulsions are utilized in numerous products to protect sensitive ingredients, control dosage, make application easier, or conceal or adjust taste. The culinary field contains many classical examples of emulsions, including milk, beverages, mayonnaise, chocolate, and sausages. Life science products with emulsion structures include pharmaceutical and cosmetic creams, lotions, microencapsulated drugs, and bioactive compounds, some of which may have designated release points in the gastrointestinal tract.30 Technical emulsions are applied in paints, where the dispersal of binders decreases viscosity and facilitates spreading and drying of the coating layer.14,31 Emulsions are also applied in chemicals, such as those involved in polymerization reactions, as a way of controlling the contact between reagents.32

Emulsions have multiple uses, numerous alternative ingredients, and diverse physicochemical and functional properties. Thus, the requirements regarding emulsifiers and stabilizing agents vary. Lipid phase, pH, and the ionic strength of the aqueous phase play a major role in emulsions' stability. For amphiphilic stabilizers, the size and proportion of the polar and nonpolar parts determines the position at which the stabilizer is anchored at the droplet interface (i.e., hydrophilic–lipophilic balance, HLB).21 This, in turn, determines whether the stabilizer is applicable to o/w or w/o emulsions. The size, shape, and surface chemistry of particles define their ability to assemble at an interface, and the macromolecular properties of hydrocolloids, such as hydrodynamic volume and polymer entanglement, determine the associations between stabilizer molecules and emulsion droplets.23

Food emulsions are commonly stabilized with starch derivatives,9 phospholipids (e.g., soy lecithin), or synthetic emulsifiers (e.g., polysorbates).21 However, the abundance of allergies among consumers and demand for “clean-label” food is increasing consumers' interest in new stabilizers. Synthetic emulsifying and stabilizing agents with HLBs optimized for various products can be manufactured from either petroleum-derived or bio-based alkyls. Wood biomass is an attractive material that can lead to an increase in the share of bio-based emulsifiers and stabilizers and replacement of non-renewable ones, exploration of new alternatives for green chemicals, and the achievement of good functional properties without compromising environmental and human safety. In addition, production of wood biomass does not compete with food production.

### 3. Lignocellulosic materials – bioresources and structural characteristics

Wood biomass is mainly composed of lignocellulosics, generally containing 40–50% cellulose, 20–35% lignin, and 20–35% hemicelluloses (Fig. 1).33,34 However, the composition of a tree varies depending on its species, age, growing conditions, and harvesting season. To release and recover individual components, wood biomass is commonly subjected to pretreatment, which can take the form of mechanical milling, extraction, acid, alkaline, or organosolv treatments, oxidation, ionic liquids, or hot water extraction.35–38 Green biomass treatment methods include deep eutectic solvents, steam explosion, supercritical fluids, and microbial degradation, and emerging lignocellulose pretreatment methods include microwave irradiation, ultrasound, gamma radiation, electron beam irradiation, pulsed-electric field, high hydrostatic pressure, and high pressure homogenization.39 Also, we recently presented centrifugation as a solvent-free method of separating lignin- and hemicellulose-rich fractions in softwood extracts.40

#### 3.1. Cellulose

At the molecular level, cellulose consists of long and linear β-(1 → 4)-linked glucopyranosyl chains (Fig. 2). Industrially prepared wood-based cellulose samples from acid sulfite process showed molar mass up to 1.5 × 10⁶ g mol⁻¹.32 Due to the large molar mass and regularity of the structure, numerous hydroxyl groups cause hydrogen bonding and van der Waals forces between the individual chains.43 Cellulose is organized into repeated crystalline structures and forms microfibrils in the wood cell wall, which in turn form larger macroscopic fibers.42 Native cellulose is practically insoluble in water, but it can be dissolved in other solvents, such as acids. Treatment of dissolved cellulose with a non-solvent, such as water, results in regeneration of cellulose in solid form.43 Cellulose pulp can also be dispersed in an alkaline solution and then treated with appropriate reagents to substitute the anhydroglucosyl monomers of the cellulose chain and yield water-soluble derivatives. The products of chloromethane, propylene oxide, mixed chloro-
methane and propylene oxide, mixed chloromethane and chloroethane, and monochloracetic acid are methyl cellulose (MC), hydroxypropyl cellulose (HPC), hydroxypropyl methyl cellulose (HPMC), methylcellulose (MCC), and carboxymethyl cellulose (CMC), respectively (Fig. 3). These are the chemical derivatives of cellulose that are most widely used as emulsion stabilizers. However, numerous other pathways for cellulose modification have been reviewed by others.\textsuperscript{44,45}

A hierarchical cell wall structure is the basis of cellulose fibers, microcrystalline and microfibrillated cellulososes (MCC and MFC, respectively), nanofibrils (CNF), and nanocrystals (CNC). Preparation of MCC, MFC, CNF, and CNC involves breaking down the hierarchy into individualized micro- or nanostructures with high crystallinity, therefore reducing the amount of amorphous material present.\textsuperscript{4,46} CNF is prepared by extracting fine nano-sized fibrils from pulp via mechanical processing and/or homogenization. Oxidation by (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) or enzymatic pretreatment processing and/or homogenization. Oxidation by (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) or enzymatic pretreatment process.\textsuperscript{47} For analytical purposes, lignin can be isolated from pre-treated, disrupted wood biomass by removing carbohydrates after hydrolyzation or by extraction. Lignin is nonpolar and shows low solubility in common solvents.\textsuperscript{33} Chemical derivatization introduces functional groups and solubilizes lignin, after which it can be separated from solid cellulose and hemicelluloses. In industrial scale, large quantities of lignin are released in the spent liquor of sulfite and Kraft pulping processes (40–50%\textsuperscript{49} and 30–35%\textsuperscript{50} of the spent liquor, respectively). Sulfite pulp is performed in the presence of sulfur dioxide and sulfate ions\textsuperscript{51} and it produces lignosulfonic acids and salts in the spent liquor.\textsuperscript{51} Lignosulfonates are anionic polymers in which the essentially hydrophobic lignin backbone is rendered hydrophilic by substitution of sulfonate groups. Lignosulfonates are highly crosslinked and contain some carboxylate groups. The polyelectrolyte nature of lignosulfonates gives them dispersive and adhesive properties.\textsuperscript{51,52} In Kraft pulping, wood is treated at elevated temperature with a mixture of sodium hydroxide and sodium sulfide.\textsuperscript{33} Phenolic hydroxyl and carboxyl groups as well as sulfur are introduced in the lignin structure.\textsuperscript{53} and simultaneously, side chains and substructures may be slightly altered.\textsuperscript{54} Other variations of pulping processes yielding lignin are also used and developed. For example, one type of biorefinery concept applies hot water extraction of wood to recover hemicelluloses, and sequential alkaline extraction to separate lignins from the pulp.\textsuperscript{55}

Traditionally, lignin was treated as waste and used for low-value applications, such as energy production. However, advances in lignin modification chemistry have produced a number of functional lignin-derived polymers that exploit both the intrinsic features of lignin and the properties of grafted functional groups. Current applications of lignin-derived bio-polymers include reinforcement fillers, antioxidants, UV absorbents, antimicrobial agents, carbon precursors, biomaterials for tissue engineering and gene therapy, and smart materials, which were recently reviewed by Kai et al.\textsuperscript{55}

### 3.2. Lignin

Lignin is a complex aromatic polymer located mainly in the secondary cell walls of wood.\textsuperscript{55} In contrast to cellulose, the structure of lignin is not uniform and lacks a repetitive polymeric pattern. The structure of lignin varies remarkably between wood species, and even between parts of individual trees, so there is a low probability that two lignin macromolecules will be identical.\textsuperscript{48} Furthermore, lignin is highly reactive and tightly bound with cellulose and hemicelluloses in the cell wall. Thus, its structure is often altered during isolation, which complicates efforts to define its native formulation in detail. Lignin is composed of 4-hydroxyphenylpropa-noid units that polymerize to form a netlike structure. Three different phenylpropanoid molecules are known to function as major precursors to lignin polymers: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. These precursors polymerize via radical oxidative coupling and form p-hydroxyphenyl, guaiacyl, and syringyl units (Fig. 4).\textsuperscript{48}

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### 3.3. Hemicelluloses

Hemicelluloses are heteropolysaccharides that are closely associated with cellulose and lignin in wood cell walls. The

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**Fig. 3** Partial structures of cellulose derivatives with (a) methyl, (b) hydroxypropyl methyl, (c) methyl ethyl, and (d) carboxymethyl groups.

**Fig. 4** The (a) p-hydroxyphenyl, (b) guaiacyl, and (c) syringyl units that comprise lignin. For a comprehensive description of lignin structure, a review by Ralph et al.\textsuperscript{48} is recommended.
most abundant hemicelluloses in hardwoods are xylans (25–35% of wood mass), and mannans are most abundant in softwoods (about 20% of wood mass). Softwoods contain 5–10% xylan, and hardwoods contain a minor quantity of glucuronomannan (2–5%) (Fig. 5).33,34 Hardwood xylans consist of β-D-xylopyranosyl units linked by (1 → 4)-bonds and substituted with (1 → 2)-linked 4-O-methyl-α-D-glucopyranosyl uronic acid and acetyl groups (glucuronoxylans, GX).33,34 Xylans from softwoods are substituted with (1 → 2)-linked 4-O-methyl-α-D-glucopyranosyl uronic acid and (1 → 3)-linked α-L-arabinofuranosyl units (arabinoglucuronoxylans; AGX).56 On average, seven of ten xylopyranosyl residues derived from hardwood GX carry an O-acetyl group at the C-2 and/or C-3 position. Softwood xylans are not acetylated.34 The molar mass of pressurized hot water extracted (PHWE) birch GX is about 6500 g mol\(^{-1}\).12

The backbones of GGM and glucomannan consist of alternating β-D-glucopyranosyl and β-D-mannopyranosyl units attached with (1 → 4)-bonds. Softwood GGM contains α-L-galactopyranosyl units (1 → 6)-linked to the backbone mannosyl units. The C-2 and C-3 positions of mannosyl units are partially substituted by O-acetyl groups, on the average one group per 3–4 backbone hexopyranosyl units.33,57 The molar mass of GGM from thermomechanical pulping process water of spruce is approximately 30 000 g mol\(^{-1}\) (ref. 58) and that from PHWE is about 10 000 g mol\(^{-1}\).12

However, the composition of isolated GX and GGM extracts is more complex than that described above, as the extracts often contain co-components, such as lignin fragments or other wood-derived extractives.39-61 Pressurized hot water-extracted hemicelluloses are characterized by up to 70 mg gallic acid equivalent per g hemicelluloses,14 indicating presence of lignin.61 Covalent bonding may occur between the polysaccharide chains and lignin residues, creating lignin–carbohydrate complexes (LCC).61-63 These may either originate from native structures in wood or form through reactions that occur during the extraction process.

Hot-water-extracted hemicelluloses are largely watersoluble, but they may exhibit macromolecular assemblies or aggregates in aqueous environments.64 The aggregation phenomenon is time- and pH-dependent.65 Alkali treatment of hardwood pulp removes side groups from xylans and decreases their water solubility. Due to their intermediate molar mass, the viscosity of aqueous GX and GGM solutions is low, even at high concentrations.12

4. Strategies for achieving emulsion stability

4.1. Amphiphilic surfactants

To introduce surface activity to wood cellulose and lignin, they are functionalized with nonpolar groups in cellulose18 and either charged groups66,67 or alkyl chains68 in lignin, which bring amphiphilic properties to their structures (Fig. 6).
Tailored amphiphilic stabilizers may contain various proportions of polar and nonpolar structures, and they have the capacity to assemble into an oil–water interface and reduce interfacial tension. Hemicellulose-rich aqueous extracts exhibit native surface activity without chemical derivatization. 12

4.1.1. Cellulose derivatives. Cellulose derivatives are attractive as hydrocolloids since the fact that they are produced by chemical modification of cellulose ensures that they have uniform properties. 69 Numerous methods for cellulose modification have been explored, 44,45 but the most common methods for producing emulsion stabilizers are the etherification reactions of cellulose into MC, HPC, HPMC, MEC, and CMC (Fig. 3). 18 After these reactions, cellulose ethers can be further hydrophobized through the attachment of alkyl chains of different lengths. 70 The properties of modified cellulose are determined by the type of substitution, the degree of polymerization (DP) of the cellulose chains, and the degree of substitution (DS) with functional groups. 71 For example, the above-mentioned cellulose ethers are soluble in cold water, and CMC is also soluble in hot water.

MC and HPMC exhibit some surface activity. 18 HPC has high surface activity compared to most hydrocolloids, and MEC shows very high surface activity and the capacity to decrease the surface tension of water. 18 CMC is not surface-active, 72 and its effects on emulsion stability are related to regulation of the viscosity of the continuous phase, as discussed further in section 4.3.

Many cellulose ethers are commonly used to stabilize o/w emulsions. 73,74 However, ethylcellulose (EC), which is water-insoluble, can stabilize w/o emulsions. 75 HPC, HPMC, and hydrobically modified hydroxyethyl cellulose (HMHEC) adsorb at the oil–water interface and form a solid film that prevents coalescence of the droplets. 76–78 Camino et al. compared several grades of HPMC with varying methyl and hydroxypropyl content, methyl/hydroxypropyl ratio, molar mass, and DS and found that the highest surface activity were achieved with the HPMC sample with the highest content of methyl groups and lowest molar mass. 72 Low molar mass has also been correlated with small emulsion droplet size, which is related to high stability. 79 The self-assembly of HPMC in a solution is driven by hydrophobic interactions between the hydrophobic substituents, mainly methyl groups. 77 However, at pH 3, adsorption at the droplet surface and interfacial film formation was hindered. At low pH values, there are a higher number of hydrogen bonds between the protons of the solvent and the HPMC. Thus, because of the interactions between the molecules and the surrounding medium, the hydrophobic interactions and interfacial film formation were weaker. 79,80 Controlling emulsion stability with cellulose derivatives therefore requires an understanding of the structural proportions and molecular interactions between the polar cellu-lose chain and the nonpolar functional groups introduced to it.

4.1.2. Lignin derivatives. To stabilize emulsions, the stabilizer is commonly dissolved or dispersed in the continuous phase. Kraft lignin shows tendency to form aggregates in aqueous environment, 53 whereas lignosulfonates are readily dispersible in water. 81 Both can be viewed as spherical poly-electrolytic microgels. 81,82 Due to the ionizable groups, both lignosulfonates and Kraft lignin act as polyelectrolytes and may stabilize emulsions through repulsion via an electrical double layer. 66,67,83,84 Unsubstituted regions of lignin remain nonpolar and hydrophobic, and they are likely to induce adsorption at dispersion interfaces. 85 Notably, Kraft lignin exhibits higher surface activity, which can be explained by its lower polyelectrolytic expansion and degree of sulfonation compared to lignosulfonates. 66 The former implies that the swollen core of lignosulfonates is more amenable to the ionization of acidic groups, so lignosulfonates may be richer of ionizable groups in the interior of the molecular matrix. 66 However, the surface activity is not directly linked to efficient emulsion stabilization capacity 86 and the molar mass of the lignin fraction also plays a role. For example, high-molar-mass lignosulfonates and Kraft lignin can act via multilayer adsorption to provide both steric and electrokinetic stabilization. 83

Lignosulfonates can be combined with other surfactants to achieve higher stability. For example, lignosulfonates engage with cationic surfactants and adsorb at the oil phase through hydrophobic interactions. 52 Changes in pH and presence of multivalent cations may affect the colloidal behavior by causing coagulation of sulfonated lignins. 82 Surfactants and other designed additives, such as sodium salts and bile acids, may enhance the colloidal stability of lignins under challenging conditions, such as alkaline solutions, elevated temperatures, and high ionic strengths. 87

To utilize sulfur-free industrial lignins, such as those recovered from pre-hydrolysis, as emulsifying agents, they can be modified by, for example, alkylation to improve their surface activity. 69 The surface tension of alkylated lignins is associated with their capacity to emulsify and stabilize paraffin w/o emulsion, as can be observed by monitoring the formation of a creaming layer. 68 Another approach is to introduce polar groups via carboxymethylation to make lignins water-soluble, adjust the balance of affinity between the oil and water phases, and optimize their surface activity. 19,20 The solution-related properties of carboxymethylated lignins are dependent upon DS and pH. In one study, the droplet size of carboxymethyl lignin-stabilized kerosene o/w emulsion remained relatively constant for one month. 19 The complexity of lignins’ structure and the numerous possibilities for further derivatization makes lignins a challenging, but versatile, raw material for producing effective emulsion stabilizers.
4.1.3. Native hemicellulose-rich extracts. The polysaccharide structure of wood hemicelluloses is composed of chains of monosaccharides with short branches and some backbone monosaccharides partially substituted with acetyl groups. The carbohydrates are polar in nature, whereas the acetyl groups are slightly nonpolar. However, the plain polysaccharide structure of hemicelluloses lacks considerable amphiphilicity that would make them interfacially active.

The water-solubility of hemicelluloses is dependent upon their molar mass and the presence of side groups, which hinder close packing and association of adjacent hemicellulose chains. Additionally, the alkaline conditions under which extraction is performed remove a major part of the side groups and make hemicelluloses water-insoluble. The first studies to report the use of wood hemicelluloses in emulsions performed hydrophobic modification by grafting insoluble beech GX, its sulfoethyl derivative, and viscose effluents with alkyl or p-carboxybenzyl groups. After treatment, the samples showed water solubility, moderate surface activity, and the ability to form and stabilize paraffin o/w emulsions. This experiment was conducted simply using a laboratory mixer and observed visually by monitoring the level of the cream layer or separated oil. In a different study, controlled etherification of Kraft GX and GGM into water-soluble hydroxypropylated and butylated derivatives was performed to tune the amphiphilicity of hemicelluloses for emulsifying octane.

Water-extracted hemicellulose samples are largely watersoluble, but they are rarely composed of pure polysaccharides. Depending on the lignocellulosic raw material and isolation method, the amounts and types of lignin residues and extractives accompanying the carbohydrate structure may vary. These provide hemicellulose samples with amphiphilic properties and the capacity to lower the surface tension of water. For example, native beech GX isolates that contained residual lignin showed the capacity to stabilize emulsions. In addition, spruce GGM extracts often contain varying amounts of lignin residues, and they have been shown to stabilize colloidal wood resin emulsions as well as orange o/w emulsions. Furthermore, GGM adsorbed at the rapeseed o/w emulsion droplet interface and stabilized it. Rheological characterization of GGM- and GX-stabilized emulsions indicated that stability was at least partially due to the steric mechanism. Most work on hemicellulose-stabilized emulsions has been performed with o/w emulsions, but Xu et al. prepared and stabilized w/o emulsions using carboxymethylated GGM.

In addition to surface activity and the physical capacity to stabilize emulsions, phenolic compounds such as lignin fragments introduce antioxidant properties to hemicelluloses. This was shown by Wrigstedt et al., who synthesized ferulic acid and sinapic acid esters on birch GX and testing the antioxidant and emulsification properties. In a different study, spruce GGM containing phenolic residues efficiently inhibited lipid oxidation of rapeseed oil o/w emulsions, as indicated by the resulting peroxide values, volatile oxidation products, and analysis of polymerized lipids. Naturally associated lignin residues in GGM are believed to anchor polysaccharide structures at the oil droplet interface and enable stabilization of emulsions. Lehtonen et al. suggested that the native interactions of GGM and phenolic residues could be retained by adjusting the isolation methods, and that this could achieve efficient physical stabilization and extended protection against lipid oxidation. Indeed, water-extracted hemicelluloses are exceptionally attractive emulsion stabilizers due to their multifunctionality, which is obtained through environmentally advantageous and safe aqueous isolation without further derivatization.

4.2. Pickering stabilization by particles

In contrast to amphiphilic compounds and dissolved macromolecules, Pickering emulsions are physically stabilized by solid colloidal particles that are wetted partly by oil and partly by water (Fig. 7). The position of such particles at the oil-water interface depends on their relative affinity for both phases; their interface bends toward the phase for which their affinity is lower. Particles that are preferentially wetted by water are suitable for forming o/w emulsions, whereas particles that are preferentially wetted by oil are suitable for forming w/o emulsions.

4.2.1. Micro- and nanocelluloses. MCC has been employed by the food industry as an emulsion and foam stabilizer for over 40 years. It functions as an emulsion stabilizer and thickener because it has a strong affinity for both oil and water, resulting in its orientation at the o/w interface. MCC particles form a three-dimensional network structure, developing viscosity and thickening the continuous water phase between oil droplets, thus preventing collision and subsequent coalescence. The combined functional effects of interfacial adsorption and thickening can be utilized to stabilize emulsions under challenging process and storage conditions. Multiple w/o emulsions in which both of the interfaces were stabilized using MCC in the external and internal aqueous phases have been prepared. In addition to physically stabilizing emulsions, MCC reduced the rate of lipid oxidation in sunflower o/w emulsions.

Cellulose nanoparticles have gained increasing attention as Pickering stabilizers. Chemically unmodified CNF, TEMPO-oxidized CNF, and CNC can act as Pickering stabilizers of o/w emulsions against droplet coalescence, but not against creaming or flocculation. The performance of CNC prepared to become Pickering stabilizers by various methods of conversion, including oxidative reaction and deep eutectic solvents, was comparable. Near-critical water treatment and high-
shear homogenization of MCC produced nanocellulose particles that acted as Pickering stabilizers.\textsuperscript{108} CNC can also be combined with CNF, the former acting as a Pickering stabilizer at the o/w interface and the latter inducing depletion stabilization.\textsuperscript{109}

Hydrophobization of CNF by surface silylation functionalized it as a w/o emulsion stabilizer.\textsuperscript{101,110} CNF occurred as single, dispersed fibrils or formed large, network-like aggregates at the o/w interface. Fibrils that were insufficiently hydrophobized did not stabilize emulsions, as they were only partially deposited, and formed small, compact aggregates. Network formation by CNF was identified as the main mechanism preventing coalescence of oil droplets.\textsuperscript{111} Treatment of CNF with octadecylamine or poly(styrene-co-maleic anhydride) also resulted in hydrophobic fibrils, which were tested by Lif et al.\textsuperscript{112} Anionic CNC was combined with cationic surfactants to tailor Pickering emulsions to have the capacity for phase-inversion.\textsuperscript{113} Dried, water-redispersable emulsions were obtained by combining tannic acid and water-soluble cellulose derivatives (i.e., MC or HEC) with CNC. Tannic acid formed complexes with the cellulose derivatives, leading to the condensing of a protective “shell” around the oil droplets.\textsuperscript{114}

Chemical modification of CNF and CNC with lauroyl chloride resulted in nonpolar nanofibers that were able to stabilize w/o emulsions. Combining lauroyl chloride-modified and native nanocelluloses led to new surfactant-free o/w/o double emulsions that could be stabilized by nanocelluloses at both interfaces. High nanofiber length was associated with high emulsion stability.\textsuperscript{115}

In summary, versatile cellulose nanoparticles can be prepared and functionalized into designed stabilizers.

4.2.2. Regenerated cellulose. Another method for preparing cellulose nanoparticles that can stabilize emulsions is regeneration of dissolved cellulose in a non-solvent. The hydrophilic cellulose derivative hypromellose phthalate (HP) is dissolved in acetone, an ethanol/water mixture, or acetate buffer with a pH of \(>5\), and then it is sheared in aqueous non-solvent media to produce micron-sized particles.\textsuperscript{116} During coagulation, the HP particles are deformed into far-from-equilibrium shapes because of the low interfacial tension and turbulent flow in the blender after solvent attrition.\textsuperscript{116} The particles, which have intermediate hydrophobicity, adsorb at the oil–water interfaces and stabilize them.\textsuperscript{116} Dissolution of cellulose into phosphoric acid causes esterification, and subsequent regeneration in water yields amorphous cellulose particles that efficiently stabilize o/w emulsions through a combination of Pickering and network mechanisms.\textsuperscript{117,118} Regenerated cellulose particles prepared with phosphoric acid also showed stabilization capacity in combination with sodium caseinate.\textsuperscript{119}

Cellulose derivative particles may be a type of regenerated cellulose when they form dispersions in emulsions’ continuous phase instead of solutions. EC and HPMC were characterized as Pickering stabilizers in o/w and w/o emulsions. The average particle sizes \(D_{3,2}\) of HPMC and EC dispersed were 22 and 0.7 \(\mu\)m, respectively, in oil and 0.2 and 110 \(\mu\)m, respectively, in water. Particles’ size was further reduced by sonication. Emulsification of sunflower oil with EC particles resulted in small water droplet size in w/o emulsions, while HPMC was a more effective stabilizer for o/w emulsions.\textsuperscript{120}

4.2.3. Lignin particles. There are numerous possibilities for converting lignin into chemicals and derivatives. One interesting approach to developing new materials is preparation of lignin nanoparticles, as reviewed by Beisl et al.\textsuperscript{121} and Bai et al.\textsuperscript{122} For example, alkaline lignin extracted from the residues resulting from furfural production is soluble in basic water. In acidic conditions, lignin becomes insoluble and forms particles that are an effective emulsifier for o/w Pickering emulsions.\textsuperscript{123,124} Combination of acid precipitation of alkaline lignin with sonication is a rapid method to produce nanoparticles that provide extended emulsion stability.\textsuperscript{123} Control over the regeneration of solubilized lignin enables reducing the particle size to nanoscale (Fig. 8).\textsuperscript{126} Interestingly, small angle X-ray scattering revealed that the morphology of lignin nanoparticles may be heterogenous, as they can form clusters of aggregated sub-particles (Fig. 9).\textsuperscript{125} This corresponds with earlier observations of the microgel-like morphology of lignin.\textsuperscript{81,82}

Composite nanoparticles for Pickering stabilization can be prepared by acid precipitation of alkaline lignin together with sodium dodecyl sulfate.\textsuperscript{127} Lignin can also be cross-linked to produce Pickering stabilizer particles.\textsuperscript{128} Particles grafted from a lignin macroinitiator with hydrophilic polymers using reversible addition-fragmentation chain transfer polymerization have structural features similar to those of the nanoparticles used in Pickering emulsions, but the former are surface-active. In addition, those particles have the capacity to stabilize w/o emulsions.\textsuperscript{129,130} Fully bio-based Kraft lignin nanoparticles were surface-treated by adsorbing cationic lignin, to extend the emulsion stabilization array.\textsuperscript{131} Kraft lignin nanoparticles were also coated with chitosan, used as emulsifiers, and further crosslinked with sodium tripolyphosphate to achieve a strong stability against emulsion coalescence.\textsuperscript{132} Recent efforts in lignin nanoparticle research tackle the challenge of their continuous production by using a microchannel\textsuperscript{126} and a potentially scalable preparation by spray-freezing.\textsuperscript{133}

4.2.4. Hemicellulose particles. In contrast to PHWE, alkali extraction of hemicelluloses modifies (i.e., deacetylates) polysaccharides, resulting in reduced water solubility and concomitant extraction of some lignin.\textsuperscript{134} In fact, alkali-treated polymeric hemicelluloses, such as those recovered from Kraft pulp, are not water-soluble without chemical derivatization. We suspended alkali-extracted xylan from beech and birch (sigma) in 25 mM sodium citrate buffer at a pH of 4.5 and used the suspension as the continuous phase of rapeseed o/w emulsions with 1 wt% xylan and 5% oil (previously unpublished data). The emulsions were prepared and their droplet size distributions were characterized by static light scattering according to Lehtonen et al.\textsuperscript{97} The \(D_{3,2}\) surface average droplet size of beech xylan-stabilized emulsions was 0.49 \(\mu\)m immediately after preparation and 0.54 \(\mu\)m after a one-month accelerated storage test at 40 \(^\circ\)C. The \(D_{3,2}\) values of birch xylan-stabilized
emulsions were 0.43 µm fresh and 0.42 µm after one month. The results showed that the water-insoluble xylan particles acted as efficient emulsifiers and stabilizers. Fig. 10 illustrates the droplet size distributions of beech and birch xylan-stabilized emulsions immediately after preparation and after storage for one month. A narrow distribution of small droplets was detected, with little indication of large droplets. Optical microscopy was performed according to Lehtonen et al.’s method for visualizing droplets, and the microscopy images (Fig. 11) supported the findings of the droplet size distribution analysis.97

According to our results, insoluble hemicelluloses, such as xylans obtained from alkaline processes, can be used as efficient emulsion stabilizers. It is hypothesized that xylan particles act as Pickering stabilizers, adsorb at the droplet interface, and form a protective film that prevents coalescence.

4.3. Control over the viscosity of the continuous phase
The shelf life of emulsions can be remarkably extended by increasing the viscosity of the continuous phase (Fig. 12). Of the wood-based stabilizers, CNF is particularly suited for
increasing the viscosity of water, as it consists of long, flexible, and entangled fibrils that form a gel network that can entrap emulsified droplets and prevent them from undergoing creaming and coalescence. An ionic surfactant, sodium dodecyl sulfate, was used to prepare o/w and w/o emulsions, and then the emulsions were further co-stabilized by addition of CNF or less polar aqueous counter collision-treated CNF.135

The solution viscosity of cellulose derivatives depends on DP and, to some extent, on DS. CMC is not surface-active and does not show an emulsifying capacity as such,73 so its effects on stability are related to controlling the viscosity. It has been found that 1% aqueous solutions of CMC show viscosity of up to 5000 mPa s at ambient temperatures.18 CMC solutions exhibit a reversible reduction of viscosity upon heating, but they do not gel alone or with other hydrocolloids.18 The stabilizing capacity of other cellulose derivatives results from combined effects of interfacial activity and viscosity increase.71,75

5. Potential of lignocellulosic stabilizers

5.1. Stabilization mechanisms and performance

Current literature presents clear evidence of the functionality of lignocellulose-derived compounds and particles as emulsion stabilizers. However, quantitative comparison and evaluation of their performance is complicated due to high variation in emulsion composition, preparation, and characterization methods used in different studies (Table 1). The oil type and polarity, content and ratio of stabilizer and oil, and the intensity of the emulsification process affect the emulsion formation and resulting oil droplet size. Furthermore, the emulsion stability assessment is subject to storage time and conditions as well as characterization methods, such as visual inspection or droplet size analysis (Table 1). The envisioned application determines whether emulsification and short-term stability is sufficient,123 or whether long-time stability against coalescence and creaming, for example, is needed.14 To compare the performance of lignocellulosic emulsion stabilizers, systematic studies at standardized conditions are needed.

Lignocellulose-derived components, either soluble molecules or insoluble particles, stabilize emulsion systems via different mechanisms depending on their colloidal properties (Table 1). Cellulose derivatives,76 lignosulfonates,67 Kraft lignin,83 native97 and modified90 hemicelluloses, as well as insoluble nanoparticles from cellulose,106,109 lignin,125,127 and hemicelluloses (please see section 4.2.4) adsorb at oil droplet interface either through amphiphilic structures or the
Pickering mechanism. The amphiphilic structures may be derived from natural associations between hemicelluloses and lignin\(^\text{97}\) or they can be achieved by modification during the pulping process\(^\text{67,83}\) or by derivatization of the isolated lignocellulosics.\(^\text{90}\) The emulsion stabilization mechanisms of amphiphilic lignocellulose-derived molecules resemble those of abundant surfactants, such as polysorbates and lecithin.\(^\text{12,21}\) Even though the interfacial activity of lignocellulosic stabilizers may not compare to that of small-molecule amphiphilic surfactants, their higher molecular mass brings additional functionality through steric stabilization.\(^\text{12}\)

Pickering particles can be formed from each: cellulose,\(^\text{117}\) lignin,\(^\text{115,127}\) and hemicelluloses through solubilization and regeneration, and they show capacity to adsorb at oil–water interfaces and stabilize them. Pickering particles are well known for emulsion stabilization.\(^\text{99}\) To compete with inorganic particles or starch granules,\(^\text{99}\) lignocellulose-derived particles should provide at least comparable performance, price, and availability.

Cellulose derivatives\(^\text{76}\) and CNF\(^\text{135}\) may also stabilize emulsions by increasing the viscosity of the continuous emulsion phase, inhibiting droplet coalescence and emulsion creaming/sedimentation. A surface active emulsifier is usually first needed to reduce droplet size.\(^\text{122}\) Viscosity optimization is essential for many common industrial applications. To facilitate processing of certain products, such and paints\(^\text{144}\) and heavy crude oil,\(^\text{67}\) low viscosity is desired, so interfacial stabilization of emulsions is preferred over viscosity increase. Thickening agents are abundantly used in other products, including cosmetic creams and certain foods.\(^\text{21}\) The combination of price and performance determines whether lignocellulosic stabilizers will find use in these products.

### 5.2 Applications in technical emulsions

Lignocellulosic stabilizers are an attractive option for technical dispersions as their bio-based nature and, in many cases, biodegradability are favored over the less sustainable characteristics of non-renewable stabilizers. One type of technical dispersion in which they might be used is petroleum-based emulsions. Heavy crude o/w emulsions have been emulsified with sodium lignin sulfonates to decrease their viscosity for pipeline transportation.\(^\text{85}\) In addition, the stabilizing capacity of lignosulfonates has been compared with that of more surface-active Kraft lignin in an emulsion model with dispersed bituminous crude oil containing large amounts of polar asphaltenes.\(^\text{66}\)

Decreasing the viscosity of crude bitumen and refined oil were achieved by emulsification with carboxymethylated Kraft

| Stabilizer type (and content) | Oil type and content | Emulsification method | Stability evaluation | Stabilization mechanism |
|-------------------------------|----------------------|-----------------------|---------------------|-------------------------|
| Hydrophobically modified HEC\(^\text{76}\) (0.2–1%) | Paraffin | Mixing at 6000 rpm for 10 min | Droplet size 10–30 µm, stable for at least one month | Adsorption effect |
| Lignosulfonate\(^\text{67}\) (0.0625–0.5%) | Geisum | Mixing at 1200 rpm for 15 min | Visual observation, stable for at least 3 days | Surface activity, electrostatic interactions |
| Kraft lignin\(^\text{63}\) (0.5–2%) | Exxol D80 48% | Mixing at 8000 rpm for 2 min | Visual observation, phase separation in 25–240 min | Adsorption, steric and electrokinetic stabilization |
| Etherified Kraft GGM or GX\(^\text{90}\) (1%) | Octane | Mixing with Ultra-Turrax T8 at speed 6 for 2 min | Droplet size below 100 µm for at least 22 days | Amphilic structures |
| GGM-rich spruce extract\(^\text{97}\) (1%) | Rapeseed oil 5% | High-pressure homogenization, three passes at 800 bar | Stable for at least 6 weeks | Adsorption, amphiphilic hemicellulose-lignin structures |
| CNC, TEMPO-oxidized CNF, or CNC\(^\text{106}\) (0.1–1.5%) | Dodecanol 20–35% | Mixing at 24 000 rpm for 90 s | Droplet size 10–40 µm, stable against coalescence for at least one month | Adsorption, electrostatic interactions |
| CNC and/or CNF\(^\text{109}\) (0–1%) | Sunflower oil 1–10% | Ultrasonication for 90 s at a power level set at 40% strength | Visual inspection and microscopy for 7 days, stability dependent on component ratios | CNC: Adsorption |
| Regenerated cellulose particles\(^\text{118}\) (0.1–1.25%) | Kerosene | Mixing at 10 000 rpm for 3 min | Visual inspection; stable after 1 day | Combination of adsorption and network formation |
| Nanoparticles from alkaline lignin\(^\text{125}\) (0.15–0.6%) | Rapeseed oil 10% | High-pressure homogenization, four passes at 88 bar | Turbiscan analysis and visual inspection; stable for at least 22 days | Adsorption, electrostatic interactions |
| Nanoparticles from black liquor lignin with sodium dodecyl sulfate\(^\text{127}\) 0.6% | Cyclohexane | Mixing at 11 000 rpm for 3 min | Droplet size 10–20 µm for 2 months | Adsorption, electrostatic interactions |
| Insoluble beech and birch xylan | Rapeseed oil 5% | High-pressure homogenization, three passes at 800 bar | Droplet size 0.4–0.5 µm for at least one month | Adsorption |
| Sodium dodecyl sulfate (0.01–1.2%) and CNF (0–0.5%)\(^\text{135}\) | Toluene | Mixing at 9000 rpm for 5 min | Visual inspection for stability against creaming | Viscosity modification and electrostatic interactions |

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and organosolv lignins. Overall, the complex structure of lignins makes them complicated to use, but they are inexpensive, and their numerous reactive groups enable derivatization and upgrading for functional stabilizers.

Di Marino et al. exploited the emulsification capacity of Kraft lignin during in situ extraction in an electrochemical depolymerization system to obtain monomers for further reactions. Prior studies have also found that lignin-derived fragments or lignin nanoparticles can be applied to surfactants for emulsion polymerization of latexes. In a different study, hemi-celluloses derived from pre-hydrolysis of Kraft-based dissolving pulp were used to aid the creation of a stable latex with enhanced capacity for absorbing dyes and to improve the biodegradability of the latex. Further, softwood GGM and hardwood xylans have been tested as stabilizers of alkyl-based paint emulsions to decrease viscosity and ensure easy application on painted surfaces. Examples of technical emulsions stabilized with cellulose include o/w emulsion droplets characterized as a substrate for cellulose hydrolysis for advanced conversion processes. Svagan et al. crosslinked hexadecane o/w emulsions stabilized by a mixture of CNC and CNF using aromatic polyurea to produce a protective mechanical barrier for liquid-core microcapsules.

5.3. Food and other life science applications

Cellulose derivatives are widely used and well-known as food emulsion stabilizers. Recent research on the topic has applied them as fat replacers in biscuits, muffins, and stabilizers and texturing agents in emulsion-type sausages. Cellulose derivatives are also suitable for pharmaceutical applications, such as HPMC-stabilized emulsion for treatment of dry eye syndrome.

MCC, nanocelluloses, and hemicelluloses are of interest for their ability to naturally emulsify and stabilize ingredients and additives in food products, including salad dressings, whipped toppings, sauces, foams, soups, puddings, dips, and many others. The use of MCC and MFC in food was first suggested in Japanese and US patents developed by Turbak et al. in the 1980s, as noted by Gómez et al. Later, application of CNF as a stabilizer for frozen dessert was proposed in a patent application by Yano et al. In addition, Mikulcová et al. proposed emulsification and stabilization of antimicrobial oils (i.e., cinnamaldehyde, eugenol, and l-moment) by CNF and CNC as a way to achieve a longer shelf life for perishable food. Multiple w/o/w emulsions stabilized with MCC may be of interest for drug release applications, such as carriers of isoniazid for tuberculosis therapy.

Hu et al. characterized regenerated cellulose particles as sausage emulsion stabilizers when combined with sodium caseinate. Use of soybean oil as a lipid phase enabled the authors to reduce the saturated fat content of pork sausages. Substitution of 50% pork fat with emulsified soybean oil resulted in products that were acceptable by a sensory panel. In other studies, regenerated cellulose and softwood GGM functioned as stabilizers of citrus o/w beverage model emulsions. GGM-stabilized rapeseed o/w emulsions have also been proposed for use in food applications. Vegan and dairy beverages stabilized with GGM were characterized as model product prototypes. Additionally, GGM-stabilized emulsions in which α-tocopherol (a model hydrophobic core compound) is the dispersed phase were lyophilized to produce edible microcapsules that could be applied to a variety of foods.

Various wood-derived compounds are used as food additives or ingredients, including MCC and several types of cellulose derivatives, vanillin aroma, glycerol esters of wood rosins, xylitol, and sterols/stanols. Cellulose, hemicelluloses, and lignins are present in all terrestrial plants and thus in common diet, and they are classified as dietary fibers. However, food-grade assessment and related safety evaluation of isolated wood lignins and hemicelluloses has not been conducted. According to legislation, the risk assessment and safety evaluation considers the preparation method and toxicity of novel foods, taking account of the anticipated intake.

Pitkänen et al. highlighted the safety of softwood GGM as a food ingredient or additive as major safety hazards were not identified in their literature review; on the contrary, successful animal feeding tests indicated the non-toxicity of GGM. A study using an in vitro digestion model suggests that birch pulp xylan is slowly fermented in colon. Pressurized hot water extraction of hemicelluloses is advantageous, because hazardous chemicals are avoided. The presence of process chemicals in Kraft lignin and lignosulfonates raise concern regarding their use in life-science products, unless they are carefully purified. Alkali-extracted birch lignin from the residual solids after hot water extraction is free from sulfur, so it is advantageous compared to Kraft lignin and lignosulfonates. However, the latter are still extensively studied for their beneficial effects on human health. Those effects include the capacity of lignin’s complex polyphenolic structure to bind bile acids in the intestine, inhibit tumor growth, and act as antioxidant, for examples.

Physical modifications (e.g., particle size reduction) and chemical derivatization (e.g., introducing charged groups) may affect the function of lignocellulosic materials in digestion. The interactions of nano-sized materials with their biological surroundings can be unpredictable. The nanosized structure of CNC has raised concern due to its capacity to pass through the cell membrane and cause cell death. However, the cytotoxicity of CNC is strongly dependent on the nanoparticle concentration.

6. Future perspectives

Due to depletion of non-renewable resources, increasing greenhouse gas emissions, and extremes of weather becoming more frequent than before, the need for sustainable technologies and green materials is urgent. Since forests play a key role as a carbon sink, their cutting and industrial exploitation should be balanced with their growth rate. This emphasizes the need to use the wood mass economically, so that all frac-
tions of harvested wood are valorized. Ideally, lignocellulosic components can be used in various upgraded materials to replace fossil resources or other biomass types, such as those that could be preferably used as energy nutrients. To realize this aim, both the price and performance of lignocellulose-derived materials should match or outperform those of conventional alternatives. A key parameter to determine the price of wood biomass fractions is scale of production. The fact that forest industries operate at scale of thousands of tonnes of forest biomass fractions per year causes a bottleneck for commercialization of new products, since small-scale production is rarely profitable, and large-scale production is challenged to find markets at early stages of development. Small- and medium-sized players and start-ups may find opportunities to develop new types of operations besides or in conjunction with established forest industries.

Lignocellulosic biomass treatment can target obtaining highly pure fractions. Alternatively, certain processes result in heterogeneous mixtures of lignin and hemicelluloses, whose purification would require extra process steps. On the other hand, less pure multicomponent fractions may exhibit additional functionality compared to pure lignocelluloses. A new interesting opportunity would be to use whole wood particles as stabilizers, after dissolving wood in water or ionic liquids. Safety aspects of novel products are of utmost importance before commercialization. On the other hand, legislative matters often slow down the route of new products to market. Thus rapid development of reliable safety assessment methods is needed to evaluate emerging technologies, including lignocellulosic stabilizers. Acceptance of novel products further requires a dialogue between researchers, authorities, industries, and consumers. For example, different grades of nanocelluloses are gradually appearing to market after decades of research and development. Questions still remain on their upscaling, practical applications, markets and business models, toxicity and environmental issues, characterization, and fundamental features.

7. Conclusions

The three unique types of biopolymers that form the vast majority of wood mass—namely, cellulose, lignin, and hemicelluloses—can be recovered from forest industry processes and valorized into bio-based emulsion stabilizers. Functionalization of cellulose and lignin provides them with amphiphilic properties and the capacity to assemble at the water–oil interface, whilst hemicellulose-rich aqueous extracts exhibit native surface activity derived from the associations between polysaccharides and phenolic structures. Many wood-derived materials are poorly soluble in water, but they can be used as insoluble particles ranging in size from nanometers to micrometers that have capacity to stabilize oil–water interfaces. Cellulose nanofibrils and carboxymethyl cellulose form viscous aqueous suspensions and solutions, respectively, that restrict the mobility of oil droplets and extend emulsions’ stability. The properties of lignocellulosic stabilizers make them particularly suitable for technical emulsions, such as those made from crude oil, as they can decrease the emulsions’ viscosity. In addition, food and other life science industries have long used cellulose derivatives in their products. There is the potential for broad use of sustainable and functional wood-based stabilizers in life sciences after performing the necessary safety evaluations of novel ingredients.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

I thank Satu Kirjoranta for providing technical assistance with preparation and analysis of emulsions created with water-insoluble birch and beech xylans. In addition, I am grateful to Julia Varis for drawing the graphical abstract and Fig. 1, 5, 7 and 10 as well as Dr Maarit Lahtinen for drawing the chemical structures in Fig. 2, 3, 4 and 6. Finally, I thank Prof. Maija Tenkanen for our fruitful discussions.

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