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LIGNIN AND HEMICELLULOSE IN DISPERSIONS – AS SURFACTANTS AND FUNCTIONAL MATERIALS

ABSTRACT

Patrik Borenius: Lignin and hemicellulose in dispersions – as surfactants and functional materials
Master of Science thesis, 80 pages, 2 Appendix pages
Tampere University
Master's Degree Program in Engineering and Natural Sciences Technology
Major: Chemistry
Examiners: Adj. Prof. Terttu Hukka and Prof. Jurkka Kuusipalo
Advisors: Dr. Hanne Wikberg and Adj. Prof. Terttu Hukka
October 2019

The aim of thesis was to understand how lignins and hemicelluloses work as plasticizers, dispersing agents, emulsifiers and stabilizer in dispersion applications from the chemistry point of view. An alkali-O_2 oxidation (LigniOx) of lignins was discussed in more detail because relevance to the applied part of this thesis.

In the applied part, two organosolv and soda lignins provided by Fortum, and oxidized by VTT Technical Research Centre of Finland, were evaluated in special carbon black and titan dioxide dispersions. Rheological measurements and optical microscopy were used as analysis methods. The aim of the applied part was to increase the knowledge of the new type of lignin-based dispersants and give background information for the development of Fortum's lignins as dispersants in paint, coating, ink, plastic and other dispersion-related applications.

The research literature of lignins and hemicelluloses in different dispersion-related applications is broad. However, this does not directly translate to broad amount of developed and existing applications. Hemicelluloses have chemical analogies, such as gums and other hydrocolloids, which are commercially used for example as texture modifiers in foods and cosmetics. The public research of hemicelluloses as dispersants and texture modifiers in other dispersion applications than foods and cosmetics is however still in early phases.

The research of new lignin-based dispersants has focused on the applications in which lignosulfonates are already commercially utilized, such as cement plasticization. In these cases, the new lignin-based dispersant should perform better than lignosulfonates, especially if the production costs are higher for these new lignin-based dispersants. Alternatively, new dispersion applications should be found, in which lignosulfonates have not been used or do not work well.

In the applied part of the thesis, the rheological measurements and complementary optical microscopy imaging showed that alkali-O_2 oxidized (LigniOx) lignins have potential as dispersants especially in carbon black dispersions and to an extent in the titan dioxide dispersions. All the oxidized organosolv and soda lignins had very similar behavior in these dispersions. The optimum amounts of lignin dispersants (7.5-20 wt% lignin of carbon black) in carbon black dispersions were slightly lower compared to commercial lignosulfonate and synthetic polymer references. The lignin dispersants were especially suitable for the special carbon black dispersions because good dispersing performance and no visible change in the color of the dispersions even with high amounts of lignin dispersants.

In the case of titan dioxide dispersions, the required amount of lignin dispersants was lower (0.125-0.5 wt% lignin of titan dioxide) compared to the references. However, the brown color of lignin affects the color of titan dioxide dispersions to an extent and the storage stability of titan dioxide dispersions with lignin dispersants needs to be further investigated.

Keywords: lignin, hemicellulose, dispersion, carbon black, titan dioxide

TIIVISTELMÄ

Tämän diplomityön tarkoituksena oli perehtyä ligniinien ja hemiselluloosien käyttöön dispergointiaineina, emulgaattoreina ja pinta-aktiivisina aineina erilaisissa teknisissä dispersioissa. Erityisesti alkali-happi hapetettuja ligniinejä (LigniOx) ja niiden käyttöä dispersioissa tarkasteltiin lähemmin.

Diplomityön kokeellisessa osassa Fortumin kahta organosolv ja kahta sooda ligniiniä, jotka olivat hapetettu Teknologian Tutkimuskeskus VTT:n toimesta, testattiin erikoishiilimusta ja titaanidioksidi dispersioissa. Hiilimustan ja titaanidioksidin dispersioita tutkittiin reometrin ja valomikroskoopin avulla. Kokeellisen osan tarkoituksena oli lisätä tietoa uudentyyppisten ligniini-dispergointiaineiden käytöstä ja antaa Fortumin ligniineistä perustietoa jatkotutkimuksille.

Ligniinien ja hemiselluloosien käyttöä erilaisissa dispersioissa ja sovelluksia on tutkittu paljon. Laaja perustutkimus ei kuitenkaan ole suoraan johtanut laajaan sovellusten jatkokehitykseen ja kaupallistumiseen. Hemiselluloosien tapauksessa samankaltaisia yhdisteitä kuten erilaisia luonnonkumeja, on kaupallisessa käytössä esimerkiksi sakeuttamisaineina ja koostumuksen parantajina ruoka- ja kosmetiikkateollisuudessa. Hemiselluloosien julkinen tutkimus muissa kuin ruoka- ja kosmetiikkateollisuuden dispersiosovelluksissa on kuitenkin vielä varhaisessa vaiheessa.

Uusien ligniini-dispergointiaineiden tutkimus on keskittynyt sovelluksiin, joissa lignosulfonaatteja käytetään kaupallisesti, esimerkiksi betonin notkistimina. Uusien ligniini-dispergointiaineiden täytyy toimia paremmin kuin lignosulfonaatit, varsinkin jos tuotantokustannukset ovat korkeammat näille uusille ligniinipohjaisille dispergointiaineille. Uusien sovellusten löytäminen, joissa lignosulfonaatteja ei käytetä tai ne eivät toimi halutulla tavalla, on toinen mahdollisuus uusille ligniinipohjaisille dispergointiaineille.

Kokeellisessa osassa havaittiin reologisten mittausten ja valomikroskopian avulla, että alkali-happi hapetetut ligniinit ovat potentiaalisia dispergointiaineita vesipohjaisille erikoishiilimusta ja titaanidioksidi dispersioille. Kaikki alkali-hapetetut organosolv ja sooda ligniinit toimivat ja käyttäytyivät samankaltaisesti hiilimusta- ja titaanidioksididispersioissa. Alkali-hapetettujen ligniinien optimaaliset määrät suhteessa pigmentteihin olivat alhaisemmat kuin verrokki dispergointiaine lignosulfonaatilla ja synteettisellä polymeerillä. Hiilimustadispersioissa optimaalinen määrä alkali-hapetettua ligniiniä oli 7.5-20 p.% ligniiniä hiilimustasta ja titaanidioksididispersioissa 0.125-0.5 p.% ligniiniä titaanidioksidista. Erityisesti hiilimustan dispersioissa alkali-hapetetut ligniinit toimivat hyvin ja ligniinin ruskea väri ei vaikuttanut hiilimustadispersioissa. Titaanidioksididispersioissa alkali-hapetut ligniinit värjäsivät dispersioita isoilla pitoisuuksilla ja dispersioiden säilyvyys vaatii lisää tutkimusta.

Avainsanat: ligniini, hemiselluloosa, dispersio, hiilimusta, titaanidioksidi

PREFACE

This thesis was conducted for Laboratory of Chemistry and Bioengineering at Tampere University and Fortum Innovation Acceleration in Bio2X development project. Furthermore, the applied part of the thesis was conducted at VTT Technical Research Centre of Finland, in Rheology Laboratory in Espoo, Finland.

I would like to thank M.Sc. Risto Sormunen, who allowed me to be part of the Bio2X team and the interesting work and topics the Bio2X deals with. I would also like to express my deepest gratitude for Dr. Hanne Wikberg and M.Sc. Matti Sonck for their never-ending support and guidance throughout this thesis work at Fortum.

I want to also thank Dr. Adj. Prof. Terttu Hukka from Tampere University, who trusted and gave me the freedom to conduct the thesis project in my own manner.

I am grateful for Dr. Anna Kalliola and Dr. Tiina Liitiä for trusting me and giving me the opportunity to do laboratory work at VTT. Furthermore I want to especially thank Dr. Anna Kalliola and personnel at VTT for guiding and supervising the applied part of the thesis.

Lastly, I want to give my humblest thanks to a person, who does not need to be named and knows her enormous role in my life. Thank you.

Helsinki, 15.10.2019

Patrik Borenius

CONTENTS

LIST OF SYMBOLS AND ABBREVIATIONS

APG	Alkyl polyglycoside
APP	Alkyl polypentosides
BET	Brunauer-Emmett-Teller
CB	Carbon black
DBP	Dibutyl phthalate
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DS	Degree of substitution
GA	Glucuronic acid
GAX	(Glucurono)arabinoxylan
GGM	(Galacto)glucomannan
GGMEtOH	Ethanol-precipitated (galacto)glucomannan
GGMSpDr	Spray dried (galacto)glucomannan
GX	Glucuronoxylan
KL	Kraft lignin
kta	10^3 metric ton per year
LS	Lignosulfonate
MeGA	Methyl glucuronic acid
Mta	10^6 metric ton per year
OL	Organosolv lignin
O/W	Oil-in-water
PAA	Poly(acrylic acid)
PCE	Poly(carboxylate ether)
SDS	Sodium dodecyl sulfate
SL	Soda lignin
Surfactant	Surface active agent
t	Metric ton (1000 kg)
VTT	VTT Technical Research Centre of Finland Ltd
wt%	Weight percent
W/O	Water-in-oil

$Đ$	Dispersity
DP	Degree of Polymerization
M_n	Number Average Molar Mass
M_w	Weight Average Molar Mass
pK_a	Negative logarithm of acid dissociation constant
γ	Surface or interfacial tension

1. INTRODUCTION

The search for novel uses of biomass, biochemicals and replacing of petroleum-chemicals is more intensive than ever. The reasons for this search are for example the climate change, plastic pollution, increasing awareness of the limited fossil feedstocks and overall need to develop sustainable global economy [1]. Economic reasons for the development are for example volatile crude oil and petrochemical prices, the desire to reduce dependency on crude oil imports [2], decline in conventional paper demand and possibility to make profit out of all components of the biomass and not just cellulose.

Lignin and hemicelluloses are polymers produced in millions of metric tons for example in conventional pulp mills [3]. However, currently these byproducts are mostly burned to recover the pulping chemicals and to provide energy for the mill. As major components of woods and plants, lignin and hemicellulose have further potential to be feedstock for variety of applications. Lignin is an aromatic phenolic polymer, characterized by its recalcitrance chemical structure and light brown-to-dark black color. [4] Hemicelluloses are class of polysaccharides in woods and plants that are not cellulose. Similar polymers have already established commercial applications as hydrocolloids and gums for example in food and cosmetic industries.

New technologies apart from conventional sulfate and sulfite processes to fractionate biomass allow cellulose, hemicellulose and lignin to be obtained in high purity and quality. This creates the demand to develop and find commercial applications for all three chemicals, especially for the new raw materials hemicellulose and lignin. There are existing applications for natural polymers similar to hemicellulose and lignosulfonates as surface active materials, dispersants, emulsifiers, rheology and texture modifiers. This indicates that there are promise and possibilities for new type of hemicelluloses and lignins for example in dispersion-related applications.

To find new application possibilities for biorefinery hemicellulose and lignins, this thesis concentrates on the use of hemicellulose and especially lignin as surface active and functional materials. The relevant theoretical background of dispersion and surfactants are discussed in Chapter 2. In the Chapter 3, different lignins and their physicochemical properties relevant to dispersions are discussed. The Chapter 3 is concluded by introducing few of the proven and potential applications of lignin-based dispersants. Chapter 4 discusses the wood- and straw-based hemicelluloses, xylans and mannans, in a

similar manner to lignins in Chapter 3. Chapter 5 is the applied part of the thesis and focuses on the preliminary study of novel alkali-oxygen oxidized (LigniOx) lignin dispersants in carbon black and titan dioxide suspensions.

2. DISPERSIONS AND SURFACTANTS

This chapter introduces the main concepts of the thesis. Dispersions, surfactants and functional materials and their properties, requirements and chemistry are discussed. The focus is on the liquid-containing dispersions and polymeric surfactants, as the main subjects of the thesis are biopolymers.

2.1 Dispersion

Dispersion is by definition a two-phase system, in which discontinuous, but finely divided, substance particles (gas, liquid or solid) are dispersed in a continuous phase that is different composition or state from the dispersed phase. The substance that is dispersed in the continuous phase is called the **dispersed phase** or discontinuous phase. [5, 6] Different dispersions can be discussed by phrasing *dispersed phase*-in-*continuous phase*. For example, a solid-in-water dispersion means that the dispersed phase is solid phase particles dispersed in the continuous phase consisting of water.

Dispersion contains the dispersed phase particles with sizes of 1 nm–1000 µm [7]. If the dispersed phase particles have at least one dimension in range 1 nm–1 µm, the dispersion can be referred as a **colloid** [5, 6, 7]. The dispersed phase particles are aggregates of multiple molecules [8].

While particle size is one way to identify and characterize dispersions, other properties are also helpful. Dispersions are not stable indefinitely and can separate to different phases over time. Dispersions can be separated by centrifugation or filtration. Furthermore, dispersions are often opaque, turbid and scatter light. [8]

Dispersions can be considered as ''solutions of greater particle size'' in which the chemical structure of the dispersed phase still matter. As dispersions are formed by partly immiscible chemicals, there are unattractive forces between the molecules of the dispersed phase and continuous phase. The dispersed phase and continuous phase tend to minimize the unattractive forces by decreasing the interfacial area between the phases. [7, 9] The tendency of substances to decrease the surface area is often characterized by quantity called **surface** or **interfacial tension**, γ (mN m^{-1}). Higher the surface tension, more strongly the substance tries to minimize its surface area. [6]

Table 1. Type of dispersions. Adapted from [7].

Dispersed Phase	Continuous Phase	Name	Example
Liquid	Gas	Liquid aerosol	Hair sprays
Solid	Gas	Solid aerosol	Smoke
Gas	Liquid	Foam	Shampoos, fire foams
Liquid	Liquid	Emulsion	Foods, cosmetics, latex
Solid	Liquid	Suspension	Paints, pesticides, cement
Gas	Solid	Solid foam	Polyurethanes, styrofoams
Liquid	Solid	Solid emulsion	Gelatin, silica gel
Solid	Solid	Solid suspension	Dried concrete, alloys

Dispersions appear in wide variety of applications, products and industrial processes, either as a desired or undesired phenomena. The stability of dispersion means that dispersion has constant properties and appearance for the desired time. A look at the amount of different dispersions and combinations of dispersed and continuous phase reveal the complexity of the subject of dispersions and their stability (Table 1). The most familiar and common dispersions are those in which liquid is the continuous phase: foams, emulsions and suspensions.

2.1.1 Emulsion

An **emulsion** is by a definition a dispersion in which the dispersed phase and the continuous phase are immiscible liquids [5, 6, 7]. The dispersed phase particles of emulsion are often referred as droplets, emphasizing their liquid state [5, 6].

The typical emulsion is combination of water and hydrophobic liquid, often referred simply as oil [7]. The oil can vary from vegetable and food-related lipids to petroleum crude oils. As emulsions contain often water either as the dispersed or continuous phase, emulsions are often categorized as **oil-in-water (O/W)** or **water-in-oil (W/O)** emulsions (Table 2). In the O/W emulsion, water is the continuous phase and oil is the dispersed phase, and in the W/O emulsions vice versa. [6, 7]

Emulsions are a subclass of dispersions and therefore behave as such: they are generally cloudy or turbid in appearance because the average droplet size of the dispersed phase is large enough [10], typically 0.1–100 µm in diameter [11]. However, emulsion can be transparent to the naked eye, but still be an emulsion and for example cause light scattering.

Table 2. Examples of emulsion applications in different industries. O/W = oil-in-water emulsion, W/O = water-in-oil emulsion. Adapted from [7].

Industry	Application	Type
Environmental and agriculture	Insecticide and herbicide formulations	O/W
	Water and sewage treatment emulsions	O/W
	Oil spill emulsions	W/O, O/W
Home and personal care	Hair and skin creams and lotions	O/W, W/O
	Hair dye emulsions	W/O
Materials science	Asphalt (paving) emulsions	O/W
	Latex paint, polish, coating emulsions	O/W
	Metal working fluid emulsions	O/W
Medicine	Emulsion encapsulated drugs	O/W, W/O
	Vesicles	W/W
Petroleum industry	Drilling emulsions	O/W, W/O
	Reservoir emulsions	W/O
	Heavy-oil pipeline emulsions	O/W
	Well-stimulation emulsions	O/W, W/O
	Enhanced oil recovery emulsions	O/W
	Emulsified fuel	O/W, W/O
	Oli-flotation froth	O/W
Mineral and mining industries	Emulsion flotation	O/W
Foods	Milk, creams, soft drinks, mayonnaise	O/W
	Butter, margarine, salad dressings	W/O

As almost all dispersions, emulsions are unstable and tend to separate to two separate liquids during storage [10, 12], even though the time for separation can be long (minutes to years). The separation of an emulsion to distinct phases (for example water and oil) is called demulsification or breaking of the emulsion [6, 7]. **Flocculation**, **coalescence**, **creaming** and **sedimentation** of the dispersed phase are the mechanisms that decrease the interfacial area between the phases in emulsions and cause demulsification (Figure 1).

Emulsions, as all dispersions, occur in variety of products, processes and disciplines. Emulsions can be the desired outcome, for example in cosmetic creams and lotions, but also unwanted and costly problem, such as water emulsions in crude oil upgrading (Table 2). [7]
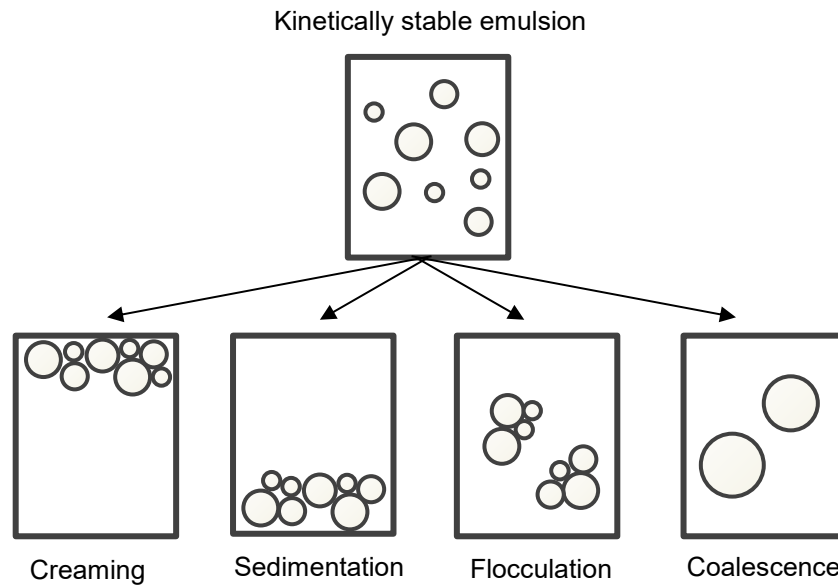
Figure 1. Illustrative mechanisms of dispersion breaking.

2.1.2 Suspension

Dispersion of a solid substance (dispersed phase) in a liquid (continuous phase) is known as a **suspension** [5, 7]. The solid dispersed phase is in form of particles and the particles have dimensions of 1 nm–100 µm [7]. The particles can be single molecules or aggregates of these primary particles. Furthermore, the shape of the particles in suspension can be variant: circles, rods, plates or any kind of loose aggregate shape. [7, 13]

The unstable suspended particles tend to minimize the surface area in contact with continuous phase by increasing the average particle size. Examples of the mechanisms that can increase the particle size and decrease amount of suspended particles, are sedimentation and flocculation (Figure 1) [6]. When suspension is set undisturbed for enough time, the solids tend to separate out of the continuous phase. Alternatively, the suspension can be separated by centrifugation or filtration.

In addition to the stability, suspensions must be well-flowing and workable, and suspended solid particles must have the right surface charge and average particle size in various applications (Table 3). To understand the details of the application and type of suspension are important, as suspensions can be desired or undesired phenomena. For

Table 3. Examples of suspension applications in different industries. S/W = solid-in-water suspension, S/L = solid-in-liquid (other than water) suspension. Adapted from [7, 9].

Industry	Application	Type
Environmental and agriculture	Suspended soils and sediments	S/W
	Insecticide and herbicide suspensions	S/W, S/L
Home and personal care	Exfoliating scrubs	S/W
	Facial Masks	S/W
	Lipsticks, lip balms and glosses	S/L
Materials science	Cellulose fiber pulp slurries	S/W
	Pigment and dye containing paints	S/L
	De-inking pulp slurries	S/W
Medicine	Polymer encapsulated drugs	S/W
	Biodegradable drug suspensions	S/W
	Diagnostic suspensions	S/W
Petroleum industry	Drilling fluid (mud) suspensions	S/W
	Hydraulic fracturing suspensions	S/W
	Well cementing slurries	S/W
	Oil-sand slurries in bitumen recovery	S/W
	Migrating fines in reservoir or oil recovery	S/W
	Asphaltene suspensions in crude oils	S/W
Mineral and mining industries	Mineral-processing slurries	S/W
	Mineral-flotation froths	S/W
	Mineral-tailing slurries and ponds	S/W

example, sedimentation is sometimes desired in the waste water treatment, while in paints or coatings the suspension must be well-flowing and stable over long periods of time. [7]

2.2 Small-Molecule Surfactants

Surface active agent (surfactant) is a chemical which at low concentration is adsorbed at the different interfaces and lowers the surface tension of the medium in which it is dissolved (for example water) or the interfacial tension between two or more phases (for example oil and water) [5, 14]. Surfactants are amphiphiles, while not all amphiphiles exhibit surface active properties. An amphiphilic molecule exhibits affinity towards different phases [14, 15].

An organic **amphiphilic** molecule consists of at least two parts: **lyophobic** (solvent-rejecting) and **lyophilic** (solvent-preferring) parts, which describe the interactions with different phases and solvents. If water is part of the system, then terms **hydrophobic** (water-rejecting) and **hydrophilic** (water-preferring) are used, respectively [6, 7]. The am-
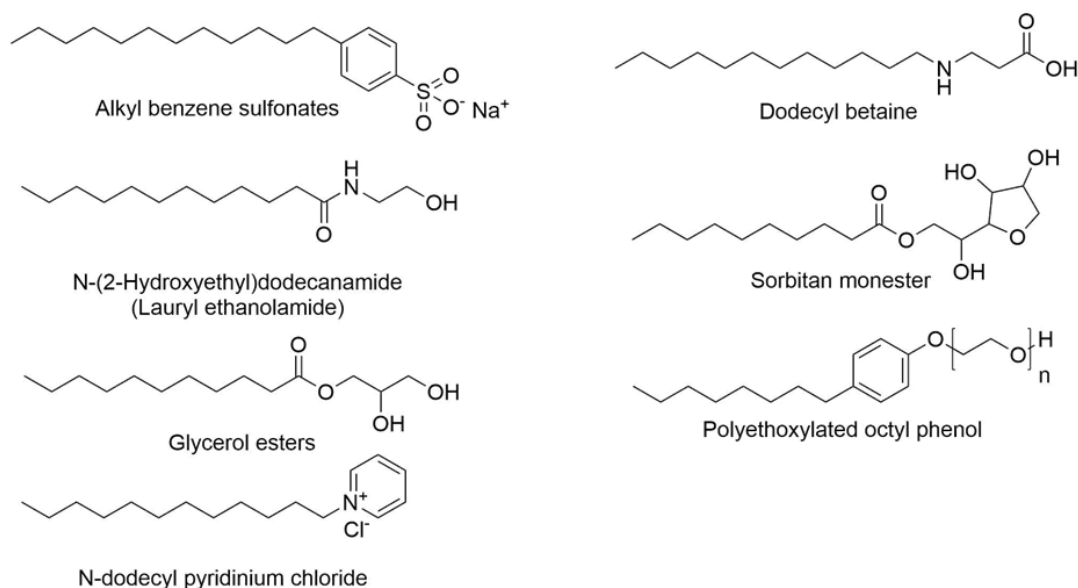
Figure 2. Examples of small molecular surfactants. Adapted from [15].

phiphiles have strong tendency to migrate to surfaces and interfaces. Amphiphiles orientate so that hydrophilic part is in contact with the more polar phase, such as water, and hydrophobic part is in contact with the nonpolar phase, such as oil or air. [14, 15]

The polar, hydrophilic, portion of amphiphile often contains heteroatoms, such as oxygen, sulfur, nitrogen or phosphorus in form of functional groups like alcohol, thiol, sulfate, sulfonate, ether, ester, carboxylic acid, phosphate, amine or amide (Figure 2). This polar portion has strong affinity for polar liquids, especially water. On the other hand, the nonpolar, hydrophobic portion of amphiphile is generally an alkyl or alkylbenzene type, with possible halogen or non-ionizable oxygen atoms. [14, 15]

The term **tenside** is used as a synonym to a surfactant, which highlights the (surface) tension lowering property of the surfactant. [15] To highlight the other functions of surfactants, surfactants are described according to use, function or dispersion structures (Figure 3).

While classifying surfactants based on their use and function is sensible from the commercial point of view, the division does not tell about chemistry of the surfactants. From the chemical point of view surfactants are classified based on the type and structure of the hydrophilic part and behavior of surfactants in water. [15] Surfactants are classified to anionic, cationic, nonionic and amphoteric surfactants [14, 15].The ''fifth'' class of surfactants is sometimes introduced: surface active polymers (polymeric surfactants) [15, 16]. Polymeric surfactants obey the similar rules as classical small molecule ionic because (1) the same functional groups and structures that are present in small molecule surfactants, are present in multiples in polymeric surfactants. Furthermore, (2) the division between single molecule and polymeric surfactant is sometimes labile.

Surfactants classified by use and function				Structures which surfactants aid to form	
Soap	Dispersant	Emulsifier	Bactericide	Micro-emulsions	Gel
Detergent	Wetting Agent	Foaming Agent	Antistatic Agent	Liposomes/ Bilayers	Liquid crystallines
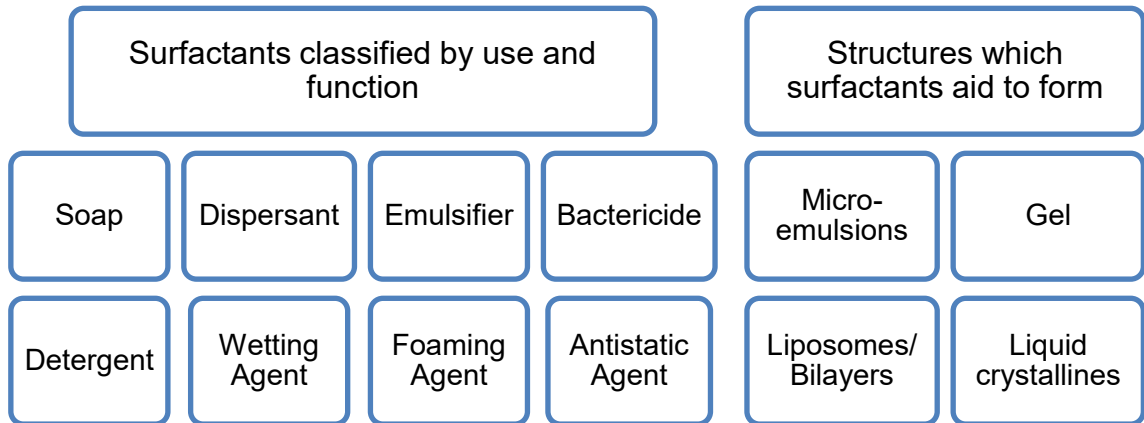
Figure 3. Example functions of surfactants other than decreasing surface or interfacial tension and different structures surfactants help to build. [15, 16]

2.2.1 Anionic Surfactant

Anionic surfactants dissociate in water as an anionic amphiphile (actual surfactant), with the counter ion being alkaline metal, such as K^+, Na^+, or a quaternary ammonium. The most common anionic surfactants are based on carboxylates, sulfonates, sulfates and phosphates. [15, 16]

Anionic surfactants are the most widely used surfactants [15, 16] because relatively low cost of manufacturing and their wide range of applications in the food, chemical and petroleum industries [10]. Anionic surfactants have distinctive uses and properties, such as solubility in alkaline and acidic solutions, hydrophilicity, chemical stability against hydrolysis and resistance to hardness of water (Mg^{2+} and Ca^{2+} ions). [16] Examples of anionic surfactants are alkylbenzene sulfonates (Figure 2), soaps (fatty acids), lauryl sulfates (foaming agents) and lignosulfonates (dispersants) [15].

2.2.2 Nonionic Surfactant

Nonionic surfactants do not dissociate to ions in aqueous solutions, because they contain hydrophilic parts that are less easily ionizable, such as hydroxy, ether, ester and amide functional groups. The common hydrophilic part is poly(ethylene glycol) chains, and corresponding nonionic surfactants are called (poly)ethoxylate surfactants (Figure 2).

Nonionic surfactants are the second most used surfactant type after anionic surfactants [15] and there is great variety in nonionic surfactants. Ethoxylate, sorbitan and alkyl polyglycoside (APG) surfactants are examples of nonionic surfactants [15]. Especially APG surfactants have gained interest in the last decades because of low toxicity [15] and various production possibilities from different renewable feedstocks [17].

2.2.3   Cationic Surfactant

Cationic surfactants dissociate in water as an amphiphilic cation with the counter ion being often a halogen, such as Cl⁻ or Br⁻. Almost all cationic surfactants are amine salts and quaternary ammoniums. The properties, such as water solubility, of cationic surfactants depend on the amount of hydrophobic long fatty alkyl substituents attached to the nitrogen. [15]

Cationic surfactants are less widely used than anionic or nonionic surfactants, mainly because more expensive manufacturing. Therefore cationic surfactants are only used in applications in which (1) no cheaper substitute is available, such as biocides, or as positively charged substances that adsorb to negatively charge substrates to provide anti-static effects or corrosion inhibition. [15] Examples of cationic surfactants are *N*-dodecyl pyridinium chloride (Figure 2) and 1-hexadecylpyridinium chloride (cetylpyridinium chloride).

2.2.4   Amphoteric Surfactant

Amphoteric or **zwitterionic surfactants** are single molecules that exhibit both anionic and cationic dissociation in water [15]. The hydrophilic part of the amphoteric surfactant contains both the negatively and positively charged functional groups, often only separated by a few carbon atoms. The hydrophobic part is similar to other surfactants, for example a long alkyl chain.

Amphoteric surfactants are based on synthetic betaines or sulfobetaines and natural compounds, such as amino acids or phospholipids, such as lecithins. The ionizable functional groups and properties, such as water solubility and surface activity, of amphoteric surfactants can be pH insensitive (sulfobetaines) or pH sensitive (amino acids).

Amphoteric surfactants are generally expensive and therefore used (1) as co-surfactants to modify and improve the performance of a primary surfactant because compatibility with both anionic and cationic surfactants [17]. Other uses are (2) when biocompatibility and low toxicity override the higher price of surfactant, such as in cosmetics [15]. An example of amphoteric surfactant is dodecyl betaine (Figure 2).

2.3   Polymeric Surfactants

Surface active polymers (polymeric surfactants) are macromolecules which are surface active and have multiple polar hydrophilic and nonpolar hydrophobic parts, and are surface active [15]. The location and segregation of the nonpolar and polar functional

Figure 4. Types and examples of polymeric surfactants. Adapted from [15].

groups is not however as well-defined as for small molecule surfactants. [15] The detailed chemical structure of especially bio-based polymers and to an extent of synthetic polymers varies more than for small surfactant molecules.

Polymeric surfactants can be either polyelectrolytes or nonionic polymeric surfactants. Polyelectrolytes are polymers with ionizable anionic, cationic or amphoteric functional groups, such as poly(carboxylate ethers) (PCE) (Figure 4).

Polymeric surfactants can be divided to block and graft polymers (Figure 4). In the block polymer, hydrophilic monomers (H) are linked to each other and lipophilic (L) monomers have done the same. In graft-polymers different functional groups and small segments of other monomers are attached to the main polymer chain. [15, 18] While the graft polymers are the more common type of a polymeric surfactant [15], synthetic polymeric surfactants can be block or graft polymers.

Polymeric surfactants are a loose class of surfactants that can be divided to synthetic, petroleum-based, polymeric surfactants and to bio-based surfactants. The petroleum-derived polymeric surfactants are made from well-defined monomers, for example ethylene oxide, while bio-based polymeric surfactants are extracted and modified from natural sources as the main- or byproduct.

2.3.1 Synthetic Polymeric Surfactants

Homopolymers such as polyethene or polypropene have poor surface activity, especially at liquid/liquid interfaces. This is because simple polymers made from one monomer does not have hydrophilic and hydrophobic parts [18]. The common synthetic polymeric

surfactants are made from two or more monomers that provide hydrophobic and hydrophilic parts.

Synthetic polymers are the most used polymeric surfactants. Main examples of synthetic polymeric surfactants are poly(ethylene oxide)-*block*-poly(propylene oxide copolymers, PCEs [15, 18], ethoxylated or sulfonate condensates [15], such as naphthalene sulfonate condensates (Figure 4).

2.3.2 Bio-Based Polymeric Surfactants

A bio-based polymeric surfactant means a natural or slightly modified polymer that is derived from non-petroleum origins. Bio-based polymeric surfactants can be loosely described as graft-type polymeric surfactants with more complex structures than synthetic polymeric surfactants.

Commercially used examples of bio-based polymeric surfactants are lignosulfonates, (modified) polysaccharides, such as starch, carboxymethyl and carboxyethyl cellulose, gum arabic, xanthan gum and pectin. [15] Especially derivatives of polysaccharides have been studied and applied as bio-based polymeric surfactants [19]. The polysaccharides have monosaccharides linked by glycosidic bonds to form the main chain of the polymer and multiple graft-like substituents attached to the main polymer chain. Even as complex polymers as lignins have three monomers that repeat throughout the polymer, covalently bonded in different ways and to which different functional groups are attached, depending on the botanical origin but also on the extraction process.

2.4   How Surfactants Work and Why Are They Needed?

The migration and adsorption of a surfactant to the surface alters the Gibbs free energy of the surface. All surfaces have surface or interfacial tension (γ) that describes how easy or difficult it is to increase the surface area. Substances that have high surface tension, such as water in contact with air, have high attractive, intermolecular forces between the
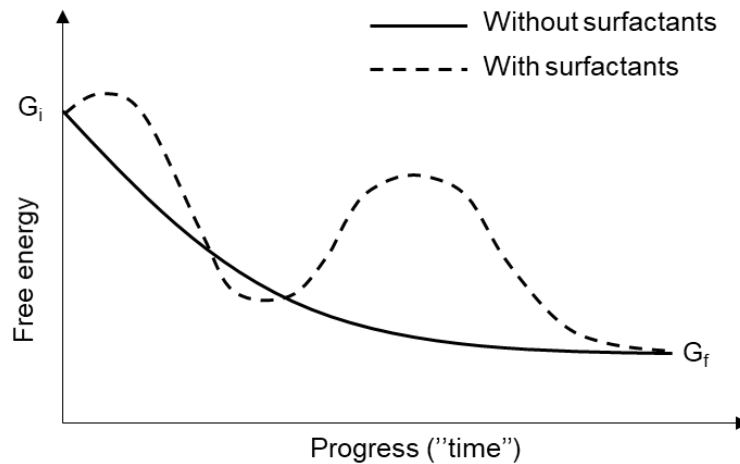
Figure 5. Schematic representation of (free) energy path for dispersion breakdown. Solid and dashed line indicate breakdown without and with surfactants, respectively. Adapted from [16].

molecules of the substance. As surfactants adsorbs to the interfaces, they break these intermolecular interactions and decrease the surface or interfacial tension. The surface tension changes depending on (1) how much surfactant is adsorbed to the surface and (2) orientation of the surfactant molecules on the surface. A lower surface tension means that it requires less energy to increase surface area of a substance. [16]

Surface and interfacial phenomena are crucial in dispersions. As dispersion is mixture of small particles of one substance (dispersed phase) evenly spread in other substance (continuous phase), there is huge interfacial areas between the two phases [7]. While surfactants decrease the interfacial tension and therefore allow for more surface area between different phases, the thermodynamics most often favor the decrease in surface area. [16] How can dispersions then seem stable for extended periods of time and how to prevent sedimentation, creaming, flocculation or coalescence that are caused by intermolecular forces between dispersed phase particles?

Surfactants can stabilize a dispersion by forming activation energy barriers for the dispersion breakdown (Figure 5). To counteract attractive forces between dispersed phase particles, it is necessary to create repulsive forces between them that, which make stable dispersions. [16]

There are two main types of stabilizing repulsions that surfactants can facilitate between the dispersed phase particles: electrostatic repulsion and steric repulsion (Figure 6). **Electrostatic repulsion** is a mechanism that prevents aggregation of dispersed phase particles by electrostatic forces and prevents the attractive shorter-distance intermolecular forces [5]. The electrostatic repulsion is an especially important phenomenon for aqueous dispersions and ionic surfactants. The role of the electrostatic repulsion with

Electrostatic repulsion/stabilization

Steric repulsion/stabilization

Attractive Van der Waals interactions
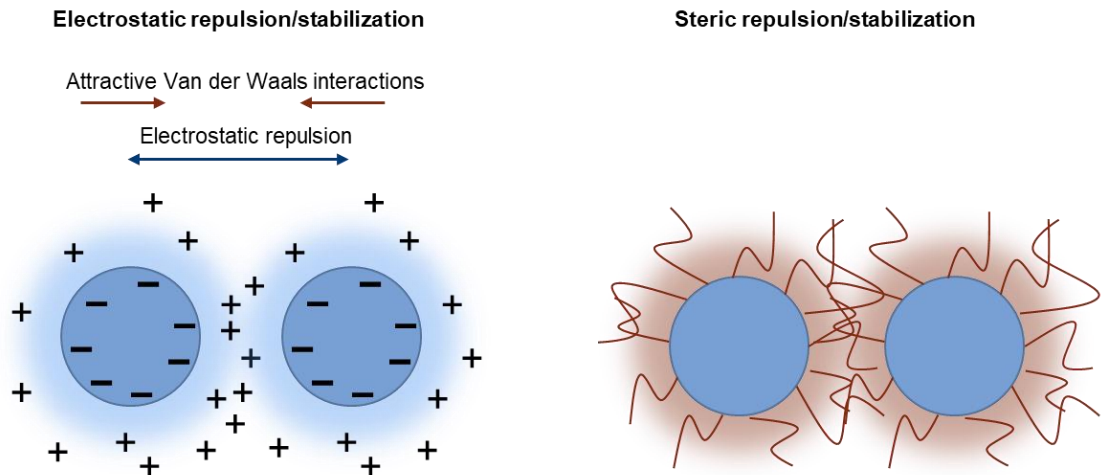
Electrostatic repulsion

Figure 6. Schematic presentation of repulsion mechanisms to stabilize dispersed phase particles; on the left, electrostatic repulsion and on the right steric repulsion.

nonionic surfactants or non-aqueous dispersion is more unclear. On the other hand, **steric repulsion** is related to all polymeric and nonionic surfactants, which adsorb to the surface of the dispersed phase particles. Steric repulsion caused by large polymeric surfactants works by volume-restriction and making the approach of dispersed phase particles energetically unfavorable. [7, 16] The type and structure of surfactants have significant effect whether electrostatic, steric or both mechanisms are important for dispersion stability.

2.4.1 How Polymeric Surfactants Work?

For polymeric surfactants to work as efficient surfactants and to be able to stabilize dispersions, they must fulfill certain criteria: (1) they must adsorb strongly to the surface of the dispersed phase particles, (2) completely cover the dispersed phase particles with proper orientation, (3) strong solvation of the relevant parts of the polymeric surfactant in the continuous phase to stabilize dispersions and (4) reasonably thick adsorbed layer of polymeric surfactant. [18]

Firstly, to work as surfactants polymers need to adsorb on the surface of the dispersible particles [18, 20]. Polymeric surfactants are adsorbed to interfaces by different intermolecular interactions, such as van der Waals forces, hydrogen bonding and ion exchange. The combination and strength of the different adsorption forces depend on the surface of the dispersed phase particles and type of the polymeric surfactant.

Secondly, adsorbed polymeric surfactants must cover the interface completely to provide dispersion stability [18]. Polymeric surfactants cannot pack as many molecules and as tightly to the interfaces as small molecule surfactants. With uncomplete coverage of the dispersed phase particle, a single polymer has room to adsorb to the surface of two

different dispersed particles and thus link the dispersed particles. In this case, bridging flocculation and breakdown of dispersion can happen instead of repulsion and dispersion stability. [7, 13] The bridging is a desired phenomenon for example in waste-water treatment or other sedimentation processes, but not when stable dispersions are desired.

Because less tight packing of polymeric surfactants to the surfaces, polymeric surfactants are not as good as small molecule surfactants in decreasing the surface or interfacial tension [10]. High concentrations of polymeric surfactant is required to achieve similar reduction in surface tension as small molecule surfactants [19]. Polymeric surfactants are also less optimal in applications in which kinetics and fast reduction in interfacial tension are important [10], such as manufacturing of dispersion with small particle sizes in short time. Polymeric surfactants might not reach adsorption-desorption equilibrium at the surface of dispersed particle instantly, especially if polymeric surfactants have low diffusion rates and electrical charges are involved [21]. However, polymeric surfactants excel when long-term dispersion stability is important. While polymeric surfactants reduce interfacial tension only to an extent, electrostatic repulsion, steric stabilization and viscosity are the primary mechanisms how polymeric surfactants stabilize dispersions. The most significant factor that affect the steric stabilization is the thickness of the adsorbed polymeric surfactant layer on the surface of the dispersed phase particles [7]. Often polymeric surfactants, especially polyelectrolytes, cause both electrostatic and steric repulsion (**electrosteric** stabilization) and the more dominant mechanism for dispersion stability depends on myriad of factors [6, 7]. The structure, type and concentration of the surfactant and dispersion, but also temperature, pH and electrolyte content affect dispersion stability [22].

Polymers also often affect the bulk viscosity of the dispersions. Higher viscosity of dispersions reduce the rate of creaming and sedimentation and thus increase the dispersion stability. [7, 16] Sometimes the main function of a polymer in a dispersion is to work as ''viscosity enhancer'' [7, 15]. An example of a polymeric surfactant that work mainly as **thickening agent** is carboxymethyl cellulose [15]. Other hydrophilic biopolymers, gums, that work by modifying the rheology and texture of dispersions are often referred as **hydrocolloids** especially in food and cosmetic products [7, 13, 23].

Surfactant related parameters

- Surface/interfacial tension
- Electrostatic repulsion
- Steric repulsion
- Bulk viscosity and rheology
- Affinity/solubility of surfactant to dispersed phases

Dispersion "environment" related parameters

- Temperature
- pH
- Salinity
- Impurities (proteins, etc.)
- Unadsorbed polymers and amphiphiles

Dispersion preparation related parameters

- Particle size of dispersed phase
- Dispersity

Dispersion phase related parameters

- Dispersion type (emulsion, suspension, foam)
- Density difference between phases
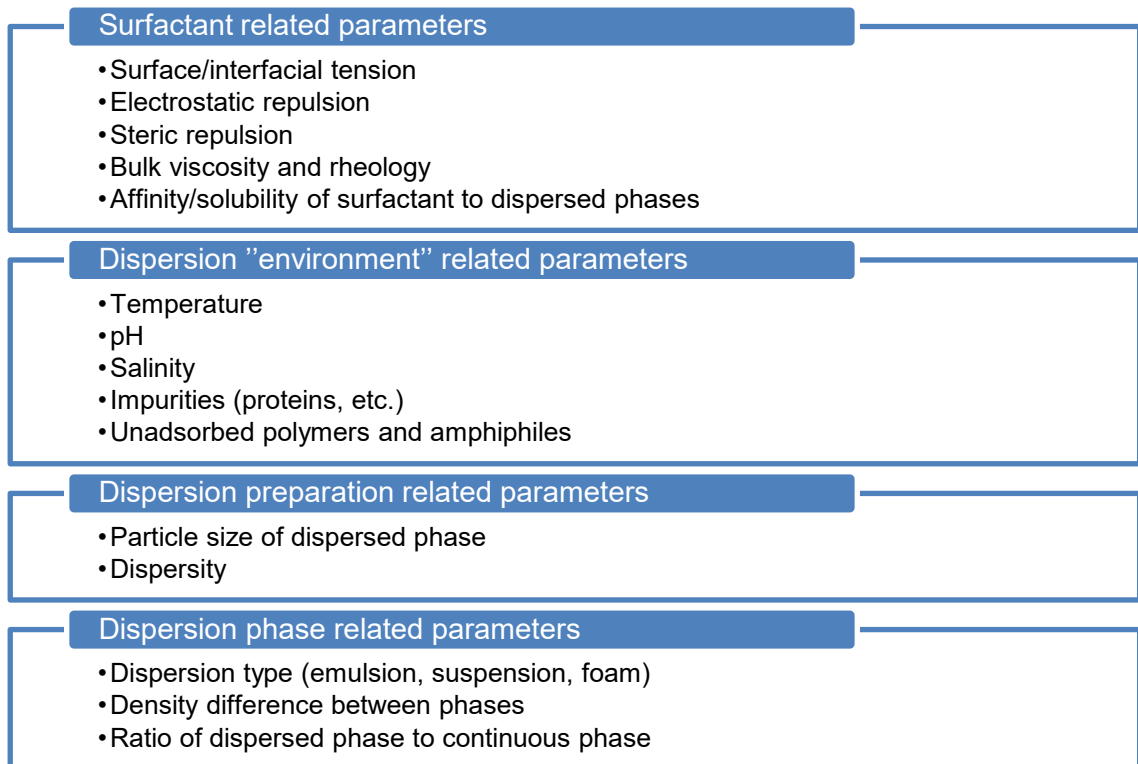- Ratio of dispersed phase to continuous phase

Figure 7. Parameters that affect stability of dispersions. There is correlation between different parameters, for example temperature affects solubility of surfactants.

The discussed mechanisms (interfacial tension, electrosteric stabilization, viscosity) for dispersion formation and stability are those related to surfactants. Moreover, there are various other factors that affect stability, structure and other properties of dispersions (Figure 7). There is also correlation and interplay between different phenomena of dispersions. For example, solubility of a surfactant and viscosity of dispersion are temperature related phenomena.

3. LIGNIN

Lignin is a complex amorphous, phenolic biopolymer found in the cell walls of lignocellulosic biomass, such as woods and annual plants [4, 24]. It is the main constitute of lignocellulose, alongside cellulose and hemicellulose [4] and the most abundant natural aromatic polymer [24, 25]. Amount of lignin is 24–33 wt% (weight percent) of dry mass in softwoods (gymnosperms), 18–28 wt% in hardwoods (angiosperms) and 15–25 wt% in cereal straws, bamboo or bagasse [4, 26]. The biochemical function of lignin in cell walls is to provide rigidity, aid in water transport and to provide resistance to degradation by micro-organisms [26].

Lignin is a polymer of 3 precursors (monolignols): coniferyl, sinapyl and *p*-coumaryl alcohols. In lignin polymers, the monolignols are referred as guaiacyl (G), syringyl (S) and *p*-hydroxyphenyl (H) units, respectively (Figure 8). The amount of these monolignols vary depending on the botanical origin of the lignin. Softwood lignins contain mainly G-units and little H-units (Figure 9), while hardwood lignins contain mixture of G- and S-units. Straws and grasses have greater mixture of all the three monolignols. [4, 17, 27]

There are various covalent bonds between the different monolignols to form the lignin polymer, but the bonds can be roughly divided to carbon-carbon (C-C) or carbon-oxygen (C-O) bonds [27]. The C-O bonds in lignin are alkyl or aromatic ethers or ester bonds, and the most abundant bond type is the aryl ether β-O-4 linkage (Figure 10), which is the main covalent bond susceptible to pulping, bleaching and biological degradation [24,
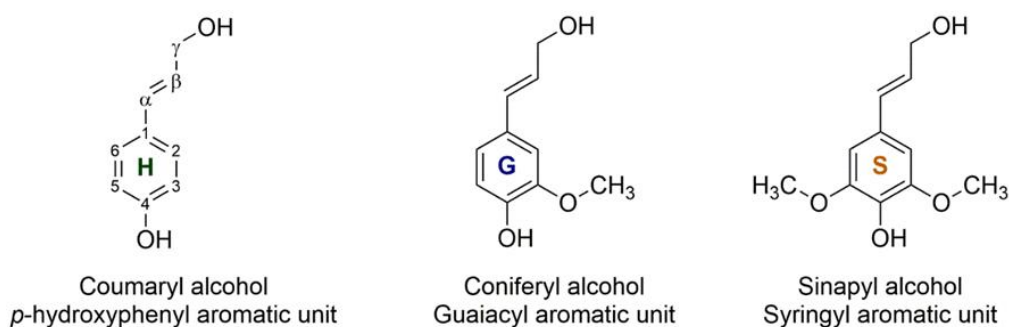

Coumaryl alcohol
p-hydroxyphenyl aromatic unit

Coniferyl alcohol
Guaiacyl aromatic unit

Sinapyl alcohol
Syringyl aromatic unit

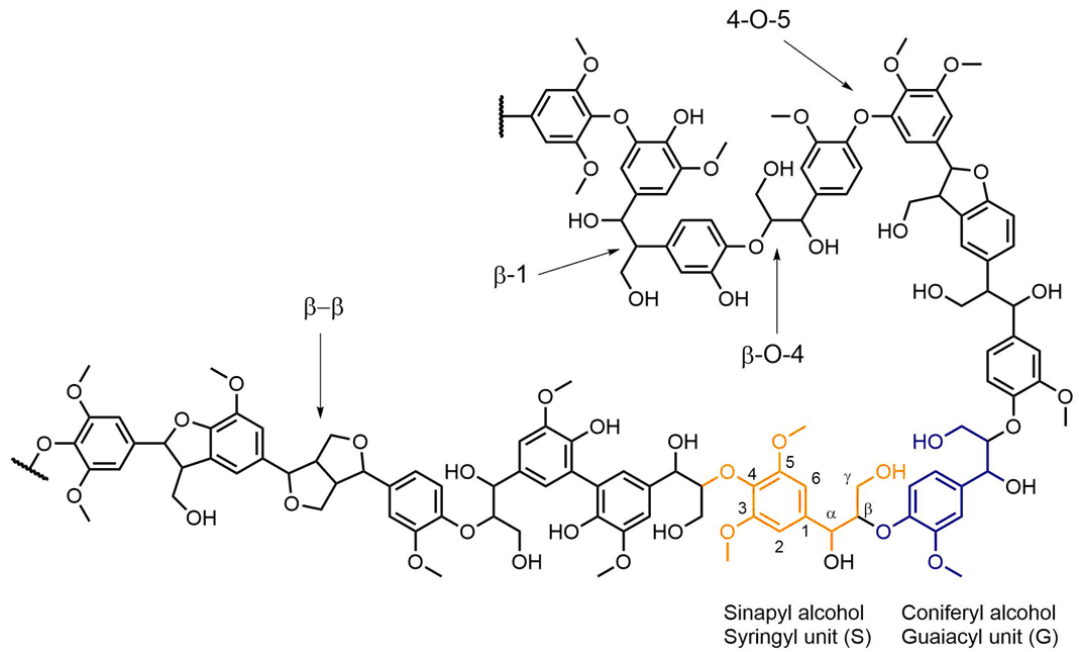*Figure 8. Chemical structures of lignin precursors (monolignols).*

Figure 9. Illustration of hardwood lignin structure. Adapted from [157].

27]. The C-C linkages are more difficult to break without significant fragmenting of the lignin structure [27].

Lignin contains naturally many functional groups, which of phenolic and aliphatic hydroxy, methoxy, carbonyl and carboxylic acid functional groups have the greatest impact on the reactivity of lignin. The type and amount of different functional groups, and other features of lignin, depend on the botanical origin but also on the pulping technology. [27, 28]
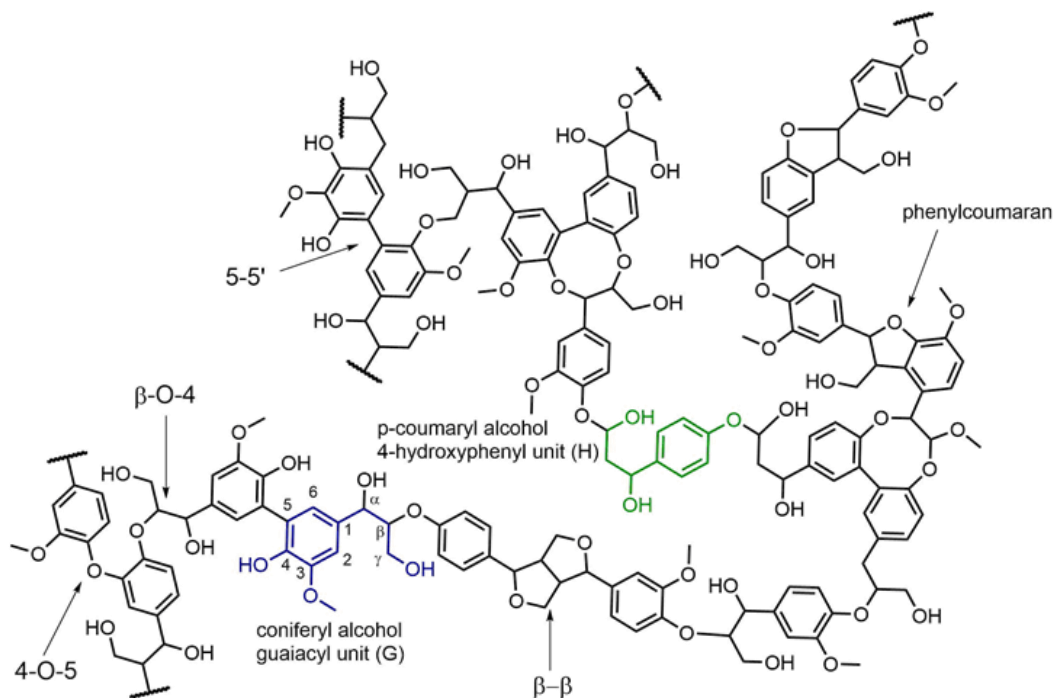

Figure 10. Illustration of softwood lignin structure. Adapted from [157].

3.1 Technical Lignins

Lignocellulosic biomass contains cellulose, hemicellulose and lignin, which are tightly bounded together in the plant cell walls. The lignin crosslinked with celluloses in woods and other lignocellulosic biomasses is often referred as a **native lignin**. Fractionation of lignocellulose to its main components is required to obtain isolated cellulose, hemicellulose and lignin, which have a technical and commercial value. The lignins obtained from different pulping and fractionation processes are referred as **technical lignins** [26] and the fractionation processes can be physical, chemical, biochemical or thermomechanical treatments [24].

Chemical fractionation technologies are utilized to fractionate lignocellulose to cellulose, hemicellulose and lignin. Chemical fractionation technologies are often referred as pulping processes or technologies. At the commercial scale the main pulping technologies are sulfite and sulfate (kraft) pulping (Figure 11) [4, 25], while soda pulping is used in some small pulp mills for non-wood feedstocks [25]. In addition to the sulfur-based pulping technologies, there are under renewed development interest alternative pulping technologies [25]. The alternative pulping technologies aim to separate cellulose, hemicellulose and lignin with good yields and qualities, avoid wasting any material and thus create increased value [24] compared to conventional pulp mills, that focus mostly on cellulose (pulp) recovery, while the rest of the biomass is typically burned for energy as a form of black liquor. However, the existing sulfite and sulfate pulp mills are also increasingly
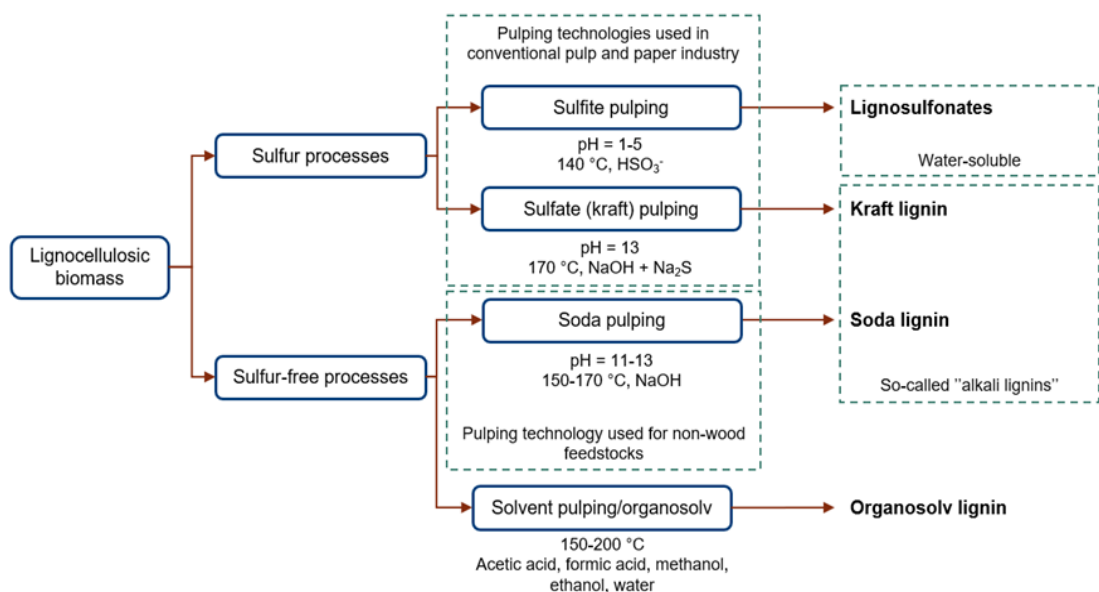

Figure 11. Representation of chemical pulping technologies, example pulping conditions and chemicals, and what type of lignin is obtained. Depending on the pulping technology, lignins can be water-soluble (lignosulfonates), alkali lignins or organosolv lignin. Adapted from [24].

developed towards the ''biorefinery'' concept, with extraction and recovery of other lig-nocellulosic components than just cellulose. The commercial examples of other components produced during the conventional pulping processes are technical lignin, turpentine and tall oils. The global production volume of different lignins by chemical pulping technologies was 50–70 x 10⁶ metric tons per year (Mta), of which only 1–2 % is actually is isolated from the black liquor [24, 25].

While lignin is produced during the chemical pulping processes, residual lignins are also available as a by-product from bioethanol production and steam explosion technologies [4]. These technologies and residual lignins are however quite different in their chemical structure compared to lignins obtained from chemical pulping processes and are thus not considered further in this thesis.

The chemical pulping technologies aim to dissolve lignin from the lignocellulosic matrix with aid of heat and chemicals [29]. Lignins from different pulping processes are different in terms of their chemical structure and properties. Terms like lignosulfonate, organosolv lignin, kraft and soda lignin (alkali lignins) are used to classify and highlight the differences between the lignins and pulping processes (Figure 11). Different lignins are discussed in greater detail in subsections, but overview of the lignins is presented in Table

Table 4. Comparison of some physicochemical properties of technical lignins. SW = softwood, HW = hardwood, annual = grasses, straws. LS = lignosulfonate, KL = kraft lignin, SL = soda lignin, OL = organosolv lignin.

	LS	KL	SL	OL
Feedstock	SW, HW, annual	SW, HW	HW, annual	SW, HW, annual
Production Scale	Industrial	Industrial	Industrial	Demonstration/Pilot
Separation methods	Ultrafiltration	Precipitation (pH), Ultrafiltration	Precipitation (pH), Ultrafiltration	Precipitation, Dissolved air flotation
Solubility (example solvents)	Water	Alkali, DMF, Pyridine, DMSO, 2-methoxyethanol	Alkali	Alkali, organic solvents
M_w (10³ g mol⁻¹)	3-150	1.5-5.0	0.8-3.0	1.0-8.0
Đ	4.0-8.0	2.0-4.0	2.5-3.6	1.5-2.7
Total phenolic OH (mmol g⁻¹)	3.0-4.0	3.2-5.6	2.2-2.7	3.3-4.0
Total carboxyl (mmol g⁻¹)	0.4	0.4-0.9	0.6-1.0	0.3-0.4
Acid soluble lignin (wt%)	-	1-5	1-11	1-8
Polysaccharides (wt%)				
Monosaccharides (wt%)	0-28	0-14	1-7	1-5
Sulfur (wt%)	4-9	1-3	traces	traces
Nitrogen (wt%)	0.02	0.05	0.2-1.0	0-0.3
Sources	[24, 30, 55, 107]	[24, 30, 107]	[3, 24, 30]	[24, 25, 26, 30]

4, from the perspective of few physicochemical properties relevant to dispersion applications and use of lignins as polymeric surfactants.

3.1.1 Lignosulfonates

Lignosulfonates (LSs) are water-soluble polyelectrolytes obtained from sulfite pulping of lignocellulosic biomasses. Extracted LSs are commercially available with multiple established applications [4, 30] as dispersants, binders, dust-control agents, adhesives and antioxidants [24]. Of the isolated ~2 Mta of lignins globally, the vast majority are lignosulfonates, with approximate volume above 1 Mta [26, 29].

Sulfite (SO_3^{2-}) and bisulfite (HSO_3^-) ions are the reactive species in sulfite pulping [31], because of the pulping chemical sulfurous acid (H_2SO_3) and its salts. Sulfite pulping can be done in various conditions, but typically acidic conditions (pH 1–5) are used. At a temperature of 140 °C [24], lignin is depolymerized by acidic cleavage of ether bonds [31], but mainly lignin is dissolved to white liquor by introduction of sulfonate functional groups to the structure of lignin. LSs are generally soluble in a wide pH range (2–12) and thus recovered from black liquor by ultrafiltration, ion exchange or in the special cases by excess lime precipitation (Howard process) [26, 32].

Lignosulfonates (LSs) are unique compared to other lignins because they are soluble in alkaline but also acidic solutions in a wide pH range [24, 26, 30]. LSs are also soluble in some highly polar organic solvents and amines [26]. LSs are soluble in aqueous solutions because high degree of ionizable sulfonate functional groups, mainly attached to the aliphatic side chain of monolignols (Figure 12) [24, 31].
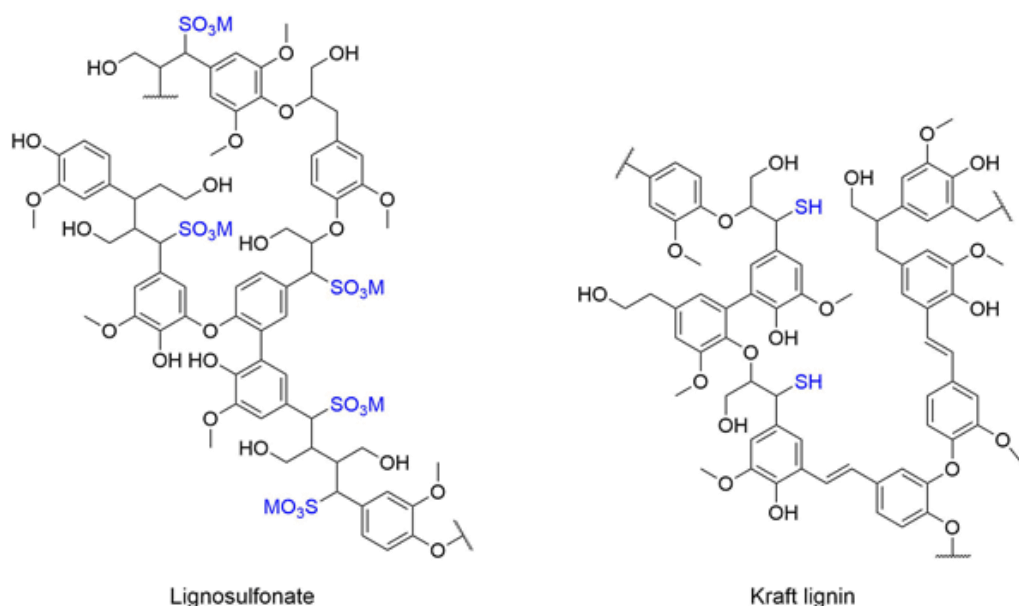

Figure 12 Illustrative structures of lignosulfonates and kraft lignins. M in lignosulfonate indicates counterion, such as Na^+ or Ca^{2+}. Adapted from [26, 29, 30].

Types and quality of different lignosulfonates vary largely. LSs have high number (M_n) and weight average molar masses (M_w) and dispersity ($Đ$ = 6–8) compared to other lignins [24, 26]. LSs can have M_w as high as 150 000 g mol^{-1}, but more typical is 5 000–20 000 g mol^{-1} [26]. Unpurified LSs have lignin contents of ~70–75 wt% of the dry matter [26]. Contamination by the carbohydrate residues [25, 26], cations used in the sulfite pulping (Na^+, NH_4^+, Ca^{2+}, Mg^{2+}) and ash affect the properties, reactivity and hence usability of LSs [24, 25, 26]. Furthermore, compared to kraft lignins, LSs contain more sulfur [24, 26], mainly in form of aforementioned sulfonate functional groups. High amounts of inorganic sulfur is undesirable, as its removal add environmental problems and expenses to the sulfite process and lignin extraction. [26]

Lignosulfonates are well-established components in formulations of various dispersants, plasticizers and other surface- and dispersion-related applications. The water solubility and anionic sulfonate functional groups allow LSs to be readily used in dispersion applications. As a high molar mass polymer, adsorption and thus dispersion performance of LSs is however hindered in specific applications.

3.1.2 Kraft Lignin

Lignins from sulfate pulping are referred as sulfate lignins or **kraft lignins** (KLs). Sulfate pulping is the dominant pulping technology of the pulp and paper industry, but KLs isolated from black liquor are only available in quantities of 100–200 x 10^3 metric ton per year (kta). [4] Most of the lignin is burned for energy in the recovery boiler [29]. However, if the recovery boilers are the bottleneck of the pulp production, there is incentive for lignin extraction. Additional driver for lignin production is the desire to sell lignin for higher value applications than burning and energy.

Sulfate pulping uses mainly sodium hydroxide (NaOH) and sodium sulfide (Na_2S) as pulping chemicals [24]. Lignin is partially depolymerized in the alkaline conditions at temperatures of 150–180 °C for 2 hours and thus dissolved in the white liquor [4, 26]. KL is isolated from black liquor by different extraction technologies consisting of acid (CO_2 and H_2SO_4) precipitations and ultrafiltrations [26, 33]. Few commercially available extraction technologies focusing on KL extraction are for example Lignoforce™ and Lignoboost™ (developed by Innventia, owned by Valmet) [33].

KLs are characterized by small amount of sulfur (1–3 %) covalently bound to lignin [24, 26] in form of aliphatic thiol (-SH) groups (Figure 12), which give KLs a characteristics odor especially during heating [25]. The thiol functional groups are introduced mainly to β-carbons of KLs [29] because of sulfide (S^{2-}) and polysulfide chemicals used in the sulfate pulping [34]. Episulfide and subsequent thiol functional groups increase the sulfur

content of KLs, but these functional groups are unstable and easily lost during the pulping processes [35], and thus KLs have lower sulfur content than LSs [24, 35].

Incorporation of thiol (pK_a = 13) and phenolic hydroxy functional groups (pK_a = 10) [24, 25], and high amounts of condensed structures [24], KLs are poorly soluble in anything else but alkaline solutions and few selected organic solvents [25], such as pyridine, di-methyl sulfoxide (DMSO) and dimethylformamide (DMF) [30]. The presence of hydrox-ide, sulfide and bisulfide (HS⁻) ions during sulfate pulping also cause decrease in M_w of KL by cleaving the ether bonds of lignin [34], especially the β-O-4 bonds.

Few commercial applications have been developed for KLs in the recent years. KLs can replace for example phenol in phenol-formaldehyde resins used for plywood, laminated veneer lumber and oriented strand board gluing. Other potential high value applications are for example carbon fiber production, biocomposites and energy storage applications.

3.1.3 Soda Lignin

Alkaline or soda pulping is used to produce **soda lignins** (SLs), mainly from annual plants, such as straws, bagasse and flax, and to some extent from hardwoods [24, 25, 29]. Soda pulping with NaOH is used in small capacity commercial pulp mills utilizing agricultural residues or annual plants as feedstocks. Because of the smaller size of con-ventional soda pulp mills compared to sulfate and sulfite pulp mills, soda pulp mills can-not develop capital-intensive systems for handling and recycling large amounts of spent cooking chemicals. However, the recovery of lignin could reduce the environmental im-pact of these smaller mills. In addition to the conventional soda pulping, new pilot scale (modified) soda pulping technologies have emerged with concept to produce high quality cellulose, hemicellulose and lignin as a primary focus. [25] The global production volume of these new SLs is 5-10 kta [29].

In soda pulping NaOH is used fractionate lignocellulosic biomass at pH = 11–13 and temperatures of 150–170°C [24]. Lignin is partially depolymerized and dissolved to the white liquor, of which it can be extracted by acid precipitation with mineral acids, followed by subsequent purification steps, similarly to kraft lignin [24, 25]. Soda lignins do not contain covalently bound sulfur and only trace amounts of sulfur, if SL is acid-precipitated in the isolation process with H_2SO_4. Structurally SLs are relatively unmodified especially compared to KLs and LSs [30], but also even to organosolv lignins, because lack of harsh reactive chemicals like sulfate or sulfite ions or organic acids (Figure 13).

Solubility of SLs is quite similar with those of other alkali lignins, such as KL [24]. SLs are soluble in alkaline solutions [24] and in selected organic solvents. Absence of sulfur,
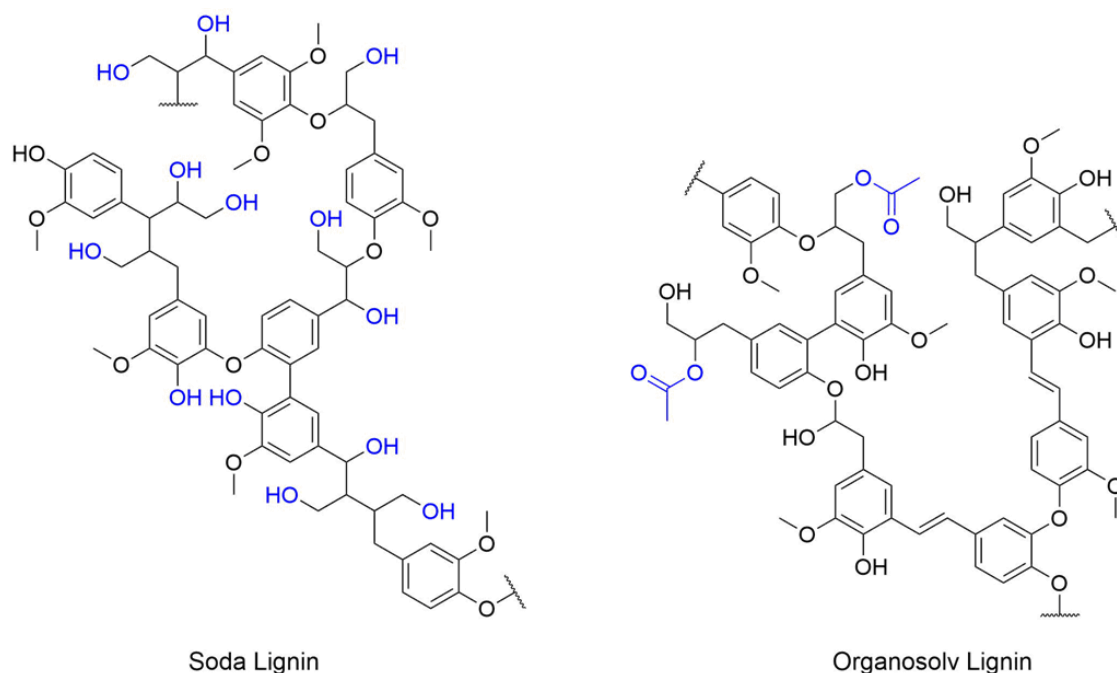
Figure 13. Illustrative structures of soda and organosolv lignins. Adapted from [26, 29, 30].

low average molar masses, low Đ, high phenolic hydroxy content are some of the properties that make SLs attractive towards high-value applications. [24, 25].

3.1.4 Organosolv Lignin

In the organic solvent processes water-soluble organic solvents are used to fractionate lignocellulosic biomass. The main products of organosolv processes are cellulose and **organosolv lignin** (OL) [24, 29]. Depending on the details of the organosolv process, hemicelluloses in form of monosaccharides and other side products, such as furfural, are possible. While utilization of organic solvents for pulping of biomass has been proved at a demonstration scale since the 1989 [25, 26], in recent years the field has gained renewed interest and more demonstration scale facilities because emergence of biorefinery concepts. Currently, there are handful of pilot and demonstration scale organosolv pulping processes under development, and small quantities of OLs are available (~3 kta) [29].

Organosolv pulping technologies vary on the choice of organic solvents, catalysts and temperatures. For example processes based on ethanol, formic acid and acetic acid are proven at pilot scales. [24] Organic acids and bases with organic solvents or water are often used to enhance pulping rates. Process temperatures of 100–220°C, pressures of 1–5 bar and reaction times of 1–4 h indicate the variance in organosolv processes. OLs are extracted from the black liquor by adjustment of pH or temperature and solvent distillation. [26]

Organosolv lignins do not contain sulfur in their structure [30], because the process is done without sulfur-containing chemicals (Figure 13). OLs are hydrophobic, and thus mainly soluble in nonpolar organic solvents and to some extent in alkaline solutions. [24, 25] The physicochemical properties and potential applications of OLs are quite similar to other alkaline soluble lignins, such as soda and kraft lignins [24, 25]

3.2 Lignins As Surfactants and Relevant Physicochemical Properties

Lignins can be described as grafted polymers that have hydrophobic, aromatic backbone and grafted hydrophilic functional groups. Thus lignins show properties of amphiphilic polymeric surfactants, similar to other anionic polyelectrolytes. [19, 21, 36]

Kraft lignins can reduce surface tension of water down to 45–65 mN m^{-1}, depending on concentration (0.01–2 wt%) and M_w of the KL [37, 38]. With high concentration of KLs (10 wt%), surface tensions as low as 30–35 mN m^{-1} have been achieved [19, 39], while typical surface tension values are higher. KLs show the most surface activity in the first 10–20 minutes, but equilibrium activity and adsorption are reached only after 3–20 h [19, 37]. This kinetic behavior is similar to other polymeric surfactants, such as LSs [37], which show slow diffusion rate and kinetics of adsorption to the surfaces. Adsorption of KLs as surfactants is suspected to be irreversible [19].

Soda lignins show surface activity in alkaline solutions, with surface tensions of 45–70 mN m^{-1}. The surface tension decreases more with increase in concentration (0.01–5 wt%) and pH (7–10) of the alkaline solution. As for KLs and LSs, the complete equilibrium surface activity is achieved after about 10 h for SLs. The pH of acid-precipitation and drying of the SL during the isolation of SL from the pulping processes have none or minor effects on the dispersion performance of SLs. As higher M_w lignin polymers are precipitated first at higher pHs because less ionizable functional groups per polymer, the effect of low M_w lignin polymers precipitated at lower pH have no significant additional effect on the dispersion performance or surface activity of the SLs. Thus, the alkaline black liquor and dried SL have quite similar surface activities. [21]

Lignosulfonates reduce surface tension to values of 40–65 mN m^{-1} at concentrations of 0.1–10 wt% [40, 41, 42], indicating weak surface activity. While increase in concentration of LS decrease the surface tension, the dependence of surface tension on pH is not as clear as for alkali lignins. Reduced surface tension caused by LSs is constant for pH range 7–12 and decrease when pH decrease below 5–7. [40, 41] Similarly to other lignins, the static (equilibrium) surface tension is achieved only after 1 hour or later. [40]

In addition to the increased water solubility compared to alkali lignins, the sulfonate functional groups of LSs influence the adsorption and dispersion performance of lignosulfonates [43, 44, 45] and thus can result in different dispersing behavior than caused by alkali lignins. Adsorption of LSs to the surface of dispersed phase particles is important for the overall dispersion performance of LSs and stability of dispersions. LSs have anionic sulfonate functional groups, in addition to carboxyl functional groups found in all technical lignins, that provide dispersion stability via electrostatic repulsion. Furthermore, hydrophobic and aromatic phenyl propane structures found in all lignins can facilitate pi-interactions with aromatic hydrophobic dispersed phases particles, such as disperse dyes or carbon blacks. [46]

3.2.1 Purity

Purity of lignins depend on the botanical origin, pulping conditions [28] and washing of the lignin in isolation processes. Main impurities of lignins are ash, mainly in form of silicates and metallic cations, carbohydrates and proteins. Sulfur is not a significant natural constituent of lignin, but more of a result of sulfite and sulfate pulping and isolation processes of lignins [25].

The ash content of different dry alkali lignins varies between 0.2–13.7 wt% [28], while LSs can have ash and impurity contents as high as 18–33 wt% [28, 42]. Especially alkali lignins and organosolv lignins obtained from non-wood feedstocks, such as rice straws, contain large amounts of silica. Silicates can co-precipitate with the lignin for example during the acid precipitation of alkali lignins [25]. Inorganic content can be reduced by efficient washing of raw material feedstock before the pulping and further washing of the isolated lignin.

The carbohydrates in form of (hemi)celluloses and monosaccharides can affect how lignins perform in dispersions as polymeric surfactants. The amount of monosaccharides in the technical lignins are typically below 3 wt% (Table 4) [28, 36], while amount of oligo- and polysaccharides can be higher. A low carbohydrate content is important when lignin is used for example as a concrete plasticizer, as sugars can retard the hardening of cement or concrete. Typically, carbohydrates contents below 2 wt% in LSs is desired for these applications [28]. On the other hand, less purified LSs show more decrease in surface tension of water. [36, 40]. Thus, the role of carbohydrates in lignins used as polymeric surfactants is application dependent and not yet clear.

Another impurity found in lignin can be proteins, which can be coextracted from lignocellulosic biomass during the pulping and fractionation processes. The amount of amino acids and proteins in lignins can be up to 7–8 wt% [28], especially when non-wood based

feedstocks, such as wheat and rice straw, are used. How protein residues and other contaminants affect the dispersion performance of lignins is application dependent and often unclear [25].

3.2.2 Solubility

Lignins can be divided to two classes based on their solubilities in water at different pHs. Sulfonated lignins (mainly lignosulfonates) are water-soluble because they contain sulfonic functional groups [25], which have pK_a less than 2. On the other hand, alkali lignins including kraft and soda lignins, and organosolv lignins are completely soluble in alkaline solutions when pH is above 10. Alkali and organosolv lignins have phenolic hydroxy groups (pK_a = 9–10) as the main ionizable functional groups, which when deprotonated, make alkali lignins soluble in water. [25, 47] Presence of other functional groups, such as carboxyl functional groups (pK_a = 4–5) [48] and possible thiol functional groups (pK_a = 13), molar mass, average particle size and degree of condensation are few of the other parameters that affect lignin solubility in different solvents.

The higher the pH of aqueous solution, more surface active and better dispersants alkali lignins are [21, 38, 39]. Higher the pH of the solution, more of the ionizable phenolic hydroxy and carboxyl functional groups of alkali lignins are deprotonated. This makes alkali lignins more water-soluble, increases electrosteric repulsion potential of lignins as surfactants and possibly allow for improved adsorption of lignin at the surface of dispersed phase particles.

3.2.3 Molar Mass

Weight average molar masses (M_w) of technical lignins vary depending on the pulping process. LSs have M_w = 5 000–150 000 g mol^{-1}, while KLs, SLs and OLs have typically M_w below 10 000 g mol^{-1}. Dispersity ($Đ$) of lignins can be significant [49] and mainly dependent on the pulping process and post-treatments, but also to some extent on botanical origin of the lignin. Softwoods have generally higher M_w than hardwoods [37] and often LSs have higher $Đ$ (=4–8) than alkali and organosolv lignins (Table 4).

Surface activity and dispersing performance of KLs and LSs are dominated by their average molar masses (Table 4) [38, 49]. Higher M_w lignins are better at reducing surface tension [19, 37, 38] and for example as dye dispersants [49, 50], because increased adsorption to surface of the dispersed phase particles than lower M_w lignins [49]. Furthermore higher M_w lignins have more favorable hydrophobic and hydrophilic balance caused by aromatic lignin backbone and ionizable functional groups, respectively [38]. Higher M_w of lignin can however increase the time to reach adsorption equilibrium [19,

37], because of increased size of lignin molecules and therefore decreased diffusion rate. To further add complexity, the correlation between M_w and surface activity of lignins is most certainly application dependent and cannot be extended cases where lignins are chemically modified.

3.3 Chemical Modifications of Lignin to Dispersants

Lignins contain variety of functional groups suitable for chemical modifications and therefore lignins are potential raw materials [24] to produce polymeric surfactants. The chemical modifications can include sulfonations (lignosulfonate-like structures), oxidations, carboxyalkylations, grafting with poly(ethylene glycol), hydroxyoxylations and many more. [20]

Alkali lignins are hydrophobic, which make their utilization difficult in water-based applications [20, 24]. Dispersions often involve water as a continuous phases or dispersed phase, and alkali lignins are insoluble in aqueous solutions below pH ~10, which are typically required for many dispersion applications. Improved water solubility is achieved by introducing hydrophilic and ionizable functional groups, and altering the M_w and Đ of lignins. Furthermore, chemical modifications can for example increase the adsorption of lignins to the surface of the dispersed phase particles and improve stability of dispersion by enhancing the electrosteric repulsions. Overall, lignins need to be modified to be used in high-value dispersion applications [51].

In comparison to for example cellulose, which has more well-defined and understood structure, the modifications of lignins are however challenging due to structural complexity and steric hindrance. The most reactive positions for chemical modifications of lignins are *free,* non-condensed, phenolic hydroxy functional groups and unsubstituted aromatic *ortho*-positions next to those phenolic hydroxy groups, aliphatic hydroxy groups and *α*-carbons of phenyl propane monomers (Figure 8). [52]

Table 5. Summary of the few potential chemical reactions to modify lignins towards dispersion applications. Oxidation reactions are discussed further in the subsections.

Modification	Sulfonation	Oxidation	Carboxyalkylation	Amination
Purpose	Introduce sulfonate functional groups and slightly changes to molar mass and dispersity of lignin.	Introduce carboxyl functional groups to the lignin, with controlled degradation of lignin.	Introduce carboxyl functional groups to lignin without degradation of lignin.	Introduce cationic amine functional groups to lignin and make lignin a cationic dispersant.
TRL and scale	7-9 Commercial scale at least in the past	5-7 Pilot and demonstration	3-4 for lignin (9 for cellulose)	1-3
Reagents	Na_2SO_3, formaldehyde	O_2 or H_2O_2 or O_3	Chloroacetate	Non-tertiary amine, formaldehyde
Solvent	Alkaline solution	Alkaline solution	Water, ethanol	Water, dioxane
Reaction conditions	50-140 °C pH 9-12 2.5-4.0 h	25-100 °C pH 2-14 0.1-3.0 h	40-90 °C 1.0-4.0 h	50-100 °C 2.0-4.0 h
Pros	Makes lignin water-soluble. Well-known, similarity to lignosulfonates. Improve dispersion performance of alkali lignins by introducing ionizable sulfonate groups. No pressure required.	Makes lignin water-soluble. Can be done with known bleaching chemicals and even with environmentally-friendly oxygen. Can be done directly from alkaline black liquor. Sulfur-free can be an advantage. Short reaction time.	Controllable degree of substitution. No degradation of lignin. Sulfur-free can be an advantage. No pressure. Reaction known at industrial scale from carboxymethylcellulose production.	Produces cationic surfactant for possibly higher value applications. No degradation of lignin. Sulfur-free can be an advantage. No pressure.
Cons	Toxic formaldehyde as one of the reagents. Sulfonated lignins are not the best performing dispersants. Economical attractivity can be questionable. Requires separation of lignin from black liquor.	Pressure required. Small molecule acidic degradation byproducts.	Long reaction times. and poor reactivity (degree of substitution). Possible alcohol solvents. Chloroacetic acid is hazardous alkylating agent.	Low degree of substitution and reactivity. Possible non-water solvents. Low TRL.

Summary of few of the chemical reactions to produce water-soluble and better performing polymeric surfactants and dispersion additives from lignins, is presented in Table 5. These class of reactions are chosen based on the different technological readiness levels and type of lignins they produce. The different oxidations and especially alkali-oxygen oxidation (LigniOx technology) is discussed in more detail, because of its relevance to this thesis.

3.3.1 Oxidations

To obtain sulfur-free and high-performing lignin dispersants, other modifications than sulfonations need to be considered. Alkali lignins can be oxidized to improve solubility of lignins in aqueous solutions below pH 10 [35, 53] and make lignins more suitable as

dispersants for aqueous solutions. [54] The improved water solubility can be caused by introduction of carboxyl functional groups either as substituents to the lignin structure or via depolymerization and oxidation reactions [35]. Different reagents, such as ozone (O_3) and hydrogen peroxide (H_2O_2) in alkaline conditions have been used to oxidize lignins.

Alkali lignins can be oxidized with **ozone** (O_3). Alkali lignins can be used directly, as part of the black liquor, in oxidation reactions or lignins can be acid-precipitated and resolubilized with NaOH, before following oxidiation with ozone. Typical ozone consumption is 10–40 wt% of lignin and with increasing degree of ozonation, the pH of the aqueous solution in which lignin is soluble decreases (as low as pH 2). The increased solubility is mainly caused by formation of ionizable carboxylic functional groups followed from O_3 consumption. [54, 55] On the other hand, the M_w of ozonated kraft lignin increased from 5000 g mol^{-1} up to 10 000 g mol^{-1} with steady increase of O_3 consumption (10–40 wt% of lignin) [55]. While lignin undergoes oxidative cleavage of the aliphatic side chains and aromatic structures during the initial stages of the oxidation, the dehydrogenative repolymerization of phenolic fragments occur during the ozonation by oxygen radicals; superoxides ($\cdot O_2^-$) and hydroperoxyl radicals ($\cdot OOH$) at pH 10.5–12.4 and hydroxyl radicals ($\cdot OH$) at pH 8.1–8.7. The increase in the amount of incorporated carboxylic acid functional groups to the lignin and small degradation products decrease the pH steadily during the ozonation if pH is not kept constant by steady addition of an alkali. [48, 55]

Lignins can be also oxidized with another strong oxidizer, **hydrogen peroxide** (H_2O_2). The oxidation with H_2O_2 can be done in acidic [56] or alkaline conditions to dissolve lignin and to promote hydroperoxyl formation and thus oxidation efficiency of H_2O_2 [53].

The endothermic oxidation reaction with H_2O_2 is done at 60–100 °C, for 0.5–4 h, but it is suspected that oxidation with H_2O_2 is a fast process and reaction time can be shorter (Table 6). The oxidation with H_2O_2 increase the carboxyl group content and thus charge density of lignin and causes slight de- and repolymerization of the lignin, without affecting average molar mass significantly (Figure 14). [53, 56] As a result of the oxidation with H_2O_2, oxidized lignin becomes soluble in pH as low as 5. Side reactions include H_2O_2
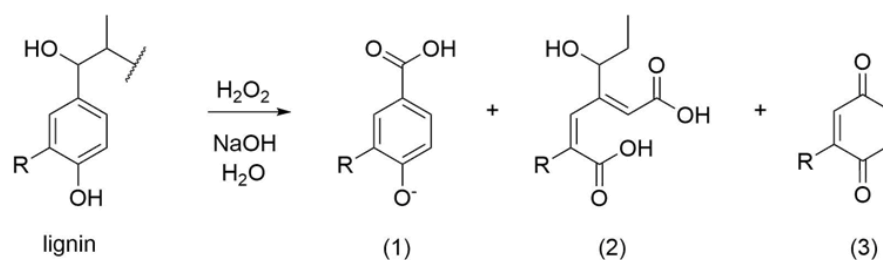

Figure 14. Hydrogen peroxide oxidation products of alkali lignins. R indicates the rest of the lignin polymer. Adapted from [53, 56].

decomposition and formation of quinone chromophores, which cause dark color of lignin (Figure 14 (3)). [53]

According to a study, the estimation of raw material costs other than lignin to produce oxidized lignin with H_2O_2 from kraft lignin are \$358–\$845 per product metric ton, assuming that no chemicals are recycled [53]. Hydrogen peroxide has the advantage of being used already in the bleaching of cellulosic pulp and therefore widely available and known among the pulp and paper industry [53, 56].

While oxygen (O_2) is not as strong oxidizers as ozone or hydrogen peroxide [59], technologies based on O_2 in alkaline conditions have been developed due to economic and environmental interests. One of these technologies is discussed in the next section in more detail.

3.3.2 Alkali-Oxygen Oxidation – LigniOx Technology

LigniOx technology, an alkali-oxygen oxidation of lignins towards dispersant applications is developed and patented by VTT Technical Research Centre of Finland Ltd [57, 58]. The LigniOx oxidation increases hydrophilicity and solubility of various technical lignins in water and makes lignin suitable for example as a plasticizer in concrete and as a dispersant for TiO_2, $CaCO_3$ and gypsum suspensions [59, 60, 61]. Oxygen is environmentally friendly oxidizing agent and widely used in the modern pulp bleaching industry [62].

In the LigniOx technology, dissolved lignin is oxidized under alkaline conditions by oxygen (O_2). The reaction conditions are represented in Table 6 and compared to other oxidation reagents and reactions discussed previously.

Alkali-oxygen oxidation causes degradation of the lignin and increases the amount of carboxyl functional groups in the lignin macromolecule. The formation of the ionizable

Table 6. Lignin oxidation conditions by different oxidation reagents and conditions. LigniOx technology is patented by VTT Technical Research Centre of Finland Ltd.

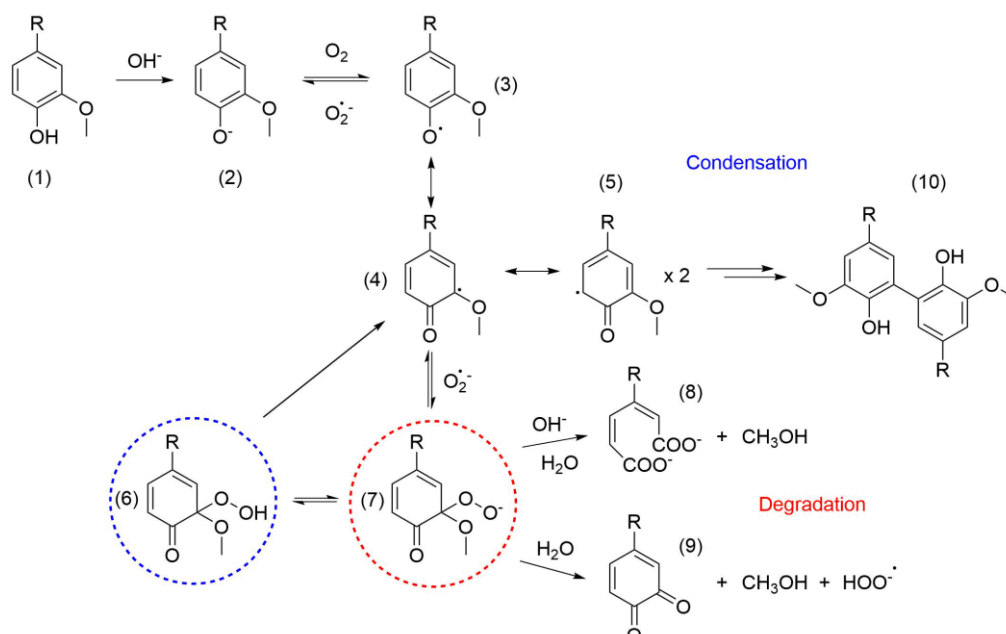| Process	LigniOx	H_2O_2	O_3
Temperature (°C)	60-80	25-100	25-100
Time (h)	0.1-0.8	0.1-4.0	1.0-3.0
Lignin concentration (wt% of solution)	0.75-25	10-24	1-25
Oxidizer load (wt% of lignin)	12-50	12-60	-
Oxidizer consumption (wt% of lignin)	8-13	-	10-40
NaOH (wt% of lignin)	23-45	6-50	20-40
Reaction pH	10-14	2-12	3-7
Sources	[60, 62]	[53, 56]	[54, 55]

Figure 15. Lignin reaction schemes in alkali-oxygen oxidation. Reaction path is pH dependent; below pH 12 condensation reactions occur and above pH 12 degradation reactions. Adapted from [164].

functional groups in the lignin is mainly to due to conversion of the phenolic hydroxy functional groups to carboxylic acid functional groups. [20, 60] In the alkaline conditions, O_2 reacts with phenolates (Figure 15 (2)) to form phenoxyl radicals (3). The phenoxyl radicals of the lignin are further oxidized to a short-living hydroperoxide anion (4) key intermediate (pK_a = 12–13) that rearranges to primary oxidation products, resembling muconic acid or carbonyl structures. [62]

Control of the pH above or below 12 determines the protonation of hydroperoxide anions of lignin and thus further degradation to secondary oxidation and small molecular products (Figure 15) [62]. The protonation of hydroperoxide anions (6, 7) of lignins occur below pH 12 and results in decomposition back to phenoxyl radicals (4) [62], which without further oxidation can cause lignin condensation by 5-5 coupling reactions (5, 10) [35, 62]. On the other hand, above pH 12, the degradation and depolymerization continues to secondary and small molecule degradation products. [62] Condensation by 5-5 coupling does not consume phenolic hydroxyl groups in lignin, which are thus still able to react with O_2 (10) [62].

The charged functional groups caused by LigniOx oxidation should preferably be part of the lignin polymers [35, 62], mainly in form of muconic acid-type structures (Figure 15 (8)) [62]. In addition, there are degraded small molecule acids that have also ionizable carboxyl functional groups which make LigniOx lignin solutions more hydrophilic. The amount of these low molar mass acids contributing to the charge measurements of lignin

Table 7. Weight average molar mass (M_w), dispersity (Đ) and charge density of unmodified and LigniOx oxidized soda lignins (LigniOx SL), commercial lignosulfonate (WRDA 90D, Grace) and synthetic polycarboxylate (Glenium C151, BASF) dispersants. [62]

Dispersant	M_w	Đ	Negative charge (at pH 6)
Units	g mol^{-1}		mmol g^{-1}
Soda lignins	3800	1.9	1.5
LigniOx soda lignins	3200-7300	1.9-2.8	3.2-6.9
WRDA 90D	3000	1.8	-
Glenium C151	16000	3.1	-

maybe up to 10 wt% of the LigniOx lignins at pH 6. [60, 62] It is argued that alkali-oxidation should minimize the degradation of lignin to small molecule non-lignin products; minimize condensation of lignin to less water-soluble material; and maximize the formation of carboxylate functional groups in the lignin structure [35].

While alkali-oxygen oxidation causes minor degradation of lignin, there are possible condensation reactions in form of 5-5 coupling (Figure 15 (5, 10)) [35, 62]. In addition to the choice of pH during the oxidation, the increase in lignin concentration (from 0.75 wt% to 25 wt%) cause increase in M_w and Đ, which are indicators of the condensation reactions. [60, 62] The high lignin concentration favors the condensation coupling reactions because phenoxyl radicals are closer to each other during the oxidation [62]. Furthermore, increasing the lignin concentration makes the reaction solution more viscous, which makes diffusion of O_2 harder and restricts availability of O_2 taking part in degradation reactions during the reaction. This can result in higher pressures required during the oxidation. However, the high lignin concentration is desired if the product LigniOx lignin solution is used as such for example as a concrete plasticizer [62] and to reduce the production costs.

Properties of unoxidized and LigniOx oxidized soda lignins and commercial dispersants are presented in Table 7. LigniOx oxidation increase the solubility of oxidized lignins down to pH 4–6 [62, 63]. The solubility of oxidized lignins increased despite the increase in M_w and Đ, because the increase in amount of ionizable carboxylic functional groups attached to the lignins [62]. Furthermore, the LigniOx lignins had similar or lower M_w and Đ as commercial lignosulfonate (WRDA 90D) and synthetic polycarboxylate dispersant (Glenium C151).

3.4 Applications of Lignins in Dispersions

Polymeric surfactants are used in various applications and for example in cosmetics, paints, pharmaceuticals, oil drilling muds, cement, ceramics, asphalt, scale/corrosion prevention and waste water treatment. Besides synthetic polymers, sulfonated lignins are also used commercially as dispersants in some of these applications, such as in cement dispersing [52], dust control and pesticide formulations as a binder. [20] Kraft, soda and organosolv lignins are still under development phase towards dispersion applications and used in much less quantities than for example lignosulfonates.

The dispersion applications where anionic polyelectrolytes are used are currently the most promising choice for lignin-based dispersants. Current examples of commercially used polyelectrolytes are different poly(carboxylate ethers) (PCEs), poly(acrylic acids) (PAAs), naphthalene sulfonate condensates and lignosulfonates. Dispersion applications which use lignosulfonates or have active patents related to other lignins are discussed in more detail below. However, as mentioned, there are myriad of other applications in which lignin-based dispersants could possibly be used.

In the final section, oxidized LigniOx lignins and their potential, researched, applications are discussed separately because of relevance to this thesis.

3.4.1 Cement and Concrete Plasticization

Concrete is a mixture of aggregates (sand and coarse inorganic substances), cement, water and additives [60, 62]. Water is an essential part of the concrete mixture and plays a dual role: it provides concrete mixture a paste-like form that can flow easily, but also reacts with the cement to set and strengthen the concrete via hydration reactions [60]. While high amount of water is required for well-flowing concrete, low water-to-concrete ratio is required for strong and durable concrete [60, 62]. Therefore, a dispersant is added to a cement mixture to provide a well-flowing concrete, while the water-to-concrete ratio can be kept as small as possible [60]. An ideal dispersant would not affect any other properties than those desired; better flow and more even cement dispersion. However, any real dispersant causes unwanted side-effects such as, retardation of hydration reactions or introduction of air to the concrete mixture.

Currently water-soluble sulfonated lignins are utilized in concrete as plasticizers. While the term plasticizer is often used when discussed about concrete formulations, the mode of action of lignin-based surfactants is to work as a dispersant of the cement. The commercial dispersants for cement and concrete in order of decreasing performance: synthetic PCEs > naphthalene sulfonate condensates > lignosulfonates [28, 62]. These are

anionic polyelectrolytes (polymeric surfactants) that adsorb to the surface of the cement particles (calcium aluminates and calcium silicates). Dispersing of the cement particles is caused by electrostatic repulsion of carboxylic and sulfonic functional groups of the adsorbed polyelectrolytes, while the branched and polymeric structure of these polyelectrolytes cause steric repulsions between the cement particles. [60, 62, 64] It is suspected in a study that steric repulsion is more effective mechanism of dispersion compared to electrostatic repulsion in cement and concrete applications [20]. The steric repulsion was the dominant plasticizing mechanism for PAA dispersants, but for naphthalene sulfonate condensates the electrostatic repulsion was more dominant dispersive mechanism of the cement particles [64].

3.4.2 Carbon Black and Kaolin Dispersions

Special carbon blacks (CBs) are used as black color pigment for example in paints, inks and plastics. Amount of CB in a pigment suspension is 1–40 wt%, depending on the application. [20, 65] CB contains mainly carbon but is often grouped with other inorganic pigments, such as titan dioxide (TiO_2) [66]. There is great variation on manufacturing process, particle size, color, exact composition and surface functional groups of different CBs [67].

Dispersants used for CB dispersions are anionic polyelectrolytes, for example PAA [20], LS [20, 65], naphthalene sulfonate condensates and alkyl benzene sulfonates [65]. Non-ionic dispersants have been also used for CB suspensions [65]. The amount of dispersant in CB suspension varies between 0.02–30 wt% of the suspension [65, 66], depending on the application and the dispersant.

Kaolin is a major clay mineral used in paper [68], mining and ceramic industries, for example as a pigment and a filler. Kaolin is aluminosilicate and the kaolin particles have both positive and negative surface charges over wide pH range (3.5–8.5). The commercial dispersants for kaolin suspensions can be inorganic or organic [52]. Inorganic dispersants include sodium silicates, sodium carbonates and inorganic polyphosphates [52], while organic dispersants are PAAs [52, 61, 68], naphthalene sulfonate condensates and LSs [68]. Examples of the chemical modifications to make lignin more suitable for dispersing kaolin are carboxymethylation [69], sulfomethylation [52] and oxidation [61, 63].

3.4.3 Disperse Dyes

Disperse dyes are hydrophobic dyes, that are insoluble in aqueous solutions [9, 70, 71]. They are azobenzene or quinone derivatives [50, 72] and used as dyes to color hydrophobic natural and synthetic fibers (polyesters) [50].

A great amount dispersant is required to form small particle size and stable dye suspensions. Furthermore, the dispersant solution also work as a diluent of the dye. [50] During the dyeing process, only the dye should exhaust itself onto the fiber, while dispersant and other components should be left in the waste liquor [47, 50]. Dispersant should exhibit excellent heat stability, coupled with low dye reducing and staining properties [9, 47, 72]. Furthermore, dispersant should also minimize foaming [9, 72] and reduce or maintain low viscosity of the dye dispersion [47, 72]. Usually, there is no single dye dispersant that is capable of performing all the above mentioned traits and thus there is demand for different dye dispersants [47].

Weight ratios of 0.75–2 (dispersant to dye) are preferred in the dye dispersions [49, 71]. The current dye dispersants are LSs, naphthalene sulfonate condensates [49, 50] and phenol-formaldehyde condensates [49]. Various lignin dispersants for dye dispersions have been patented. Chemical modification reactions to make lignin dye dispersants include, but are not limited to, ozonation [54], Mannich reactions [70], sulfonation [47], crosslinking with epoxide [47] and reaction with methylol hydroxybenzene [72].

LS dispersants have the advantages of being readily available [50] and having a high temperature stability [49, 50, 72], which is achieved with a lower degree of sulfonation. Nevertheless, the temperature behavior of LSs is complex and at the dyeing temperatures (130–220 °C) LSs can cause possible dye reduction and fiber staining [9]. Other disadvantages of LSs as dye dispersants are high dispersity [71], which results in poor dispersion performance [49], fiber staining resulting from the dark color of lignin, which limits lignin applications with light-colored dyes [50, 72] and possible dye reduction [72], especially at the elevated dyeing temperatures. To reduce the fiber staining and dye reduction of LS dispersants, the free phenolic hydroxy functional groups should be blocked, for example by etherification or crosslinking through phenolic hydroxy functional groups [49, 71, 72].

3.4.4 Asphalt Emulsions

An asphalt emulsion consists of asphalt (50–80 wt%), water (~40 wt%) and emulsifier (1–2 wt%) [73, 74]. Emulsifiers are required in preparation of asphalt emulsions, but also

to improve the storage stability of the asphalt emulsions [74, 75]. Multiple type of surfactants can be used as asphalt emulsifiers, but most commonly used ones are cationic polymers, such as alkyl amide polyamines [74], ammonium lignin derivatives [73, 74, 75] or resin acids [74].

Lignin has been incorporated to asphalt formulations as a binder to replace bitumen at a demonstration scale. However, currently lignin is more expensive than bitumen, but price increase and quality decrease of bitumen and improving economics of the lignin production can shift the balance in 5–10 years. [76] The higher value application of lignin can be as an emulsifier for asphalt emulsions.

Various alkali lignins have been used as asphalt emulsifiers, such as lignin quaternary ammonium salts [75] and ethylene amine/formaldehyde lignins [75, 77]. These are slow-set asphalt emulsifiers, that allow for maximum mixing time, longer workability and flow of the asphalt [77].

Various lignin emulsifiers require that lignin adsorbs to the surface of dispersed phase bitumen droplets or particles. After the adsorption, the cationic lignins cause electrostatic repulsion, but also steric stabilization that prevent aggregation of bitumen particles. [75] An emulsifier is required to keep asphalt emulsion applicable and workable, but when asphalt emulsion is laid for example as a pavement, the asphalt emulsion needs to break down and harden for example via water evaporation [34].

The interfacial tension between asphalt and water is around 40 mN m^{-1}. When emulsifier is adsorbed to the asphalt-water interface, the interfacial tension decreases to 10–20 mN m^{-1}. [75] Various quaternary ammonium and amine lignins had surface tensions of 34–56 mN m^{-1} [75, 77] and caused average asphalt particle size to be 0.8–10 μm in the asphalt emulsions. The decrease in interfacial tension with addition of hydrophobic dodecyl functional group to the quaternary ammonium lignin structure causes decrease in the asphalt particle size. The optimal asphalt particle size in asphalt emulsions is 1–20 μm. [75]

The doses of quaternary ammonium and amine lignins in the asphalt emulsions had optimum around 0.8 wt% according to emulsifying performance and storage stability. With insufficient amount of lignin emulsifier, the adsorbed layer of emulsifier is too thin and results in too little electrostatic repulsion between the bitumen particles. On the other hand, lignin concentrations higher than 1.1 wt% also cause decrease in electrostatic repulsion due to excess counter-anions in the diffuse layer around the asphalt droplets. [75]

3.4.5 Pesticides

Pesticides are hydrophobic compounds that are solids or liquid at room temperatures. [46, 78] Typical pesticides are for example thiocarbamates [78, 79, 80], haloacetanilides, nitroanilines [78], organophosphates [78, 80], pyrethroids [78], strobilurins [78, 79] and dimethomorph [79, 81].

Pesticides have to be dispersed to form concentrated suspensions (solid pesticide) or emulsions (liquid pesticide) in water, which allow for easy application of the pesticides for example by spraying [78, 82]. Furthermore, the dispersion can be dried to produce powder or granule pesticide, in which for example LS can work as water-soluble matrix allowing for redispersion at the later time with readdition of water. [78] Wet alkali lignin concentrates have been patented in the past as dispersants in flowable, organic solvent-containing pesticide formulations [80]. Alkali lignins without sulfonation are less re-searched as pesticide dispersants. Other techniques than sulfonations to make alkali lignins suitable as pesticide dispersants have been grafting and crosslinking lignin with epichlorohydrin-poly(ethylene glycol) to make water-soluble and more hydrophilic lignin. [83]

Lignins are used as dispersants of pesticides to provide dispersion stability and possible solvent-soluble matrix for granule or powder pesticides [78, 79]. LSs with M_w = 40 000–60 000 g mol^{-1} were patented as dispersants for concentrated pesticide suspensions (less than 44 wt% water) [78], while concentration of LS is up to 10 wt% of the suspension [78, 81]. Furthermore, LSs with M_w > 10 000 g mol^{-1} were found to be better dispersants for fungicide suspensions that lower M_w LSs. The dispersion performance of LSs increased with increase in M_w, because increased adsorption of LSs on the surface of hydrophobic pesticides and improved steric repulsion between the pesticide particles. [44, 46, 84] Increased steric repulsion caused by higher M_w is related to the increased adsorption layer thickness when M_w of lignin increases [85].

Also charge density was found to be an important for effectiveness of LSs, indicating importance of the electrostatic repulsion as dispersion mechanism of lignosulfonates [84, 85]. If the M_w is too high, it is possible that some of the sulfonate functional groups are screened by intertwined and bundled lignin polymers and cannot effectively cause elec-trostatic repulsion between the dispersed pesticide particles [44, 85]. Different cations of LSs did not have significant effect on properties of pesticide dispersions [86].

3.4.6 Coal-water Slurries

While the invention of a coal-water slurry is old, the modern day coal-water slurries are coming to use in heat generation facilities as an alternative to natural gas and heavy fuel oils [87, 88]. The main advantage of the coal-water slurry as a fuel is low cost ($35–$50/t [89]), with comparable heat values of 15–20 kJ kg^{-1} to more expensive natural gas and fuel oils [87].

A coal-water slurry is concentrated suspension of finely dispersed coal (50–75 wt%) in water (25–48 wt%). Purpose of adding water and formation of slurry from coal is to make coal a safe fuel in terms of explosion and fire hazard, reduce emissions [87] and convert coal to heavy fuel oil-like liquid [45].

Manufacturing of a coal-water slurry consists of 1) preliminary crushing of coal slag to 3–12 mm particles, 2) wet grinding the coal particles to size of 3–150 µm in a ball mill 3) and homogenization of the coal-water slurry suspension and addition of dispersants [87]. Dispersants are mandatory in coal-water slurries, as coal is a hydrophobic material [90] and viscosity [87, 90, 91], yield stress and stability of coal-water slurry are important [87, 90]. A single dispersant cannot be used to achieve all the desired properties, such as good dispersion and long-term stability, so the final coal-water slurry is usually compromise between the low viscosity and good slurry stability [90].

At the industrial scale, nonionic and anionic polymers with molar masses of 10 000–80 000 g mol^{-1} are used as coal-water slurry dispersants in amounts of 1 wt% [90, 91]. Examples are polystyrene and naphthalene sulfonate condensates, humic acids [45, 90, 92] and PAAs [90]. For purpose of stabilizing coal-water slurries, high molar mass polysaccharides, such as gums, are also used [90]. Dispersants work by adsorbing to the surface of the coal particles, rendering them more hydrophilic and improving their wettability [45, 90, 92]. While anionic dispersants adsorb less densely on the coal surfaces compared to nonionic dispersant, they are much stronger dispersants for coal-water slurries [90], as they cause electrostatic repulsion in addition to the steric repulsion [90, 92].

Lignosulfonates have been found as potential dispersants of coal-water slurries. Sodium LSs with M_w of 10 000–30 000 g mol^{-1}, $Đ = 2.9$ and overall charge density of 2.6 mmol g^{-1} were found as optimal to reduce viscosity of a coal-water slurry. [91] Oxidized and sulfomethylated hardwood KL ($M_w = 21\ 300$ g mol^{-1}, $Đ = 1.3$ and 4.4 mmol g^{-1}) [92] and wheat straw alkali lignin [43] have also shown to work as coal-water slurry dispersants. For coal-water slurry suspensions, the lignin dispersant with $M_w > 10\ 000$ g mol^{-1}, high anionic charge (> 2.0 mmol g^{-1}), and possibly low $Đ$ seems to be desired [45, 92].

3.4.7 Enhanced Oil Recovery

Extraction of crude oil from underground reservoirs is complex process consisting of multiple steps. Primary and secondary recovery steps have combined recovery factor of 35–45 %. To obtain 5–15 % more crude oil from the oil reservoir, tertiary or enhanced oil recovery methods are utilized; one of them being chemical enhanced oil recovery or chemical injection. The process involves use of surfactants, polymers or alkali flooding to reduce the interfacial tension between oil and water and increase the viscosity of water to improve oil recovery. Furthermore, cost-effective and cheap co-surfactants and polymers, referred as sacrificial agents, are used to reduce the undesired adsorption of primary surfactants and flooding chemicals during the enhanced oil recovery. [31, 93] Examples of sacrificial agents used in the oil industry are alkalis, cellulose and starch derivatives [93], lignosulfonates [31, 93], polyglycol ethers, petroleum sulfonates [31] and poly(carboxylic acids) [93].

Lignosulfonates and black liquors from sulfate process have been used as the low cost sacrificial agents in the enhanced oil recovery since 1977 [31]. However, even these low-cost lignins have shown to sometimes outperform the primary chemicals used in chemical enhanced oil recovery. [93] Therefore, lignins can be considered as a potential polymeric surfactants with high performance for enhanced oil recovery.

Alkali lignin (0.4 wt%), octadecylamine (0.3 wt%) and sodium dodecyl sulfate (SDS) (1.3 wt%) surfactant blend showed lower, but decent performance with 11.1 % of oil recovery, compared to standalone 2 wt% of SDS surfactant (17.4 % oil recovery) [94]. Furthermore, sulfonated KL (1.2 wt%), hexamethylenetetramine (0.2 wt%) and sodium dodecylbenzenesulfonate (0.6 wt%) surfactant blend showed oil recovery of 15 %, while sodium dodecylbenzenesulfonate alone (2 wt%) recovered only 5 % of the oil [95].

While decreased interfacial tension between water and oil can generally predict improved oil recovery, other factors are also important after certain interfacial tension has been reached (0.001–10 mN m^{-1}) [94, 95, 96]. For example, alkali amount (0.2–1.0 wt% NaOH) affects the interfacial tension of lignin-based surfactant blends and thus oil recovery [96].

3.4.8 Applications of Alkali-Oxygen Oxidized LigniOx Lignins

While the dispersing mechanisms of LigniOx lignins is similar to commercial cement dispersants [20], LigniOx lignins have comparable or better dispersion performance than commercial lignosulfonate [62]. LigniOx lignins caused less retardation of the strengthening hydration reaction and increased the slump of concrete compared to reference

LS. [60, 62] The air content in the concrete was slightly increased compared to LS when LigniOx lignins were used. The addition of defoaming agent, tributylphosphate (2.5 wt% of lignin) [20, 62] reduced the air content of concrete to the level of high performing PCE dispersants [62].

Compared to commercial PCE dispersants with concentration of 0.2 wt%, similar or better plasticizing performance of concrete was obtained for LigniOx lignin with concentration of 0.4 wt% [63]. In another studies, LigniOx OL and KL showed equal or increased plasticizing than PCEs, naphthalene sulfonate condensates or LSs with equal amounts of plasticizer (0.6 wt% on cement) [20].

LigniOx kraft and hydrolysis lignins of different M_w have been tested as dispersants (0.25–7.5 wt% of CB) in specific <u>special carbon black</u> (10 wt%) suspensions. At dispersant concentration of 2.5 wt% of CB, LigniOx lignins decreased viscosity of suspension more than reference PAA and similarly as commercial LS. Storage for 7 days did not affect the viscosity of LigniOx dispersed suspensions. [20] When dispersant doses was decreased to 0.75 wt% of CB, separation in performance between LigniOx lignins was found. The 7000 g mol^{-1} LigniOx KL showed still low viscosity compared to PAA and LS. Furthermore, LigniOx KLs also facilitated smaller particle size of CB in suspension compared to PAA and similar to LS, which agree with the viscosity results. [97, 20]

<u>TiO_2</u> is used as a white pigment in white paints but also in colored paints due to the excellent opaqueness it provides. The LigniOx lignins do not alter the white color of TiO_2 suspensions and showed similar shear stress as PAA dispersant with concentrations of 0.05–0.06 wt% [61, 63]. LS was not able to disperse TiO_2 paste (70 wt%) enough to measure the shear stress [61].

LigniOx lignins showed decreased shear stress compared to commercial LSs in <u>calcium carbonate ($CaCO_3$)</u> suspensions. Compared to PAA with 0.5 wt% concentration, LigniOx lignins were comparable at concentration of 1.0 wt%. [61, 63] However, the brown color of LigniOx lignins affected the color of white $CaCO_3$ suspension at lignin concentration of 0.25–1 wt%. Unmodified alkali lignins did not provide decent dispersions of $CaCO_3$ [61].

In <u>gypsum</u> ($CaSO_4 \cdot 2H_2O$) plasters, lignin-based chemicals can work as plasticizers or set retardants. In the gypsum plaster mix LigniOx SL was comparable to commercial dispersants, such as citric acid or polycarboxylate. Compared to LSs, the time to maximal exothermic heat flow caused by the hydration reaction rate increased by 65 minutes when LigniOx SL is used, which is equal to the synthetic PCE dispersant. This allows for

long working time of the gypsum plaster. When comparing LigniOx SL to the best performing dispersant and set retardant (citric acid) in gypsum plaster, dispersion performance and total heat released from hydration are comparable, while maximal hydration reaction rate is slightly lowered. [61, 63]

4. HEMICELLULOSE

Hemicelluloses are heteropolysaccharides found mainly in woods, grasses and other plants and are the main constituent of plant cell walls (20-30 %), along cellulose and lignin. [98] Hemicelluloses are the second most abundant class of polysaccharides after cellulose [99, 100, 101] and chemically similar to various gums (hydrocolloids) and cellulose, while being less complex than gums, but more complex than cellulose [102].

Hemicelluloses are polysaccharides with *O*-glycosidic linked backbones of different pentose and hexoses. The sugars in the backbone chain of hemicellulose include xylose (xylan hemicelluloses), mannose (mannans) and glucose (glucans), while substituents can be arabinose, galactose and methyl glucuronic acids (MeGAs). [102, 103] The structure of hemicelluloses and the exact sugar composition depend on the plant species [103, 104], on the extraction and isolation processes [98] and even on the analysis techniques. The compositions of the hemicelluloses are listed in the Table 8.

Table 8. Composition of the selected hemicellulose in different feedstocks. In parentheses are the values of Fortum's hemicelluloses.

Components in hemicelluloses (wt%)	Birch	Softwood	Wheat straw
Arabinose	0-1 (0-1)	2 (8)	6-30 (7-14)
Galactose	1 (3)	11 (9)	1-5 (4)
Glucose	6 (2-3)	10-16 (10)	1-15 (7-11)
Mannose	1-2 (2)	30-68 (33)	0-1 (1-2)
Xylose	45-60 (54-55)	5-25 (14)	55-70 (36-42)
Uronic acids	5 (5-9)	1-2 -	2-6 -
Ash	1 (1-2)	0-1 -	9 (4-5)
Phenolics	0-7	0-5	2-7
Sources	[162]	[131]	[141, 161]

4.1 Hemicellulose Types

Scheller et al. have suggested that hemicelluloses should be defined as those polysaccharides that contain mainly equatorial β-(1→4)-linked backbone structure of pentoses

and hexoses. Therefore, hemicelluloses can be divided to four groups based on the structure [104, 105]:

- xylans
- mannans
- xyloglucans
- mixed-linkage β-glucans.

In subsections only the relevant hemicellulose to the scope of the thesis are discussed. These include hemicelluloses that can be found in different woods (hardwoods and softwoods), wheat straw, rice straw and bamboo. Only those hemicelluloses that are present in significant amounts and extractable from applications perspective are discussed further. The hemicelluloses of interest are mannans and xylans (Table 9), and even among them there is great variety in type of substituents and glycosidic linkages [104].

4.1.1 Xylans

Xylans are one of the most abundant class of naturally occurring polysaccharides besides cellulose, and an important renewable biopolymer source [103, 106]. Different xylans are the major hemicellulose in hardwoods, softwoods [107] brans and cereals [98, 108] and certain algae [109]. The variety of different xylans is immense, but the xylans discussed in greater detail are different glucuronoxylans and arabinoxylans, which are important woods, straws and bamboos [102, 110].

All xylans constitutes of β-(1→4)-linked D-xylopyranose units [98, 107, 109]. There is however structural variation in xylans, such as different substituents attached to the main backbone [106]. Main substituents are acetyl, glucuronosyl and arabinosyl residues [98, 108] and depending on different substituent abundance, the xylans are classified further.

Table 9. Estimates of types and amounts of polymeric hemicelluloses (of total hemicellulose content) in selected feedstocks. In parentheses are the values of Fortum's hemicelluloses. SW = softwood, WS = wheat straw, RS = rice straw.

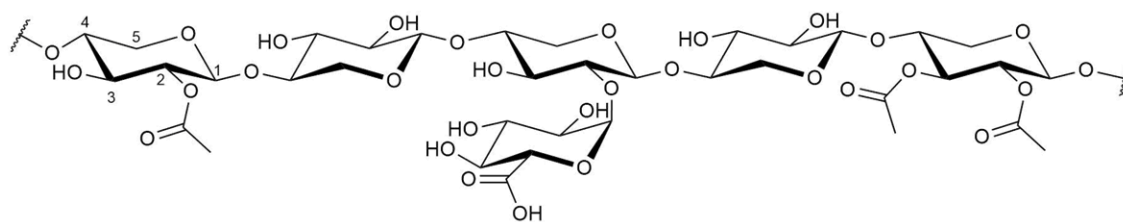| Type of hemicellulose (% of total hemicellulose)	Birch	SW	WS	RS	Bamboo
Glucuronoxylan	60-90 (86)	5-15 (-)	- (-)	- (-)	- (-)
(Glucurono)arabinoxylan	trace (trace)	15-50 (30)	70 (~90)	85-95 (~95)	~90 (~95)
(Galacto)glucomannan	2-5 (14)	35-90 (70)	5 (9)	5 (5)	2 (3)
Sources:	[104, 111]	[98, 111]	[161]	[163]	[122, 160]

*Figure 16. Illustrative scheme of glucuronoxylan (GX) structure found in hardwoods.
Adapted from [104, 105].*

Glucuronoxylan (GX) is the main hemicellulose found in various hardwood species, such as beech [102] and birch [111]. The amount of GX of hardwood hemicellulose is 60-90 wt% [98]. The main substituents are 4-*O*-methylglucuronic acid and acetylated derivative of it, attached to the backbone of β-(1→4)-linked D-xylopyranose units (Figure 16) [98, 105].

The substitution occurs at regular intervals with glucuronic acids (GAs) joined to the xyloses by α-(1→2)-linkages. The ratio of different glucuronic acid substituents to xylose monomers is about 0.7–2.5 : 10, corresponding to the degree of substitution (DS) of 0.07–0.25. [97, 108, 111] This means that on average every 10th D-xylose monomer is substituted with a GA substituent.

As is common for many hemicelluloses, various hydroxy functional groups of main D-xylose chain and substituents sugars are acetylated [98]. In GXs the degree of acetylation is 0.4-0.7 [111, 107], but deacetylation occurs readily in alkaline conditions, while hot-water treatments can preserve the acetyl functional groups [111].

GXs are soluble in alkaline solutions and partly soluble in dimethyl sulfoxide (DMSO). The β-(1→4)-linkages between D-xylose units in GXs are easily hydrolyzed by acids, whereas the α-(1→2)-linkages between 4-*O*-MeGAs and xyloses are quite resistant to hydrolysis. [107]

Xylans that contain many L-arabinose monosaccharides attached to the D-xylose backbone are known as arabinoxylans or (glucurono)arabinoxylans. The distinction is not always clear between the two, and depending on the botanical origin different degrees of substituents are present in different (glucurono)arabinoxylans.

(Glucurono)arabinoxylans (GAXs) are quite similar to glucuronoxylan of hardwoods [104]. However, GAXs are found in wheat straws, softwoods, lignified grasses and annual plants [112], rather than in hardwoods [107].
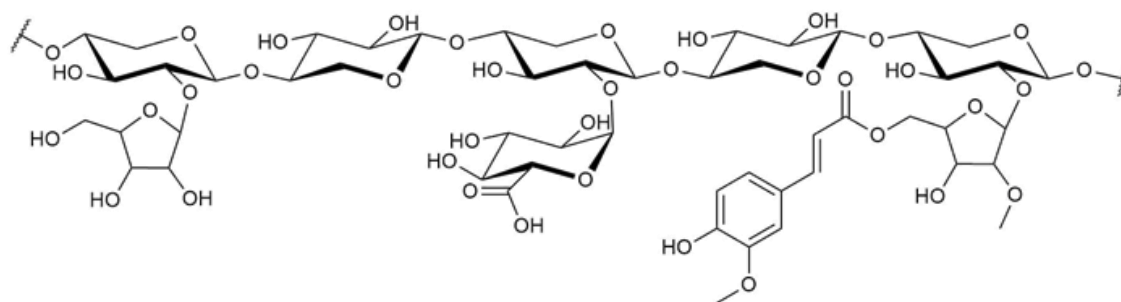
Figure 17. Illustrative scheme of (glucurono)arabinoxylan (GAX) structure found in lignified grasses and straws. Adapted from [104, 105].

Softwood hemicelluloses are 20–40 wt% of GAXs [98, 107, 111], only galactoglucomannans being more abundant of softwood hemicelluloses. The DS by arabinose units is 0.13 in GAXs of softwoods, while DS of GA substituents is 0.2. GAXs found in softwoods are soluble in alkaline solutions, and partly soluble in neutral water and DMSO [107].

GAXs are the dominant hemicellulose for example in lignified grasses, straws, cereal grains and bamboos. There is great variation in the ratio of GA : xylose : arabinose units (3–9 : 10 : 1–10), and degree of acetylation. In a contrast to the GAXs found in softwoods, GAXs in grasses, straws and other lignified annual plants are more heterogeneous, with greater variance in the degree of substitution. [104, 108] For example, disubstitution of arabinose units to C2 and C3 of a same xylose monomer is possible [104, 108]. Furthermore, GAXs of grasses have presence of ferulic acid esters mainly attached to *O*-5 of the arabinofuranosyl residues (Figure 17) [104, 105].

Part of GAXs in annual plants are soluble in water, but the main fractions are soluble in alkaline solutions. The solubility of GAXs in water depend on the amount and distribution of α-L-arabinofuranose substituents. For water-insoluble GAX, the DS is 0.2–0.35, while for water-soluble GAX, the DS is 0.5–0.9 [104], meaning that more α-L-arabinofuranose substituents, more branched and more water-soluble the GAX.

4.1.2 Mannans

Mannans can be divided to two groups: galactomannans and (galacto)glucomannans [104, 107]. The classification between different (galacto)glucomannans is not exact and is based on the amount of substituents and botanical origin [107]. The amount of D-galactose substituents varies depending on the botanical origin and extraction techniques of the (galacto)glucomannans.

(Galacto)glucomannans (GGMs) are the dominant hemicellulose in most softwoods [12, 111] and part of the structural cell walls of softwoods [12]. The amount of different
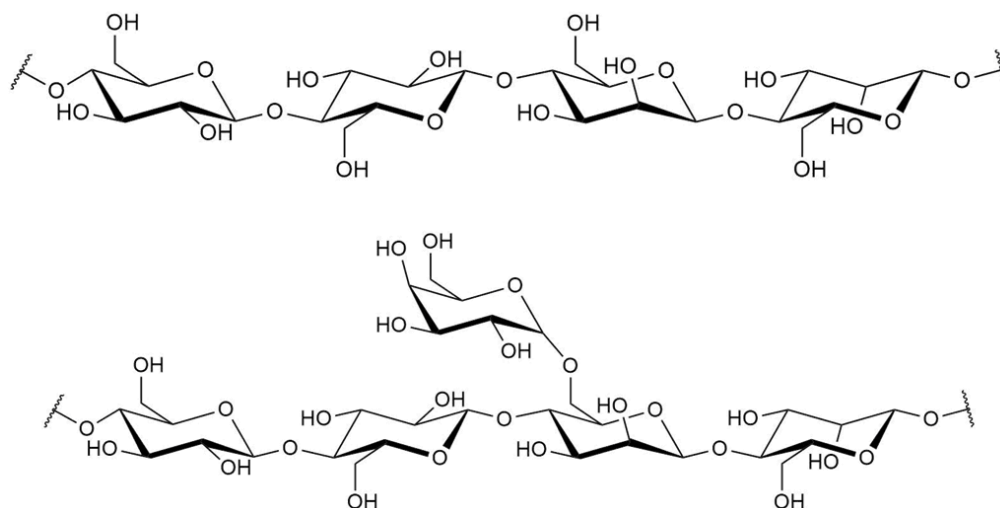
Figure 18. Illustrative schemes of glucomannan (above) and (galacto)glucomannan (be-low). Adapted from [104, 105, 107].

GGMs is 60-90 wt% of softwood hemicelluloses [105, 111]. The backbone of GGM consists of randomly distributed β-(1→4)-linked D-glucopyranose and D-mannopyranose units (Figure 18) [98, 107]. GGMs have monosaccharide ratios of 0.2–1 : 1 : 2–6 (galactose : glucose : mannose) [104, 98, 107].

The main substituent of GGM is α-D-galactose, which is linked to both D-glucose and D-mannose units via α-(1→6)-glycosidic linkages [98, 113]. In contrasts, some suspect that α-D-galactose substituents are attached only to D-mannose units [104, 111] and that also β-D-galactose is a possible substituent [113]. In addition to the D-galactose substituents, the typical degree of acetylation of GGMs is 0.15–0.4 [107, 111] and acetylation occurs at C2 and C3 hydroxy functional groups of D-mannopyranose units [22, 111, 113, 114]. The acetylation does not occur in the D-glucose units [114].

Those (galacto)glucomannans with low amount of D-galactose are often called just **glucomannans**. While the GGMs are found in softwoods, glucomannans with lower amounts of D-galactose substituents are found in softwoods and to some extent in hardwoods in amounts of 5–20 wt% of hemicellulose composition (Figure 18) [104, 107, 111]. Glucomannans have monosaccharide ratios of 0.1 : 1: 1–4 (galactose : glucose : mannose), depending on the softwood or hardwood species [104, 114]. The DS by D-galactose units is lower in glucomannans of hardwoods compared to GGMs of softwoods. The degree of acetylation is 0.2–0.3 for water-soluble glucomannans of birch [114].

Glucomannans are more difficult to dissolve than GGMs, because cellulose-like backbone of glucomannans [104] with strong intramolecular hydrogen bonding. The glycosidic bonds between mannose units are more readily hydrolyzed by acids than corresponding glucosidic bonds, but overall glucomannans are easily depolymerized by acidic

conditions [107]. As with all hemicelluloses, GGMs are easily extracted by alkaline treatment from delignified or lignocellulosic biomasses [104].

4.1.3 Antisolvent Precipitation of Hemicelluloses

Hemicelluloses are the most readily extracted and hydrolyzed constituent of the lignocellulose [115]. Examples of technologies to obtain hemicelluloses from wood and straw biomass are pressurized hot-water extractions, alkaline extractions, purification and concentration of thermomechanical pulp process waters and pre-hydrolysis of hardwood dissolving pulp. [111] As for all components of the lignocellulose, the extraction technology affects the physicochemical properties of the hemicelluloses. Some of the properties that are affected are the weight average molar mass (M_w), degree of polymerization (DP) and exact chemical structure and functional groups of the hemicelluloses, such as degree of acetylation [115].

While hemicelluloses can be used as such from the abovementioned processes, different aftertreatment purification and isolation technologies can be used to alter for example the purity, M_w and DP of hemicelluloses. Spray-drying and ethanol precipitation are few of the purification, isolation and drying techniques of hemicelluloses, especially used for hardwood GXs and softwood GGMs.

Ethanol precipitation (EtOH-precipitation) is used to isolate or further fractionate hemicellulose, such as GX [111] or GGM [116], into high, medium and low molar mass fractions [111]. The EtOH-precipitation can also increase the purity of the hemicellulose [111, 116, 117], by removing lignin-related compounds and extractives (triglycerides and fatty acids) [117]. A water-miscible organic solvent, such as ethanol, will first precipitate polymeric hemicelluloses and leave oligo- and monomeric hemicelluloses dissolved [116]. Methanol, C3-C4 alcohols, acetone and methyl *tert*-butyl ether are other water-miscible organic solvents suitable for the precipitation [117, 118], while ethanol has the advantage of cost-effectiveness, availability and low toxicity. If hemicellulose are precipitated from impure compositions containing for example cellulose and lignin, hydrogen peroxide or another oxidizing compound can be added during the precipitation or as a separate step to improve purity and color of the hemicellulose [118].

The ratio of ethanol to hemicellulose concentrate determines the yield and properties of the precipitated hemicellulose [111, 119, 120]. For softwood (GGM) and hardwood (GX) hemicelluloses, high molar mass fractions precipitate first at lower ethanol-to-hemicellulose ratios, followed by precipitation of lower molar mass fractions with increase in ethanol volume [111, 120]. On the other hand, an opposite trend was observed for GAXs of

grasses, such as bagasse and bamboo, meaning that higher M_w GAXs were observed with higher ethanol-to-supernatant ratios (0.2–3) [121, 122].

In EtOH-precipitation of aspen hemicelluloses, with increase in ethanol-to-supernatant ratios (1–4), EtOH-precipitated galactoglucomannans (GGMEtOHs) contained more mannose and less xylose, galactose and to an extent arabinose units [114]. In the another study of pine hemicellulose GGMs, similar trend was observed for amount of mannose and xylose, but amount of galactose increased with increase of ethanol (0.2–9 ratios). The amount of arabinose in precipitated GGMEtOH had no clear trend with ethanol volume. [120]

For GAXs of grasses and straws, the amount of xylose decreased and arabinose : xylose ratio increased with increase in ethanol volume [121, 122, 123, 124]. The higher arabinose-to-xylose ratio indicates more branched GAXs, which are more soluble in water and thus require higher ethanol volumes to precipitate [122, 123].

4.1.4 Spray Drying of Hemicelluloses

Spraying drying is a drying technique for a wide variety of biomolecules and biopolymers, such as proteins and carbohydrates. Spray drying has a few advantages over other drying technologies of sensitive polymers, such as freeze drying [125], refractance window-drying and radiant zone-drying [126]. Spray drying produces dry powders of spherical particles [125, 126], with controllable particle size, morphology and density in a single process step. Drying techniques cannot often control the morphology of powder particles and therefore further process steps are required, such as crushing and screening. [125] Spray drying causes also only minor color alterations to the dried the mannan polysaccharide, compared to other industrial drying techniques [126].

Yields and structure of polysaccharides are altered during different industrial drying processes, and thus also during the spray drying. The drying temperature, drying time and heat transfer mechanism, but also initial extraction techniques affect the structures and properties of dried hemicelluloses. For example, drying causes decrease in galactose content and degree of acetylation of GGM-like polysaccharides. [126] However, if hemicelluloses are extracted by alkali or hot-water treatments from the lignocellulosic biomass, degree of acetylation is already reduced to an extent and drying might not alter the structure or properties of hemicelluloses much further.

The purity of EtOH-precipitated hemicelluloses is higher than those of spray dried hemicelluloses. The content of phenolic compounds and extractives are more abundant in

spray dried (1–11 mg/g) than EtOH-precipitated hemicelluloses (0.1–1 mg/g). [111] However, whether these ''impurities'' affect positively or negatively the surface activity and other dispersion-related effects of the hemicellulose fractions is unclear.

4.2   Hemicelluloses in Dispersions and Physicochemical Properties

Hemicelluloses are considered as potential emulsifiers, dispersants and foam stabilizers [103]. Hemicelluloses work in dispersions mainly by increasing the viscosity of the dispersion media, which reduce the rate of creaming, flocculation and coalescence of the dispersed phase according to the Stokes' Law. [102, 127]. In addition to the changes in viscosity, purified and modified hemicelluloses act by forming multimolecular films around dispersed particles or droplets [103] and thus can cause steric stabilization [115, 127]. This hydrophilic barrier between the oil- and water-phases stabilize the O/W emulsions, which hemicelluloses most often form [102, 127]. The dispersing mechanisms of hemicelluloses in dispersions are combination of macromolecular hydrocolloids (gums) that affect the rheology of the dispersions and those of classical surfactants [111].

There are certain challenges in using hemicelluloses as surfactants and rheology modifiers. In general, polysaccharides have lower surface activity than other biopolymers, such as proteins. This is characteristic to hydrophilic polymers with monotonic structures. [113] Only a modest decrease in the interfacial and surface tension is achieved with wood hemicelluloses, such as spruce GGM and birch GX [127].

Another challenge of hemicelluloses are batch-to-batch variation, which might relate to variation in the feedstock source and the extraction technology [102]. Susceptibility to microbial contamination is also an important consideration when hemicelluloses are used in dispersions as texture modifiers or polymeric surfactants, as this reduces the shelf-life of the products containing hemicellulose [102] and limits the potential applications with strict regulations (pharmaceuticals, foods and cosmetics). Hemicelluloses are also more susceptible to chemical degradation by oxidiation and hydrolysis [102], than for example lignin and cellulose, which might limit use of hemicellulose in high temperature and acidic conditions.

Xylans have shown to exhibit emulsifying properties [103, 127] and foam stabilizing effects [103]. Different xylans produce stable O/W emulsions, comparable to nonionic polymeric polysorbate surfactant (Tween 20) [127, 128]. As expected, hardwood GXs decrease the surface tension of water only slightly, to 61 mN m^{-1}, and cannot form micelles [128]. Similar results were found for birch GXs in O/W emulsions, in which reduction of

interfacial tension was only 0.4 mN m^{-1} [127]. GAXs obtained from barley straws provided equal average droplet size (diameter 1–3 μm) and 7 day stability in O/W emulsions as corn fiber gum [124].

Hardwood GXs have been shown to work in dispersions via combination of mechanisms that are common to hemicellulose: 1) steric repulsion which is typical for polymeric surfactants, 2) increase in viscosity of continuous phase which prevents dispersion breakdown 3) possibly electrostatic repulsion, as GXs contain ionizable glucuronic and galacturonic acids as substituents. [127] Hence, GAXs are not classical surfactants that work by reducing the surface or interfacial tension, but combination of surfactant, dispersion stabilizers and rheology modifier.

Mannans have been shown to work as emulsifiers, emulsion stabilizers and to extent as rheology modifiers. GGMs are assumed to work as surfactants by increasing viscosity of dispersions, but also by adsorbing to the surface of oil droplets and thus providing steric stabilization. [127] The accumulation of mannans around hydrophobic droplets in O/W emulsions maybe be explained by limited water solubility or by conformational changes of mannans in the solution giving mannans hydrophobic sites that can interact with hydrophobic dispersed phase droplets. [115] The effects of proteins [23], phenolic compounds and other extractives [111] attached to hemicelluloses are also possible factors in the performance of mannans in dispersions [23]. Proteins can work as the hydrophobic anchor of hemicellulose-protein complex, which attach the complex to the surface of the hydrophobic dispersed phase particles.

GGMs overall show only minor changes in surface and interfacial tensions as is typical for polymeric surfactants. Spruce GGMEtOHs decreased the interfacial tension of O/W emulsions by 0.4–1 mN m^{-1} [127]. In another study, spray dried (galacto)glucomannan (GGMSpDr) and GGMEtOH did not show significant reduction in surface tension. GGMSpDr reduced the surface tension of water to 65 mN m^{-1} at concentration of 5 wt%. [113] In another studies of thermomechanical pulp and hot-water extracted GGMSpDrs, the surface tension was reduced to 42 mN m^{-1} and 50 mN m^{-1}, respectively, at 5 wt% concentrations. Spray dried hemicelluloses reduced surface tension more than EtOH-precipitated hemicelluloses. It was suspected that higher amount of hydrophobic extractives and phenolics (impurities) of spray dried hemicelluloses improved their surface activity. [111] It is important to note that to significantly change water's surface tension of 71.1 mN m^{-1} at 25 °C, concentrations of GGMs up to 5 wt% are required.

Overall, the addition of GGMEtOH and GGMSpDr (0.003–0.03 wt%) enhanced the O/W emulsion (0.16 wt% oil) formation and stability compared to other mannans like galactomannan (guar gum) during 14 day test period, at temperatures of 4–25 °C. The optimal concentration of GGM was dependent on the M_w of GGM and botanical origin, and requirements of the O/W emulsion storability. Storage at an elevated temperature (45 °C) caused rapid emulsion breakdown with all mannans. [12]

GGMEtOHs show good O/W emulsion stability over 30 days with O/W ratios of 0.05–0.6, measured by the average particle size increase of the oil droplets and rheological measurements [11]. At low concentrations of oil (0.16 wt%) and GGMs (0.008–0.03 wt%) O/W emulsions stabilized by GGMEtOH had greater turbidity and stability than the GGMSpDr-containing emulsions. As there was no difference in contaminants between the GGMEtOH and GGMSpDr, it was suspected that harsher conditions associated with spray drying than EtOH-precipitation caused the difference in their emulsion stabilizing performance. [12] GGMEtOH and carboxymethylated GGMEtOH (1 wt%) provided better O/W emulsion stability and smaller average particle size than gum arabic or corn fiber gum [11].

As can be seen, the åhysicochemical characteristics and dispersion-related properties of hemicelluloses depend on purity, average molar mass (M_w), degree of polymerization (*DP*) and substituents of hemicelluloses [98], and will be discussed in more detail.

4.2.1   Hemicellulose Purity

While the carbohydrate composition of hemicellulose is determined by botanical origin, purity of hemicelluloses is controlled by extraction technologies of the biomass [111].

The presence of covalently or physically bound proteins are suspected to be responsible for some dispersion stabilizing effect of hemicelluloses [104, 124]. However, there are conflicting results on the role of residual proteins on the surface activity and stability of dispersions when hemicelluloses are used [12, 115]. The protein content is naturally higher in grass- and straw-based lignocellulosic feedstocks, than in softwoods and hardwoods, and thus can affect the amount of proteins in final hemicellulose fractions. GAXs of rice or wheat straws can therefore contain higher amounts of proteins than GGMs of softwoods or GXs of hardwoods.

Residual lignin, phenolics and other extractives can also be advantage in hemicellulose emulsifiers and foam stabilizers [104, 111]. Proteins, phenolics and other extractives bound to hemicelluloses can provide the anchor or hydrophobic character required to adsorb to the surface of oil droplets or other hydrophobic surfaces [111].

4.2.2 Solubility

For hemicellulose to work as emulsifiers and surfactants in dispersion, they must be at least partly soluble in water or oil. Solubility of hemicelluloses is affected by monosaccharide composition, degree of substitution and acetylation, branching and average molar mass. These properties of hemicelluloses are controlled by the choice of feedstock, extraction conditions and possible aftertreatments, such as ultrafiltrations, precipitations or spray drying.

For **xylans** of annual plants and hardwoods, the ratio of arabinose-to-xylose indicate the degree of branching. The water solubility of GAXs increase with increase in arabinose-xylose ratio, which correspond to a higher DS and branching. [122] The formation of extensive hydrogen bonding in GAXs, especially with less branched GAXs, result in partial solubility or even in insolubility of GAXs in water [129].

As for most hemicelluloses, deacetylation of xylans is caused by alkaline extraction conditions [122, 130], while hot-water treatment or steam extraction partially preserve the acetyl functional groups [103]. However, while the degree of acetylation affects the water solubility of xylan, it did not correlate with emulsion performance of GXs (8 wt%) in O/W alkyd resins emulsions [111].

GGMs are soluble in alkaline solutions, while only smalls fractions are soluble in neutral water. [104, 116] It is suspected that differences in solubilities of GGMs of the same botanical origin are caused by the extraction and isolation technologies affecting the structure of GGMs and uncertainties in analytical methods used to characterize GGMs [116].

Solubility of GGMs relate to the amount of galactose and acetyl substituents and overall surface area of the GGM polymer [113]. The degree of acetylation is especially critical for solubility of GGMs, as GGMs will retain their solubility even though galactose substituents, but not acetyl functional groups, are removed from the polymer [116]. Deacetylated GGMs are less water soluble than acetylated GGMs and form more ordered and compact structures [115]. Deacetylation of the GGMs can cause flocculation of the GGMs in water, because of the decreased water solubility [113]. The amount of galactose substituents in GGMs did not affect the emulsion performance in O/W emulsions [115].

Deacetylation of GGMs by alkali extraction conditions [107, 115] occur more readily than in acidic conditions. Alkali (NaOH) concentration above 0.05 wt% is enough to deacetylate GGMs [116]. On the other hand, in the acidic conditions GGMs hydrolyze more readily than in alkaline conditions. Especially the galactose substituents [107, 116], but also

mannose units in the main polymer chain hydrolyze easily in acidic conditions [116] and result in residual monosaccharides.

4.2.3 Molar Mass

It is argued that average molar mass of hemicelluloses is considered to be one of the main properties controlling the dispersing performance of hemicelluloses [111]. For a non-ionic organic polymer to provide emulsion stability via steric repulsions, M_w greater than 10 000 g mol^{-1} is typically required. This is because polymer dimensions are then comparable or greater than range of attractive intermolecular forces between the dispersed phase particles [131]. The typical DP of hemicelluloses is 50–300 [108, 132], corresponding roughly to molar masses of 7 500–50 000 g mol^{-1}.

In alkaline conditions the M_w of **xylans** decrease from 10 000–50 000 g mol^{-1} down to 10 000–20 000 g mol^{-1} [130], with dependence on the alkali concentration. Increase in the alkali concentration decrease the M_w of xylans. [133] However, the extraction conditions, botanical origin, impurities and even analysis technique alter the M_w, meaning that the M_w values should be taken as estimates and rough guidelines.

Unfractionated **GGMs** have M_w = 20 000–78 000 g mol^{-1}, indicating that GGMs have wide molar mass distributions. As for other structural features of GGMs, the biomass feedstock and extraction and isolation technologies strongly affect the M_w. [116]

It is the M_w of GGMs that mainly affect their effectiveness in O/W emulsions [115]. In alkyd resin O/W emulsions, higher M_w of the hemicellulose was one of the properties that improved the O/W emulsion. It was suspected that the higher M_w was required for the hemicellulose polymers to have large enough dimensions to cause steric stabilization between the dispersed phase particles. [111] The GGMEtOH with higher M_w (61 900 g mol^{-1}) was associated more at the O/W interface than the lower M_w GGMs [11]. GGMs with M_w above 30 000 g mol^{-1} were able to stabilize wood resin O/W emulsions [131].

4.3 Chemical Modifications of Hemicellulose for Dispersion Applications

Properties of hemicelluloses for dispersion application can be altered by various chemical modifications [102, 134]. The variation in monosaccharide composition, glycosidic linkages, substituents and abundance of hydroxy functional groups offer possibilities for the chemical modifications [103, 134]. The amorphous character, relatively low M_w and

better water solubility imply that chemical reactivity of hemicelluloses is better compared to other lignocellulosic components, such as cellulose and lignin [132].

Hemicelluloses have been successfully modified for interfacial and dispersion applications by altering their ionizable functional groups (cationic or anionic), solubility in water [102, 109, 132], viscosity and thermal properties [102, 109]. The chemically modified hemicelluloses are also more resistant to microbial and chemical degradations, while providing better emulsifying properties [103]. Examples of the chemical modifications are various esterification, alkylation, crosslinking and grafting reactions [102, 134]. The most relevant chemical modifications for dispersing performance and surface activity of hemicelluloses are introduced in the following subsections, and with different ionizable functional groups (anionic, cationic, nonionic).

Carboxyalkylation and amination are chemical modification that alter hemicelluloses to anionic and cationic polymeric surfactants, respectively. The alkyl polypentosides, made either from D-xylose or different xylans, are a promising alternative to small molecule nonionic surfactants. Alkyl polypentosides allow hemicellulose valorization to wider range of dispersion applications, for example in cosmetics, detergents and food applica-

Table 10. Summary of the discussed chemical reactions to modify hemicelluloses towards dispersion applications.

Modification	Carboxyalkylation	Amination	Alkyl polypentosides
Purpose	Introduce ionizable carboxyl functional groups to hemicelluloses.	Introduce cationic amine functional groups to hemicelluloses.	To transform polymeric xylans or D-xylose to a small molecule nonionic surfactant.
TRL	2-4 for hemicellulose (9 for cellulose)	1-3	6-9 (8-9 for glucose and starch)
Reagents	Chloroacetate	Chlorine- or epoxide-containing amines.	C4-C22 *n*-alcohols
Solvent	Isopropanol, water	Alkaline solution	C4-C22 *n*-alcohols, water
Reaction conditions	25-65 °C 1-5 h	25-75 °C 2-22 h	80-130 °C 1-6 h
Pros	Controllable degree of substitution. Makes hemicellulose anionic and polyelectrolyte. Low reaction temperature. No degradation or changes in molar mass of hemicellulose. No pressure. Reaction known at industrial scale from carboxymethylcellulose production.	Produces cationic surfactant for possibly higher value applications. No degradation or changes in molar mass of hemicellulose. No pressure. Water as a solvent.	Produces small molecule nonionic surfactants. High TRL. Flexibility of raw material (xylan or monosaccharides). No pressure. Alkyl polyglucosides are already a niche surfactant product with established production technologies.
Cons	Long reaction times and poor reactivity (degree of substitution). Isopropanol solvent is required. Chloroacetic acid is hazardous alkylating agent.	Possible long reaction times. Possible low reactivity. Low TRL.	High temperature and reaction time. Different feedstocks can affect the final product quality.

tions, to function as foaming and wetting agents and degreasers. Summary of the different ''modifications'' are presented in Table 10. Once again, it is important to note these are only a few selected, but promising, modification technologies of hemicelluloses.

4.3.1 Carboxyalkylation

Carboxyalkylations are common chemical reactions to modify polysaccharides. The well-known example is carboxymethyl cellulose, which is used a thickener, filler and stabilizer in food and cosmetic products, with E number E 466. Carboxyalkylation introduces anionic carboxyl functional group to natively nonionic hemicelluloses and the modification have been done at laboratory and pilot scales for hemicelluloses, such as xylans and mannans [11, 22, 106, 135].

The most common carboxyalkylation is carboxymethylation (Figure 19). Carboxymethylation introduces carboxymethyl substituents onto the hydroxy groups of hemicelluloses. The reaction is done in alkaline (NaOH) isopropanol or water solvent with sodium monochloroacetate at temperatures of 25–65 °C for 1–5 h. [22, 136, 135] The degree of substitution by carboxymethyl functional groups is 0.25–1.3 [11, 136, 137], depending on the solubility of the hemicellulose in isopropanol or alkaline solution, ratios of xylan, sodium monochloroacetate and NaOH, concentration of NaOH, reaction temperature and time [135]. The dominating positions of substitution are C6 primary hydroxy groups of glucose and mannose units [11, 22], followed by hydroxy groups at C2 and C3 in all hemicelluloses [11, 22, 135]. Monosubstitution by carboxymethyl functional groups was the most dominant form of substitution [22], but disubstitution was also possible depending on the exact reaction conditions [135].

Carboxymethylated GGMEtOH with DS of 0.25 gave stable O/W emulsions at concentration of 3–7 wt%, even after 7 days and at temperatures up to 60 °C. On the other hand, carboxymethylated GGMEtOHs with DS = 0.1 and DS = 0.5–1.5 did not produce stable O/W emulsions. [22] Carboxymethylated GGMEtOH (1 wt%) was found to be comparable emulsifier to unmodified GGMEtOH and better than arabic gum or corn fiber gum in O/W emulsions [11].
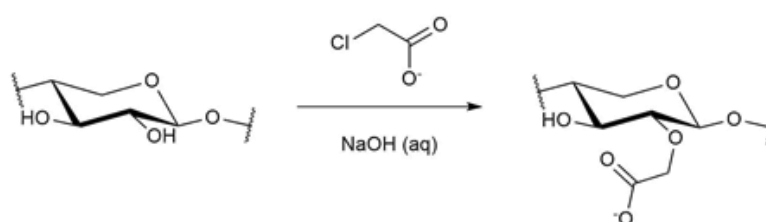

Figure 19. The reaction scheme of carboxymethylation of xylan.

Carboxymethylated GXs reduced interfacial tension by 15 mN m^{-1} compared to unmodified GX [136]. Carboxymethylated GAXs from different feedstocks and with different DS reduced surface tension of water by 15–27 mN m^{-1} as 1 wt% solutions. Furthermore, carboxymethylated GAXs were water-soluble and showed dispersion viscosity of (8–140 mPa s) at concentrations of 5 wt%. [135] The average molar mass of GXs is not significantly affected by carboxymethylation [137].

4.3.2 Amination

In the cationization reactions, positively ionizable functional groups are introduced to the hemicellulose polymers. The most common cationic functional groups in surfactants are nitrogen containing amines and ammonium salts.

Various reagents can be used to functionalize xylans with amine functional groups. While the exact structure of the ammonium-reagent differ, the chemical reactions are similar. The hydroxy functional groups of xylans react as nucleophiles with an epoxide- or a chlorine-containing ammonium reagents [109]. With the epoxide electrophiles, such as glycidyltrimethylammonium chloride [109, 132] or 3-hydroxypropyltrimethylammonium chloride [129, 138], which reacts *in situ* with NaOH to an epoxide structure, the reactions are ring-opening etherifications (Figure 20).

Reactions are done in aqueous solution with NaOH catalyst, at 25–70 °C for 2–22 h [109, 129, 138]. For poorly water soluble GAXs, hot-water pretreatment can improve the swelling and homogeneity of GAXs in the aqueous solution, which facilitate better reactivity
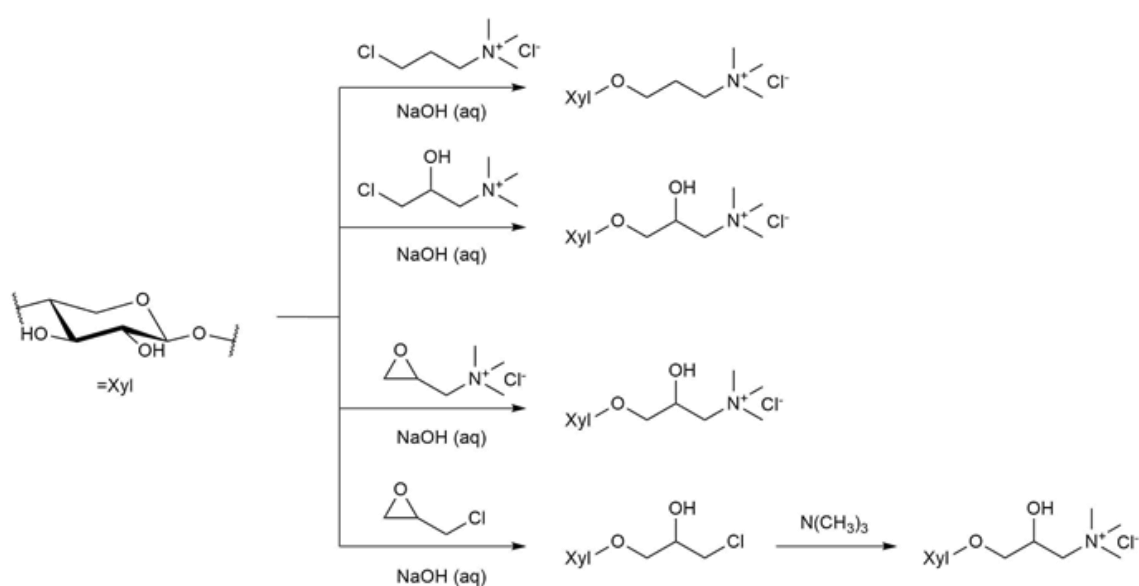

Figure 20. Different amination reactions and reagents to make cationic xylans. Adapted from [132, 138].

[129]. The chemically modified hemicellulose product is often isolated by precipitation with ethanol [132, 138].

Concentrations and ratios of hemicellulose, ammonium reagent and NaOH, the reaction time and reaction temperature affect the degree of substitution (0.19–1.2) and cationic charge of the modified hemicellulose [109, 129, 138]. The botanical origin and corresponding minor differences in the structure of GAXs had no significant influence on the reactivity towards the amination reaction. The amination reaction did not degrade the polymeric structure of xylans [129]. The cationic hemicelluloses have been patented and studied as paper additives [129], paper sizing agents [109, 138] and coagulant aids in water treatment [132].

4.3.3 Alkyl Polypentosides

Alkyl and alkenyl polypentosides (APPs) are a subclass of alkyl polyglycosides (APGs) surfactants, which are non-ionic surfactants used as foaming agents and detergents. While APGs are dominantly alkyl polyglucosides based on D-glucose, the main APPs are alkyl polyxylosides, based on D-xylose. [139, 140, 141] The alkyl polyxylosides are gaining increased interest as surfactants, as a result of the valorization of agricultural residues, such as wheat straws. The availability of high quality and pure non-food hemicelluloses, such as xylans and hydrolysis products of them, have been previously unavailable in significant quantities. [139]

Alkyl polyxylosides can made from D-xylose by glycosylation, using the same reactions as APGs or by catalyzed telomerization of butadiene [139]. While telomerization with butadiene is an attractive reaction to produce alkenyl polyxylosides from xylose, the technique is still is in early laboratory phase and is not considered further here.

The direct and easy route to obtain alkyl polyxyloside surfactants are from D-xylose monosaccharides via glycosidation, similar to APGs. Use of C4-C22 alkyl alcohols and acidic catalyst with xylose results in alkyl polyxylosides, either by direct glycosidation or transglycosidation after use of short chain alkyl alcohols, such as butanol (Figure 21). [140, 142] The Fischer glycosidation is an equilibrium reaction that needs to be thermodynamically driven with excess of aglycone (alcohol), while controlling the reaction temperature to avoid degradation of sugars. The Fischer glycosidation is applied at an industrial scale to glucose, but also in a lesser extent to xylose. Furthermore, the reaction remains more productive than enzymatic processes to obtain APGs and APPs. [139]
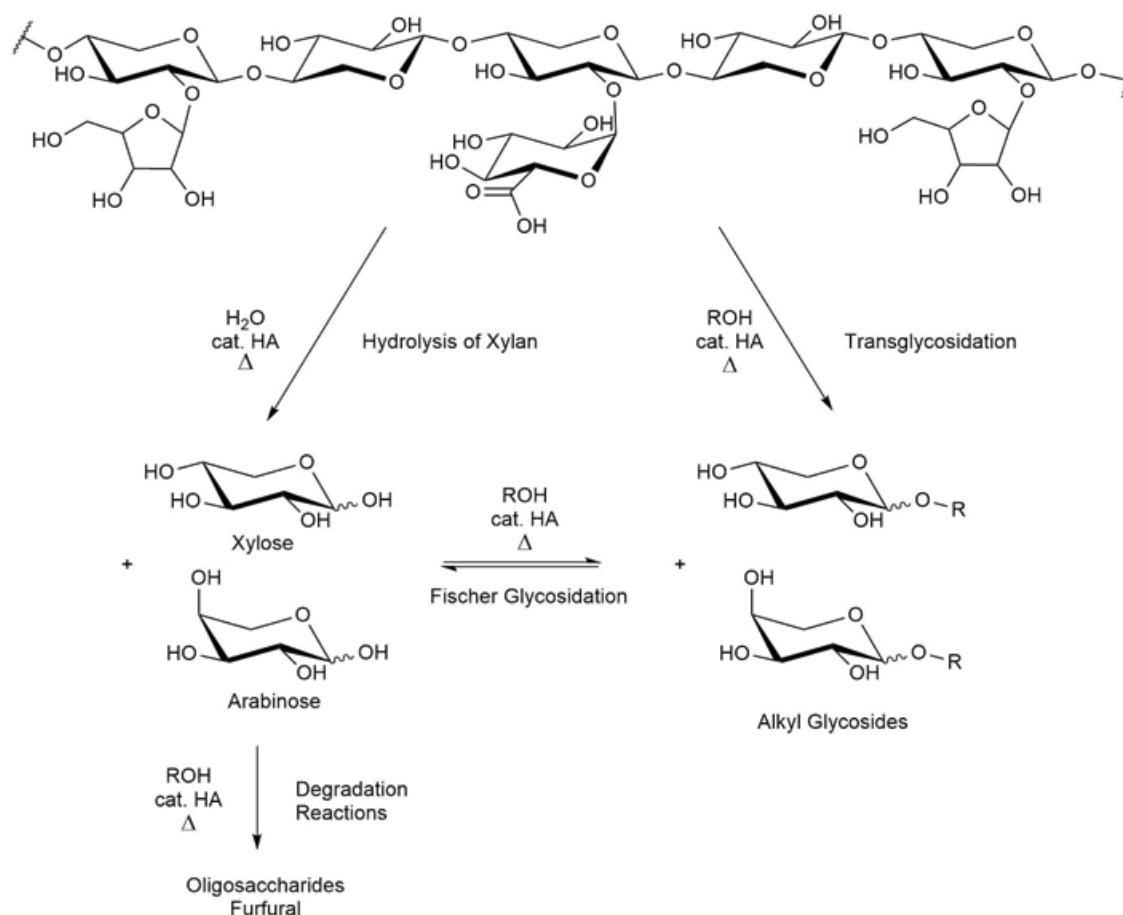
Figure 21. Reaction schemes of alkyl polypentosides from xylan. Polymeric xylan can be directly converted to different glycosides (transglycosidation) or via hydrolysis to monosaccharides and subsequent Fischer glycosidation. R = long alkyl or alkenyl chain, HA = acid catalyst. Adapted from [143].

Pentoses (xylose) and hexoses (glucose) have different reactivity in alkyl polyglycoside reactions. Pentoses are more reactive towards glycosidation and require lower temperatures than glucose. [108, 139] Preparation of alkyl polyglucosides are done at temperatures of 100–150 °C [139, 140], while APPs can be done in milder conditions (80 °C), which reduce degradation of sugars [108, 139] and staining of the final product [140]. Therefore, it is possible to obtain higher quality surfactants in a more cost-effective manner from xylose than glucose. Furthermore, it is easier to control *DP* of alkyl polyxylosides than *DP* of alkyl polyglucosides [108, 139]. This is an important characteristic when applications of APGs are considered, as the *DP* affects the electrolyte stability, surface activity and foaming behavior of APGs [108].

Use of xylose for a surfactant production require an effective hydrolysis of hemicelluloses from biomass to monosaccharides, and isolation and purification of the resulting monosaccharides. Therefore, there is an interest in using low cost materials, such as starch and polymeric xylans that are rich in xyloses, but in still polymeric form, to produce APPs. It would ideal to produce APPs with directly from the corresponding polymers (xylan) by

transglycosidation reactions (Figure 21), with reduction in production costs and steps. [139, 143]

Wheat bran containing 13–25 wt% of xylan has been used directly to convert xylan to alkyl polyxylosides with decanol or hexadecanol and an acid catalyst, at 90–130 °C and reaction times of 1–5 hours [99, 143]. Similar reactions as above have been done with oat spelt xylan (containing 53 wt% of D-xylose) and butanol, octanol or decanol [144], hardwood beech xylan (60 wt% of D-xylose) with decanol [141] and wheat straw with decanol [101] and hexadecanol [99]. With the increase in *n*-alcohol chain length, the required reaction temperatures and times increased [99, 144]. A small amount of water is required for production of alkyl xylosides from polymeric xylan materials to facilitate an effective rate limiting hydrolysis reaction of the polymeric xylan [101, 144].

Decyl xylosides showed similar critical micelle concentration and surface tension, increased foaming ability [144, 143] and wetting time compared to decyl xylosides obtained from pure D-xylose [101, 143]. All these results were obtained even though the APPs obtained from polymeric xylans had less pure starting materials, contained more impurities and mixture of xylosides, arabinosides and glucosides than alkyl xylosides made from pure D-xylose sources [99, 101, 144].

GAXs of different botanical origin and extraction technology show different reactivity towards the APP reaction. The botanical origin influences the details of monosaccharide composition (xylose, arabinose and glucose), amounts of substituents (uronic acids and acetyl groups) and ash, which can affect the reactivity of GAXs toward APP formation. [141] An increased amount of arabinose substituents make GAXs more soluble in *n*-alcohols and the arabinose substituents are also readily glycosylated, thus allowing better glycosylation of GAXs under milder conditions. The rate of different alkyl glycoside formation from GAXs is in a decreasing order: alkyl arabinosides > alkyl xylosides ≈ alkyl glucosides [99, 101, 141]. On the other hand, increased glucuronic acid content makes GAXs more resistant to mild acid hydrolysis. For above mentioned reasons, hardwood GXs with higher glucuronic acid and lower arabinose substituents require higher temperatures to gain similar yields than non-wood GAXs. However, the formed APP surfactants from different xylans are equal in terms of their surfactant properties (critical micelle concentration, foaming and reduction in the surface tension). [141] The hydrophobic chain length of alkyl polyxyloside also affects the emulsifying properties (stability and foaming). An increase in the chain length seems more favorable for emulsions and the optimal chain length was found to be 10 carbons (decyl xylosides). [100]
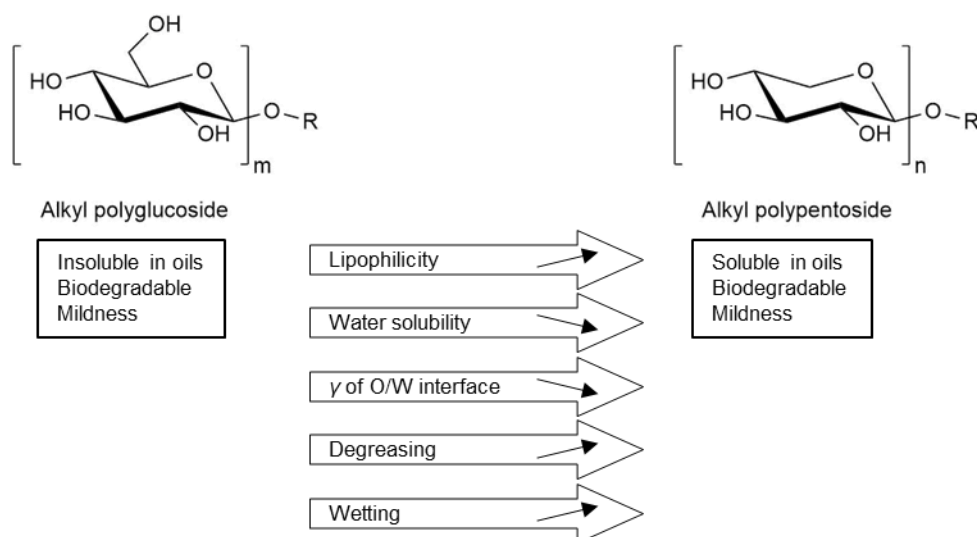
Figure 22. Comparison of dispersion-related properties of the alkyl polyglucosides and alkyl polypentosides. Adapted from [139].

Despite the similarities of alkyl polyglucosides and alkyl polyxylosides as non-ionic surfactants, there are difference in their properties (Figure 22). Alkyl polyxylosides are more lipophilic than alkyl polyglucosides, which result in lower critical micelle concentration. [108, 139] Furthermore, in applications where the oil solubility of the surfactant is important, alkyl polyxylosides are superior to alkyl polyglucosides because of increased lipophilicity. Commercial alkyl polyxylosides also show good wetting power and degreasing ability when compared to alkyl polyglucosides and alcohol ethoxylate surfactants. [139] Furthermore, APPs obtained directly from wheat bran GAXs showed better wetting than APGs [101, 143].

Alkyl polyxylosides are not considered acutely toxic or harmful and can therefore be used in agrochemicals, laundry detergents, cosmetics and cleaning products, with comparable biodegradability to conventional surfactants. [108]

4.4 Potential Applications of Hemicelluloses in Dispersions

Non-food hemicelluloses as dispersants, emulsifiers and stabilizers in technical applications have not been fully commercialized. Overall, only few products based on xylans (alkyl polyxylosides) have been commercialized [103]. However, many food-based or gum-type hydrocolloids such as galactomannans, konjac glucomannan and tamarind xyloglucan are commercially utilized in foods and cosmetics [104].

The current status of hemicellulose commercialization and utilization is assumed to change for a few reasons. First, there is an increased knowledge and (economical) motivation to create biopolymer-based materials and surfactants. Secondly, the availability of non-food hemicelluloses is increasing steadily as increased valorization of the non-

food biomass and development of the biorefinery concepts. There is commercial and an economical interest and demand to make valuable products of all the components of lignocellulose and not just cellulose. [103] Thirdly, the use of the non-food hemicelluloses, such as xylans from hardwoods and annual plants and GGMs from softwoods, do not compete with food production like some other commercially used polysaccharides, such as starch [141, 143].

The following subsections further discuss those applications for which different xylans and wood-based GGMs are considered promising in light of existing patents. Food hydrocolloids and thickeners are not discussed here, as they are out of the scope of this thesis.

4.4.1 Paper Sizing Formulations

Hemicelluloses have potential in dispersions of sizing agents, which are used in the papermaking and the textile production. Common sizing agents used in paper making are alkyl ketene dimers and alkenyl succinic anhydride, which improve the glaze, printing and other surface properties of papers. Sizing agents are introduced to papers as aqueous dispersions, and therefore dispersion stabilizers are required. Depending on the temperature, sizing agents can form emulsions or suspensions. Cationic starch and guar gum (galactomannan) are commonly used stabilizers for dispersions of sizing agents and as surface sizing agents themselves. However, both polysaccharides are source of nutrition and therefore non-food hemicelluloses, like GAXs or arabinogalactan has been considered as alternatives. [109]

Ammonium cationized xylan and arabinogalactan as stabilizing agents in sizing formulations have a granted patent, assigned in 2018. A decreased water adsorption of paper and reduced concentration of dispersion stabilizer in sizing formulations are advantages of cationic xylans and arabinogalactans over cationic starch. [109]

4.4.2 Films and Coatings

Hemicelluloses are a potential raw material for films used for example in food and cosmetics packaging and biomedical films. Hemicelluloses are mostly researched as the main material in the packaging films, but the same physicochemical properties of hemi-

Table 11. Water vapor permeability (WVP) and water vapor transfer rate (WVTR) of films produced from different synthetic and bio-based materials. Adapted from [134].

Material	WVP	WVTR
Units	10^{-11}	10^{-3}
	$g \, m^{-1} \, Pa^{-1} \, s^{-1}$	$g \, m^{-2} \, s^{-1}$
Low-density Polyethene (LDPE)	0.2	6.2
Poly(ethylene terephthalate) (PET)	0.28	0.04
Polystyrene (PS)	0.42	0.06
Poly(lactic acid) (PLA)	1.34	0.18
Hydroxypropyl methylcellulose (HPMC)	10.0	-
Cellophane	6.9	6.2
Amylose	120	-
Amylopectin	115	-
Different Xylans (GAXs)	2.3–21	1.5–9.3

celluloses are important as for dispersion- and surfactant-related applications of hemi-celluloses. The water solubility and hydrophilicity of hemicelluloses and the chemical modifications to alter these properties are important, whether the application of hemicellulose is films, surfactants or texture modifiers.

Required properties of flexible packaging films are low oxygen or water permeability, mechanical strength and flexibility. In the food packaging applications it is also desired that films are transparent and of low cost. [134, 145] While mechanical strength and flexibility are required, the water- and oxygen permeability of hemicellulose films is the biggest hurdle currently (Table 11). The oxygen-barrier properties of hemicellulose films are favorably comparable to poly(vinyl alcohol), poly(lactic acid) and poly(hydroxyalkanoate) films and packaging materials. [134] Hemicelluloses with higher molar masses are more suitable to produce films with desired properties. However, with increase in molar mass of hemicellulose, the handling of increasingly viscous hemicellulose solutions and production of films become increasingly difficult. The oxygen barrier films made from xylans with molar masses of 8 000–50 000 g mol^{-1}, mixed with plasticizer, cellulose or poly(vinyl alcohol) oligomers have been patented. [145]

Films and coatings produced from different GAXs, using mainly glycerol as a plasticizer, have higher water vapor permeabilities and transfer rates compared to the commercial petroleum-based plastics, such as poly(ethylene terephthalates). Chemical modifications or addition of hydrophobic compounds via mixing or emulsifications are ways to decrease the hydroscopicity of GAX films. On the other hand, compared to other bio-based derivatives, such as cellulose and starch derivatives (amylose and amylopectin), films made from GAXs have comparable or decreased water vapor permeability (Table 11). [134]

In a different approach to produce hemicellulos films, water-soluble films made from xylans have been patented. Composition includes hydroxyalkylated xylan, glycerol as a plasticizer and water as a solvent. The solution is cast on a synthetic polymer web, for example polypropene, at which the film is dried on and subsequently separated from. Potential applications are heat sealable packages and water-soluble detergent, food and pharmaceutical films. [146]

4.4.3   Primer Compositions and Alkyd Resins

Primer compositions are used to precoat or undercoat for example paper before liquid toner can be applied via laser printing [102]. Also in various other applications primer compositions are used to precoat surfaces like plastics and woods to ensure better adhesion of a paint and increase durability of the paint, and to provide additional protection. Xylans have been used in water-based primer compositions containing mainly dispersed silica, starch and xylan varnish. Most preferably GAX is used in amounts of 4 wt%. Other hemicelluloses, such as mannans, are also possible in the primer dispersions. [102]

Alkyd resins are polyesters made by a condensation polymerization of polyols, fatty acids or triglycerides and polyprotic acids. They are viscous and tacky materials which make them difficult to handle as such. Emulsification of the alkyd resins in water solutions facilitate their handling and use as coatings or paints. [111]

Ethanol-precipitated hemicellulose and hemicelluloses as such have been researched as emulsifiers in alkyd resin W/O emulsions. Only whole fraction GX, high molar mass part of GX and GGMEtOH were able to function as alkyd resin (40 wt%) emulsifiers (8 wt%). The low and medium molar mass part of GX and GGM did not form emulsions as the alkyd resins and hemicellulose solutions separated into liquid and semi-solid phases. The main properties that governed the emulsifier performance were combination of high M_w of hemicellulose and some impurities or extractives, such as phenolics in the hemicellulose. [111]

4.4.4   Wood Resin Emulsions

Wood resin is a term used for lipophilic extractives that occur in pulp and paper processes [131]. Stability of the wood resin emulsion is an essential part of the pulp and paper making processes, as collapse of the wood resin emulsion causes pitch and deposit problems on the processing equipment [116]. Components of the wood resin are fatty acids and triglycerides.

GGMs are able to stabilize wood resin emulsions against NaCl and CaCl$_2$-induced aggregation, while lowering the agglomeration of wood resin droplets, at GGM-to-resin weight ratios of 0.7–1.1 [116, 131]. Deacetylated GGM (60 °C, pH 11, 1 h, dialyzed M_w = 12 000–14 000 g mol^{-1} [115]) is not able to stabilize wood-resin emulsion [115] or W/O emulsions [22]. It was suspected that deacetylated GGM cannot accumulate around wood resin droplets or cannot extend far enough into the solution when adsorbed to the surfaces of the resin droplets, and therefore cannot cause adequate steric repulsion. [115] However, there are conflicting results of deacetylated GGMs being able to stabilize wood resin emulsion as well as acetylated GGM, indicating that interfacial phenomena of wood resin emulsions and polysaccharides are complex [131]. Proteins [115, 131], lignin-carbohydrate complexes, residual poly(galacturonic acids) (pectins) and effect of bleaching are few of the phenomena which can affect wood resin emulsions [131].

GAXs are able to stabilize wood resin O/W emulsion more effectively than guar gum (galactomannan). Even at 5 parts per million concentrations xylans were able to stabilize wood resin emulsions completely. [115]

4.4.5 Other Proven Applications

Most commonly non-wood based polysaccharides and hemicelluloses (gums) are used in food applications to provide texture, viscosity, dispersion stability and other rheological properties for the food products.

In cosmetics, utilization of wood-based hemicelluloses, such as GAXs or GGMs is still scarce. One main reason has been lack of good quality and pure hemicelluloses from softwood and hardwood feedstocks. However, there are some examples in using (hydrolyzed) xylans obtained from hardwoods in cosmetic products as ''moisturizing the skin and preserving the barrier function'' [147].

Monosaccharide xylose and its hemicellulose precursor, xylan, have gained interest in production of various APP surfactants. Similar technologies as in existing large scale and optimized production of APGs can be used to produce APPs. Various APG and APP surfactants with long hydrophobic alkyl parts can be used as foam boosters in cosmetics, skin-care products and shampoos, as degreasing agents in detergents [141, 144] and as wetting agents in paper impregnation resins [148]. APGs and APPs are a potential substituent for widely used nonionic ethoxylate alcohol surfactants [99].

5. APPLIED PART

The applied part of the thesis aimed to increase the knowledge of the new type lignin-based dispersants and give background information for the development of Fortum's lignins as dispersants in paint, coating, ink, plastic and other dispersion-related applications. Lignins were alkali-O_2 oxidized (LigniOx) organosolv and soda lignins and they were evaluated as dispersants in special carbon black (CB) and titan dioxide (TiO_2) pastes. The lignins were property of Fortum and the alkali-O_2 oxidation technology (LigniOx) is property of VTT Technical Research Centre of Finland.

Some of the materials were provided specifically for this thesis by different companies. LignoStar Group BV, Altana Group and Penta Carbon GmbH are acknowledged for their contributions.

5.1 Materials and Methods

The materials, instrumentation and measurements are described in this Chapter. Materials include carbon black and titan dioxide used to prepare the pigment suspensions (pastes). The studied dispersants are alkali-O_2 oxidized lignins and commercial references. The methods to prepare the samples and instrumentation for the rheological and optical microscope measurements are also introduced.

5.1.1 Materials

The overview of the materials used in this thesis are presented in Table 12. The carbon black (CB) and titan dioxide (TiO_2) are used to prepare the aqueous CB- and TiO_2-suspensions, respectively.

Special carbon blacks are utilized in various applications, such as inks, plastics and coatings, as a coloring, ultraviolet-protection and conductivity agent. The CB used in this thesis is a powder special carbon black with the brand name P-200Z, by Penta Carbon GmbH. [149] Some of the technical specifications of the P-200Z are presented in Table 13.

Titan dioxide is used as white pigment in white paints but also in colored paints due to the excellent opaqueness TiO_2 provides. Moreover, TiO_2 is found in different forms in plastics, paper, inks, cosmetics, pharmaceuticals, foods and cosmetics. The TiO_2 used

Table 12. Overview of the materials used in the applied part. The A and B indicate the fractionation process to produce the lignin and ''b'' = birch and ''s'' = straw indicate the botanical origin. All the new lignin-based dispersants were concentrates, with lignin contents of 10–15 %.

Material	Type	Use
Penta Carbon P-200Z	Powder Special Carbon Black	Main material in the pigment suspensions
Uula Titan Dioxide 104	Powder Titan Dioxide	Main material in the pigment suspensions
Disperbyk-190	Block co-polymer	Reference dispersant
Vanillex N	Sodium lignosulfonate	Reference dispersant
JH101-Bb	Alkali-O_2 oxidized soda-wheat straw lignin concentrate	New lignin-based dispersant
JH104-Bs	Alkali-O_2 oxidized soda-birch lignin concentrate	New lignin-based dispersant
JH111-As	Alkali-O_2 oxidized organosolv-wheat straw lignin concentrate	New lignin-based dispersant
JH113-Ab	Alkali-O_2 oxidized organosolv-birch lignin concentrate	New lignin-based dispersant

in this thesis is a pigment-grade titan dioxide-104 by Uula Color Oy. The published properties of TiO_2 are presented in Table 13.

The commercial polymeric dispersants used in this thesis as references are partly desulfonated sodium lignosulfonate (Vanillex N) and synthetic ''high molecular weight block copolymer with pigment affinic groups'' (Disperbyk-190). The technical specifications of these references are presented in Table 14.

Table 13. Relevant technical specification of studied carbon black (P-200Z) and titan dioxide (Uula 104 TiO_2 Pigment). DBP = dibutyl phthalate, BET = Brunauer-Emmett-Teller. ASTM D standards are for the carbon black P-200Z.

	Standard	P-200Z	TiO_2
Manufacturer		Penta GmbH	Uula Color Oy
Type		Powder	Powder
Density (kg dm^{-3})			1-1.5
DBP absorption number (0.01 cm^3 g^{-1})	ASTM D 2414; -	116±5	
Relative Tint Strength (%)	ASTM D 3265; -	116±5 %ITRB	
pH-value	ASTM D 1512; -	6–10	6–8.5
Iodine absorption number (g kg^{-1})	ASTM D 1510; -	121±5	
Ash content (%)	ASTM D 1506; -	0.45	

Table 14. Commercial reference dispersants.

	Disperbyk-190	Vanillex N
Manufacturer	Altana Group	Nippon Paper Group
Type	Synthetic block copolymer	Purified, partly de-sulfonated sodium lignosulfonate
Phase	Viscous aqueous liquid	Water-soluble solid
Dry Matter (%)	40	> 95
Density (kg m^{-3}, 20°C)	1060	700
pH (5 % solution)	-	7.5–8.5
Mineral ashes (%)	-	22
Sodium (%)	-	10
Inorganic salts (%)	-	9
Weight average molar mass (10^3 g mol^{-1})	-	2–10
Sugar derivatives (%)	-	8
Acid value (mg KOH g^{-1})	10	-

The technical lignins used in this thesis are manufactured by pilot and demonstration scale processes. The technical lignins are named by their manufacturing process as **A** and **B**. The **A** process is a organosolv process which uses mixture of organic acids and water. The lignin is separated by solvent evaporation and pH adjustment from the black liquor. On the other hand, the **B** process is a modified soda process in which hemicelluloses are hot-water extracted before the pulping process. The lignin is precipitated from the black liquor with pH adjustment. Both A and B lignins are obtained from two feedstocks: birch and wheat straw.

Both the A and B lignin are soluble in water at pH ~10. They must be chemically modified to increase their water solubility at lower pH and to produce high-performing dispersants for aqueous dispersions. The LigniOx technology, an alkali-oxygen oxidation, is developed and patented by VTT Technical Research Centre of Finland Ltd [57, 58]. The oxidation alters the average molar mass, dispersity and amount of ionizable functional groups of the lignin, depending on the amount of oxygen, NaOH, pH, reaction time and pressure. The oxidized A and B lignins are concentrates (Table 12), received and used as such in the dispersion tests. The concentrates are brown thick solutions and contain 10–15 wt% of lignin according to the ultraviolet measurements at wavelength of 280 nm.

5.1.2 Methods

The experimental part of the thesis was done at VTT Technical Research Centre of Finland, in the rheology laboratory in Espoo, Finland. The work included preparation of the

CB and TiO$_2$ pastes and their rheological measurements. The pigment pastes were also characterized by optical microscopy.

Figure 23. The equipment used for mixing of suspensions and rheometer. Left: Omni Mixer Sorvall, middle: Heidolph Diax 600, right: Texas Instruments AR-G2 rheometer.

The CB pastes were prepared from Penta Carbon P-200Z. The concentration of CB was 15 wt% in the pastes, which was chosen based on the earlier studies of LigniOx dispersants [97]. 5–30 wt% of CB is the typical concentration for CB in aqueous suspensions [66]. Estimates of required dispersants doses were done based on the earlier studies of LigniOx dispersants with different CBs. For the reference, the required dispersant demand can be estimated from the surface area of the pigments. Dibutyl phthalate value (DBP) or Brunauer-Emmett-Teller (BET) value are typically used techniques to measure the surface area of pigment particles. [150]

The procedure used to **prepare the carbon black suspensions** (overall 20 g) is presented below:

1. Weighted required amount of distilled water into the mixing container

2. Added 15 % CB (3 g) into the water in 3 portions, with shake between each addition

3. Added dispersant solution to final weight of 20 g of suspension

4. Shook and left the mixture wet for 15 minutes under parafilm

5. Mixed with Heidolp Diax 600 Laboratory Stirrer for 2 minutes

6. Mixed with OCI Instruments Omni Mixer Sorvall for 3 minutes

7. Suspension/paste was left to cool down for 10–30 minutes in a closed container before rheological measurements and optical microscopy analysis

The TiO$_2$ suspensions were prepared from the TiO$_2$-104 powder by Uula Oy. The concentration of 75 wt% TiO$_2$ was chosen based on the earlier work done at VTT. The concentrations of dispersant for inorganic pigments, such as TiO$_2$, are usually lower than for CBs [150], in range of 0.1–2.0 % dispersant active matter of TiO$_2$ weight.

The procedure used to prepare the TiO$_2$ suspensions (overall 20 g) is presented below:

1. Weighted calculate amount of distilled water into the mixing container

2. Added required amount of dispersant solution

3. Added 75 % TiO$_2$ (15 g) into the water/dispersant solution in 3 portions, with shake between each addition and making sure the TiO$_2$ is not floating on the top of the mixture

4. Shook and left the mixture wet for 15 minutes under parafilm

5. Mixed with OCI Instruments Omni Mixer Sorvall for 2 minutes

6. Suspension/paste was left to cool down for 10–30 minutes in a closed container before rheological measurements and optical microscopy analysis

The rheological measurements were done to evaluate the flow properties of the CB and TiO$_2$ suspensions with different dispersants and doses. The rheometer was AR-G2 rheometer by Texas Instruments (Figure 23). The measurements were conducted with a Peliter plate steel cone geometry (40 mm diameter and 2.0° angle). For pourable suspensions the amount of paste for the rheological measurements was 600 µl. For non-pourable pastes, the amount of paste was estimated so that the paste spread to cover the surface area of the rheometer head.

The rheological measurement procedure was a logarithmic sweep, with 1 minute soak time, shear rate between 6–600 s^{-1}, 5 points per decade and averaging time of 30 s at each measured shear rate. CB and TiO$_2$ suspensions were measured similarly, except for TiO$_2$ pastes, the edges of the paste on the rheometer plate were covered with small layer of silicone oil (1 Pa s) to avoid drying of the paste during the measurement. The rheological measurements were done at 25 °C.

Each paste was measured twice, except in the cases were the paste was clearly unstable (measured only once) or the two first measurements showed clear variance, in which case a third measurement was made. Each paste was measured right after preparation (day 0) and after 7 days, while storing the paste in a closed container. Before the day 7 measurements, the pastes were mixed by hand.

The optical microscopy samples were prepared by diluting the original suspensions. First, about 100 µl of suspensions was diluted in 900 µl of water. Secondly, from this 1:10 dilution, 200 µl sample was diluted in 800 µl of water, giving a total dilution of 1:50. Small drop of the diluted sample was placed between the glass plates and sealed with varnish to avoid drying of the sample. The optical microscope was Zeiss Axio Imager M2.

5.2 Results and Discussion

This chapter presents the observations and results obtained during the sample preparations, rheological measurements and optical microscopy analysis of CB and TiO_2 pastes.

5.2.1 Carbon Black Pastes

Viscosity of pigment dispersions is often measured as a function of stress, shear rate and dispersant concentration (dose) [151]. To find the optimum dispersant concentration for the specific pigment, a ladder study was performed [150]. Three-to-four doses of dispersant was estimated for each dispersant to see if the L-shaped viscosity curve could be achieved (Figure 24).

Firstly, the required doses of dispersants were typical for aqueous CB suspensions. Special CBs require high doses of dispersants and the exact amount depends on the specific application. The typical doses are 5–50 wt% active matter of dispersant of CB weight [152]. Secondly, the L-shaped curves were incomplete, indicating that even higher doses (+30 wt% of CB) are required to confirm the optimum doses. Thirdly, while the minimum
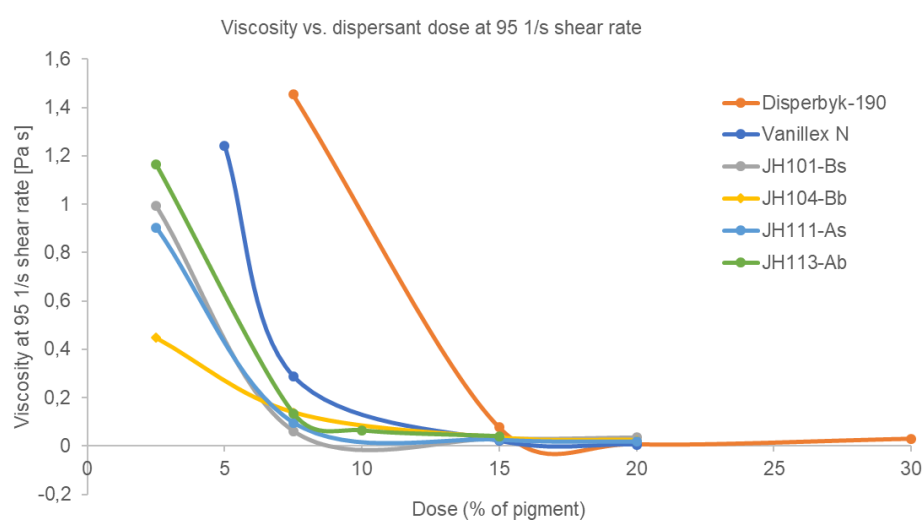

Figure 24. Viscosity (Pa s) vs. dispersant dose (wt% of pigment) at 95 1/s shear rate in 15 % carbon black suspensions.
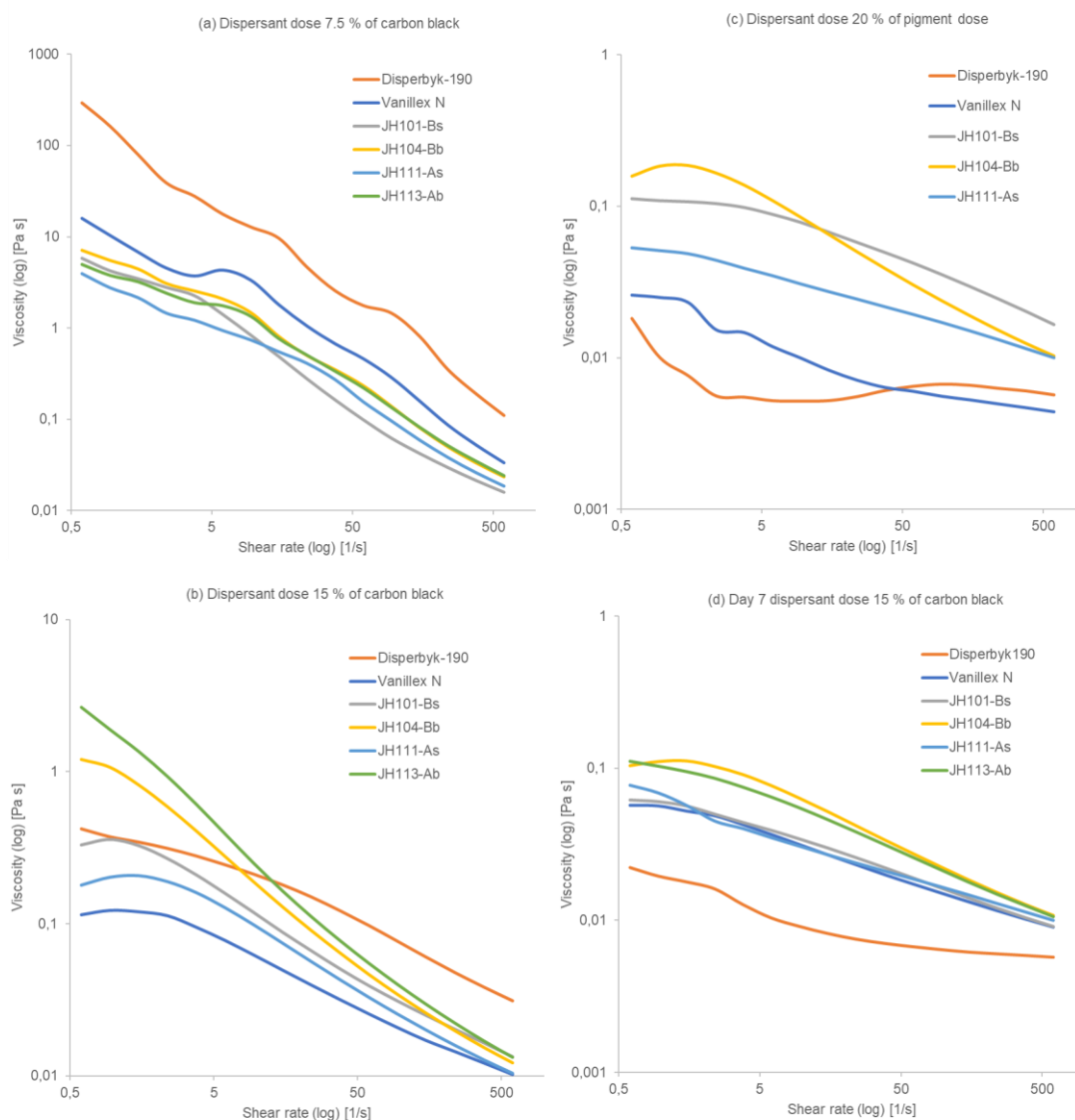
Figure 25. Viscosity (Pa s) vs. shear rate (1/s) at different doses of dispersant (active matter wt% of carbon black). (a) 7.5 wt%, (b) 15 wt%, (c) 20 wt%, (d) 15 wt% at day 7. The scales are logarithmic.

dispersant dose in final application is desirable from the economic perspective, the optimum dose of dispersant depends also on the type of the dispersant and other properties of the suspension [150]. Dispersant affects for example the pigment color, gloss and storage stability, which are important properties in the final product and also determine the optimum dose of dispersant.

The JH104-Bb, JH101-Bs, JH111-As and JH113-Ab oxidized lignins had lower optimum doses of dispersant compared to reference dispersants. However, the viscosities were quite similar for all dispersants at their respective optimum doses (7.5–15 wt% of CB for lignins) and (+15 wt% of CB for references). Viscosities of 0.01 Pa S at a shear rate of 95 1/s were achieved for all the dispersants at their respective optimum doses.

Viscosity vs. shear rate at different doses of dispersant are presented in Figure 25. Overall, all the CB dispersions showed (slight) shear thinning behavior. Newtonian behavior was observed at small shear rates for specific doses of dispersant. Similar rheological behavior has been observed for CB suspensions with ~8500 g mol^{-1} polyacrylate dispersant [151]. Moreover, the LigniOx oxidized kraft lignins show shear thinning behavior at doses of 0.75 wt% of CB, in 10 % CB suspensions [97].

With low doses of dispersants (below 7.5 wt% of CB), the viscosities were high, especially at low shear rates (Figure 25 (a)). The suspensions were more viscous and showed heterogeneity after the rheological measurements, when the dispersant dose was too low (Appendix B, Figure 34 (a) and (d)). The average particle size of CB was also larger in the optical microscope images when the dispersant dose of lignin dispersants is 2.5 wt% of CB (Figure 26). Larger agglomerates of carbon black indicate that the amount of dispersant is insufficient.

The viscosities measured at day 7 were equal or lower than at day 0 for nearly all dispersants when the CB suspensions were pourable, wet and liquid-like (Figure 25 (d) and Appendix A, Figure 32). The lower viscosity at day 7 can be a result of sedimentation, which decreases the CB amount in the actual suspension. The light remixing without high energy mixers is probably not enough to completely disperse the CB particles after 7 days of storage.
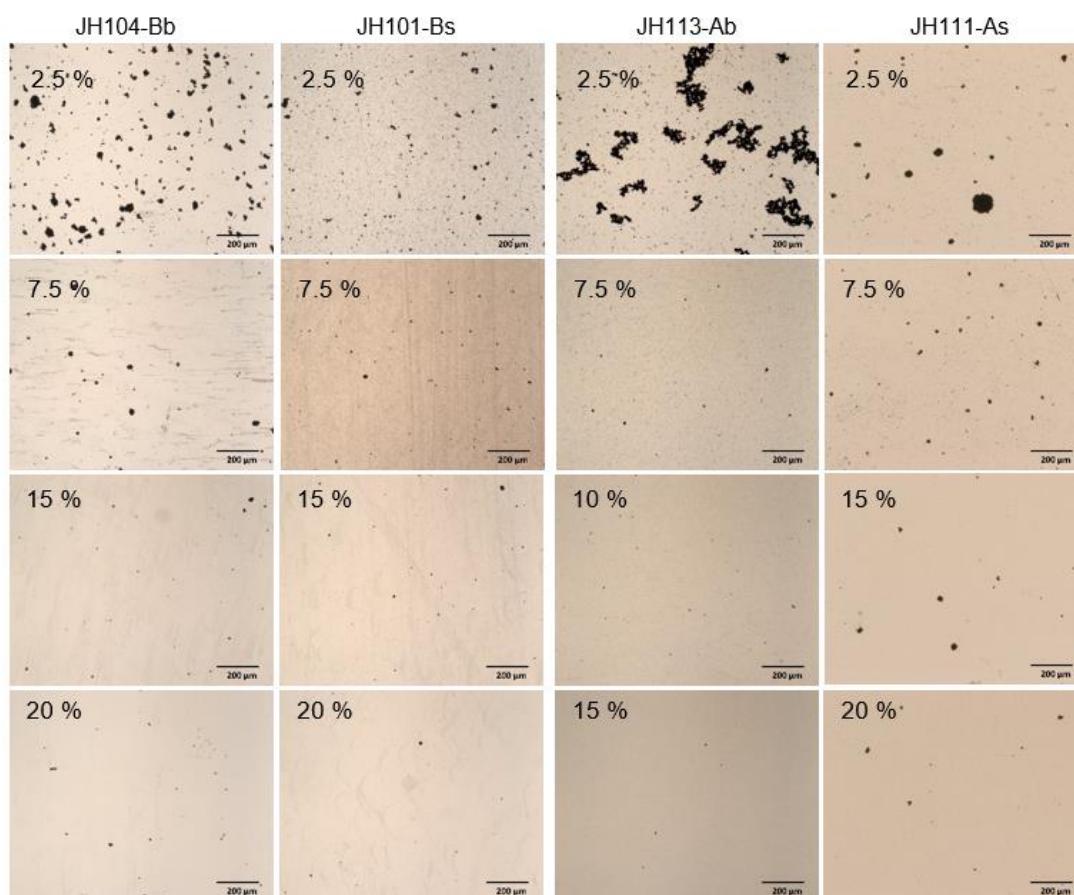
Figure 26. Optical microscopy images of carbon black suspensions with different doses of lignin dispersants. In all images, the black scale bar is 200 µm. The suspensions with lignin dispersant doses of 2.5 % show large agglomerates of carbon black.

The optical microscopy images were taken to see if there is relation between the high viscosity and particle size of CB particles. The optical microscopy images had no greater differences except at low dispersant doses (2.5 wt% for lignins). At these low dispersant doses the average CB particle sizes were larger than at more optimal dispersant doses of 7.5–20 wt% of CB (Figure 26 and Appendix A, Figure 31). Furthermore, the shape of the CB particles with JH113-Ab dispersant was different compared to the other dispersants. The suspensions with higher particle sizes were more uneven and thicker in their appearance (Appendix B, Figure 34). The effect of diluting the CB suspensions (1:50) for the optical microscopy study is unknown and requires further studies.

5.2.2 Titan Dioxide Pastes

For the 75 % TiO_2 suspensions, the viscosity vs. dispersant dose (of pigment) at shear rate of 95 1/s is presented in Figure 27. The L-shaped curves are visible for all dispersants, except for Disperbyk-190. The suspension with 0.25 wt% Disperbyk-190 of TiO_2 was done, but the suspension was unmixable and dry, and the rheological measurement could not be done.

Lignin dispersants had lower optimum doses than the reference dispersants (Figure 27). The optimum dose of lignin dispersants was around 0.15–0.3 wt% lignin of TiO_2 and there was no clear difference between types of lignins. These doses are within the lower range (0.01–3 wt%) of typical dispersant amount used in TiO_2 suspensions [150]. The lignin dispersants showed the greatest differences at dispersant doses of 0.05 wt% of TiO_2, but these differences are likely insignificant. The 0.05 wt% dose was below the optimum dose and the suspensions with this dose were dry, thick and unstable (Appendix B, Figure 33) For the reference dispersants (Vanillex N and Disperbyk-190), the optimum doses of dispersant were +0.6 wt% of TiO_2, which is higher than for oxidized lignins, but still within the typical doses used for TiO_2 pastes (Figure 27).
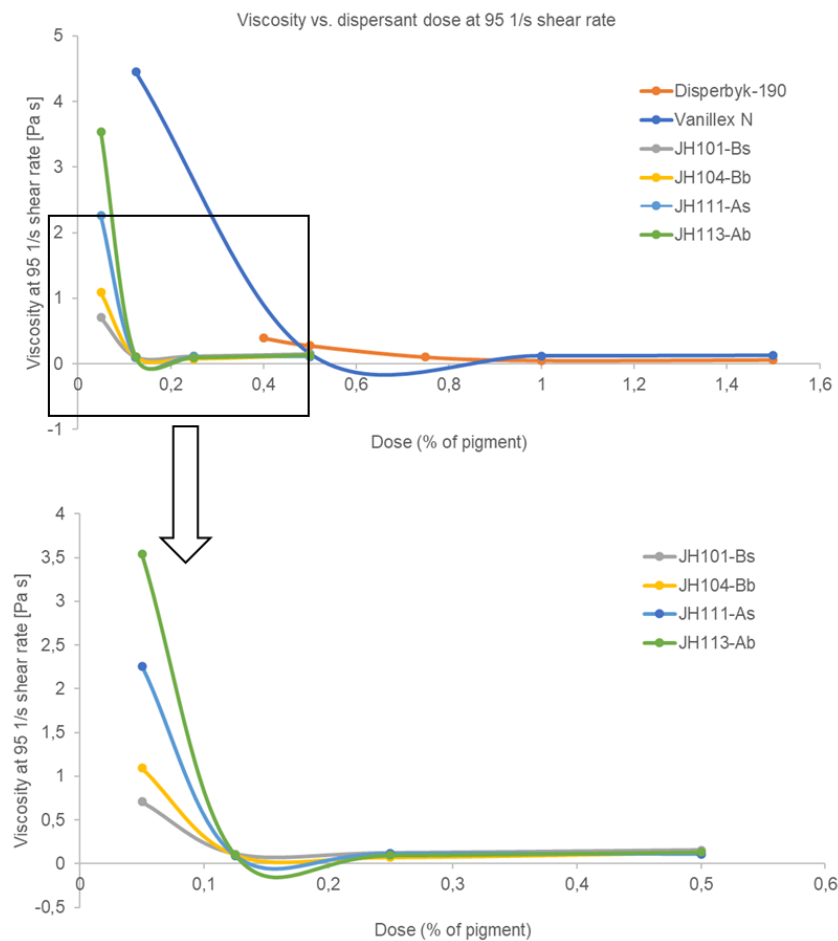

Figure 27. Viscosity (Pa s) vs. dispersant dose (wt% of pigment) at 95 1/s shear rate in 75 % TiO_2 suspension.
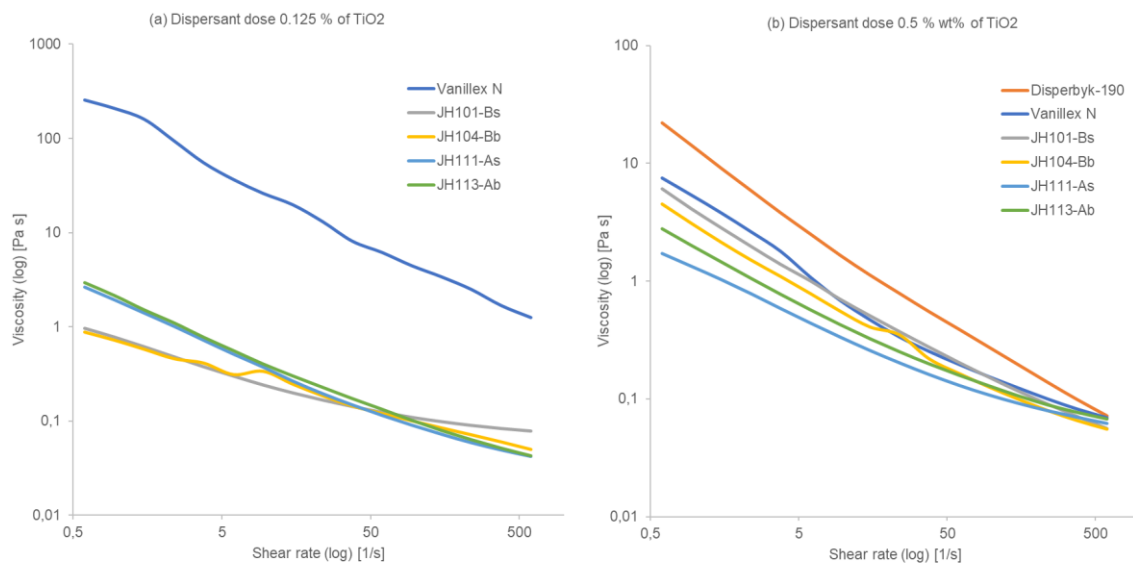
Figure 28. Viscosity (Pa s) vs. shear rate (1/s) at different doses of dispersant (wt% of TiO_2). (a) 0.125 wt%, (b) 0.5 wt%. The scales are logarithmic.

The viscosity vs. shear rate of TiO_2 suspensions are presented in Figure 28. Similar viscosity vs. shear rate behavior have been observed for aqueous TiO_2 suspensions with sodium hexametaphosphate (0.15 wt% of TiO_2) [153] and dethylenetriamine alkylamide (0–5.0 wt% of TiO_2) dispersants [154]. In these studies it is suspected that pH between 5–13 affects the rheological behavior of TiO_2 suspensions significantly [153].

When oxidized lignin dispersants were tested at dispersant doses of +1.0 wt% of pigment, the TiO_2 paste began to get brownish shade. Similarly to the oxidized lignins, lignosulfonate Vanillex N at higher dispersant doses of 1.0 wt% and 1.5 wt% affected the white color of TiO_2. For Disperbyk-190, color of TiO_2 was bright white for all the tested doses of dispersant (0.4–1.5 wt%). A slight color change with the lignin dispersants can be seen in the images of Appendix B, Figure 33 (b) and (d).

The optical microscopy analysis of TiO_2 suspensions do not show large difference in the particle size of TiO_2 agglomerates between different dispersants and different doses. However, Vanillex N and JH111-As at day 0 and JH113-Ab at day 7 showed brown spots in the microscopy images, with dispersant doses of 0.05 wt% and 0.125 wt% of TiO_2 (Figure 29). The brown spots are most likely droplets of lignin solution. Possible reasons
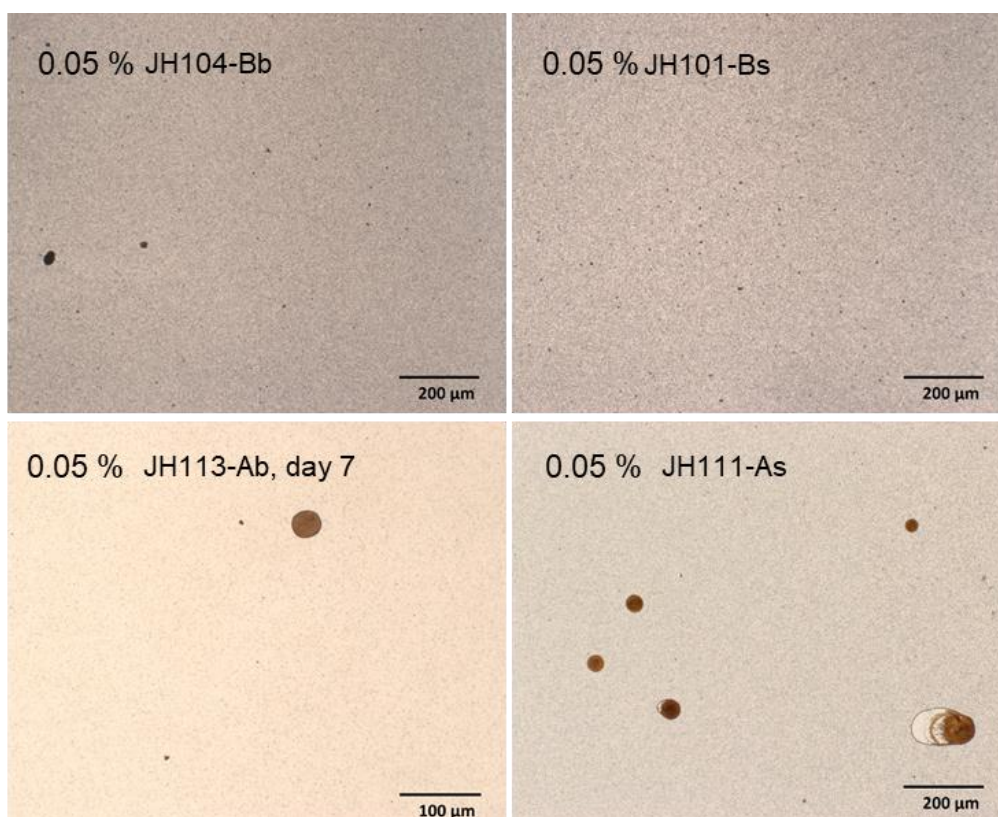
Figure 29. Optical microscopy images of TiO₂ suspensions with dispersant doses of 0.05 wt% of TiO2. The JH111-As and JH113-Ab lignin at 0.05 wt% dose show brown, large spots, in addition to fine small TiO₂ particles found in all other samples. The brown spots are most probably unmixed lignin dispersant. The lignin dispersant dose of 0.05 wt% is below the optimum dispersant amount for TiO₂ pastes, but similar spots were obtained with lignin doses of 0.125 wt% of TiO₂.

for these are (1) unproper mixing of the TiO₂ suspensions, which were thick and dry to begin with, or (2) incompatible of the dispersants with TiO₂ at low doses of dispersant. Some incompatability between the lignin-containg dispersants (LigniOx lignins and lignosulfonates) were seen even at higher doses of dispersants after storing the TiO₂ pastes for 7 days. All the lignin-containing TiO₂ suspensions had slight layer of brown liquid on the top of the TiO₂ pastes after 7 days, but in nearly all cases the phases were

Figure 30. Suspension with 75 % TiO₂ and 0.5 wt% JH113-Ab of TiO₂ after storing of 7 days and before remixing.

remixable by light shaking. 0.5 wt% JH113-Ab of TiO_2 had the most clear separation of brown layer and TiO_2 suspension, as seen in Figure 30.

6. CONCLUSIONS AND OUTLOOK

The aim of thesis was to understand how lignins and hemicelluloses work as plasticizers, dispersing agents, emulsifiers and stabilizer in dispersion applications from the chemistry point of view. The options to modify and alter the structure of lignins and hemicelluloses to be more suitable surfactants and dispersants were introduced shortly. An alkali-O_2 oxidation (LigniOx) of lignins was discussed in more detail because relevance to the applied part of this thesis. In the applied part, two organosolv and two soda lignins provided by Fortum and oxidized by VTT Technical Research Centre of Finland were evaluated in special carbon black and titan dioxide dispersions. Rheological measurements and optical microscopy were used as analysis methods. The aim of the applied part was to increase the knowledge of the new type of lignin-based dispersants and give background information for the development of modified Fortum's lignins as dispersants in paint, coating, ink, plastics and other dispersion-related applications.

Firstly, the literature about use of lignins and hemicellulose in different dispersion-related applications is broad. However, this does not directly translate to myriad of existing applications that would have been developed past the initial tests. Hemicelluloses have chemical analogies, such as gums and other hydrocolloids, which are commercially used for example as texture modifiers in food and cosmetic-related applications. The public research of hemicelluloses past the food- and cosmetics is however still in the early phases.

The research of new lignin-based dispersants has focused on the applications in which lignosulfonates are already commercially utilized, such as in cement plasticization. In these cases, the new lignin-based dispersants should perform better than lignosulfonates if the production costs are higher for the new lignin-based dispersants. Alternatively, new dispersion applications should be found in which lignosulfonates have not been used or do not work efficiently.

In the applied part of the thesis, the rheological measurements and complementary optical microscopy imaging showed that alkali-O_2 oxidized LigniOx lignin dispersants have potential especially in carbon black dispersions and to an extent in the titan dioxide dispersions. All the oxidized organosolv and soda lignins of Fortum had very similar behavior in the dispersions. The optimum amounts of lignin dispersants (7.5—20 wt% of carbon black) were slightly lower compared to commercial lignosulfonate and synthetic polymer references. The lignin dispersants were especially suitable for the special carbon black

dispersion, because of good dispersing performance and no visible change in the color of the dispersion even with high amounts of lignins.

In the case of titan dioxide dispersions, the required amount of lignin dispersants was lower (0.125—0.5 wt% of titan dioxide) compared to the references. However, the color of lignin-containing titan dioxide dispersions with high amounts of lignin dispersants and stability of the dispersions over 7 days need further optimization.

The experimental work performed here is the background and initial research on the new lignin-based dispersants in pigment applications. Therefore, extensive further research is needed and only few of the topics are mentioned as suggestions for future research. It would be worthwhile to

- study how the new alkali-oxygen oxidized lignin-based dispersants work in carbon black and titan dioxide dispersions when other chemicals and components of the common pigment formulations are added.

- study how pH and elevated temperature affect the dispersing performance of the new alkali-oxygen oxidized lignin-based dispersant and stability of the carbon black and titan dioxide dispersions.

- perform the draw-down and rub-out tests to evaluate color, gloss and opacity of the dispersions when the new alkali-oxygen oxidized lignin-based dispersants are used.

The experimental findings of this thesis should give the basepoint for the further research.

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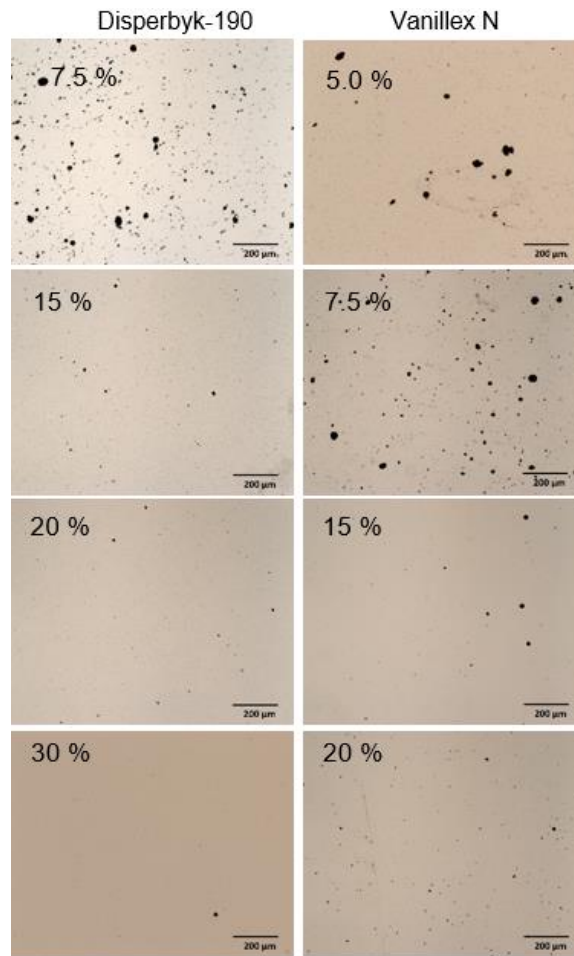
APPENDIX A

Figure 31. Optical microscopy images (10x magnification) of carbon black suspensions with different doses of reference dispersants. In all images, the black scale bar is 200 µm. The suspensions with lignin dispersant doses of 2.5 % (of carbon black) show large agglomerates of carbon black.
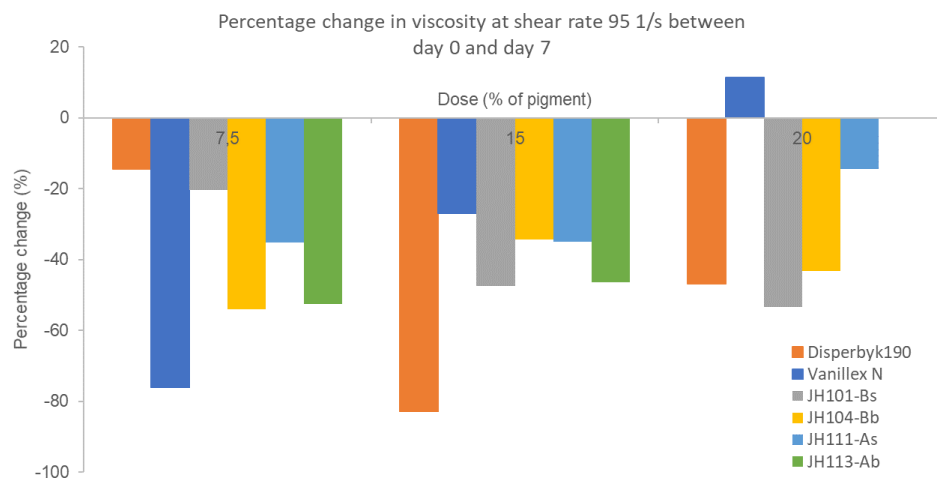

Figure 32. Percentage change in viscosity of carbon black suspensions at shear rate of 95 1/s between day 0 and day 7 rheological measurements. The suspensions were remixed by hand-shaking for 1 minute before the measurements at day 7.
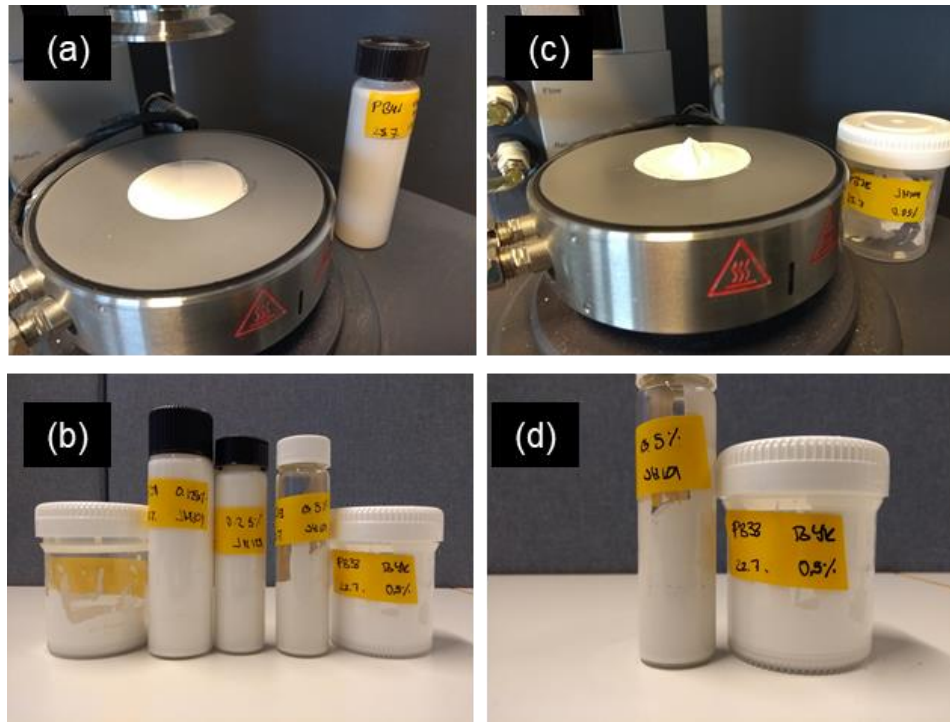
APPENDIX B

Figure 33. 75 % TiO$_2$ suspensions. (a) JH104-Bs (0.5 wt% of TiO$_2$), (b) from left, first four contain JH101-Bb at doses of 0.05–0.5 % of TiO$_2$, on right Disperbyk-190 (0.5 wt%), (c) JH104-Bs (0.05 wt%), (d) left: JH101-Bb (0.5 wt%), right: Disperbyk-190 (0.5 wt%). There is slight color difference between the lignin dispersants and synthetic dispersant (Disperbyk-190). The brown color increases with doses of lignin above 0.5 wt% of pigment.
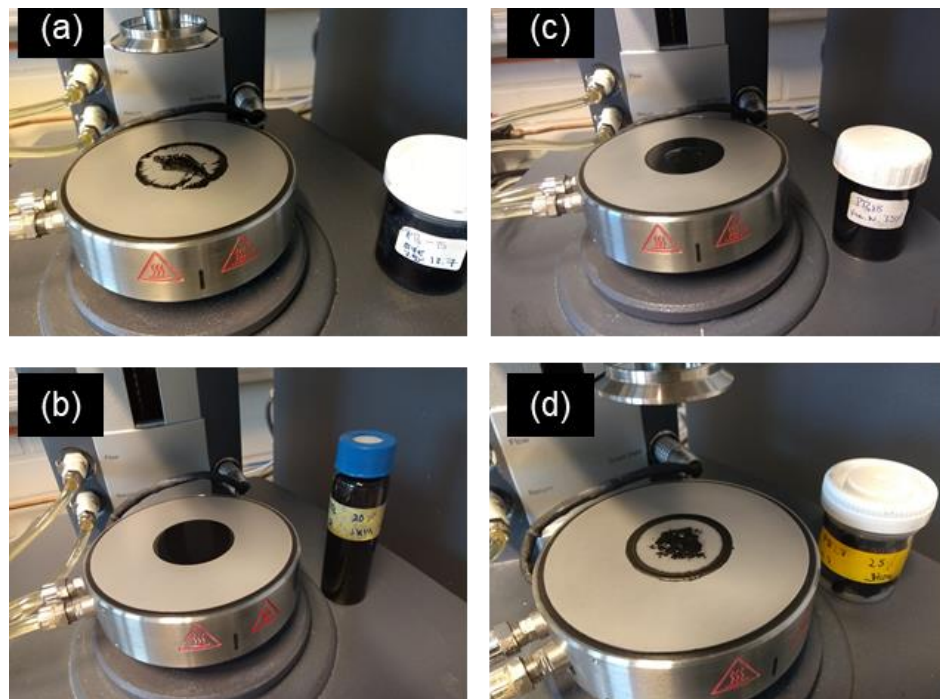

Figure 34. 15 % carbon black suspensions on the rheometer plate after the measurements. Dispersant in (a) is Disperbyk-190 (7.5 wt% of carbon black), (b) JH111-As (20 wt%), (c) Vanillex N (7.5 wt%), (d) JH104-Bs (2.5 wt%). When the dispersant dose is significantly below the optimum, the suspension is heterogenous and shows clear separation after the measurement, as in (a) and (d).