CHARACTERIZATION AND EVALUATION OF LIGNIN-BASED SURFACTANTS

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Miko Suominen

Examiners: Docent Ikenna Anugwom, D.Sc. (Tech.)

Principal Scientist Anna Kalliola, D.Sc. (Tech.)

Supervisors: Senior Scientist Stefania Bertella, D.Sc. (Tech.)

Principal Scientist Anna Kalliola, D.Sc. (Tech.)

ABSTRACT

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Miko Suominen

Characterization and evaluation of lignin-based surfactants

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Surfactants are molecules which possess both hydrophilic and hydrophobic moieties. Surfactants are critical ingredients in several applications, most notably in hard surface cleaners, detergents, personal care formulation and agrochemicals. Majority of globally used surfactants are from fossil-based origin. Lignin, a complex molecule from nature, possesses both hydrophilic and hydrophobic functional groups, deeming it a possible renewable alternative to fossil-based surfactants.

In this work, novel hardwood lignin-based surfactants produced with methods aiming to decrease the molecular size of lignin and control the hydrophobicity and hydrophilicity were evaluated. Chemical characterization methods were used to characterize the lignin-based samples. The evaluation included measurements of surface tension, emulsion stabilization and pigment suspending ability against selected commercial references.

Based on the results, some of these novel lignin-based surfactants possessed similar surface-active properties as commercial reference surfactants. The lignin-based surfactants were able to reduce surface tension to values similar to the reference. The best performance of lignin-based surfactants was seen as emulsifying and suspending agents, where they exceed the performance of the commercial references. The results indicate that the functional groups and the structure have the highest effect on the surface-active properties of lignin-based surfactants. Other parameters, such as molecular size and molecular charge as well as the pH conditions also affect the performance. The required characteristics of lignin-based surfactants seem to be dependent on the application.

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Pinta-aktiiviset aineet ovat molekyylejä, joiden rakenteessa on sekä hydrofiilisiä että hydrofobisia funktionaalisia ryhmiä. Pinta-aktiiviset aineet ovat tärkeitä aineisosia useissa sovelluksissa, kuten yleispuhdistusaineissa, pesuaineissa, kosmetiikassa ja maatalouskemikaaleissa. Suurin osa maailmanlaajuisesti käytetyistä pinta-aktiivisista aineista on fossiilipohjaisia. Ligniini, kompleksinen luonnon molekyyli omaa sekä hydrofiilisia että hydrofobisia funktionaalia ryhmiä, tehden siitä mahdollisen uusiutuvan vaihtoehdon fossiilisille pinta-aktiivisille aineille.

Tässä diplomityössä arvoitiin ja karakterisoitiin uusia ligniinipohjaisia pinta-aktiivisia aineita, jotka olivat valmistettu ligniinimolekyylin pienentämiseen ja hydrofobisten ja hydrofiilisten ominaisuuksien kontrollointiin tähtäävillä menetelmillä. Näytteiden ominaisuuksia arvioitiin mittaamalla niiden kykyä alentaa veden pintajännitystä, stabiloida emulsioita sekä ylläpitää pigmenttisuspensiota.

Tulokset osoittivat, että ligniinipohjaisilla pinta-aktiivisilla aineilla oli samankaltaisia ominaisuuksia kuin kaupallisilla pinta-aktiivisilla aineilla. Ligniinipohjaiset pinta-aktiiviset aineet onnistuivat laskemaan pintajännitystä samalle tasolle kuin kaupalliset referenssit. Parhaiten ligniinipohjaiset pinta-aktiiviset aineet toimivat emulsioiden stabilointiin sekä pigmenttisuspension ylläpitämiseen, päihittäen referenssit. Tulosten perusteella vaikuttaa siltä, että molekyylirakenteella on suurin vaikutus pinta-aktiivisten aineiden tehokkuuteen, mutta myös molekyylikoolla ja varauksella sekä pH olosuhteilla huomattiin olevan vaikutusta ligniinipohjaisten pinta-aktiivisten aineiden toimintaan. Ligniinipohjaisilta pinta-aktiivisilta aineilta vaadittavat ominaisuudet näyttävät riippuvan käyttökohteesta.

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"Opinpahan"

26.8.2025 Espoo

Miko Suominen

ABBREVIATIONS

2D-HSQC	2-Dimensional heteronuclear single quantum coherence
AS	Alkane sulfonate
CIPAC	Collaborative International Pesticides Analytical Council
CMC	Critical micelle concentration
EC	Emulsion concentrate
EW	Aqueous O/W emulsion
FAO	The Food and Agriculture Organization of the United Nations
FTIR	Fourier-transform infrared spectroscopy
G	Guaiacyl
H	P-hydroxyphenyl
HL	Hydrolysis lignin
HLB	Hydrophilic-lipophilic balance
IR	Infrared
LABSA	Linear alcohol benzene sulfonic acid
LAS	Linear alkylbenzene sulfonate
LBS	Lignin-based surfactant
NMR	Nuclear magnetic resonance
OECD	Organization for Economic Co-operation Council
O/W	Oil-in-water
O/W/O	Oil-in-water-in-oil
PD	Polydispersity
PSD	Particle size analysis
RCF	Reductive catalytic fractionation

S	Syringyl
SEC	Size Exclusion Chromatography
SC	Suspension concentrate
SLS	Sodium lauryl sulfate
ST	Surface tension
UV-VIS	Ultraviolet-Visible spectroscopy
W/O	Water-in-oil
W/O/W	Water-in-oil-in-water

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DECLARATIONS

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1 Introduction

Surfactants are multifunctional molecules that have a variety of applications across many different industries. Most notably, surfactants are used as an active ingredient in detergents, agrochemicals and personal care products. 18 million tons of surfactants are produced annually, out of which 96% are synthetic surfactants produced from fossil-based chemicals. (Veeramanoharan and Kim, 2024)

As industries are searching for a replacement for traditional, fossil-fuel derived chemicals and products, the bio-based solutions are gaining attraction. One of the most notable bio-based feedstocks is lignin, a naturally occurring and abundant aromatic polymer found in most of the biomass across the globe. The most significant source of lignin is currently the pulp and paper industry, where it is produced as a byproduct of pulp production (Bajwa et al., 2019).

Lignin has a heterogeneous molecular structure by nature, as it is composed by different phenolic units (monolignol) depending on the plant species, linked via different type of chemical bonds. This gives rise to a polymer comprising many functional groups, most notably aromatic rings, phenols, ethers and aliphatic alcohols (Akpan, 2019). This makes lignin an attractive feedstock for the production of bio-based products, including surfactants. The ability of lignin to work as a surfactant has been shown by numerous studies, e.g. (Bertella et al., 2022; Delgado et al., 2019; Morcillo-Martín et al., 2025).

However, the previous studies on using lignin as a surfactant have mainly focused on assessing the surfactant properties of lignin from different sources. Modification of lignin to increase surface-active properties has gained popularity among the research community, however most of the modifications have been conducted using fossil-based or hazardous chemicals or organic solvents, which diminish the sustainability aspect of lignin-based surfactants.

The aim of this thesis was to evaluate the performance of novel lignin-based surfactants, which had been produced with methods aiming to decrease the molecular size of lignin and control the hydrophobicity and hydrophilicity. The objective of the work was to find key

parameters affecting the performance of lignin-based surfactants and evaluate their possible utilization in different applications.

The thesis consists of two parts, literature and experimental part. In the literature part, the theory of surfactants, their applications and different types are discussed. The related chapters dives more in detail to lignin, its utilization and modification into surfactants. In addition, the challenges with the utilization of lignin as a surfactant and the evaluation methods are presented. In the experimental part, lignin-based surfactants are evaluated for their surface-active properties by measuring how they affect surface tension, stabilize emulsions and work as a suspending agents.

2 Surfactants

Surface active agents, or surfactants, are organic compounds consisting of two chemically distinct parts with differing polarities (Myers, 2020). As such, surfactants are classified as an amphiphiles (Tiwari et al., 2018). Surfactants reduce the surface and interfacial tension between two or more phases by adsorbing into the surface of a medium. (Shaban et al., 2020).

Amphiphilic molecules consist of at least two units, which are the lyophilic (solvent loving) and lyophobic (solvent hating) (Myers, 2020). If water is used as a solvent, the terms hydrophilic (water loving) and hydrophobic (water hating) can be used instead and these parts can be referred to as a hydrophilic head and a hydrophobic tail of the surfactant (Tiwari et al., 2018). Amphiphilic molecules orient themselves based on the preferences of their groups, with the hydrophilic part interacting with the polar phase and the hydrophobic part associating with the non-polar phase (Schramm, 2000). The typical structure of an amphiphilic molecule is presented in Figure 1.

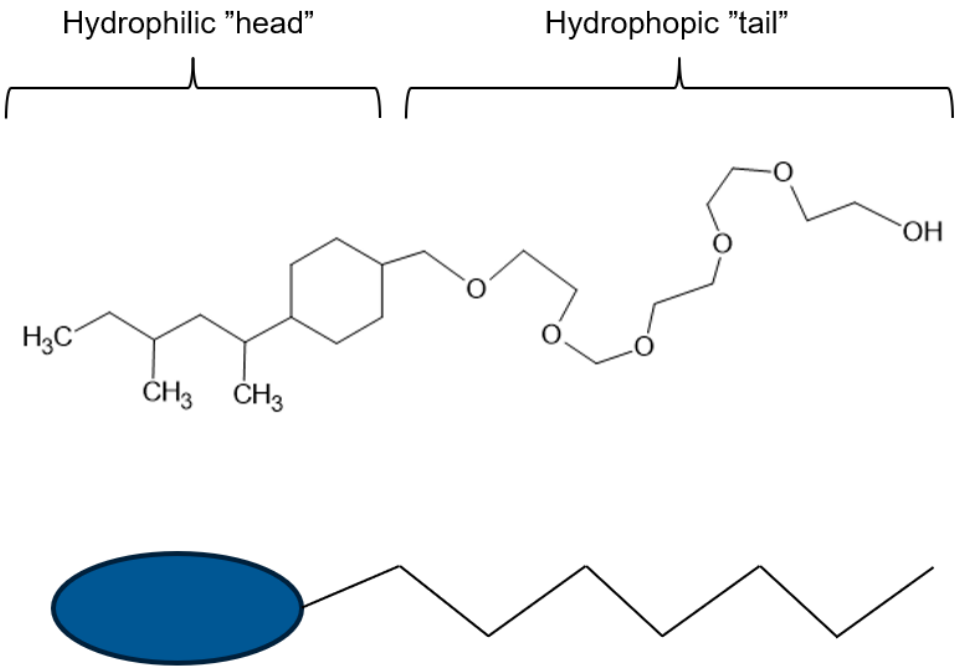


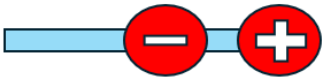
Figure 1. Typical structure of an amphiphilic molecule. Adapted from (Dave and Joshi, 2017).

2.1 Small-molecule surfactants

Small-molecule surfactants are surfactants composed of a single molecule. Small-molecule surfactants are generally classified based on the chemical properties of the polar part and their behavior in the aqueous environment. They are classified into anionic, cationic, non-ionic and amphoteric (or zwitterionic) surfactants. However, small molecule surfactants can also be classified based on their use and function, but this classification does not imply anything about the structure or functionality of the molecule. (Myers, 2020)

In this thesis, the focus is on anionic surfactants, so other surfactants are only presented briefly. The surfactant types, structure and their typical applications are shown in Table 1.

Table 1. Surfactant types, structure and typical applications.

Type of surfactant	**Surfactant structure**	**Typical applications**	**Source(s)**
Anionic		Soaps, food additives, detergents, cosmetics, pesticides, oil recovery, hard surface cleaners	(Dave and Joshi, 2017; Tiwari et al., 2018)
Cationic		Anticorrosion agent, dispersant, antistatic agent, cosmetics	(Gonçalves et al., 2023)
Non-ionic		Detergents, textile processing, cosmetics	(Alwadani and Fatehi, 2018), (Tiwari et al., 2018)
Amphoteric (Zwitterionic)		Cosmetics, personal care products	(Dave and Joshi, 2017)

2.1.1 Anionic surfactants

Anionic surfactants are a group of surfactants whose hydrophilic part is negatively charged. The most important and common forms of anionic surfactants are based on carboxylate, sulfonate, sulfate or phosphate ester groups (Myers, 2020). Examples of common anionic surfactants are presented in Figure 2.

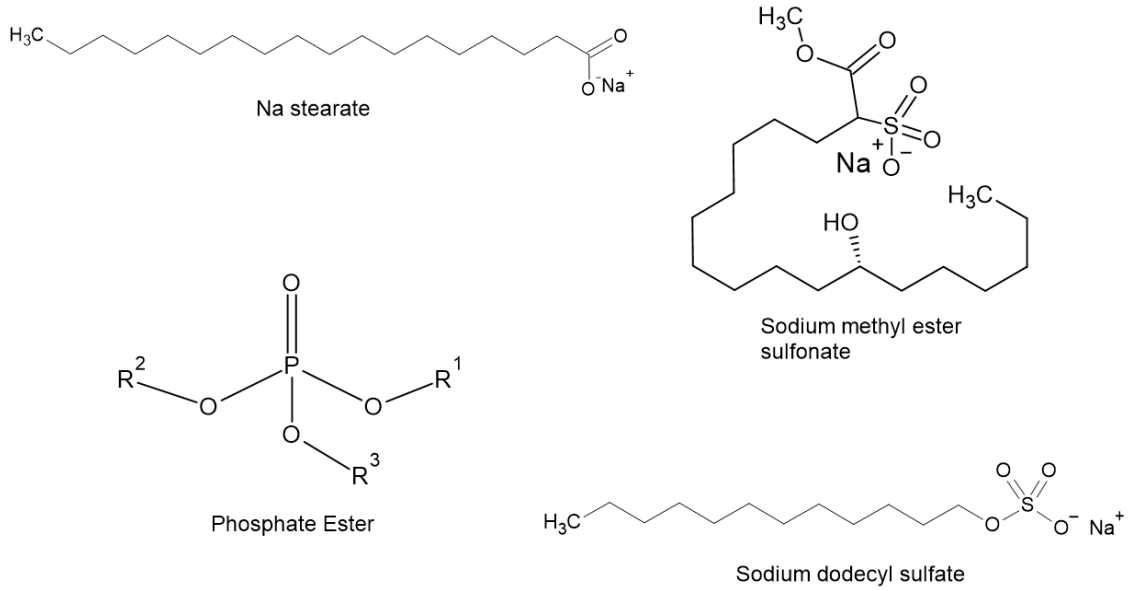


Figure 2. Examples of common anionic surfactant molecules (Alwadani and Fatehi, 2018; Dave and Joshi, 2017; Sohrabi, 2022).

Anionic surfactants are the most widely utilized group of surfactants in commercial applications, thanks to their non-toxicity, versatility and cheap cost (Dave and Joshi, 2017; Salager 2002). Anionic surfactants are used in oil recovery, pesticides, nanotechnology, as a food additives and especially as a cleaning agents in detergents, soaps, fabric softeners and other personal cleaning products due to their excellent cleaning and dirt removal properties (Alwadani and Fatehi, 2018; Dave and Joshi, 2017; Tiwari et al., 2018).

2.1.2 Other small-molecule surfactants

Other small-molecule surfactants are cationic, non-ionic and amphoteric surfactants. Cationic surfactants are a group of surfactants whose hydrophilic head is positively charged. Cationic surfactants are commonly used as a dispersants, an antistatic agents, a fabric softeners and as an anticorrosion agents. (Kronberg et al., 2014)

Non-ionic surfactants differ from other surfactants, as the molecule does not carry any ionic charge. Non-ionic surfactants are second most utilized surfactant type commercially. They are commonly used in the textile processing, cosmetics and as a foaming and emulsifying agents. (Alwadani and Fatehi, 2018)

Amphoteric (or zwitterionic) surfactants carry both positive and negative charge on their hydrophilic head. Amphoteric surfactants are the least used small molecule surfactants commercially due to their high manufacturing price. They are used mostly in cosmetics and personal care products, as they exhibit very low skin and eye irritation. Amphoteric surfactants are usually applied as a co-surfactants in combination with other surfactants, as the amphoteric nature can be used to improve the performance of the main surfactant. (Alwadani and Fatehi, 2018; Kronberg et al., 2014)

2.1.3 Bio-based small molecule surfactants

Bio-based small molecule surfactants are surfactants derived from natural origin, such as from plants, microbes, algae, fatty acids etc. Bio-based small molecule surfactants are produced by combining hydrophobic and hydrophilic compounds from natural origin either chemically or enzymatically. Common small molecule bio-based surfactants are classified into phospholipids, fatty acids, glycolipids, polyketideglycosides, lipopeptides, spiculisporic acids, isoprenoids and carotenoids. Figure 3 present corynomycolic acid, a glycolipid-based surfactant. (Hayes et al., 2019)

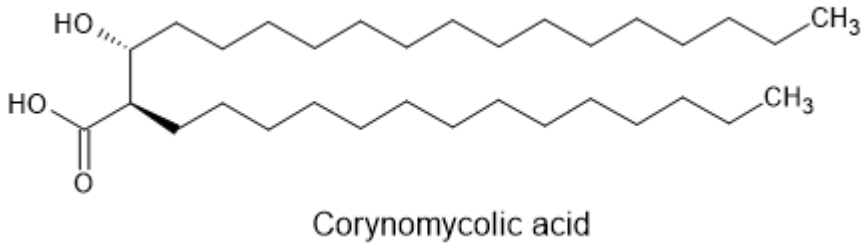


Figure 3. Corynomycolic acid. Adapted from (Hayes et al., 2019)

Bio-based small molecule surfactants are utilized widely in surfactant applications, such as in detergents, cosmetics, personal care products, paints and coatings and pharmaceuticals. Bio-based surfactants can work as an alternative to fossil-based surfactants, offering a way to make surfactant industries more environmentally benign. (Hayes et al., 2019)

2.2 Polymeric surfactants

Surface active polymers, or polymeric surfactants, are macromolecules which exhibit amphiphilic tendencies. Typically, polymeric surfactants consist of multiple hydrophilic and lipophilic parts (Salager 2002). Polymeric surfactants can be classified in several ways, but most commonly the classification is based on the structure of the polymer or the ionic charge of the hydrophilic groups. The polymeric surfactants can be divided roughly into three groups: block-, graft-, and random-type polymeric surfactants based on their structure (Salager 2002). The structure and examples of polymeric surfactant molecules are presented in Figure 4. Ionic-charge wise, just like small-molecule surfactants, polymeric surfactants can be classified into anionic, cationic, amphiphilic or non-ionic polymeric surfactants.

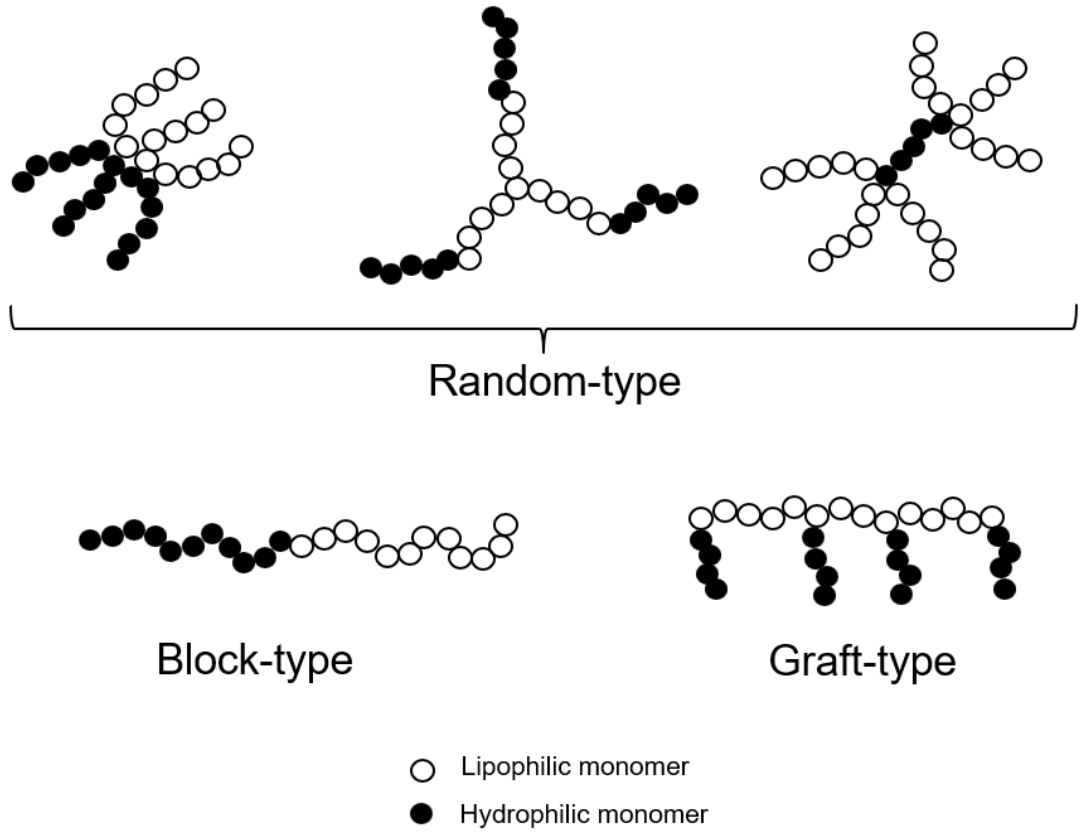


Figure 4. The three most common types of polymeric surfactants based on their structure. Adapted from (Aleid et al., 2023)

Block-type polymeric surfactants are composed of hydrophilic and hydrophobic (lipophilic) monomer segments that alternate within a linked chain, forming a polymer (Kronberg et al.,

2014). The hydrophilic part usually has hydroxyl, carboxyl, amide, ether or amino acid functional groups (Verma et al., 2023). The hydrophobic part is usually a linear alkyl chain or chain of oligomers (Verma et al., 2023).

Graft-type polymers consist of a uniform hydrophobic chain, “backbone”, with hydrophilic side chains attached onto it (Kronberg et al., 2014). The hydrophilic side chains can be either all over the backbone, with chains going in all directions, or only in one side of the backbone (Aleid et al., 2023). The lateral formation is also known as comb-type polymer, as it often has “comb-like” structure. (Aleid et al., 2023).

Random-type polymers consist of randomly distributed hydrophilic and hydrophobic segments. Random-type polymers have random structures, which varies based on the orientation of hydrophilic and hydrophobic groups, as can be seen from the Figure 4. (Aleid et al., 2023)

Polymeric surfactants generally exhibit lower surface activity than that of small-molecule surfactants, but as small-molecule surfactants, it is dependent on the surfactant concentration (Falbe, 1987). Similarly, as observed for other surfactants, the length of the hydrophobic chain in polymeric surfactants has an influence on the surface tension. Higher molecular weight polymers usually exhibit higher surface activity, as they contain more surface active functional groups (Aleid et al., 2023).

Polymeric surfactants can be derived from two different sources and thus are classified based on the origin as petroleum-based synthetic surfactants and bio-based polymeric surfactants (Foley et al., 2012; Myers, 2020). Out of these, the synthetic surfactants are more widely utilized commercially, but bio-based surfactants are gaining attraction due to their sustainability, low environmental impact and as a possible replacement for synthetic polymeric surfactants (Foley et al., 2012).

2.2.1 Bio-based polymeric surfactants

Bio-based polymeric surfactants are polymeric surfactants derived or synthetized from natural resources, such as from biomass, sugars or starches. Bio-based polymeric surfactants should not be mixed with polymeric biosurfactants, which refers to surfactants made with micro-organisms, such as with bacteria or fungi’s. (Aleid et al., 2023)

Bio-based polymeric surfactants have similar functionalities as synthetic polymeric surfactants, however, they have certain unique properties that separate them from the synthetic ones. For example, bio-based polymeric surfactants have amphiphilic structure by nature (Aleid et al., 2023). As of natural origin, bio-based polymeric surfactants are typically biodegradable and inhibit low toxicity (Aleid et al., 2023). One of the most commonly used bio-based polymeric surfactant is lignosulfonate, which structure is presented in Figure 5.

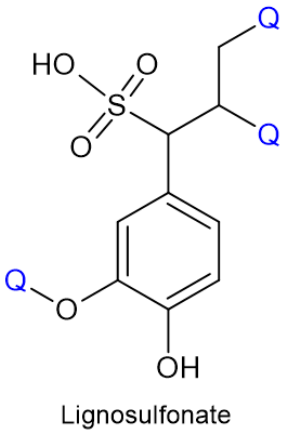


Figure 5. Structure of lignosulfonate.

Cellulose-based polymeric surfactants and lignosulphonate are an example of bio-based polymeric surfactants. These bio-based polymeric surfactants are utilized in number of applications, including personal care products, agrochemicals and dispersant applications. (Aleid et al., 2023; Ruwoldt, 2020)

2.3 Surfactant theory

Surfactants have a strong tendency to accumulate to an interface between the aqueous and the opposing phase, which can be a liquid, gas or solid. The driving force for this phenomenon is for surfactants to lower the Gibbs free energy of the phase boundary. The interfacial free energy, or interfacial tension, describes the amount of work required to increase the surface area of the boundary. For example, surface tension of water corresponds to the interfacial tension between the water and air (Kronberg et al., 2014)

Surface tension arises from the intermolecular forces acting on the top layer of a liquid. While molecules within the liquid experience equal “pull” in all directions, surface

molecules are only pulled downward and inward by the liquid phase. This imbalance creates an inward force, leading to tightly packed surface molecules and the phenomenon of surface tension. Adsorption of surfactants to the aqueous interface forces the water molecules apart from each other, breaking their hydrogen bonds, which reduces the surface tension. (Dutta, 2019)

The reduction of surface tension by surfactants is dependent on how tightly the surfactant molecules are packed (how much surfactant is adsorbed to the surface) and the orientation of the surfactant molecules on the surface. Surface tension, however, is also dependent on other external factors, such as the temperature and the electrolyte concentration of the aqueous phase. (Dutta, 2019; Kronberg et al., 2014; Rosen and Kunjappu, 2012; Tiwari et al., 2018)

The increase in surfactant bulk concentration in the solution decreases the surface tension of the medium until the phase boundary is fully saturated with surfactant molecules and the surface and internal energy of the liquid become equal (Nakama, 2017). The length of the hydrophobic alkyl chain affects the required concentration of surfactants, with longer chains requiring less surfactant (Falbe, 1987). At a point where the interface cannot absorb any more surfactant molecules, the surface tension does not drastically change. This point is called critical micelle concentration (CMC) and can be clearly seen as a sudden plateauing of the surface tension, as presented in Figure 6. (Dutta, 2019)

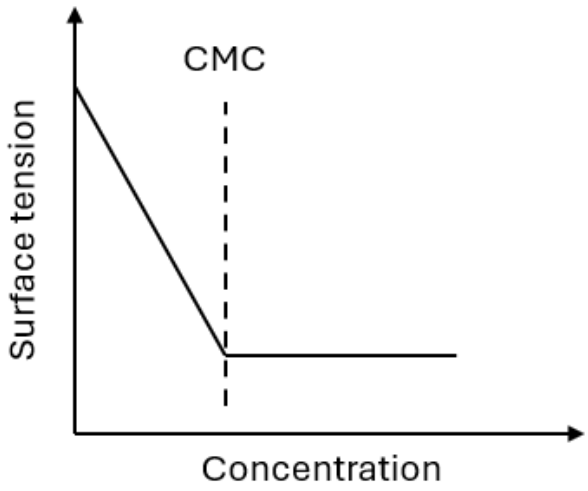


Figure 6. Illustration of CMC in surface tension vs concentration graph. The CMC is the point where the surface is fully saturated with surfactants, causing surface tension to plateau.

2.3.1 Critical micelle concentration and micelles

At CMC, the surfactant molecules in the solution start to aggregate. (Nakama, 2017). When the concentration of surfactants in the solvent is increased, the immiscible parts of the surfactants start to associate with each other, trying to minimize the contact area with the solvent (Witten, 2004). This aggregation of surfactants leads to a formation of spherical shape known as a micelle.

In aqueous solvent, the hydrophobic tails of the surfactants interact with each other, forming a micelle. If the solvent is non-aqueous, the situation is inverted, as the lipophobic heads attract each other and form the center of the micelle (Witten, 2004). In Figure 7 is presented the structure of micelles in aqueous and non-aqueous environments.

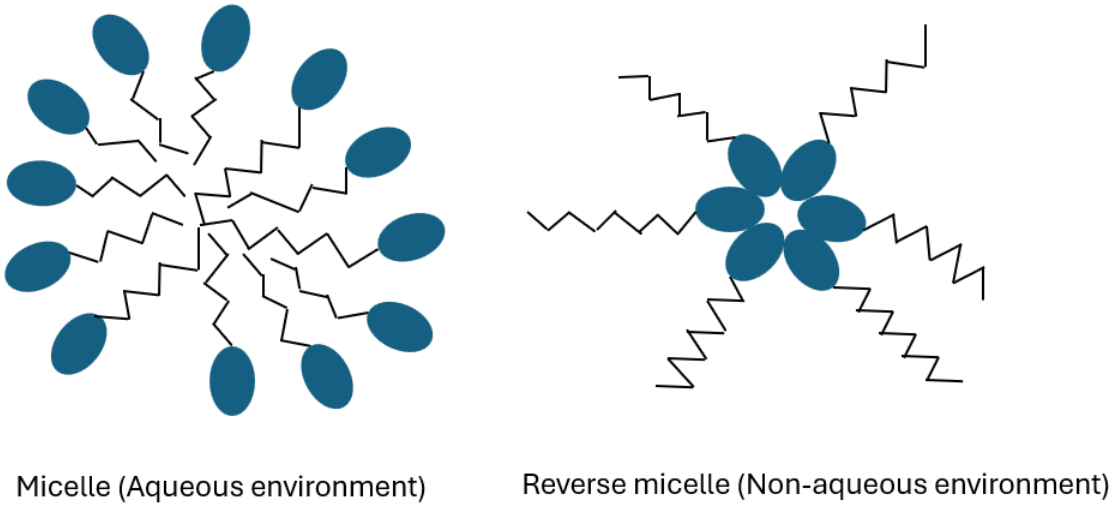


Figure 7. Shape of a micelle in an aqueous and non-aqueous environment. Adapted from (Kaur et al., 2024).

The shape of micelles in the solvent is dependent on the structure of the surfactant molecules, specifically the shape of the polar and non-polar group (Dave and Joshi, 2017). The shape of which micelles take is also affected by the bulk concentration of surfactants (Nakama, 2017). At low concentrations the micelles take the shape of sphere, which consists of 50-100 individual surfactant molecules (Hunter, 1996; Dave and Joshi, 2017). As the bulk concentration increases, micelles form more complex structures, such as rod-like, hexagonal, cubic or lamellar shapes (Moroi, 1992). Micellization is a reversible phenomenon, meaning

that if surfactant concentration decreases under the CMC-value, micelles start to decompose and freed surfactant molecules will move to the interface between the phases. (Moroi, 1992).

2.3.2 Solubilization

Surfactants have ability to make insoluble lipids and slightly soluble molecules soluble, which is known as solubilization (Nakama, 2017). Solubilization occurs in concentrations above CMC, as the phenomena is based on micelles. The micelles make the insoluble molecules soluble by absorbing them into the center or adsorbing them to the surface, depending on the polarity of the molecule. In aqueous solutions, non-polar compounds, such as hydrocarbons, absorb into the center of the micelles, which solubilizes the molecules (Nakama, 2017). Polar compounds on the other hand adsorb on the surface of the micelles (Nakama, 2017). If the solution is non-aqueous, the situation is inverted, as the micelle formation is opposite (Sakamoto et al., 2017). Figure 8 presents the solubilization mechanism of organic soil from a solid surface.

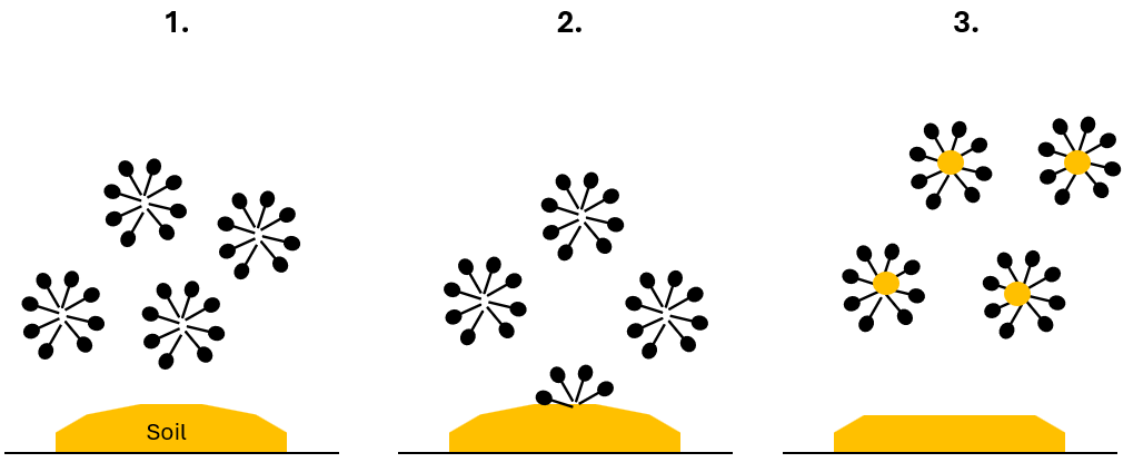


Figure 8. Solubilization of organic soil from a solid surface. (1.) Micelles exist in a solution that is applied to a solid surface. (2.) Micelles move to contact with soil. (3.) Soil particles are solubilized to the center of micelles.

2.3.3 Krafft point

Besides concentration of surfactants in solution, the aggregation of surfactant molecules into micelles is also dependent on the temperature. The minimum temperature at which micelles can start to form is known as Krafft point. Below Krafft point, surfactant molecules are too insoluble to reach CMC and therefore higher surfactant concentrations above solubility equilibrium exist as a solid crystal formations. Above Krafft point, the formation of micelles also leads to exponential increase in solubility, as can be seen from Figure 9. (Falbe, 1987; Moroi, 1992)

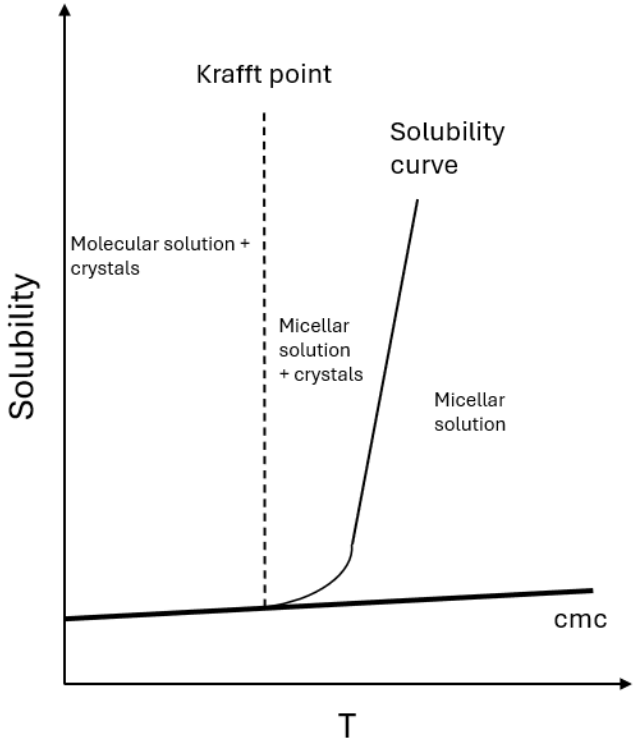


Figure 9. Phase diagram of surfactants and Krafft's point effect on solubility. Adapted from (Falbe, 1987)

The formation of solid crystals under the Krafft point is reversible phenomena, meaning that increasing the temperature above Krafft point solubilizes them into micelles (Falbe, 1987).

The Krafft point is unique for each surfactant and is dependent on variety of properties. The length of hydrophobic chain affects the Krafft point of surfactant, with Krafft point raising with increasing hydrophobic chain length. However, this is only true for every odd number of carbon atoms in the chain, which can be seen from Figure 10. (Falbe, 1987)

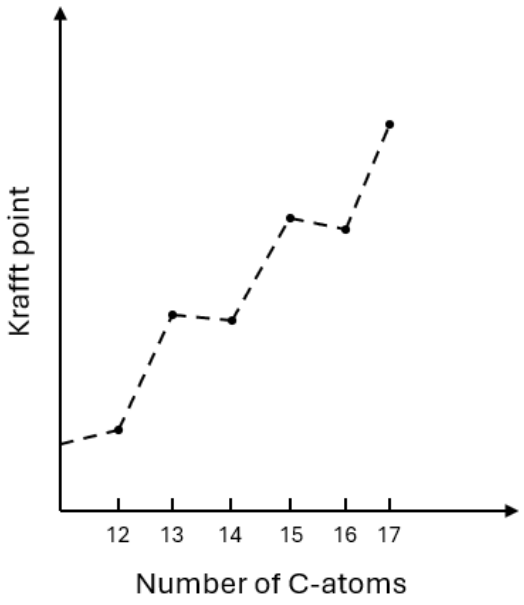


Figure 10. Krafft point as a function of the number of carbon-atoms in hydrophobic chain of the surfactant molecule. Adapted from (Falbe, 1987).

As can be observed from the Figure 10, Krafft point increases with addition of carbon atom from 12 to 13, but stays nearly identical, when the number of carbon atoms is increased from 13 to 14. This effect is due to the difference in crystal structure between odd and even number of carbon atoms in the hydrophobic chain. (Falbe, 1987)

The hydrophobic chain length also affects the CMC of the surfactant, similarly as it has effect on Krafft point. CMC increases with decreasing chain length. (Falbe, 1987)

2.3.4 Emulsions

When liquids with different polarities, such as oil and water, are mixed, they form a dispersion, known as emulsion, where droplets of oil are mixed in water and droplets of water mixed in oil. These droplets tend to separate into their respective phases, as the system is thermodynamically unstable. With the addition of surfactants, the lifetime of emulsion increases exponentially, up to years. (Falbe, 1987)

Surfactants lower the interfacial tension between two phases, as the surfactants molecules absorb to the respected interface (hydrophilic head to aqueous phase and hydrophilic tail to

organic phase). The stabilizing effect of surfactants is based on two forces, steric repulsion and electrostatic stabilization. (Falbe, 1987)

Steric repulsion is characteristic of larger surfactant molecules, particularly for polymeric surfactants. Steric repulsion is due to the physical size of these large surfactants, which prevents coalescence of droplets. Illustrative figure of this phenomenon is presented in Figure 11. (Tadros, 2014)

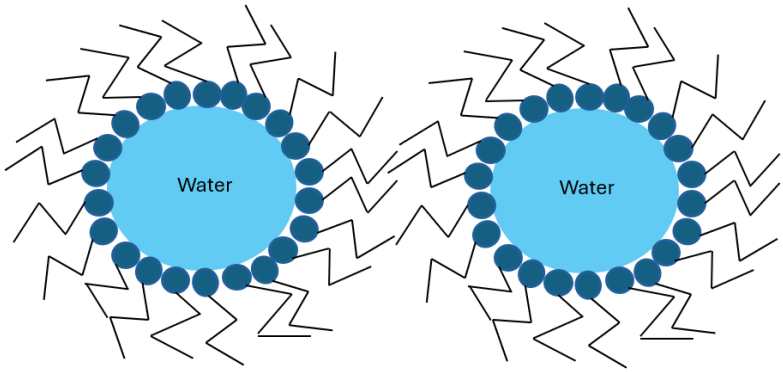


Figure 11. Steric repulsion caused by surfactant molecules on the surface of water droplets in emulsion.

Electrostatic stabilization prevents coalescence of emulsion particles by electrostatic forces. When ionic surfactants absorb into the interface of droplets, they create an electrical double layer. This double layer prevents the droplets from coming to contact with other droplets due to repulsion caused by the same type of ionic charge. Electrical double layer also prevents the attractive Van der Waals interactions between droplet molecules. (Tadros, 2014)

Emulsions can be divided into two categories based on which phase is dispersed as droplets, and which phase works as a continuous phase. In water-in-oil (W/O) emulsion, water is dispersed as droplets in continuous oil phase. In oil-in-water (O/W) emulsion, the situation is reverse, with oil dispersed as droplets in continuous aqueous phase. Furthermore, these emulsions can be mixed with a third phase to create multiple emulsion systems, such as water-in-oil-in-water (W/O/W) or oil-in-water-in-oil (O/W/O) emulsions. These different emulsions are illustrated in Figure 12. (Schramm, 2006)

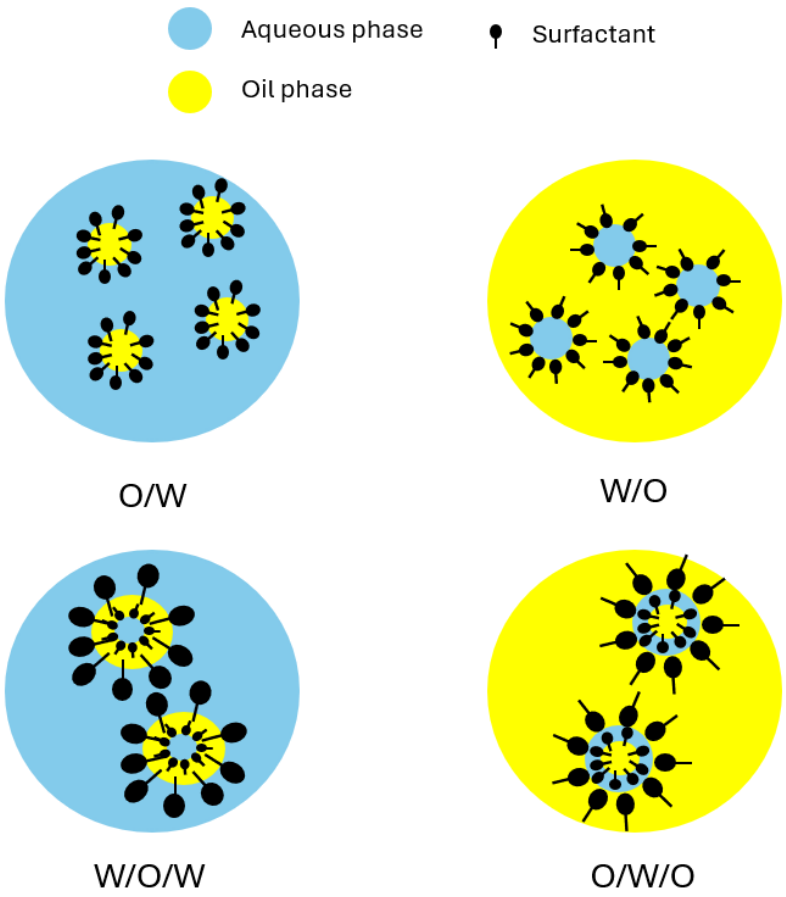


Figure 12. Structure of different emulsions.

Surfactants' performance as a stabilizer in different emulsions is based on their relative hydrophilicity or hydrophobicity. The ratio of these is known as hydrophilic-lipophilic balance (HLB). The HLB value varies from 0-20 based on the surfactant's hydrophilicity. The value of 0 corresponds to surfactants, which are very lipophilic and value 20 corresponds, that the surfactants are very hydrophilic. The HLB scale has been adjusted to go up to 40, since some of the synthetic surfactants are extremely hydrophilic. (Alwadani and Fatehi, 2018; Falbe, 1987)

Although surfactants tend to increase the lifetime of the emulsions, the unstable conditions will eventually lead to breaking of the emulsion. These emulsion breaking mechanisms are presented in Table 2 and illustrated in Figure 13.

Table 2. Emulsion breaking mechanisms (Tadros, 2016).

Emulsion breaking mechanism	**What happens**
Creaming	Larger droplets move to the top due to formation of concentration gradient in the system. Happens, if droplets are less dense than continuous phase.
Sedimentation	Larger droplets move to the bottom due to formation of concentration gradient in the system. Happens, if droplets are more dense than continuous phase.
Flocculation	Droplets aggregate due van der Walls attraction.
Phase inversion	Dispersed phase and continuous phase flip, causing the inversion of emulsion type.
Coalescence	Droplets coalesce into larger droplet.
Ostwald ripening	Small droplets dissolve and redeposit into larger droplets.

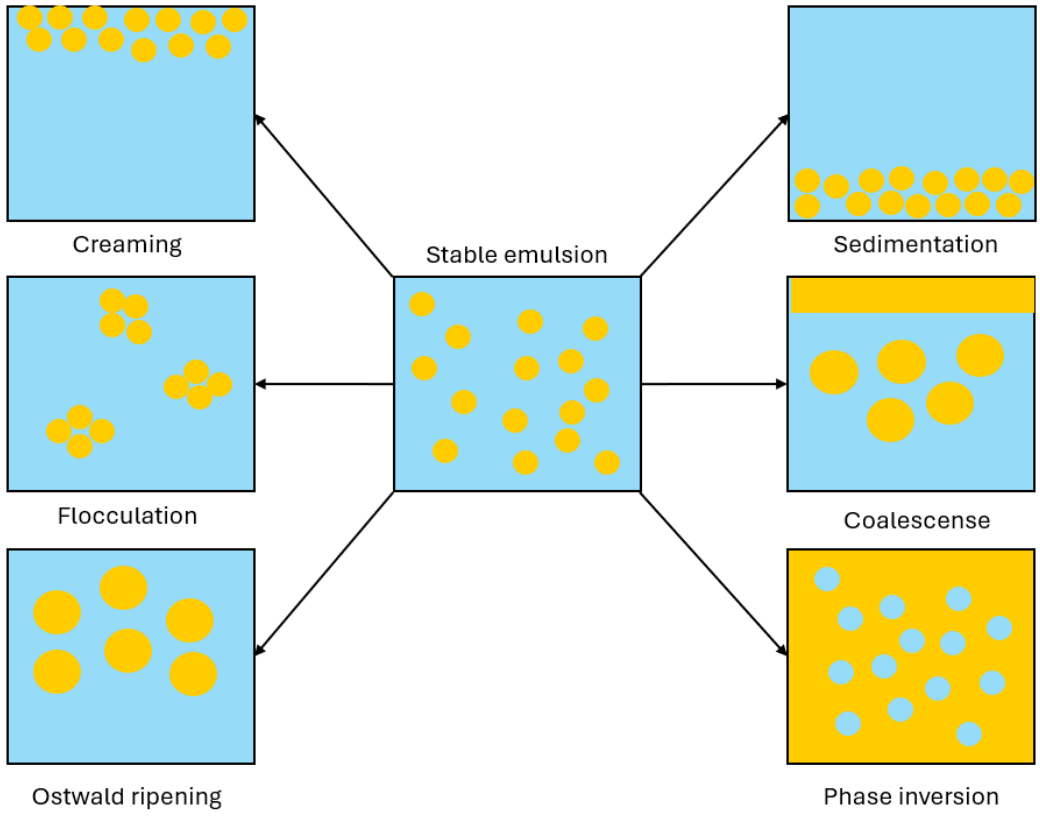


Figure 13. Emulsion breaking mechanisms. Adapted from (Tadros, 2016).

The exact breaking mechanism of emulsion can be hard to assess with bare eye or even with analytical methods. Some of these phenomena's can look rather similar, such as Ostwald ripening and coalescence.

2.4 Surfactants in home- and personal care products

Surfactants are used widely in household, personal and industrial products due to their excellent cleaning properties (Falbe, 1987). Consumer products which contain surfactants can be classified into two categories, detergents and cosmetics (Landeck et al., 2020).

Detergents are surfactants or a mixture of surfactants, which have a cleaning effect on surfaces (Falbe, 1987). The cleaning effect of detergents is based on two-step process, which in the first is removal of soil from the surface and the second is the dispersion of the soil to the washing liquid (Uner and Yilmaz, 2015). This effect was illustrated in Figure 8.

Detergents mainly consist of surfactants, with other additives designed to increase the efficiency of the product (Falbe, 1987). The exact formulation is dependent on the detergent's application (Falbe, 1987). Detergents can be classified into three categories based on their application, which are hard surface cleaners, laundry and dishwashing detergents.

Cosmetics are formulations designed to enhance or alter humans' aesthetic appeal. They can be used for different applications, such as for beautification, cleansing or grooming. From the surfactants point of view, cleansing cosmetics, such as skin- and haircare products, are especially of interest. Surfactants play vital role in these formulations, and they have many different functions, such as cleansing and stabilizing emulsions. (Tadros, 2016)

2.4.1 Hard surface cleaners and manual dishwashing detergents

Hard surface cleaners are a type of detergents designed to clean non-porous surfaces, which are mostly resistant to penetration by solid materials and do not generally absorb liquids (Uner and Yilmaz, 2015). These are, for example, materials usually found in the household, such as tiles, stone, floor, marble, plastic, metal, ceramic and porcelain (Uner and Yilmaz,

2015). Besides various surfaces, soil can also be in many forms, such as oils, fats, waxes, food residues, silicates, sand, dyestuffs etc. and can contain microbes (Falbe, 1987).

Hard surface cleaners are expected to wet the surface fast, emulsify the soil efficiently and prevent the formation of fatty streaks after cleaning. They should also exhibit good skin compatibility and be safe for humans as well as to the environment. As consumer products, hard surface cleaners should have an attractive appearance, be easy to handle, as well as emit a pleasant odor during and after cleaning. (Falbe, 1987)

The variance in material and soil makes it a challenge to formulate universal cleaning product, that would be applicable in all situations. In most cases however, the removal of soil is based on the same physicochemical mechanism and the cleaning can be accomplished with similar methods. Therefore, hard surface cleaners can be roughly classified into two categories, all-purpose cleaners and special cleaners. (Falbe, 1987)

All-purpose cleaners are mild cleaning solutions designed to be applicable to all hard surfaces. They are typically diluted and either neutral or weakly alkaline and contain 1-15% of surfactants. All-purpose cleaners are expected to remove the soil from the surface without need for rinsing. Typical surfactants used in all-purpose cleaners are anionic, nonionic or amphoteric. Out of these, anionic and nonionic are the most used surfactant types and they are typically used as a mixture in all-purpose cleaners. Cationic surfactants are not generally used as a main ingredient but are added as a disinfection agent. The most common surfactant molecules used in all-purpose cleaners are linear alkylbenzene sulfonates (LAS), alkane sulfonates (AS), sodium lauryl sulfate (SLS) and alcohol ethoxylates. (Falbe, 1987)

Special cleaners are a type of cleaners designed to remove a specific type of soil and other unwanted residue that cannot be removed by general cleaners. These could be, for example, rust stains, hardwater stains or organic material. Special cleaners can be either acidic or alkaline and are typically more diluted, although this varies depending on the application. (Falbe, 1987)

Manual dishwashing detergents are cleaning agents especially targeted to remove food residue, such as vegetable- and animal fats and proteins (Falbe, 1987). Dishwashing detergents are the only hard surface cleaning products whose cleaning properties are solely based on the surfactants (Falbe, 1987). They usually contain 10-20% surfactants (Blagojević et al., 2016). The pH of dishwashing detergents is preferred to be neutral, but it can range

between pH 5.5-8.5. Dishwashing detergents are typically mixture of two surfactants, primary and secondary surfactants due to an increase in cleaning performance (Asano et al., 2025). The primary surfactants are commonly anionic surfactants, such as LAS, AS and fatty alcohol ethyleneglycol ether sulfates (Blagojević et al., 2016). Secondary surfactants in dishwashing detergents are commonly fatty acid alkanol amides or fatty amide oxides (Blagojević et al., 2016; Falbe, 1987).

2.4.2 Laundry detergents

Laundry detergents are a type of detergents designed to clean fabrics (Bajpai and Tyagi, 2007). The laundry detergent formulations have pH-value between 10 and 12 (Dutta, 2019). The most used surfactant classes in laundry detergents are anionic and non-ionic surfactants. Laundry detergents contain mixture of different surfactants, as this improves the cleaning performance of the products (Falbe, 1987). Most commonly used anionic surfactants in laundry detergents are linear alcohol benzene sulfonic acids (LABSA), alkyl ether sulfate, fatty acid soaps, paraffin sulfonate and methyl ester sulfonate (Dutta, 2019). Common utilized non-ionic surfactants are fatty acid soaps, amine oxides, natural- and synthetic alkyl polyethyleneglycol ethers (Dutta, 2019; Falbe, 1987).

In addition to surfactants, laundry detergents contain additional ingredients, such as bleaching agents, enzymes, brighteners and auxiliary substances (Landeck et al., 2020). These additives are added to boost the performance of the surfactants, for example by softening water, as hard water reduces anionic surfactants cleaning ability due formation of ionic salts (Falbe, 1987). Other minor additives are also added to laundry detergents to make them more alluring to customers, such as colorants and perfume (Falbe, 1987).

Laundry detergents can be classified into three classes based on the fabric's color and type. These are heavy-duty-, color-, and special laundry detergents (Bajpai and Tyagi, 2007; Landeck et al., 2020). Heavy-duty detergents can used in all washing temperatures (15-95ºC) and are suitable to be used with the most common types of fabrics, such as cotton, linen and synthetic fabrics (Landeck et al., 2020; Smulders et al., 2002). Heavy-duty laundry detergents contain 10-50% surfactants (Smulders et al., 2002).

Color laundry detergents are intended to be used for colored clothes and the formulations often contain color maintaining additives, such as cellulase and dye transfer inhibitors (Smulders et al., 2002). Color laundry detergents contain 13-18% surfactants (Smulders et al., 2002).

Special laundry detergents are used for delicate and special fabrics, such as for woolens, silk, curtains and fabric's that require washing by hand (Smulders et al., 2002). Special laundry detergents contain anywhere between 7-30% surfactants (Smulders et al., 2002). Special laundry detergents differ from the two other classes of detergents, as they can be completely free of anionic surfactants and contain cationic surfactants (Smulders et al., 2002).

What is common for the different laundry detergents is that they are available both in liquid and powder form. Their cleaning ability varies based on the soil and the concentration of the surfactants. The liquid detergents are often more concentrated with surfactants compared to powder detergents. (Landeck et al., 2020)

2.4.3 Skin- and haircare products

Surfactants are used widely in many skin- and haircare products. Surfactants have many different functions in such products and work for example as a surface tension reducers, foaming or lather agents, cleansing agents and emulsification agents. Common skin- and haircare products which contain surfactants are presented in Table 3.

Table 3. Some of the skin- and haircare products, which contain surfactants in their formulations. (Sakamoto et al., 2017; Tadros, 2016; Falbe, 1987)

Skincare products	**Haircare products**
-Cleansers (foaming, gel, oil, cream, micellar water)	-Shampoo
-Toners	-Conditioner
-Facial lotions	-Hair styling (gel, spray, mousse, lotion, wax)
-Exfoliators	-Hair colorant
-Face masks	-Hair perming
	-Scalp and hair thinning care

Skincare products are used to cleanse, protect, maintain and improve skins condition with respect to its homeostatic balance (Sakamoto et al., 2017). The term "skincare products" is

generally used to refer to facial skin care products and as such, facial skincare products will be addressed in this chapter.

As described earlier, surfactants used in skincare products have different functions. They are used as solubilizers, emulsifiers, washing agents, wetting agents and as anti-foaming agents. Surfactants used in skincare formulations should fulfill essential functions, such as be gentle for the skin, bring active ingredients to the outer layer of the skin and promote their micro distribution and clean the skin's surface without increasing skins permeability to substances. (Falbe, 1987)

The function of surfactants used in skincare formulations is generally defined by their respective HLB value (Falbe, 1987). Table 4 presents HLB with respect to application of surfactant.

Table 4. HLB value of surfactants and their corresponding application in skincare formulations (Falbe, 1987).

HLB value	**Application**
15-20	Solubilizers
8-18	O/W emulsifiers
13-15	Wash active surfactants
7-9	Wetting agents
3-6	W/O emulsifiers
1.5-3	Antifoaming agents

Based on HLB values, generally surfactants with higher HLB are used in water-based products due to their foaming abilities, good cleaning abilities and effective solubilizing. Surfactants with lower HLB are on the other hand used in oil-based formulations, such in oil-based cleansers, as they dissolve better into oils and help to dissolve oils from the skin's surface.

Surfactants are a major ingredient in haircare cosmetics, where they are used as cleansers, foaming agents, emulsifiers, conditioners, wetting- and solubilizing agents and to modify the viscosity of the formulations. Haircare products are used to cleanse, maintain, protect or modify hair's structure or color. Shampoo is the most used haircare product. (Sakamoto et al., 2017)

Anionic surfactants are the most utilized class of surfactants in skin- and haircare formulations. Anionic surfactants have good cleaning abilities and emulsifying properties. Common anionic surfactant used in skin- and haircare products are carboxylate, sulphate, sulphonate and phosphate-based surfactants. Skin- and haircare formulations often contain several different types of surfactants, as a single surfactant usually cannot perform all the different tasks which are expected from the product. For example, amphoteric surfactants are used with anionic surfactants in mild formulations, such as in “everyday” shampoos. (Falbe, 1987; Tadros, 2016)

Polymeric surfactants are also used in skin- and haircare formulations. Polymeric surfactants have much lower toxicity, sensitization and irritation potential if they are not contaminated by traces of the parent monomers. Polymeric surfactants are also preferred, as they are less likely to penetrate top layer of the skin, which minimizes any medical risks associated with cosmetic formulations (Tadros, 2016). Polymeric surfactants are used as emulsifiers, dispersants, film formers, thickeners, stabilizers and destabilizers and to adjust the viscosity of the formulations (Chowdhury et al., 2019; Tadros, 2016). Block- and graft-type polymeric surfactants are typically used in these formulations (Tadros, 2016).

Also, some naturally occurring surfactants, for example phytosteroids extracted from plants, and surfactants extracted from beeswax or produced from wool fat are used in cosmetic products. However, they are not as widely used as synthetic surfactants due to their poor physicochemical properties. (Tadros, 2015)

2.5 Surfactants in agricultural products

Surfactants play an important role in many agricultural products. They are used in pesticides, herbicides, fertilizers and as a wetting agents (Tadros, 2015). Surfactants have essential functions in agrochemicals, as they are used to prepare and maintain stability of the products. Surfactants enhance the performance of agrochemicals as well improve their spreadability (Castro et al., 2014; Tadros, 2015). Agrochemical formulations contain about 1-10% of surfactants and around 230 000 tons of surfactants are used annually for these products (Castro et al., 2014).

The most used agrochemical formulations are emulsion concentrates (EC), aqueous O/W emulsions (EW) and suspension concentrates (SC). EC are a mix of agrochemical oil and organic solvents. Surfactants are added to EC solutions to produce and maintain stable emulsion and to reduce interfacial tension between the oil and the solvent. EC's contain 5-15% of surfactants. (Tadros, 2015)

EW have increased in popularity, as they are less harmful for the user and are eco-friendlier than solvent-based ECs. They can also be cheaper than EW, as they require lower amount of surfactants (0.1-10%) for the emulsion. (Tadros, 2015)

SC are a dispersion of liquid and solid, where the active ingredients are suspended in the liquid as insoluble particles. Surfactants are used as a dispersing agents to stabilize the suspension and prevent the sedimentation of the solid particles. (Tadros, 2015)

Anionic surfactants are the most widely used surfactant class in agrochemical formulations due to their relatively low price. Anionic surfactants are used in almost every type of agrochemical formulation. Structure vice, anionic surfactants with linear alkyl chain are preferred, as they are more effective and degrade more easily than branched alkyl chains. Based on the anionic surfactants hydrophilic groups, carboxylates, sulfates, sulfonates and phosphates are most used types of anionic surfactants. (Tadros, 2015)

Besides anionic surfactants, cationic, amphoteric, non-ionic and polymeric surfactants are also used in agrochemical formulations. Agrochemical formulations often contain mixes of different types of surfactants, as it improves their performance. (Tadros, 2015)

Polymeric surfactants are utilized in all major agrochemical formulations. Polymeric surfactants have different functions depending on the formulation. In EWs, polymeric surfactants are used to prevent flocculation and coalescence. In SC formulations, polymeric graft- and block-type surfactants are used to prepare and maintain the suspension. Polymeric surfactants are also utilized in other agrochemical formulations, where they, for example, provide effective steric repulsion. (Tadros, 2017a)

3 Lignin-based surfactants

Lignin-based surfactants are surfactants derived from lignin, a natural polymer found from lignocellulosic biomass. Next sections will dive more in-depth into lignin, its desired properties, chemical modification routes to surfactants and evaluation methods, which can be utilized to assess the performance of novel lignin-based surfactants. Commercial and non-commercial applications of lignin-based surfactants are also discussed.

3.1 Lignin

Lignin is complex, heterogeneous aromatic polymer found in the cell walls of plants (Poletto et al., 2018). Lignin is one of the three main components found in the lignocellulosic plants, along with cellulose and hemicellulose (Sand et al., 2023). It is the second most abundant polymer of natural origin after cellulose (Norgren and Edlund, 2014). On average, 15-25% of the cell wall is lignin (Sand et al., 2023).

Lignin has branched, three-dimensional chemical structure which composition is variable and dependent on the biomass type (Norgren and Edlund, 2014; Serrano et al., 2020). Lignin, however, has three main, repeating phenylpropane-based monomers known as monolignols: *p*-coumaryl, coniferyl and sinapyl alcohol (Poletto et al., 2018). The aromatic units of these monolignols are known as p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, respectively (Poletto et al., 2018). The quantity of these monolignols in lignin is dependent on the plant type they originate from. The chemical structure of these monolignols is presented in Figure 14.

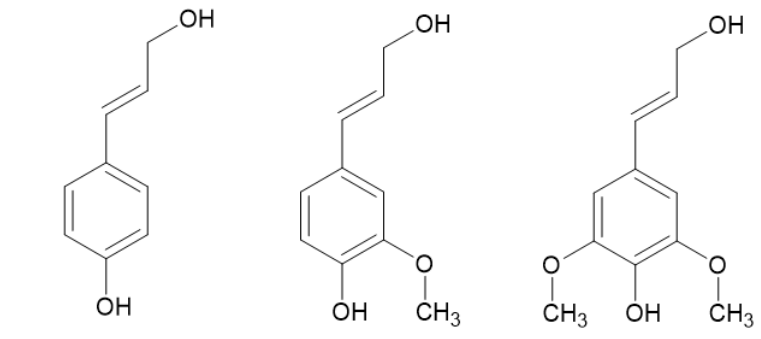


Figure 14. Molecular structure of monolignols in lignin. Adapted from (Poletto et al., 2018).

The monolignols are connected to each other via covalent bonds, and most of these are via carbon-carbon bonds (C-C) or by ether bonds (C-O-C) (Poletto et al., 2018). Out of these, the ether bond, more specifically aryl-ether linkage β-O-4, is the most abundant type, making up 60% of lignin intermonomeric linkages (Poletto et al., 2018). Common linkages found between lignin monolignols are presented in Figure 15.

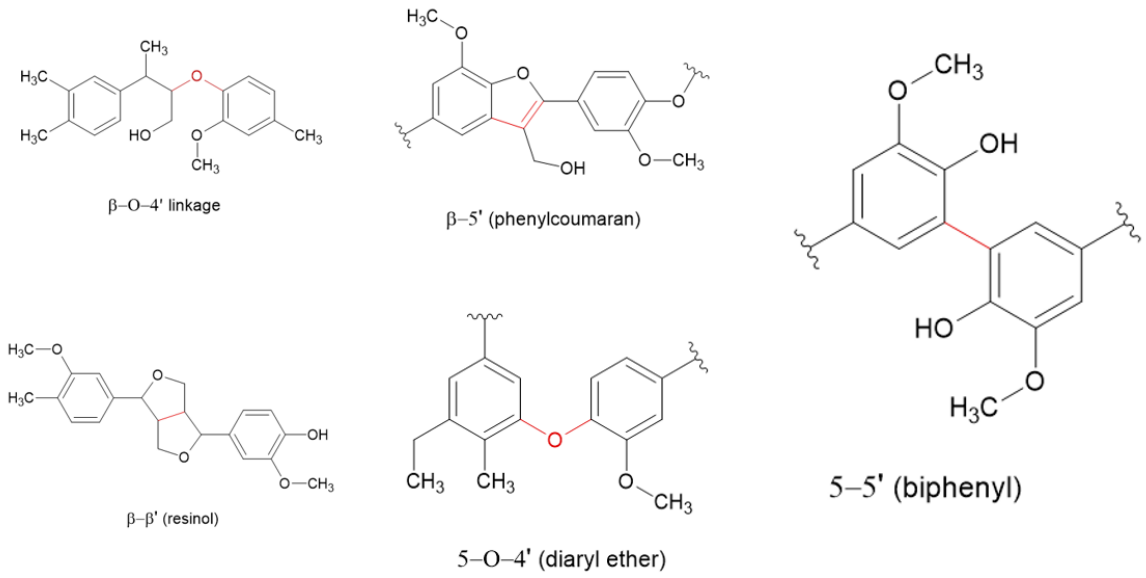


Figure 15. Common intermonomeric linkages found in lignin.

Lignin can be classified into three types based on its origin, which are softwood-, hardwood- and non-woody lignin (Akpan, 2019). Softwood lignin, also known as guaiacyl lignin, contains mainly coniferyl alcohol, making up to 90% of lignin's monolignol content (Serrano et al., 2020; Yue et al., 2016). Softwood lignin is derived from gymnosperm species (Suota et al., 2021).

Hardwood lignin, also known as guaiacyl-syringyl lignin, contains about same amount of both coniferyl and sinapyl alcohols, but their ratio can vary between plant species (Suota et al., 2021; Zhang et al., 2015). Hardwood lignin is derived from angiosperm species (Suota et al., 2021). Hardwood lignin contains higher amounts of ether bonds compared to the softwood lignin, but on the other hand the softwood lignin contains more carbon-carbon bonds (Akpan, 2019). Chemical structure of hardwood lignin is presented in Figure 16.

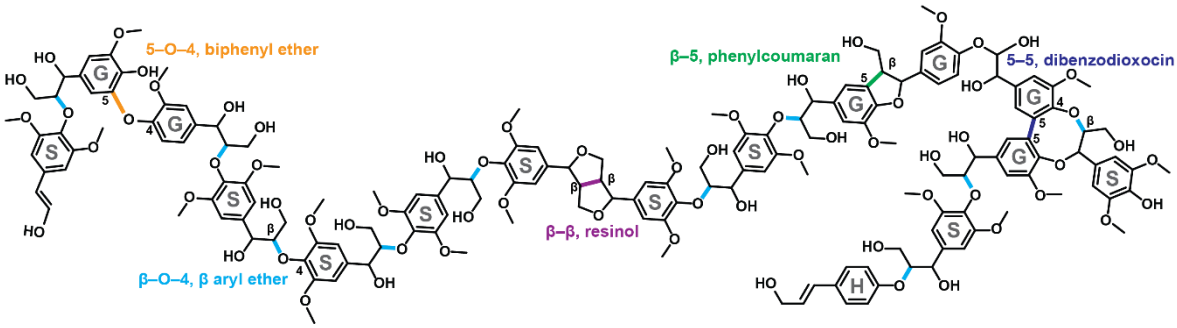


Figure 16. Chemical structure and typical linkages of hardwood lignin.

Non-woody lignin contains a mixture of all the monolignols units. Non-woody lignin is derived from graminoids and other non-woody plants. It is not as widely utilized as lignin from wood sources due to its low lignin content. (Akpan, 2019)

Lignin contains a lot of functional groups attached to its main structure. These include phenolic and benzylic hydroxy, methoxy, carbonyl and carboxylic acid groups (Lin and Dence, 2012). The specific functional groups and their quantity is dependent on the biomass type, as well as on the extraction method of lignin (Lin and Dence, 2012). The abundance of functional groups makes lignin attractive for possible subsequent modifications and applications, such as to surfactants.

3.1.1 Technical lignins

Lignin in its natural form, found in the cell walls of plants, is referred to as native lignin. In order to utilize lignin in different applications, lignin needs to be separated from lignocellulosic biomass and its components, cellulose and hemicellulose. This is done via pretreatment of lignocellulosic biomass, in which lignin is separated from the other main components. The extracted lignin is referred to as technical lignin. (Ekielski and Mishra, 2021)

The pretreatment of the lignocellulosic biomass can be classified into chemical, physical, physico-chemical or biological treatments (Eraghi Kazzaz and Fatehi, 2020). However, it should be noted that physical pretreatment does not separate lignocellulosic components from each other but rather makes them more easily accessible. Pretreatment types, common processes and their main functions are presented in Table 5.

Table 5. Common pretreatment types and processes of lignocellulosic biomass and their function.

Pretreatment type	**Pretreatment processes**	**Main function(s)**	**Source(s)**
Physical	Chipping, grinding, milling, extrusion	Reduces particle size, increases surface area and decreases crystallinity of lignocellulosic biomass	(Alvira et al., 2010)
Physico-chemical	Steam-explosion, Ammonia fiber explosion, Liquid hot water, Wet oxidation, Microwave, Ultrasound	Breaks down the structure of biomass: solubilizes hemicellulose, reduces crystallinity, separation of lignin	(Alvira et al., 2010; Mussatto, 2016; Verardi et al., 2012)
Chemical	Alkali and Acid pretreatment, Organosolv, Ionic-liquid, Ozonolysis	Removes lignin and hemicelluloses, increases accessible surface area	(Alvira et al., 2010; Mussatto, 2016; Verardi et al., 2012)
Biological	Fungal or bacterial pretreatment, enzymatic treatment	Degrades lignin and hemicelluloses.	(Mussatto, 2016; Verardi et al., 2012, 2012)

Commercially important technical lignins can be classified into five categories based on their method of extraction process and properties, which are kraft-, sulphite-, soda-, organosolv- and hydrolysis lignin (Eraghi Kazzaz and Fatehi, 2020). Out of these, kraft-, sulphite-, soda- and organosolv lignins are extracted from different pulping processes as a byproduct. Lignins extracted from pulping processes can be further divided into two categories, based on the presence of sulfur (Serrano et al., 2020). Lignins acquired through pulping will not be discussed further, as they are not relevant for the thesis.

3.1.2 Hydrolysis lignin

Hydrolysis lignin is a type of lignin that is obtained as a byproduct from hydrolysis of lignocellulosic biomass. Hydrolysis lignin can originate either from acid, alkali or enzymatic hydrolysis process (Eraghi Kazzaz and Fatehi, 2020). The primary function of hydrolysis of lignocellulosic biomass is to break down the polysaccharides (cellulose and hemicellulose)

and utilize them in different applications, such as in production of ethanol (Eraghi Kazzaz and Fatehi, 2020).

The hydrolysis lignin consists of around 50-75% lignin, 10-22% of sugars and mixture of ash, moisture and residual cellulose and hemicellulose (Chio et al., 2019; Eraghi Kazzaz and Fatehi, 2020). Hydrolysis lignin is completely sulfur-free, or contains a very little amount (<1%) (Chio et al., 2019). The exact composition is dependent on the pretreatment and hydrolysis process as well as from the source of lignocellulosic biomass.

In the acid hydrolysis process, the lignocellulosic biomass is exposed to strong acid, such as to sulfuric or hydrochloric acid, which breaks down cellulose and hemicellulose into individual sugar molecules, leaving lignin as a residue (Lenihan et al., 2010). Acid hydrolysis can done with concentrated or diluted acid and the process conditions depend on the applied method (Eraghi Kazzaz and Fatehi, 2020). With concentrated acids, the hydrolysis can be performed in temperature under 100 ºC and in ambient pressure, while high temperature (180-260 ºC) and pressure (> 1 MPa) is needed when using diluted acids (Eraghi Kazzaz and Fatehi, 2020). Downside of acid hydrolysis is that it degrades and condensates lignin, which may affect the further utilization of lignin (Ekielski and Mishra, 2021).

In alkali hydrolysis, the lignocellulosic biomass is treated with a base, such as potassium, sodium or ammonium hydroxides (Alvira et al., 2010). Alkali hydrolysis separates lignin from the cellulose and the hemicellulose by breaking the ester and ether bonds between lignin and sugars, effectively solubilizing lignin (Alvira et al., 2010). Alkali hydrolysis produces more pure lignin than acid hydrolysis, as it exhibits less cellulose and hemicellulose solubilization (Alvira et al., 2010). Alkali hydrolysis can be performed in ambient conditions or in an autoclave and high-pressure reactors (Eraghi Kazzaz and Fatehi, 2020).

Enzymatic hydrolysis utilizes enzymes in the extraction of lignin. Lignocellulosic biomass requires some type of pretreatment before the introduction of enzymes to improve enzyme access to the material, since lignin blocks the access to the polysaccharides (Chio et al., 2019). The pretreatment is usually chemical or thermomechanical-chemical (Cai et al., 2023). In the enzymatic hydrolysis, enzymes are used to break down the cellulose and hemicellulose, which leaves insoluble lignin as a residue (Cai et al., 2023). Typical enzymes

used in enzymatic hydrolysis are cellulases and hemicellulases (Verardi et al., 2012). Enzymatic hydrolysis can be performed in low temperature (< 50 ºC) and at around neutral pH, which makes the process more environmentally friendly (Eraghi Kazzaz and Fatehi, 2020). Enzymatic hydrolysis produces native-like lignin, as the lignin's structure is not altered by acids or bases (Chio et al., 2019). Enzymatic hydrolysis lignin can however be contaminated with enzymes and unhydrolyzed cellulose and hemicellulose (Cai et al., 2023). Downside of the enzymatic hydrolysis is that it has higher costs due to use of expensive enzymes (Eraghi Kazzaz and Fatehi, 2020).

Among research community, hydrolysis lignin has been experimented and valorized in adhesive, flocculant, dispersant and fire-retardant applications (Ekielski and Mishra, 2021; Eraghi Kazzaz and Fatehi, 2020). As per Eraghi Kazzaz and Fatehi (2020), not many modification reactions have been performed in the utilization of hydrolysis lignin due to low amount of free phenolic hydroxide groups present in hydrolysis lignin. Hydrolysis lignin also has low reactivity due to complex structure, hindering its modification. Impurity and low solubility of the hydrolysis lignin restricts the possible valorization of hydrolysis lignin, as it needs multiple modification and purification steps prior its utilization (Chio et al., 2019). It is stated that hydrolysis lignin would be better suitable for generating small molecules rather than larger polymers (Ekielski and Mishra, 2021).

3.2 Desired properties of lignin-based surfactants

The desired properties of lignin-based surfactants vary depending on their application area and on the function of what the surfactants are used for. Generally, lignin-based surfactants should possess similar characteristics as commercial synthetic and -bio-based surfactants. Therefore, lignin-based surfactants should have an amphiphilic structure, lower the surface and interfacial tension between two phases and self-assemble into micelles above certain concentrations and temperatures.

Lignin-based surfactants should achieve similar parameter values as commercial surfactants. In case of surface tension reduction, commercial anionic surfactants can lower the surface tension of water to 35-44 mN/m, which should be comparable with novel lignin-based surfactants (Alwadani and Fatehi, 2018).

The CMC is also an important factor for surfactants, and it should preferably be as low as possible. With low CMC, less surfactant is needed, increasing the performance and the economy of the surfactant. While there is no specific limit on what the CMC should be, it should preferably be in the same range as the commercial anionic surfactants are. A common anionic surfactant used in soaps, SDS, has CMC value of 0.01 mol/L and other common anionic surfactant, sodium tetradecyl sulfate, even lower at 0.00854 mol/L (Alwadani and Fatehi, 2018).

Although surfactants have some similar roles in both home and personal care and agrochemical formulations, the desired properties vary based on the application. The desired properties for both application areas are discussed in the next sections.

3.2.1 Desired properties in home and personal care products

Surfactants are an important part of home and personal care formulations with many different functions, as described in previous chapters. The main function of surfactants in these formulations is to work as a cleaning agent and emulsifier.

Surfactants used in home and personal care products should have good soil removal ability, which is especially important in detergent, hard surface cleaning and personal care formulations. As was previously mentioned, surfactants should not harm the material it comes in contacts with, whether it is a hard surface, textile or skin. (Falbe, 1987)

Surfactants should also be compatible with other components in the formulations. This is desired, as reacting with other components can cause the products to not work properly or lead to the formation of toxic compounds. Surfactants should also endure and work in different conditions, such as in different pH and temperature ranges, as well as in both soft and hard water. (Falbe, 1987)

From the emulsification point of view, the desired HLB value of lignin-based surfactants varies based on the application. As seen from Table 4, surfactants with lower HLB value work better in W/O emulsions while surfactants with higher HLB value are used in O/W emulsions.

Emulsions should remain stable in storage for long periods of time. According to Park et al. (2023), emulsions should stay stable for at least 1.5 years and stability of three years would

be considered excellent. Based on standard (ISO/TR 18811:2018), emulsion stability tests measure the stability of one year and above, which gives some rough indication that formulated emulsions should stay stable for at least a year. However, desired emulsion stability varies between formulations and emulsion types.

One of the most important factors, especially for personal care products, is that surfactants should be non-toxic and biologically compatible with human skin, hair or other body parts where it is applied. Surfactants in these formulations should not cause irritation, nor other unwanted effects, while still performing the expected function. Furthermore, surfactants should not penetrate through the skin, for which surfactants are preferred to be a bit higher in molecular weight rather than the smallest possible, as this reduces the risk of penetration. (Sakamoto et al., 2017)

From the environmental point of view, surfactants should not be toxic to aquatic life. As most of surfactants in home and personal care products are disposed to sewage, they should be environmentally harmless and benign. (Falbe, 1987)

Although the foaming ability of surfactants does not indicate anything about the cleaning ability or efficiency of surfactant, proper foaming is a desired characteristic in most home and personal care applications. Consumers associate foaming with the performance of the product, however, this is purely cosmetic. (Falbe, 1987)

3.2.2 Desired properties in agricultural applications

Surfactants play crucial roles in agrochemical formulations, where they are utilized as wetting agents, suspending agents and emulsifying agents.

In SC formulations, surfactants should prevent flocculation and sedimentation of solid particles, maintaining suspension. The recommended suspensibility of SC varies based on the source and suspended material. For example for pesticides, a common SC, the Food and Agriculture Organization of the United Nations (FAO) recommends that the suspensibility should be at least 60% for the active ingredient after 30 minutes. (World Health Organization, 2023)

If utilized as a wetting agent, surfactants should wet the surface and spread evenly and widely. In other terms, surfactants should lower the contact angle of water, which helps

aqueous solutions to spread evenly and widely to a solid surface. For example, surfactants should lower the contact angle of herbicide solutions, which provides more uniform spread as well as reduces the amount of herbicide solutions needed. Efficient wetting also helps with the costs, as less solution with proper wetting. (Tadros, 2018)

EC's or other agricultural emulsions should remain stable in storage conditions for at least 2 years. Small separation is acceptable, if it can be re-emulsified easily. (Azelis, 2025)

Lignin-based surfactants should also be non-toxic to the environment and be biodegradable. This is important factor, as solutions containing surfactants are applied to plants and crops. (Castro et al., 2014)

Surfactants used in agrichemical formulations should preferably be low foaming, as foaming is undesired property. (Castro et al., 2014)

3.2.3 Challenges with lignin-based surfactants

Lignin has some challenges, which limit its utilization as a lignin-based surfactant. One of the key challenges is the irregularity of lignins structure. Lignins structure varies based on which biomass type lignin originates from (softwood, hardwood, other source) and the extraction method. Extraction method of lignin from lignocellulosic biomass also alters the lignin's chemical composition, which leads to the formation of heterogenous technical lignin, varying in molecular weight and functional groups. This makes lignin hard to utilize industrially, as the chemical composition changes from batch to batch. (Alwadani and Fatehi, 2018)

Lignin has a high molecular weight, which hinders its usage as surfactant as such. Chemical treatment is needed to fractionate the lignin into smaller, homogenous molecular weight fractions. Furthermore, lignin and most of the technical lignins are insoluble in water (Alwadani and Fatehi, 2018). This hinders the usage of lignin as such, as lignin needs to be soluble in aqueous solutions for surfactant end-use.

The natural color of lignin is also a challenge. Lignin has a brown color, which affects its utilization especially in home and personal care products, where the color of the product is important. Lignin-based surfactants may need to be decolorized before they can be used in commercial formulations.

3.3 Evaluation methods for lignin-based surfactants

There are several methods to evaluate lignin-based surfactants' performance. The evaluation methods are the same that are done for evaluating synthetic surfactants. However, evaluation of lignin-based surfactants differs from the standard methods in the sense that the specific structure of lignin is unknown and varies based on the extraction conditions. This requires additional characterization methods, as to evaluate the chemical composition, especially the quantity and quality of different functional groups and linkages in lignin.

3.3.1 Surface/interfacial tension and CMC

Since one of the main functions of lignin-based surfactants is to lower surface or interfacial tension between two or more mediums, it is critical to measure both the CMC and the surface or interfacial tension. There are several methods to evaluate how the lignin-based surfactants alter the surface or interfacial tension between two phases. Table 6 presents common methods used to measure these values.

Table 6. Common methods used to measure surface and interfacial tension

Method	**Measurement type**	**Working principle**
Wilhelmy plate method	Surface & interfacial tension	Measures force on a thin plate partially immersed in liquid or between interfaces (Nalwa, 2001)
du Noüy ring method	Surface & interfacial tension	Measures force needed to detach ring from the surface/interface (Nalwa, 2001)
Pendant drop method	Surface & interfacial tension	Uses optical methods to analyze shape profile of a pendant drop suspended on a capillary tube/needle (Saad et al., 2011)
Spinning drop method	Surface & Interfacial tension	A droplet is suspended in an immersion fluid, which is then rotated at high speeds. Droplet will deform and surface/interfacial tension can be measured from it. (Rapp, 2017)
Maximum bubble pressure method	Surface tension	A gas bubble is created inside the liquid through the capillary tube. The size of the bubble is increased until it reaches maximum pressure, where the surface tension can be derived from. (Nalwa, 2001)

Wilhelmy plate and du Noüy ring methods are the most used for measuring surface or interfacial tension of a solution due to their simplicity. Both methods are based on the force generated on the measuring instrument as it interacts with the surface or interface of a liquid. (Nalwa, 2001)

In the Wilhelmy plate method, a thin plate is dipped into the liquid or between interfaces. The plate is usually made from platinum or glass. The sample is moved so that the plate just touches the surface. The surface tension creates a down pulling force to the plate, which is measured using an electro balance. (Nalwa, 2001)

The surface or interfacial tension is calculated using Equation 1.

$$\gamma = \frac{F}{2(w+d)cos\theta} \quad (1)$$

Where, γ Surface or interfacial tension, N/m

F	Pulling force of the surface/interface, N
w	Width of the plate, m
d	Diameter of the plate, m
θ	Contact angle of the liquid, º

The contact angle for the liquid can be derived from the literature, but usually complete wetting is assumed, which reduces the contact angle to 0.

In the du Noüy ring method, platinum ring is inserted horizontally below the interface and then pulled up through it. The pulling force of the liquid increases, as the ring rises from the interface. The pulling force reaches maximum value just before the lamella breaks, which is then used to calculate the surface or interfacial tension (Equation 2).

$$\gamma = \frac{F}{4\pi R f} \tag{2}$$

Where,	R	Radius of the ring, m
	f	Correction factor

Correction factor can be used to make precise measurements, which takes into account the density of the measured liquid and ring geometry. (Nalwa, 2001)

Pendant drop method differs from other commonly used surface/interfacial tensions measurement techniques, as it is based on the optical shape analysis of a droplet. In pendant drop method, a droplet of the sample liquid is formed on the tip of a needle and the surface/interfacial tension is derived based on the droplet's geometry and shape factor. The pendant drop method requires only a little amount of sample, which makes the method great alternative for force-based surface/interfacial tension methods when limited amount of sample is available. (Nalwa, 2001)

Spinning drop method is another measuring technique, which utilizes optical methods to determine surface/interfacial tension. In spinning drop method, droplet of a sample is placed to measuring liquid with higher density than that of the sample, and they are put in a rotating class tube. The tube is spun with high velocity, which causes the droplet to become cylinder shaped. The surface/interfacial tension can be derived from the dimensions of the cylinder-

shaped droplet. Spinning drop method can only be used to measure really small surface tensions. (Marquez and Salager, 2025)

Maximum bubble pressure method is based on measuring the pressure change of gas bubble in measurement medium. In the method, a capillary is placed in the sample liquid and gas bubble is created through capillary with controllable pressure. The pressure is increased, until the bubble's diameter reaches the size of the capillary. At this stage, The pressure inside the bubble has reached its maximum value, and the surface tension can be derived using the Young-Laplace equation. (Rapp, 2016)

When considering surfactants, it is also important to determine when surfactant molecules start to aggregate to form micelles. The CMC value reflects how effective the surfactant is, as low CMC suggests that less surfactant is needed to reach minimum surface tension. CMC can be determined with different methods, including conductivity measurements, UV-Vis & fluorescence spectroscopy, but most commonly CMC is acquired from surface tension measurements. (Scholz et al., 2018)

3.3.2 Emulsion stability

Lignin-based surfactants ability to form and stabilize emulsions is critical to evaluate, if lignin-based surfactants are planned to be used in personal and homecare applications, as many of the formulations are based on emulsions. Emulsion stability describes how well the emulsion can remain in stable equilibrium and resist changes to its physicochemical properties over time. (Hu et al., 2017)

Common methods to evaluate emulsion stability of lignin-based surfactants are presented in Table 7.

Table 7. Common methods used to evaluate emulsion stability (Hu et al., 2017)

Technique
Visual observation
Microscopy observation
Particle size analysis
Charge analysis

Visual observation is the simplest and quickest way to evaluate gravitational separation of emulsions, such as sedimentation or creaming. However, only a limited amount of information about the structure of the emulsion can be acquired with the human eye. Other evaluation methods should be used to study possible coalescence, flocculation and Ostwald ripening happening in the emulsion phase. (Hu et al., 2017)

Microscopic imaging of the emulsion gives better understanding of the emulsions structure. Microscopes, which could be used to assess the emulsions' structure more detailed include optical, electron, atomic force and confocal fluorescent microscopes (Hu et al., 2017). Confocal fluorescent microscope is especially great in evaluation of lignin-based surfactants, as the fluorescence can be used to observe the distribution of lignin-based surfactant molecules in the emulsion (Maceda and Terrazas, 2022). To gather more information about the emulsion, microscopy is usually coupled with analytical method, such as charge analysis or particle size analysis (Hu et al., 2017).

Analytical methods, that can be used to evaluate emulsion stability include particle size analysis and charge analysis. Particle size analysis can be used to gain information about the stability of emulsion based on the particle size distribution (PSD) of the dispersed phase. With knowledge about the PSD, stability of the emulsion can be evaluated using Stoke's law, as the stability decreases with increasing particle size. (Hu et al., 2017)

Charge analysis gives information about the emulsion by measuring the surface charge of the droplets in the emulsion. The electrostatic forces between droplets give information about the stability of emulsions, which can be measured with charge analysis instruments. These include for example light scattering, ultrasonic spectrometry and electrical probe counting. (Hu et al., 2017)

As emulsions are expected to remain stable for up to years in storing conditions, the stability of emulsions in long time period should also be evaluated. The evaluation for personal care emulsions can be conducted with accelerated stability test, according to the standard (ISO/TR 18811:2018). The standard test is based on subjecting the emulsion to an elevated temperature (40-45ºC) and observing the possible change in the emulsion properties over time. According to the standard, 2 weeks at an elevated temperature is equivalent to standard storage conditions of 6 months. The standard indicates that if emulsion stays stable for 4 weeks, the emulsion would be stable for at least 1 year, at 6 weeks at least 1.5 years, at 8 weeks at least 2 years and so forth.

Similar accelerated emulsion tests are available to agrochemical emulsions formulations, although they have slight variance depending on the method. For example, standards made by Collaborative International Pesticides Analytical Council (CIPAC) MT 46 and MT 39 can be used to assess the stability of emulsions in low and elevated temperatures. (Dobrat and Martijn, 1994)

3.3.3 Suspensibility

Suspensibility of insolubilized solids is an important factor that should be evaluated when assessing the possible use of surfactants in agrochemical or hard surface cleaner formulations. The evaluation methods for surfactants suspending ability are either done gravimetrically or with turbidity test.

Suspensibility test is an easy method to evaluate the suspending ability of surfactants. Suspensibility test consists of measuring ratio of suspended/settled solid in water medium. There are several standards for this method developed by CIPAC, for example CIPAC MT 15.1, MT 177 and 184.1 are standards used to test the suspensibility of water dispersible powders. These methods utilize gravimetrical methods to measure the suspensibility. (Dobrat and Martijn, 1994)

Turbidity measurement is another simple testing method, which can give information about the suspending ability of a surfactant. Turbidity measurement is based on measuring the light scattering from the solid particles in a suspension. The light scattering increases with concentration of suspended solids in the liquid and thus can be used to measure the

concentration of suspended particles. Turbidity can be measured with single or double beam spectrophotometer or with a nephelometer. Compared to gravimetric suspensibility test, turbidity measurement is faster and can be applied *in situ.* (Tadros, 2017b)

3.3.4 Biological and environmental tests

Surfactants need to be assessed for their biological compatibility to utilize them in commercial formulations. This is especially important, as well as mandatory process before surfactant could be used in cosmetic products. The biological testing methods have been standardized by the Organisation for Economic Co-operation and Development (OECD). In Table 8 is listed common tests and methods used for biological testing of cosmetic products.

Table 8. Biological testing methods used for safety evaluation of cosmetic ingredients (Sakamoto et al., 2017).

Testing class	**Test method(s)**
Acute toxicity	Acute oral toxicity (TG 420, TG 423), acute inhalation toxicity (TG 433, TG 436), acute dermal toxicity (TG 434)
Dermal irritation	Acute dermal irritation/corrosion (TG 404), skin corrosion (TG 431)
Skin sensitization & skin absorption	Skin sensitization (TG 429, TG 442C,D,E), skin absorption (TG 427, TG 428)
Eye irritation	Eye irritation (TG 437, TG 438, TG 460, TG 491)
Human data	Human patch test, controlled-user test
Genotoxicity	Genotoxicity (TG 471, TG 473, TG 476, TG 487, TG 490)
Phototoxicity & photosensitization	Phototoxicity (TG 432), Photo patch test
Reproductive toxicity & carcinogenicity	Reproductive toxicity (TG 414, TG 421, TG 422), carcinogenicity (TG 451, TG 453)

Surfactants, especially those in home and personal care applications, are usually disposed to sewage, where they end up to the environment. Therefore, it is important to evaluate the ecotoxicity of the surfactants. Toxicity towards water organisms is usually assessed with lethal dosing tests and chronic aquatic toxicity tests. Bioaccumulation to organisms is usually also assessed. (Falbe, 1987)

Biodegradability of surfactants is also an important factor to measure. Biodegradability of surfactants prevents the build-up of surfactant molecules to the soil or to the aquatic environment. For detergent applications, the most important biodegradability screening tests are OECD screening and OECD confirmatory test. (Falbe, 1987)

3.3.5 Contact angle

Contact angle measurement of surfactant gives information about its performance as a wetting agent. Contact angle can be determined by placing one drop of surfactant containing solution to a solid surface. By measuring the angle of the edge of droplet and the solid surface, contact angle can be determined using Young's equation (Equation 3). (Kwok and Neumann, 1999)

$$\gamma_{lv} cos\theta_Y = \gamma_{sv} - \gamma_{sl} \quad (3)$$

Where, γ_{lv} Interfacial tension of liquid-vapor, N/m

θ_Y Young contact angle, °

γ_{sv} Interfacial tension of solid-vapor, N/m

γ_{sl} Interfacial tension of solid-liquid, N/m

Figure 17 presents the different interfaces used in Equation 3.

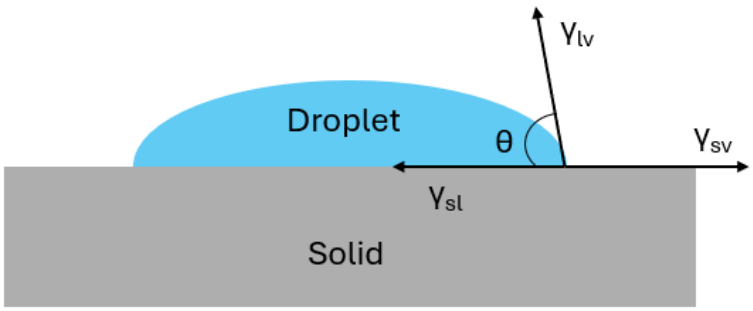


Figure 17. Contact angle of droplet on a solid surface and different interfaces used in Equation 3. Adapted from (Kwok and Neumann, 1999)

A picture of the droplet can be taken with digital camera and contact angle or image processing software can be used to determine the accurate contact angle from the picture (Akbari and Antonini, 2021). The contact angle can also be measured with instruments, such as with pendant drop analysis, which was presented previously.

3.3.6 Lignin characterization

As stated at the beginning of the chapter, it is also important to assess the properties of lignin in the evaluation of lignin-based surfactants. Important lignin properties that should be measured include molecular weight and chemical composition of lignin.

Molecular weight is important to assess, as the molecular weight affects the surface activity of lignin-based surfactants. The surface activity tends to improve with decreasing molecular weight, as lignin molecules can more easily migrate to the surface or interface. Lower molecular weight also makes lignin more soluble to water, which is an important factor when considering surfactant formulations. Molecular weight of lignin or lignin-based surfactants can be evaluated with liquid chromatography using light scattering, UV absorbance or refractive index measurements (Stark et al., 2016).

Chemical composition can be characterized using spectroscopic methods. Common spectroscopic methods include UV, FTIR, Raman, NMR and XPS spectroscopy (Stark et al., 2016). These common methods along with other chemical characterization evaluation techniques and their respective working principles are listed in Table 9. (Ruwoldt, 2020)

Table 9. Common methods used to characterize lignin's chemical structure

Method	**What information is gained**	**Reference**
UV spectroscopy	Concentration of lignin in solutions	(Stark et al., 2016)
FTIR spectroscopy	Functional groups and their relative proportions	(Melro et al., 2021)
Raman spectroscopy	Functional groups and their relative proportions	(Stark et al., 2016)
NMR spectroscopy	Functional groups, lignin linkages and their relative proportions	(Melro et al., 2021)
XPS spectroscopy	Functional groups attached to carbon atoms	(Stark et al., 2016)

Nuclear magnetic resonance (NMR) is typical method used in the characterization of functional groups and their proportions in lignin. ^{31}P-NMR, ^{1}H-NMR, ^{13}C-NMR and two-dimensional heteronuclear single quantum coherence (2D-HSQC) NMR are most common NMR techniques used in the lignin analytics (Melro et al., 2021). NMR measurements are based on applying magnetic field to an atomic nucleus, which pulses a radio frequency back to the sensor, corresponding to chemical bonds attached onto it (Stark et al., 2016). For example, in ^{13}C-NMR, carbon nuclei are placed in a strong magnetic field and irradiated with radiofrequency pulses. The nuclei absorb and re-emit energy at resonance frequencies that depend on their electronic environment. These frequency shifts provide information about the functional groups and bonding patterns associated with carbon atom.

2D-HSQC-NMR is a more precise method compared to one dimensional NMR techniques. In 2D-HSQC-NMR, carbon atoms are correlated with their attached protons. As a result, two-dimensional spectra is acquired, which can be used to observe different functional groups in the sample. In lignin-based samples, ratio of main units (H:G:S) can be also observed. For lignin-based surfactants, important features such as aromatic and aliphatic signals can be clearly distinguished. (Melro et al., 2021; Stark et al., 2016)

Fourier-transform infrared spectroscopy (FTIR) is another commonly used method in the characterization of lignin. The method is based on emitting infrared (IR) light to the sample, which either transmits through or reflects back to the sensor (Stark et al., 2016). Photons with frequencies that match the vibrational frequencies of functional groups are absorbed to

the functional groups (Stark et al., 2016). The absorbance is recorded and the information is used to generate spectra, which in turn provides information about the functional groups and their relative proportion in the sample (Melro et al., 2021). FTIR is simple and relatively fast method and the measurements can be performed to both solid and liquid samples (Melro et al., 2021).

Raman spectroscopy, similarly to FTIR spectroscopy, utilizes light to assess the functional groups present in the lignin. However, the technique differs from FTIR in a sense that rather than measuring the absorbance of the photons, Raman spectroscopy measures the change of energy level in the sample. In Raman spectroscopy, the sample is beamed with laser, which excites the molecule, leading to change in energy level. The change in energy is used to generate spectra, which gives information about the samples molecular structure and functional groups. (Stark et al., 2016)

3.4 Chemical modifications of lignin to surfactants

Chemical modification of lignin is typically needed to utilize it as a surfactant. Chemical modifications alter the reactivity, molecular size, solubility, and surface activity of lignin. Some of the chemical modification methods applied to potentially convert technical lignins to surfactants are presented in Table 10. These reactions tend to add or to decrease functional groups in lignin. (Alwadani and Fatehi, 2018)

Table 10. Chemical modification methods used to tailor lignin functionality (Alwadani and Fatehi, 2018; Bertella and Luterbacher, 2020)

Chemical modification method	**How it affects lignin properties**
Acylation	Adds acyl groups
Alkylation	Adds alkyl chains to phenolic hydroxyls
Amination	Adds amine groups to aromatic ring(s)
Carboxylation	Adds carboxylic acid groups
Halogenation	Adds halogens to lignin
Hydroxyalkylation	Adds hydroxy group to aromatic ring(s)
Esterification	Adds ester groups to lignin
Eterification	Adds ether groups to lignin
Methylation	Adds methyl to phenolic or aliphatic hydroxyls
Nitration	Adds nitro groups to lignin
Oxidation	Adds and increases carbonyl groups
Phenolation	Adds phenols to lignin
Reduction	Reduces carbonyls to alcohols & cleaves lignin bonds
Sulfomethylation	Adds sulfonic acid using methyl intermediates
Sulfonation	Adds sulfonic groups

Chemical modification reactions of lignin usually aim to increase its solubility by introducing hydrophilic groups to the lignin or reducing hydrophobic groups from the lignin.

Another chemical modification route is the size reduction of lignin. Technical lignins have high molar mass, which affects the solubility and surfactant properties negatively. Few fractionation methods exists, which could help decrease the molar mass of lignin and therefore enhance their surfactant abilities. These are for example, depolymerization and solvent fractionation. Depolymerization and solvent fractionation together with oxidation (LigniOx) will be discussed in more detail in next sections, as they were the main modification methods applied to lignin prior to the evaluation in this thesis.

3.4.1 LigniOx technology – Alkali-O_2 oxidation

LigniOx technology is a novel lignin oxidation method, which can be used to produce anionic lignin-based surfactants. In LigniOx, lignin is oxidized in alkaline conditions by molecular oxygen. LigniOx makes lignin soluble to aqueous solutions down to pH 4-6 by

the introduction of anionic groups, mainly carboxylic acids. LigniOx can be used to oxidize any type of lignin, which has phenolic hydroxyl groups in its structure. (Kalliola, 2015) The simplified reaction pathway of LigniOx-oxidation is presented in Figure 18.

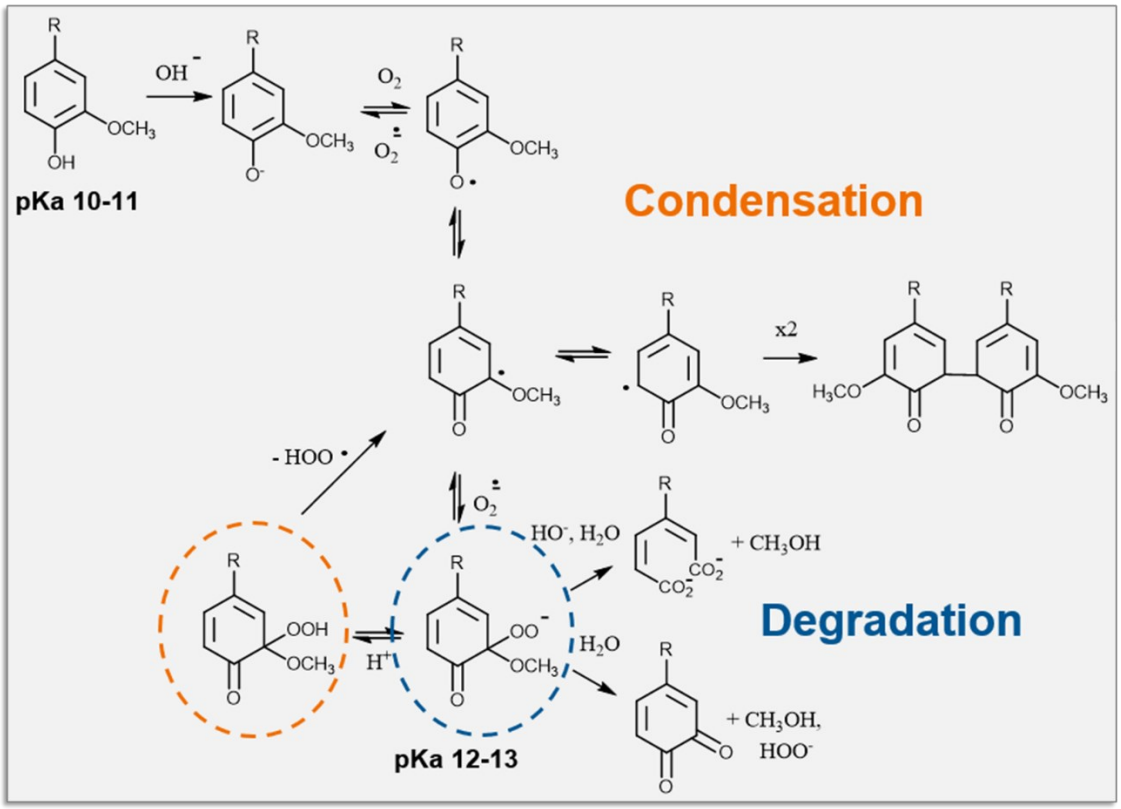


Figure 18. Reaction pathways of lignin using LigniOx-oxidation technology.

LigniOx oxidation degrades the phenolic structure and increases the amount of carboxyl functionalities in lignin. This increases the anionic charge and hydrophilicity of lignin molecules. (Kalliola, 2015)

3.4.2 Depolymerization

Depolymerization of lignin decreases the size of lignin molecules into smaller molecules. Depolymerization can offer an alternative approach of utilizing lignin, for example, as a small molecule surfactant. Preferable, depolymerization could preserve or introduce important functional groups in lignin, which enhance surface activity. These include for example, phenolic, carboxylic, sulfonic acid groups and aliphatic chains. (Chio et al., 2019)

Depolymerization of lignin can be done with several methods. These methods can roughly be classified into three classes based on the depolymerization method which are, thermochemical, chemical and biological depolymerization.

Thermochemical lignin depolymerization methods utilize temperature to degrade lignin to smaller molecule units. Currently, one thermochemical method can be used to depolymerize lignin – pyrolysis. Pyrolysis utilizes high temperature (400-600ºC) to break lignin into phenolic monomers in the absence of oxygen. With the introduction of metal catalysts, such as Fe, Al or Ni-based catalysts, the yield of phenolic monomers can be increased. (Agarwal et al., 2018)

Chemical depolymerization aims to break down lignin linkages with the use of chemicals. Several chemical depolymerization technologies could be utilized to produce lignin-based surfactants. Base-catalyzed degradation, one of the methods, uses alkali hydroxide metals to cleave ether linkages, such as α- and β-aryl (β-O-4) ethers from the lignin. These linkages are the weakest bonds in lignin molecules, which is why they specifically are targeted in this method most applicable to native or native-like lignins. Depolymerization leads to formation of lignin monomers, such as guaiacol and coniferyl alcohol. Acid-catalyzed degradation uses similar technique as the base-catalyzed degradation, but it cleaves α-aryl ethers as the linkage has lower activation energy which can lead to lignin fractioning to other monomers, such as ketones and ethylbenzene derivatives. (Agarwal et al., 2018)

Reductive catalytic fractionation (RCF) is another chemical depolymerization method, which could be utilized to generate lignin-based surfactants. RCF uses alcohols and hydrogen coupled with a Pd or Ni-based catalyst to depolymerize lignin. This reaction can lead to several lignin monomers, such as to p-coumaryl-, conferyl- and sinapyl alcohols, which could be utilized in the making of lignin-based surfactants. This technique is applicable to native-like lignins, as most technical lignins have undergone prior degradation and further condensation which hinders the use RCF. (Liu et al., 2020)

Biological depolymerization processes utilize bacteria, fungi or enzymes to degrade lignin (Zhou et al., 2022). In comparison to other depolymerization methods, biological depolymerization is the most alluring, since the energy consumption is lower, yield can be higher and production costs are smaller (Agarwal et al., 2018). Furthermore, biological depolymerization is environmentally friendly and can be tailored to produce specific

chemical compounds through bioengineering of enzymes, bacteria or fungi (Agarwal et al., 2018).

3.4.3 Solvent fractionation

Solvent fractionation of lignin aims to the production of more homogeneous lignin fractions. Technical lignin is usually highly heterogeneous, i.e. it has a broad distribution of different fractions, which differentiate in molecular weight and in chemical structure. Solvent fractionation of lignin offers a way to "filter" these different fractions based on their properties. (Xu et al., 2020)

Solvent fractionation utilizes organic, acidic or ionic liquids to divide technical lignin into fractions. For example, ammonia, ethanol, NaOH and water have been utilized in the solvent fractionation experiment. Lignin is treated with these polar liquids, which dissolves some of the lignin fractions based on their molecular weight and polarity. Low molecular weight and more polar lignin fractions dissolve into the polar solvents, while high molar weight and less polar fractions remain in the less polar solvents or precipitates. The cutoff values for lignin fractions can be altered with changing the concentration of the solvents. (Xu et al., 2020)

Solvent fractionation could also be utilized to produce lignin-based surfactants. Ghosh et al. (2024) used solvent fractionation to separate Kraft lignin into low molecular weight (≤2200 g/mol) and higher molecular weight (≥3950 g/mol) fractions. The fractionation was done using different concentrations of ethanol mixed with water. In the study, fractionated high molecular weight lignin was oxidized using LigniOx technology, which led to formation of lignin-based dispersants for special carbon black pigments. (Ghosh et al., 2024)

3.5 Applications of lignin as surfactants

Lignin, despite its complex structure and the consequent challenges, is used commercially as a surfactant. The research community has also conducted many studies about the use of lignin in surfactant applications, however most of them are not yet commercialized. Lignin-based surfactants used in commercial applications and in novel, non-commercial applications are presented/discussed in the next sections.

3.5.1 Commercial applications

Lignosulfonates are the most well-known and utilized anionic lignin-based polymeric surfactants in commercial applications. These are listed in Table 11.

Table 11. Commercial applications of lignosulfonates as surfactant (Aro and Fatehi, 2017; Ruwoldt, 2020).

Industry	**Application**
Concrete	Dispersing agent
Agrochemicals	Emulsifying agent, wetting agent, dispersing agent
Water treatment	Flocculant
Paints & pigments	Dispersing agent

Lignosulfonates are most commonly used as a dispersing agents in commercial applications, such as in the production of concrete and in paint and pigment formulations (Aro and Fatehi, 2017). Other mature commercial applications include using lignosulfonate as emulsifying agent, wetting agent or flocculant mainly in agrochemicals and water treatment applications (Ruwoldt, 2020). The annual production of lignosulfonate is around 1.8 million tons, which accounts for 90% of total commercial lignin markets (Aro and Fatehi, 2017).

Sulfonated kraft lignin is another lignin derivative used as a lignin-based surfactant. Although not as widely utilized as lignosulfonate, sulfonated kraft lignin is used as a dispersing and wetting agent mostly in agrochemical applications. Ingevity is one of the companies that produces sulfonated kraft lignin for commercial applications (Ingevity, 2025).

Based on the literature, other lignin-based surfactants have not yet been used on a commercial scale. This is due to the complex structure and low reactivity of lignin, which makes the modification of lignin-based surfactants hard from the industrial point of view. Lignin, as stated previously, also has a variable chemical structure which varies based on the extraction method as well as from the type of biomass it is extracted from.

3.5.2 Non-commercial applications

A great number of lignin-based surfactants have been experimented and tested for different applications among the research community. Table 12 presents some of these lignin-based surfactants and the end-use applications.

Table 12. Studies on non-commercial lignin-based surfactants.

Lignin-based surfactant	**Tested application**	**Reference**
Alcohol ether carboxylated Kraft lignin	Detergent	(Ou et al., 2023)
Lignosulfonate/Kraft lignin	Hair conditioner	(Wang et al., 2025)
Sulfethylated Kraft lignin	O/W emulsions	(Ghavidel and Fatehi, 2021)
Polyoxyethylated acetic acid lignin	O/W emulsions	(Homma et al., 2008)
Amine methylated & ketoamine condensated alkali lignin	W/O emulsions	(Xu et al., 2021)
Glyoxylic acid functionalized lignin	Hand-cream, O/W emulsions	(Bertella et al., 2022)
Alkali lignin	Enhanced oil recovery	(Chen et al., 2016)
Amide modified lignosulfonate	Dispersing agent in agrochemicals	(Peng et al., 2020)
Alkali-O_2 oxidized kraft lignin	Dispersing agent & concrete plasticizer	(Kalliola et al., 2022)

Lignin-based surfactants have also reported to have several application possibilities in the field of agrochemicals. For example, several lignin-based surfactants have been tested as pesticide dispersants. (Ahmad et al., 2021)

4 Experimental work

The objective of the experimental part of this thesis was to evaluate the surfactant abilities of novel hardwood lignin-based surfactants. These hardwood lignin-based surfactants were produced using chemical modification (Alkali-O_2 oxidation) and with methods aiming to decrease the molecular size of lignin (depolymerization and solvent fractionation). This experimental part focused on evaluating and characterizing different properties of the produced lignin-based surfactants and their surface-active behavior in selected applications.

The hypotheses of the thesis were:

1. By reducing the molecular size of the lignin, this becomes more surface-active and prone to diffuse on the air-water interface.

2. By utilizing alkali-O_2 oxidation the surface-active performances of the lignin can be altered.

4.1 Materials and methods

The assessed properties of lignin-based surfactants and their respective evaluation methods are presented in Table 13.

Table 13. Assessed properties and their evaluation methods.

Assessed property	**Evaluation method**
Characteristics (hydroxyl groups in lignin)	^{31}P NMR
Surface tension, CMC	Tensiometer
Emulsion stability	Visual observation
Suspending ability of $CaCO_3$	Gravimetric & turbidimetric measurement

The hydroxyl groups in hardwood hydrolysis lignin were characterized using ^{31}P NMR. Other characterization methods of hardwood hydrolysis lignin and the lignin-based surfactants included weight-average molar weight and polydispersity (PD) via alkaline SEC and average anionic charge density via polyelectrolyte titration. Surfactant properties of samples were assessed with common surfactant assessing methods, which included

evaluation of surface tension and CMC in aqueous solution, emulsion stability (W/O emulsions) and suspending ability of $CaCO_3$ pigments.

4.1.1 Lignin-based surfactants and reference materials

The hardwood lignin feedstocks used in this work, LIGNOVA^{TM} Crude and LIGNOVA^{TM} Pure, were provided by Fibenol OÜ (https://fibenol.com/), a biorefinery company located in Imavere (Estonia). Fibenol's lignins are derived from thermo-mechanically-chemically pretreated hardwood feedstock. The pretreatment includes extrusion and steam explosion processes. LIGNOVA^{TM} Crude is a hydrolysis lignin obtained after the enzymatic hydrolysis of thermo-chemically-mechanically pretreated hardwood (after C6 sugars recovery) whereas LIGNOVA^{TM} Pure is alkali extracted lignin from the microcrystalline cellulose production of the thermo-chemically-mechanically pretreated hardwood. Hydrolysis lignin and the lignin derived samples including oxidized lignins, depolymerized and solvent fractionated lignins before and after oxidation were evaluated for the ability to function as a lignin-based surfactant (LBS 0-8).

Commercial biosurfactant Rewoferm RL 100 (Rhamnolipid) by Evonik, synthetic dispersing agent Disperbyk-190 (PAA) by Altana Group and lignosulfonate Borresperse NAF (Lignosulfonate) by Borregaard were used as references. The characteristics of lignin-based surfactants (LBS) and reference materials are presented in Table 14.

Table 14. Characteristics of lignin-based surfactants and reference materials.

Sample	Mw, kDa	PD, -	Charge at pH 8, meq/g	LigniOx-oxidation status
LBS 0	10.0	3.7	-3.4	Not oxidized
LBS 1	5.5	2.2	-3.2	Oxidized
LBS 2	6.6	2.7	-2.6	Oxidized
LBS 3	7.6	2.4	-2.6	Oxidized
LBS 4	6.3	2.2	-2.8	Oxidized
LBS 5	1.9	1.4	-1.1	Not oxidized
LBS 6	1.7	1.3	-0.8	Oxidized
LBS 7	2.7	1.3	-0.8	Not oxidized
LBS 8	2.5	1.3	-1.2	Oxidized
Rhamnolipid	n.d.	n.d.	n.d.	-
PAA	n.d.	n.d.	n.d.	-
Lignosulfonate	8.3	3.0	-1.9	-

Some of the LBS were oxidized using LigniOx-oxidation. LigniOx-oxidation targets the phenolic OH groups in hydrolysis lignin and increases its hydrophilicity by formation of carboxylates. Oxidation does not alter the core structure of lignin.

Hydrolysis lignin was characterized using ^{31}P NMR before and after LigniOx-oxidation. The change in phenolic OH, aliphatic OH and carboxylic acids after oxidation is presented in Figure 19.

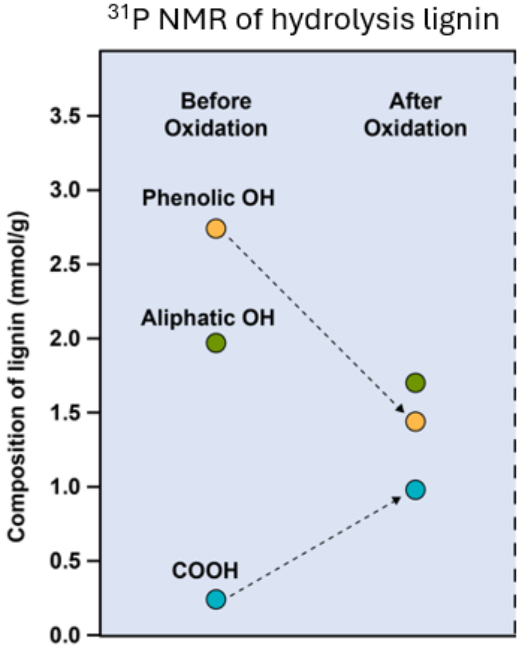


Figure 19. ^{31}P NMR of hydrolysis lignin before and after LigniOx-oxidation.

$CaCO_3$ used in the suspensibility tests was Liitujauho 105 by Uulatuote Oy. The pigment is used as a raw material e.g., in paints, coatings, mortar, and paper products.

Lignin content in the samples was determined by UV spectrometry at 280 nm after diluting with 0.1 M NaOH. The lignin contents were calculated against absorption coefficients determined outside this study. Lignin weight average molar weight was determined using alkaline Size Exclusion Chromatography (SEC), also outside this study. The lignin content was used as the active matter representing the surfactant concentration.

4.1.2 Surface tension

Lignin-based surfactants were tested for their ability to decrease surface tension in aqueous solutions. Duplicate measurements were done for each of the samples. The measurements were conducted using a Wilhelmy plate tensiometer (Sigma Force 701) equipped with platinum plate. Samples containing 0.1-10 mg/mL of lignin were prepared in pH 6 sodium maleate, pH 8 Borax-Boric acid and pH 10 Borax-NaOH buffers. Measurements were conducted for 120 minutes using continuous surface tension measurement mode with 10 second measuring intervals and the surface tension value was registered at the end of the measuring period. All testing was performed at room temperature. The tensiometer is presented in Figure 20.

Figure 20. Sigma Force 701 tensiometer with Wilhelmy plate.

4.1.3 Emulsion stability

Lignin-based surfactants were tested for their ability to stabilize W/O emulsions. For the tests, W/O emulsions with different LBS samples were prepared accordingly: 1 ml of lignin solution (10 mg/ml or 1 mg/mL) was added to the 2 ml of mineral oil. Commercial rhamnolipid and a blank sample were used as controls. The list of samples is presented in Table 15.

Table 15. Emulsion and different parameters values.

Sample	Dose (mg/mL)	pH	Emulsion	Vial nmb.
LSB 6	10	6	W/O	1
	10	8	W/O	2
	10	10	W/O	3
	1	6	W/O	4
	1	8	W/O	5
	1	10	W/O	6
LSB 4	10	6	W/O	7
	10	8	W/O	8
	10	10	W/O	9
	1	6	W/O	10
	1	8	W/O	11
	1	10	W/O	12
LSB 3	10	6	W/O	13
	10	8	W/O	14
	10	10	W/O	15
	1	6	W/O	16
	1	8	W/O	17
	1	10	W/O	18
LSB 0	10	6	W/O	19
	10	8	W/O	20
	10	10	W/O	21
	1	6	W/O	22
	1	8	W/O	23
	1	10	W/O	24
Rhamnolipid	10	6	W/O	25
	10	8	W/O	26
	10	10	W/O	27
	1	6	W/O	28
	1	8	W/O	29
	1	10	W/O	30

The prepared samples were emulsified with an Ultrasonic Processor VCX 750 tip-sonicator, which is presented in Figure 21. The emulsion stability of the samples over time was assessed visually. The visual assessments were done on days 0, 1, 3, 7, 14 and 30 following the emulsion preparation.

Figure 21. Ultrasonic Processor VCX 750 tip-sonicator.

4.1.4 $CaCO_3$ suspensibility

The suspending ability of lignin-based surfactants were tested with calcium carbonate ($CaCO_3$) utilizing VTT's in-house method. For the test, 1 gram of $CaCO_3$ was added to the measuring glass with volume of 100 ml. 20 mg of surfactant was added to the measuring glass (2% of $CaCO_3$ mass), based on the active matter content. The measuring glass was filled to 50 mL with pH 8 buffer. Each measuring glass was then sealed with parafilm.

The measuring glasses were turned upside down and then back up 30 times over 60 second period. Immediately after mixing, measuring glasses were left standing for 30 minutes. After the time period, 90% of the suspension (45 ml) was removed carefully top-down from the glass with pipette, leaving settled portion of the $CaCO_3$ at the bottom.

The top portion of the suspension was tested for turbidity with Hach 2100N Turbidimeter (Figure 22). For turbidity test, the samples were diluted 10x to pH 8 buffer solution. 30 ml of the diluted sample was placed in a turbidity vial and turbidity was measured.

Figure 22. Hach 2100N turbidimeter.

The settled mass of $CaCO_3$ was assessed from the settled part. For this, the bottom part of the measuring glass was emptied to a pre-weighted container using milliQ-water, to not leave any residue in the measuring glass. The samples were then dried in the oven for 24 h at 80ºC and the mass was measured after cooling them down to room temperature in the desiccator.

4.2 Results and discussion

Results of the measurements and discussion are presented in the following chapters.

4.2.1 Surface tension

Surface tension values of LBS samples in different concentrations at pH 8 are presented in Figure 23.

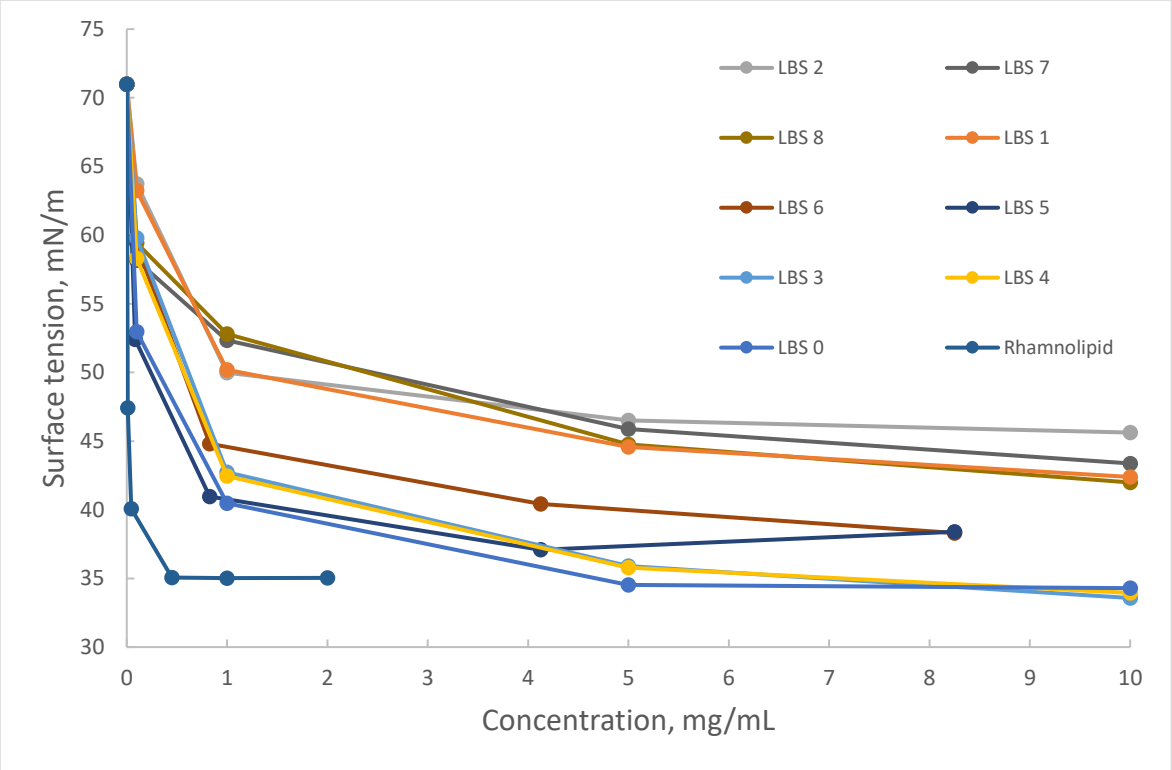


Figure 23. Surface tension of LBS samples and reference surfactant (Rhamnolipid) as a function of concentration at pH 8.

Overall, the LBS samples seemed to be divided roughly into two groups, which can be seen clearly from surface tension graph (Figure 23) for concentrations above 1 mg/mL. The best performing sample group had varying molar weight, PD and charge, which implies that the molecular structure had the highest impact to the surface tension. Out of the LBS samples, LBS 5 achieved the lowest surface tension value of 52.4 mN/m at concentration 0.1 mg/mL, while LBS 2 had the poorest performance with surface tension of 63.7 mN/m at 0.1 mg/mL. Based on the characteristics, there was no clear correlation with molar weight or polydispersity to the surface tension.

Surface tension was seen to rise a bit in sample LBS 5 from concentration 4.1 mg/mL to 8.3 mg/mL. This was most probably caused by the change in solubilized concentration of lignin, as small amount of precipitation was seen in the sample prior measurement. The precipitation was likely caused by the pH, as the sample was prepared in pH 8 buffer. This effect was also seen on other samples, when they were stored for an extensive time. To minimize the effect of precipitation on the measurements, all the samples were measured within 3 days after preparation. Thus, solubility seemed to be the issue, while the lignin

material started to precipitate at pH 8 conditions as a function of increasing lignin concentration and storing time.

The CMC for different samples was derived from the individual surface tension graphs. For this, two trendlines were constructed between two first and two last datapoints. These constructed figures are presented in Appendix 1. The CMC was the value where these trendlines intersected. The CMC and its corresponding surface tension were acquired with Excel solver using the trendline equations. The calculated values are presented in Table 16.

Table 16. CMC and corresponding surface tension of different samples.

Sample	CMC, mg/mL	ST (CMC), mN/m
LBS 0	1.4	34.7
LBS 1	1.3	46.2
LBS 2	1.2	47.2
LBS 3	1.3	37.8
LBS 4	1.3	37.1
LBS 5	1.1	36.1
LBS 6	0.9	43.0
LBS 7	1.8	47.5
LBS 8	1.9	46.5
Rhamnolipid	0.07	35.1

The CMC for LBS was quite similar, with almost all of them being above 1.0 mg/mL. LBS 6 had the smallest CMC based on calculation. As seen from the results and what was discussed in the literature part, the ST value where the CMC is reached does not indicate about the performance of the surfactant. For example, the ST value was at the same level with LBS 0 compared to the reference, rhamnolipid. The CMC between these samples however differed drastically, with rhamnolipid reaching the CMC at 0.07 mg/mL, while LBS 0 at 1.4 mg/mL.

The molar weight seemed to have some correlation with the CMC. Two of the samples with the lowest CMC value were LBS 5 & 6, which both had the smallest average molar weight (<2 kDa). This could be caused by smaller hydrophobic chain length of the LBS, which in theory reduces the CMC value.

The effect of pH to the surface tension was assessed by testing LBS 3 sample diluted to different pH buffer solutions. The results are presented in Figure 24.

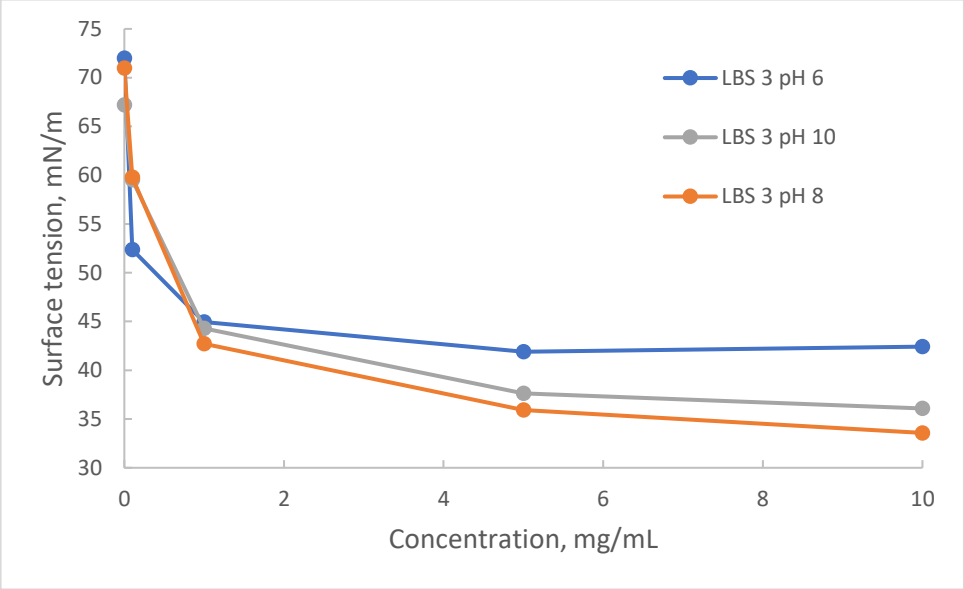


Figure 24. Surface tension of LBS 3 as a function of concentration at pH 6, 8 and 10.

The performance of the LBS increased with a decreasing pH value. This was probably caused by the protonation of LBS, which increases with decreasing pH. Protonation of LBS causes phenolates ($-PhO^-$) to turn into phenolic groups (-PhOH) (as seen in Figure 18), which reduces the negative charge of the LBS molecules. Carboxylic acid groups in the LBS tend to remain dissociated (carboxylate) at pH conditions above 4-6, while having clearly lower pKa-values compared to phenolic groups. This was confirmed by the measurement of pH vs average charge density, as seen in Figure 25. The protonation of LBS decreases their water solubility and increases the absorption to the liquid-vapor interface. Protonation of LBS increases their performance, as can be seen in Figure 24, where LBS 3 in pH 6 buffer solution had significantly lower surface tension at 0.1 mg/mL compared to corresponding in pH 8 and pH 10 buffer solutions.

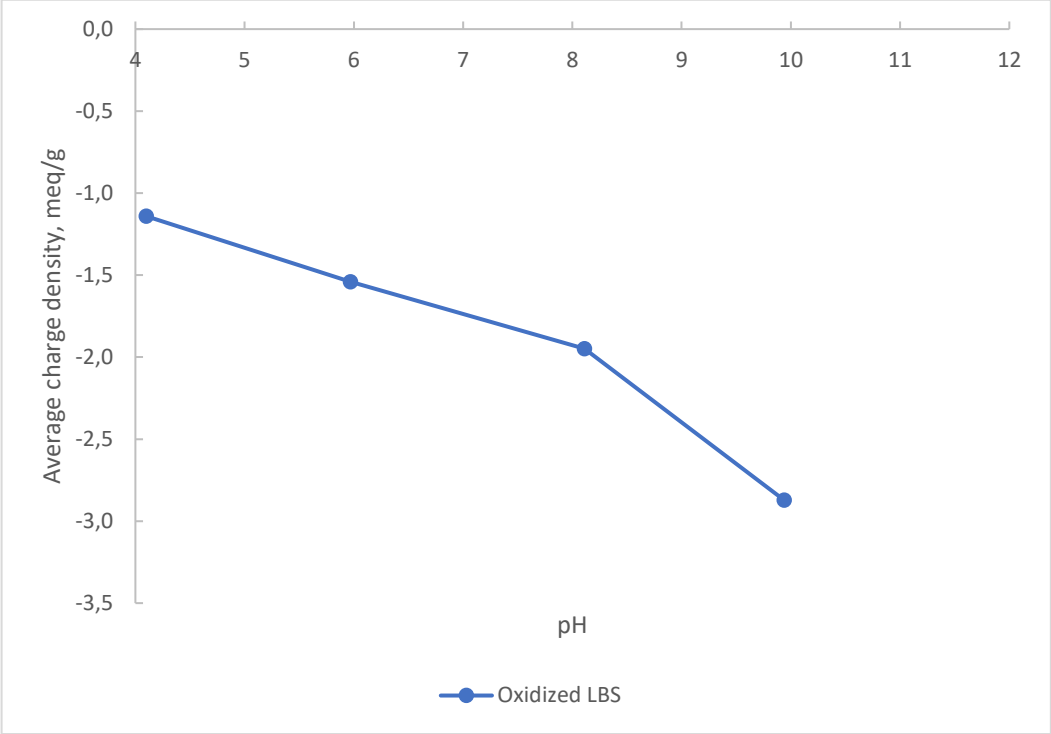


Figure 25. Anionic charge of oxidized LBS as a function of pH.

Similar results was confirmed in a study by Dickhaus and Priefer (2016), where they observed that polymeric surfactant (polyacrylic acid) which has anionic charge by COO^- groups, had a lower surface tension values at lower pH, which was caused by the protonation.

However, LBS 3 was not as effective in reducing the surface tension in higher pH, as seen from Figure 24. The surface tension plateaued at around 44 mN/m in pH 6, while in higher pH the surface tension went all the way down to 35 mN/m. Few possible reasons for this phenomenon exist, one being related to micellization. The reduction of negative charge due to protonation decreases repulsion between LBS molecules, which in turn can enhance the aggregation of LBS into micelles. The surface tension values support this theory, as based on the figure alone, LBS 3 had a lower CMC in pH 6 compared to CMC in pH 8 or pH 10. The lower repulsion between LBS molecules can hinder the reduction of surface tension in higher concentrations, as thermodynamically micellization has become more attractive than before. As the LBS molecules form micelles more easily, the liquid-vapor interface does not get as saturated with LBS molecules as in higher pH.

Protonation could also be seen between pH 8 and pH 10. LBS 3 in pH 8 had a slightly better performance than in pH 10, probably due to that phenolic groups protonate when pH is decrease from 10 to 8, according to the (Ragnar et al., 2000).

Another reason for the earlier plateau of LBS 3 in lower pH could be due to the formation of hydrogen bonds. The carboxylic acid groups in LBS molecules can form hydrogen bonds with each other, which increases the surface tension. With protonation of LBS molecules, hydrogen containing functional groups increase, increasing the possible hydrogen bonding. Hydrogen bonding can limit the orientation of LBS molecules in the surface, which further increases the surface tension.

The performance from the surface tension reduction point of view was similar as the commercial rhamnolipid. LBS 0, LBS 3 & LBS 4 reached similar ST values as the reference surfactant. Compared to other studies about the surface activity of lignin or bio-based surfactants, the best LBS in this thesis had similar performance. For example, (Morcillo-Martín et al., 2025) tested the surface activity of avocado pruning lignin in pH 10.5, which had similar ST values as LBS 0, LBS 3 & LBS 4 in pH 8.

Borrega et al. tested the surface activity of polyphenols extracted from spruce bark via alkaline extraction (Borrega et al., 2022). These polyphenols performed slightly better than the best LBS in this thesis, as polyphenols were able to reduce the surface tension down to 32 mN/m. In the same study, the surface tension of soda and kraft lignin was measured and their performance was lower than LBS in this thesis.

Overall, LBS evaluated for ST in this thesis performed rather well. The good solubility in wide range of pH of best performing LBS due to alkali-O_2 oxidation and their respective surface tension comparable to commercial biosurfactant makes the utilization of LBS in surfactant applications alluring over synthetic surfactants.

4.2.2 Emulsion stability

The results for W/O emulsion stability tests carried out under varying conditions are presented in Tables 17-22.

Table 17. Dose 10 mg/mL, pH 6, S = Stable emulsion, SS = Small separation, PS = Partial separation, F = Fully separated

Sample	Day 0	Day 1	Day 3	Day 7	Day 14	Day 30
LBS 0	S	SS	SS	SS	SS	SS
LBS 3	S	SS	SS	SS	SS	SS
LBS 4	S	SS	SS	SS	SS	SS
LBS 6	S	SS	SS	SS	SS	SS
Rhamnolipid	S	S	S	SS	SS	SS
Blank	SS	F	F	F	F	F

Table 18. Dose 10 mg/mL, pH 8, S = Stable emulsion, SS = Small separation, PS = Partial separation, F = Fully separated

Sample	Day 0	Day 1	Day 3	Day 7	Day 14	Day 30
LBS 0	S	PS	PS	PS	PS	PS
LBS 3	S	SS	SS	PS	PS	PS
LBS 4	F	F	F	F	F	F
LBS 6	S	PS	PS	PS	PS	PS
Rhamnolipid	S	S	S	SS	SS	SS
Blank	F	F	F	F	F	F

Table 19. Dose 10 mg/mL, pH 10, S = Stable emulsion, SS = Small separation, PS = Partial separation, F = Fully separated

Sample	Day 0	Day 1	Day 3	Day 7	Day 14	Day 30
LBS 0	F	F	F	F	F	F
LBS 3	PS	PS	PS	PS	PS	PS
LBS 4	F	F	F	F	F	F
LBS 6	SS	PS	PS	PS	PS	PS
Rhamnolipid	S	S	S	SS	SS	SS
Blank	F	F	F	F	F	F

Table 20. Dose 1 mg/mL, pH 6, S = Stable emulsion, SS = Small separation, PS = Partial separation, F = Fully separated

Sample	Day 0	Day 1	Day 3	Day 7	Day 14	Day 30
LBS 0	S	SS	SS	SS	SS	SS
LBS 3	S	S	S	S	S	S
LBS 4	S	S	S	S	S	S
LBS 6	PS	F	F	F	F	F
Rhamnolipid	S	F	F	F	F	F
Blank	F	F	F	F	F	F

Table 21. Dose 1 mg/mL, pH 8, S = Stable emulsion, SS = Small separation, PS = Partial separation, F = Fully separated

Sample	Day 0	Day 1	Day 3	Day 7	Day 14	Day 30
LBS 0	PS	F	F	F	F	F
LBS 3	F	F	F	F	F	F
LBS 4	F	F	F	F	F	F
LBS 6	F	F	F	F	F	F
Rhamnolipid	S	PS	F	F	F	F
Blank	F	F	F	F	F	F

Table 22. Dose 1 mg/mL, pH 10, S = Stable emulsion, SS = Small separation, PS = Partial separation, F = Fully separated

Sample	Day 0	Day 1	Day 3	Day 7	Day 14	Day 30
LBS 0	F	F	F	F	F	F
LBS 3	F	F	F	F	F	F
LBS 4	F	F	F	F	F	F
LBS 6	F	F	F	F	F	F
Rhamnolipid	S	F	F	F	F	F
Blank	F	F	F	F	F	F

Emulsion stability in W/O emulsions was highly dependent on pH of the system. All the LBS samples stayed stable for longer periods of time, as pH decreased.

Dosing of the surfactant also played a crucial role in the stability of emulsion. With higher dosing (10 mg/mL), emulsions seemed to stay rather stable, however phase separation could be seen at some point of time for all the samples. High dosing seemed to also stabilize some emulsions for longer periods, even in higher pH, as can be seen from Table 18.

In lower dosing of surfactant (1 mg/mL), surprisingly, some of the LBS performed better. LBS 3 and LBS 4 stayed stable at pH 6 with only small phase separation over the whole assessing period of 30 days. Generally, however, most of the emulsions de-stabilized above the pH 6 only after one day.

The molar weight seems to be the most significant property, which affected the stability of emulsions. The best performing emulsions were LBS 0, LBS 3 and LBS 4, which all had high average molar weight (<6 kDa). The charge of LBS molecules is also important, as was discussed in the literature part. As the negative charge of LBS decreases with decreasing pH, so should the stability of emulsions, in theory. From the results, the opposite could be observed, as emulsions were more stable in lower pH. The negative charge could have been too strong especially at pH 10, which led to de-stabilization of emulsions.

The rhamnolipid performed poorly compared to the LBS emulsions, as almost complete phase separation was observed one day after emulsification. The LBS 0 and 3 emulsions outperformed the rhamnolipid emulsion at lower dosage and pH 6, as they maintained uniformity throughout the entire assessment period.

4.2.3 $CaCO_3$ suspending ability

The results of suspensibility of $CaCO_3$ are presented in Figure 26.

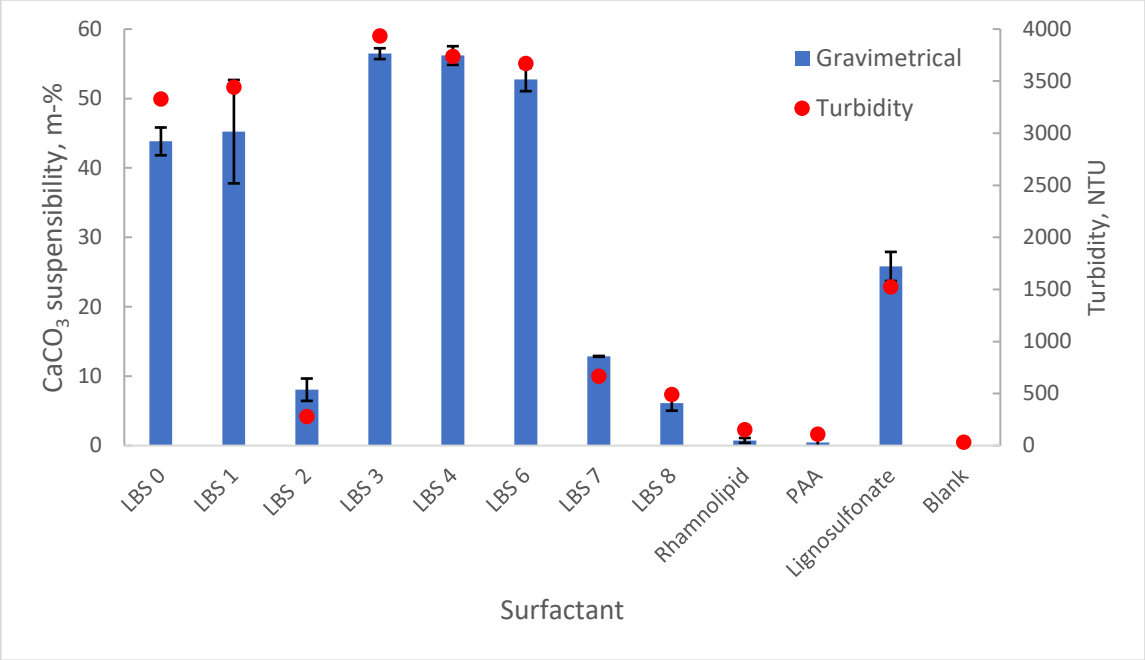


Figure 26. Suspensibility of $CaCO_3$ with different LBS and reference materials measured gravimetrically and via turbidity.

LBS 3, 4 and 6 had the best suspending ability out of LBS, with all of them reaching suspensibility of over 50 m-% or turbidity over 3500 NTU. LBS 0 and 1 were also reaching suspensibility of over 40 m-% and turbidity of over 3000 NTU. The reference materials were performing poorly compared to LBS, suggesting that LBS were working quite well as suspending agents. Turbidity measurement correlated well with the gravimetrical results, as can be seen from Figure 27.

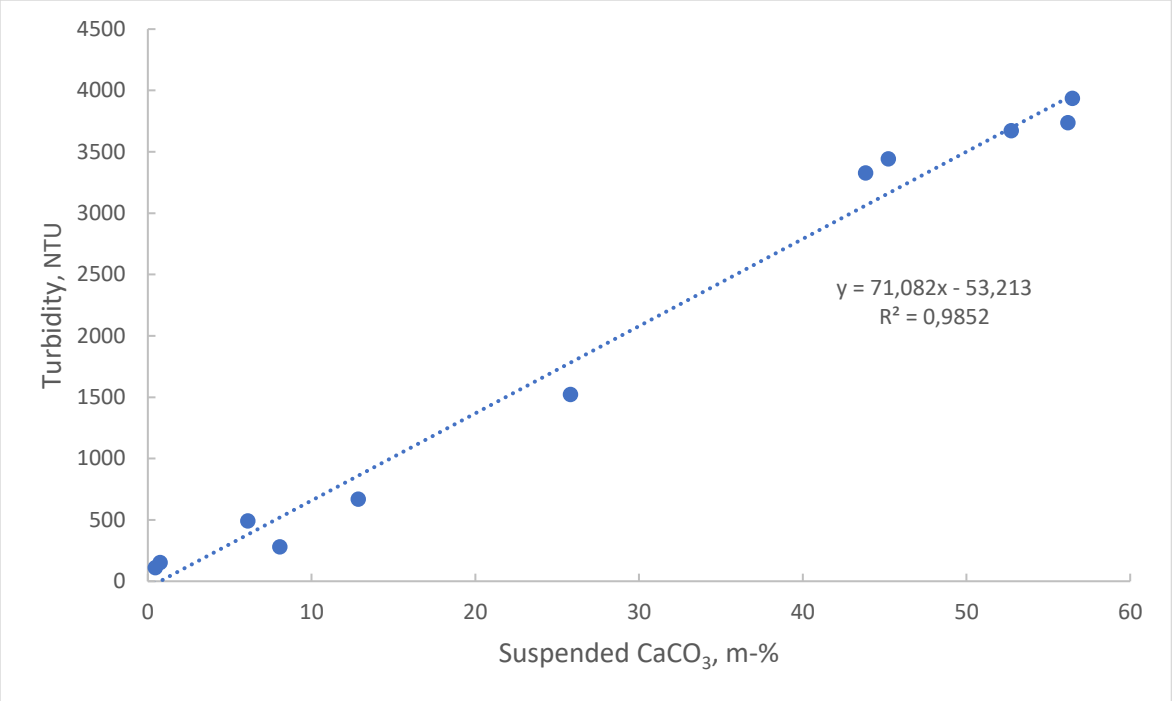


Figure 27. Correlation between gravimetric vs turbidimetric assessment in the suspensibility of $CaCO_3$.

The suspensibility of $CaCO_3$ at pH 8 seemed not to be strictly correlated with the average charge density or molar weight of the LBS. From Figure 28, where turbidity vs charge is presented, although LBS 6 had low negative charge, it still performed almost equally to LBS 3 and 4 with higher charge determined at pH 8. The opposite was seen from LBS 2, which had similar charge as LBS 3 and 4, but was performing far worse in comparison.

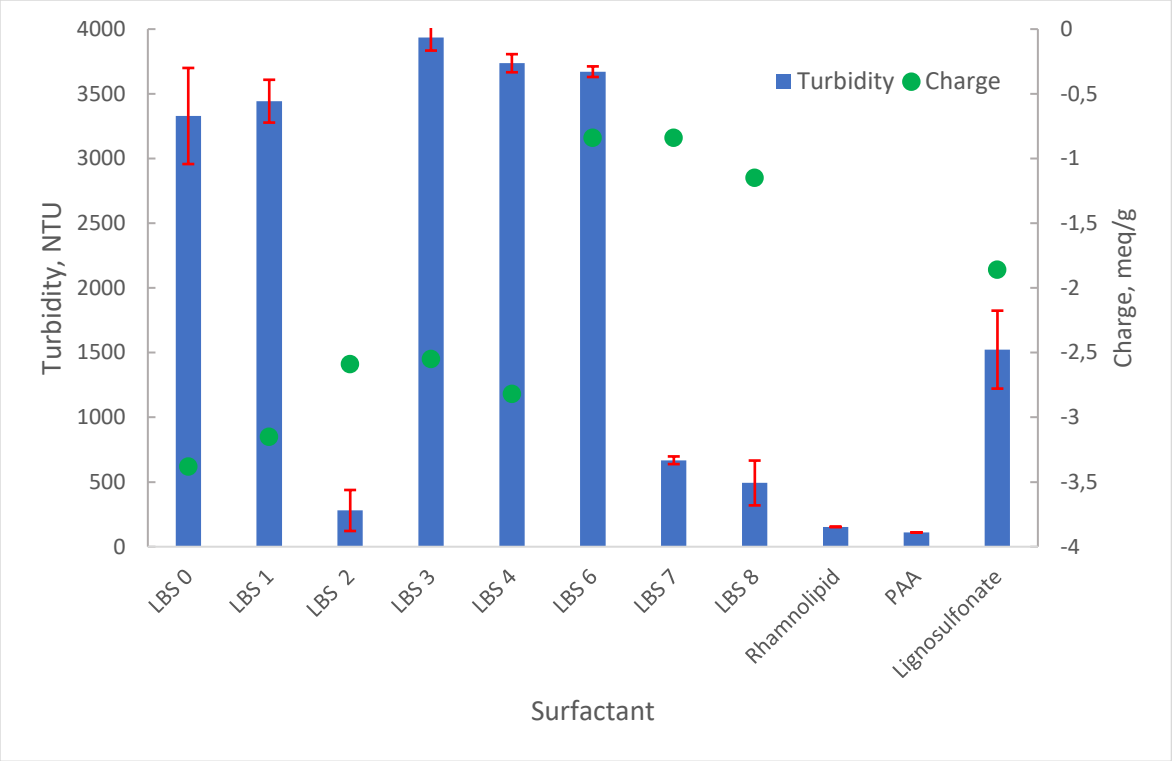


Figure 28. Turbidity of $CaCO_3$ suspension and average charge density of different LBS/surfactant samples.

Molar weight on the other hand seemed to have some effect on suspensibility, as presented in Figure 29.

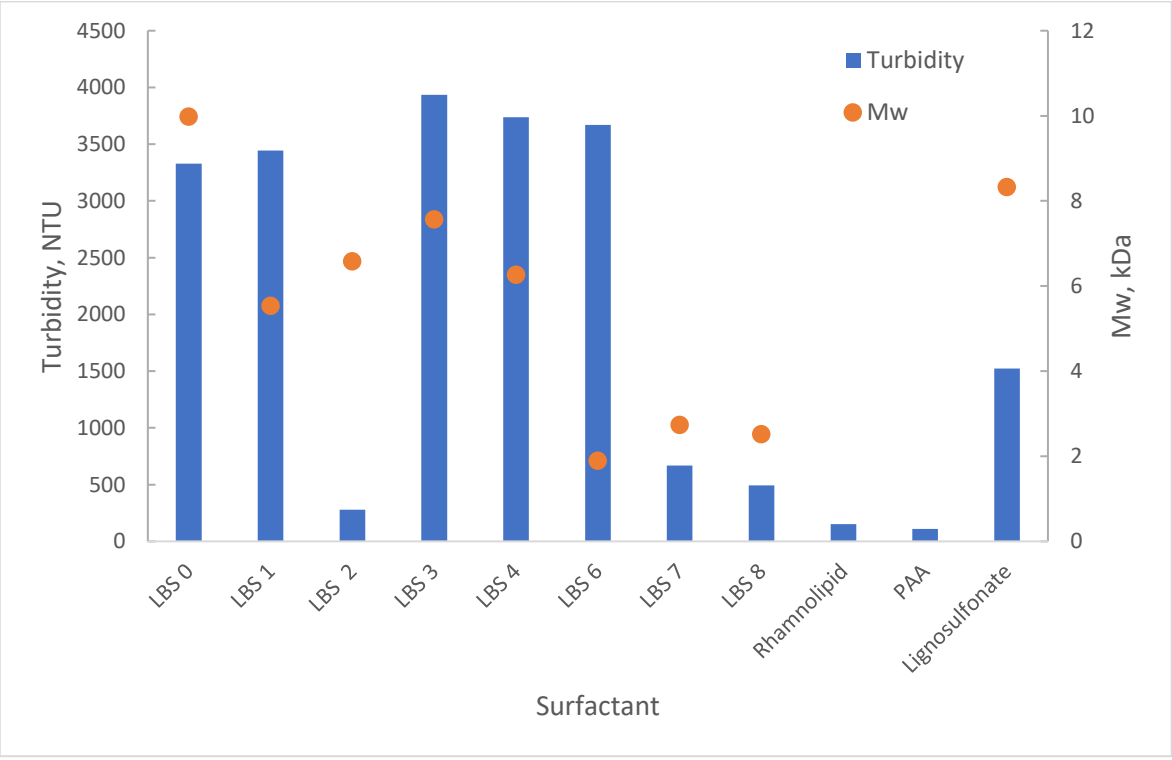


Figure 29. Turbidity of $CaCO_3$ suspension and weight average molar weight of different LBS/surfactant samples.

LBS 0, 1, 3 and 4 had good $CaCO_3$ suspending performance and their molar weight was above 5 kDa. High molar weight helps to prevent aggregation of $CaCO_3$ particles, as the LBSs are causing steric repulsion between $CaCO_3$ molecules. Based on results of the lignosulfonate reference, high molar weight did not necessarily indicate suspending ability, but the charge and molar weight together could have an effect on the suspending ability. Lignosulfonate had high molar weight, but a smaller negative charge compared to LBS 0, 1, 3 and 4.

However, the performance of suspending ability of surfactants could have been more related to the chemical composition of samples. For example, LBS 2 performed badly, although it showed similar charge and molar weight as other oxidized samples, LBS 3 and LBS 4. LBS 6 on the other hand was one of the best suspending agents, although it had low molar weight and charge.

5 Conclusions and future prospects

Bio-based surfactants are needed in replacing fossil-based surfactants in different commercial applications. Lignin could serve as a potential raw material for the bio-based surfactants. In this thesis the modified hardwood lignins were evaluated for their surface-active properties. The modification methods included alkali-O_2 oxidation, depolymerization, solvent fractionation and a combination of these methods. The aim of the thesis was to evaluate and find critical parameters or characteristics that affect the performance of lignin-based surfactants.

The performance of lignin-based surfactants was evaluated by measuring their ability to reduce surface tension in water-based solutions, to work as a stabilizing agent in W/O emulsions or as a suspending agent for $CaCO_3$. The pH conditions (pH 6, 8, 10) and lignin concentration were varied in the surface tension measurements as well as in emulsification tests to study how these variables affect the performance of lignin-based surfactants. Three commercial surfactants/dispersing agents were used as a reference.

It was found that lignin-based surfactants can reduce surface tension of aqueous solutions. Particularly oxidized samples with high molar mass performed the best, with the ability to reduce surface tension down to 34 mN/m. Compared to commercial biosurfactant, lignin-based surfactants were able to lower the surface tension to similar values, however, the needed dosage was significantly higher for lignin-based surfactants. Lignin-based surfactants in this thesis had similar surface tension performance compared to other lignin- or bio-based surfactants assessed in other studies. Results indicated that molar mass did not correlate with the surface tension reduction, suggesting that chemical structure could have the highest impact to the performance of lignin-based surfactants.

Lignin-based surfactants performed well as W/O emulsifying agents. Lignin-based surfactants were able to stabilize emulsions for over 30 days. Lignin-based samples with high molar weight had the best performance, forming stable emulsions for even longer than the commercial small-molecule biosurfactant. It was examined that pH and dosing had a strong impact on the emulsion stability.

Out of the evaluation methods used in this thesis, lignin-based surfactants worked the best as suspending agents. It was found that lignin-based surfactants can suspend $CaCO_3$ significantly better than the commercial synthetic dispersing agent. In comparison to commercial lignin-based dispersing agent i.e. lignosulfonate, the oxidized hardwood lignin-based surfactants evaluated in this thesis were able to suspend over twice the amount of $CaCO_3$.

Alkali-O_2 oxidation of hydrolysis lignin enhances lignin solubility towards mildly acidic pH conditions, which expands the end-use potential when compared to the un-modified lignin. In addition, the method utilizes environmentally benign ways to produce lignin-based surfactants, which makes the alkali-O_2 oxidized lignin-based surfactants alluring alternative for synthetic, fossil-based surfactants.

Although showing promising results, more research on lignin-based surfactants is in place. More surface tension data is needed to get accurate CMC values. For the emulsions, it would be beneficial to do more microscopic imaging, to get more in-depth information about which phenomena are causing the emulsions to destabilize. As lignin-based surfactants were found to best work as suspending agents, more research should be done in regard to their dosing affecting the suspensibility of $CaCO_3$. Chemical structure seems to have the highest impact on the performance of lignin-based surfactants. More in-depth characterization should be done to determine which functional groups in lignin polymer mostly affect the performance.

One of the key challenges with lignin-based surfactants is the dark color of lignin, which needs to be altered to utilize these novel lignin-based surfactants especially in cosmetic and hard surface cleaning applications. Furthermore, foaming and biodegradability of the lignin-based surfactants should be investigated to map their possible end-uses. Compatibility of lignin-based surfactants with the other compounds in commercial surfactant products also requires investigation to fully confirm their application potential.

Lastly, optimization of the chemical modification could be also means to increase the performance of the lignin-based surfactants. By targeting chemical functionalities that have an effect to the hydrophilicity/hydrophobicity of lignin, lignin-based surfactants could be tailored to enhance their surface-active behavior.

References

Agarwal, A., Rana, M., Park, J.-H., 2018. Advancement in technologies for the depolymerization of lignin. Fuel Process. Technol. 181, 115–132. https://doi.org/10.1016/j.fuproc.2018.09.017

Agricultural & Farming Chemicals | Suspo-Emulsions | Azelis [WWW Document], n.d. URL https://www.azelis.com/en/markets/specialty-agrihorti/products/crop-protection/suspo-emulsions (accessed 6.23.25).

Ahmad, U.M., Ji, N., Li, H., Wu, Q., Song, C., Liu, Q., Ma, D., Lu, X., 2021. Can lignin be transformed into agrochemicals? Recent advances in the agricultural applications of lignin. Ind. Crops Prod. 170, 113646. https://doi.org/10.1016/j.indcrop.2021.113646

Akbari, R., Antonini, C., 2021. Contact angle measurements: From existing methods to an open-source tool. Adv. Colloid Interface Sci. 294, 102470. https://doi.org/10.1016/j.cis.2021.102470

Akpan, E.I., 2019. Chemistry and Structure of Lignin, in: Akpan, E.I., Adeosun, S.O. (Eds.), Sustainable Lignin for Carbon Fibers: Principles, Techniques, and Applications. Springer International Publishing, Cham, pp. 1–50. https://doi.org/10.1007/978-3-030-18792-7_1

Aleid, G.M., Alshammari, A.S., Tripathy, D.B., Gupta, A., Ahmad, S., 2023. Polymeric Surfactants: Recent Advancement in Their Synthesis, Properties, and Industrial Applications. Macromol. Chem. Phys. 224, 2300107. https://doi.org/10.1002/macp.202300107

Alvira, P., Tomás-Pejó, E., Ballesteros, M., Negro, M.J., 2010. Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review. Bioresour. Technol., Special Issue on Lignocellulosic Bioethanol: Current Status and Perspectives 101, 4851–4861. https://doi.org/10.1016/j.biortech.2009.11.093

Alwadani, N., Fatehi, P., 2018. Synthetic and lignin-based surfactants: Challenges and opportunities. Carbon Resour. Convers. 1, 126–138. https://doi.org/10.1016/j.crcon.2018.07.006

Aro, T., Fatehi, P., 2017. Production and Application of Lignosulfonates and Sulfonated Lignin. ChemSusChem 10, 1861–1877. https://doi.org/10.1002/cssc.201700082

Asano, H., Nomura, M., Kaneko, Y., Oya, M., Aramaki, K., 2025. Study of Foam in Dishwashing Detergents: Effect of Nonionic Surfactant Addition on Foam Formation. J. Oleo Sci. 74, 377–384. https://doi.org/10.5650/jos.ess24197

Bajpai, D., Tyagi, V.K., 2007. Laundry Detergents: An Overview. J. Oleo Sci. 56, 327–340. https://doi.org/10.5650/jos.56.327

Bajwa, D.S., Pourhashem, G., Ullah, A.H., Bajwa, S.G., 2019. A concise review of current lignin production, applications, products and their environmental impact. Ind. Crops Prod. 139, 111526. https://doi.org/10.1016/j.indcrop.2019.111526

Bertella, S., Bernardes Figueirêdo, M., De Angelis, G., Mourez, M., Bourmaud, C., Amstad, E., Luterbacher, J.S., 2022. Extraction and Surfactant Properties of Glyoxylic Acid-Functionalized Lignin. ChemSusChem 15, e202200270. https://doi.org/10.1002/cssc.202200270

Bertella, S., Luterbacher, J.S., 2020. Lignin Functionalization for the Production of Novel Materials. Trends Chem. 2, 440–453. https://doi.org/10.1016/j.trechm.2020.03.001

Blagojević, S.N., Blagojević, S.M., Pejić, N.D., 2016. Performance and Efficiency of Anionic Dishwashing Liquids with Amphoteric and Nonionic Surfactants. J. Surfactants Deterg. 19, 363–372. https://doi.org/10.1007/s11743-015-1784-5

Borrega, M., Kalliola, A., Määttänen, M., Borisova, A.S., Mikkelson, A., Tamminen, T., 2022. Alkaline extraction of polyphenols for valorization of industrial spruce bark. Bioresour. Technol. Rep. 19, 101129. https://doi.org/10.1016/j.biteb.2022.101129

Cai, C., Zhang, C., Li, N., Liu, H., Xie, J., Lou, H., Pan, X., Zhu, J.Y., Wang, F., 2023. Changing the role of lignin in enzymatic hydrolysis for a sustainable and efficient sugar platform. Renew. Sustain. Energy Rev. 183, 113445. https://doi.org/10.1016/j.rser.2023.113445

Castro, M.J.L., Ojeda, C., Cirelli, A.F., 2014. Advances in surfactants for agrochemicals. Environ. Chem. Lett. 12, 85–95. https://doi.org/10.1007/s10311-013-0432-4

Cationic surfactants: A review, 2023. . J. Mol. Liq. 375, 121335. https://doi.org/10.1016/j.molliq.2023.121335

Chen, S., Shen ,Shicheng, Yan ,Xiang, Mi ,Jie, Wang ,Gehua, Zhang ,Jianan, and Zhou, Y., 2016. Synthesis of Surfactants from Alkali Lignin for Enhanced Oil Recovery. J. Dispers. Sci. Technol. 37, 1574–1580. https://doi.org/10.1080/01932691.2015.1118703

Chio, C., Sain, M., Qin, W., 2019. Lignin utilization: A review of lignin depolymerization from various aspects. Renew. Sustain. Energy Rev. 107, 232–249. https://doi.org/10.1016/j.rser.2019.03.008

Chowdhury, S., Rakshit, A., Acharjee, A., Saha, B., 2019. Novel Amphiphiles and Their Applications for Different Purposes with Special Emphasis on Polymeric Surfactants. ChemistrySelect 4, 6978–6995. https://doi.org/10.1002/slct.201901160

Dave, N., Joshi, T., 2017. A Concise Review on Surfactants and Its Significance. Int. J. Appl. Chem. 13, 663–672. https://doi.org/10.37622/IJAC/13.3.2017.663-672

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

Dickhaus, B.N., Priefer, R., 2016. Determination of polyelectrolyte pKa values using surface-to-air tension measurements. Colloids Surf. Physicochem. Eng. Asp. 488, 15–19. https://doi.org/10.1016/j.colsurfa.2015.10.015

Dobrat, W., Martijn, A., 1994. CIPAC Handbook: Physico-chemical methods for technical and formulated pesticides. Volume F. Collaborative International Pesticides Analytical Council.

Dutta, A.K., 2019. Introductory Chapter: Surfactants in Household and Personal Care Formulations - An Overview, in: Surfactants and Detergents. IntechOpen. https://doi.org/10.5772/intechopen.89245

Ekielski, A., Mishra, P.K., 2021. Lignin for Bioeconomy: The Present and Future Role of Technical Lignin. Int. J. Mol. Sci. 22, 63. https://doi.org/10.3390/ijms22010063

Eraghi Kazzaz, A., Fatehi, P., 2020. Technical lignin and its potential modification routes: A mini-review. Ind. Crops Prod. 154, 112732. https://doi.org/10.1016/j.indcrop.2020.112732

Falbe, J. (Ed.), 1987. Surfactants in Consumer Products. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-642-71545-7

Foley, P., Kermanshahi Pour, A., Beach, E.S., Zimmerman, J.B., 2012. Derivation and synthesis of renewable surfactants. Chem Soc Rev 41, 1499–1518. https://doi.org/10.1039/C1CS15217C

Ghavidel, N., Fatehi, P., 2021. Interfacial and Emulsion Characteristics of Oil–Water Systems in the Presence of Polymeric Lignin Surfactant. Langmuir 37, 3346–3358. https://doi.org/10.1021/acs.langmuir.0c03458

Ghosh, A., Fearon, O., Agustin, M., Alonso, S., Balda, E.C., Franco, S., Kalliola, A., 2024. Fractionation of Kraft Lignin for Production of Alkyd Resins for Biobased Coatings with Oxidized Lignin Dispersants as a Co-Product. ACS Omega 9, 46276–46292. https://doi.org/10.1021/acsomega.4c07187

Hayes, D.G., Solaiman, D.K.Y., Ashby, R.D., 2019. Biobased Surfactants: Synthesis, Properties, and Applications, Second Edition. ed. AOCS Press, London, United Kingdom.

Homma, H., Kubo ,Satoshi, Yamada ,Tatsuhiko, Matsushita ,Yasuyuki, and Uraki, Y., 2008. Preparation and Characterization of Amphiphilic Lignin Derivatives as Surfactants. J. Wood Chem. Technol. 28, 270–282. https://doi.org/10.1080/02773810802510688

Hu, Y.-T., Ting, Y., Hu, J.-Y., Hsieh, S.-C., 2017. Techniques and methods to study functional characteristics of emulsion systems. J. Food Drug Anal., Dietary Natural Compounds 25, 16–26. https://doi.org/10.1016/j.jfda.2016.10.021

Ingevity - Ingevity [WWW Document], n.d. URL https://www.ingevity.com/ (accessed 6.27.25).

ISO/TR 18811. 2018. Cosmetics - Guidelines on the stability testing of cosmetic products. The International Organization for Standardization.

Kalliola, A., 2015. Chemical and enzymatic oxidation using molecular oxygen as a means to valorize technical lignins for material applications. VTT Technical Research Centre of Finland.

Kalliola, A., Kangas, P., Winberg, I., Vehmas, T., Kyllönen, H., Heikkinen, J., Poukka, O., Kemppainen, K., Sjögård, P., Pehu-Lehtonen, L., Liitiä, T., 2022. Oxidation process concept to produce lignin dispersants at a kraft pulp mill. Nord. Pulp Pap. Res. J. 37, 394–404. https://doi.org/10.1515/npprj-2022-0017

Kaur, J., Farzeen, R., Singh, M., Thakur, N., Lal, M., Upadhyaya, S.K., Walia, Y.K., Kishore, K., 2024. Overview of Surfactants, Properties, Types, and Role in Chemistry, in: Advances in Surfactant Biosensor and Sensor Technologies. pp. 1–23. https://doi.org/10.1007/978-3-031-60832-2_1

Kronberg, B., Holmberg, K., Lindman, B., 2014. Surface Chemistry of Surfactants and Polymers. John Wiley & Sons, Incorporated, Newark, UNITED KINGDOM.

Kwok, D.Y., Neumann, A.W., 1999. Contact angle measurement and contact angle interpretation. Adv. Colloid Interface Sci. 81, 167–249. https://doi.org/10.1016/S0001-8686(98)00087-6

Landeck, L., Baden, L.A., John, S.M., 2020. Detergents, in: John, S.M., Johansen, J.D., Rustemeyer, T., Elsner, P., Maibach, H.I. (Eds.), Kanerva's Occupational Dermatology. Springer International Publishing, Cham, pp. 1131–1143. https://doi.org/10.1007/978-3-319-68617-2_75

Lenihan, P., Orozco, A., O'Neill, E., Ahmad, M.N.M., Rooney, D.W., Walker, G.M., 2010. Dilute acid hydrolysis of lignocellulosic biomass. Chem. Eng. J. 156, 395–403. https://doi.org/10.1016/j.cej.2009.10.061

Lin, S.Y., Dence, C.W., 2012. Methods in Lignin Chemistry. Springer Science & Business Media.

Liu, X., Bouxin, F.P., Fan, J., Budarin, V.L., Hu, C., Clark, J.H., 2020. Recent Advances in the Catalytic Depolymerization of Lignin towards Phenolic Chemicals: A Review. ChemSusChem 13, 4296–4317. https://doi.org/10.1002/cssc.202001213

Maceda, A., Terrazas, T., 2022. Fluorescence Microscopy Methods for the Analysis and Characterization of Lignin. Polymers 14, 961. https://doi.org/10.3390/polym14050961

Marquez, R., Salager, J.-L., 2025. Measurement Techniques for Interfacial Rheology of Surfactant, Asphaltene, and Protein-Stabilized Interfaces in Emulsions and Foams. Colloids Interfaces 9, 14. https://doi.org/10.3390/colloids9010014

Melro, E., Filipe, A., Sousa, D., Medronho, B., Romano, A., 2021. Revisiting lignin: a tour through its structural features, characterization methods and applications. New J. Chem. 45, 6986–7013. https://doi.org/10.1039/D0NJ06234K

Morcillo-Martín, R., Borrega, M., Bertella, S., Widsten, P., Rincón, E., Espinosa, E., Rodríguez, A., 2025. Lignin micro/nanoparticles from alternative biomass sources for

neutral-pH Pickering emulsions and quercetin encapsulation. Int. J. Biol. Macromol. 310, 143223. https://doi.org/10.1016/j.ijbiomac.2025.143223

Moroi, Y., 1992. Micelles: Theoretical and Applied Aspects. Springer, New York, NY, UNITED STATES.

Mussatto, S.I., 2016. Biomass fractionation technologies for a lignocellulosic feedstock based biorefinery. Elsevier, Amsterdam, [Netherlands.

Myers, D., 2020. Surfactant Science and Technology. John Wiley & Sons.

Nakama, Y., 2017. Chapter 15 - Surfactants, in: Sakamoto, K., Lochhead, R.Y., Maibach, H.I., Yamashita, Y. (Eds.), Cosmetic Science and Technology. Elsevier, Amsterdam, pp. 231–244. https://doi.org/10.1016/B978-0-12-802005-0.00015-X

Nalwa, H.S., 2001. Handbook of surfaces and interfaces of materials, 1st ed. ed. Academic Press, San Diego.

Norgren, M., Edlund, H., 2014. Lignin: Recent advances and emerging applications. Curr. Opin. Colloid Interface Sci. 19, 409–416. https://doi.org/10.1016/j.cocis.2014.08.004

World Health Organization, 2023. Manual on the development and use of FAO and WHO specifications for chemical pesticides. World Health Organization.

Ou, J., Kong ,Zhenxing, Yang ,Rui, and Dai, Z., 2023. Synthesis of a lignin-based alcohol ether carboxylate surfactant and its application as cotton fiber detergent. J. Dispers. Sci. Technol. 44, 577–584. https://doi.org/10.1080/01932691.2021.1956323

PARK, A.E., TSE, F.S.W., KAKA, P.M., 2023. Stable, low viscosity oil-in-water emulsions for skin conditioning. WO2023159295A1.

Peng, R., Pang, Y., Qiu, X., Qian, Y., Zhou, M., 2020. Synthesis of anti-photolysis lignin-based dispersant and its application in pesticide suspension concentrate. RSC Adv. 10, 13830–13837. https://doi.org/10.1039/C9RA10626J

Poletto, M., Lourenço, A., Pereira, H., 2018. Lignin - Trends and Applications, in: Lignin - Trends and Applications. IntechOpen. https://doi.org/10.5772/intechopen.68464

Ragnar, M., Lindgren, C.T., Nilvebrant, N.-O., 2000. pKa-Values of Guaiacyl and Syringyl Phenols Related to Lignin. J. Wood Chem. Technol. 20, 277–305. https://doi.org/10.1080/02773810009349637

Rapp, B.E., 2017. Chapter 22 - Measuring Surface Tension and Free Surface Energy, in: Rapp, B.E. (Ed.), Microfluidics: Modelling, Mechanics and Mathematics, Micro and Nano Technologies. Elsevier, Oxford, pp. 453–465. https://doi.org/10.1016/B978-1-4557-3141-1.50022-8

Rapp, B.E., 2016. Microfluidics: Modeling, Mechanics and Mathematics. William Andrew.

Rosen, M.J., Kunjappu, J.T., 2012. Surfactants and Interfacial Phenomena. John Wiley & Sons.

Ruwoldt, J., 2020. A Critical Review of the Physicochemical Properties of Lignosulfonates: Chemical Structure and Behavior in Aqueous Solution, at Surfaces and Interfaces. Surfaces 3, 622–648. https://doi.org/10.3390/surfaces3040042

Saad, S.M.I., Policova, Z., Neumann, A.W., 2011. Design and accuracy of pendant drop methods for surface tension measurement. Colloids Surf. Physicochem. Eng. Asp. 384, 442–452. https://doi.org/10.1016/j.colsurfa.2011.05.002

Sakamoto, K., Lochhead, R.Y., Maibach, H.I., Yamashita, Y., 2017. Cosmetic Science and Technology: Theoretical Principles and Applications. Elsevier, Chantilly, UNITED STATES.

Sand, A., Tuteja, J., Sand, A., Tuteja, J., 2023. Lignin - Chemistry, Structure, and Application, in: Lignin - Chemistry, Structure, and Application. IntechOpen. https://doi.org/10.5772/intechopen.102263

Scholz, N., Behnke, T., Resch-Genger, U., 2018. Determination of the Critical Micelle Concentration of Neutral and Ionic Surfactants with Fluorometry, Conductometry, and Surface Tension—A Method Comparison. J. Fluoresc. 28, 465–476. https://doi.org/10.1007/s10895-018-2209-4

Schramm, L.L., 2006. Emulsions, Foams, and Suspensions: Fundamentals and Applications. John Wiley & Sons.

Schramm, L.L., 2000. Surfactants: Fundamentals and Applications in the Petroleum Industry, Online-Ausg. ed. Cambridge University Press, Cambridge. https://doi.org/10.1017/CBO9780511524844

Serrano, L., Luque, R., Sels, B.F. (Eds.), 2020. Lignin Chemistry, Topics in Current Chemistry Collections. Springer International Publishing, Cham. https://doi.org/10.1007/978-3-030-00590-0

Shaban, S.M., Kang, J., Kim, D.-H., 2020. Surfactants: Recent advances and their applications. Compos. Commun. 22, 100537. https://doi.org/10.1016/j.coco.2020.100537

Smulders, E., Rähse, W., Jakobi, G., 2002. Laundry detergents. Wiley-VCH, Weinheim.

Sohrabi, B., 2022. Amphiphiles, in: Self-Assembly of Materials and Their Applications. IntechOpen. https://doi.org/10.5772/intechopen.107880

Stark, N.M., Yelle, D.J., Agarwal, U.P., 2016. Techniques for characterizing lignin. Lignin Polym. Compos. 49–66. https://doi.org/10.1016/B978-0-323-35565-0.00004-7

Suota, M.J., da Silva, T.A., Zawadzki, S.F., Sassaki, G.L., Hansel, F.A., Paleologou, M., Ramos, L.P., 2021. Chemical and structural characterization of hardwood and softwood LignoForce^{TM} lignins. Ind. Crops Prod. 173, 114138. https://doi.org/10.1016/j.indcrop.2021.114138

Tadros, T.F., 2018. Agrochemicals, Paints and Coatings and Food Colloids. Walter de Gruyter GmbH, Berlin/Boston, GERMANY.

Tadros, T.F., 2017a. Polymeric surfactants in agrochemicals, in: Polymeric Surfactants. Walter de Gruyter GmbH, Germany. https://doi.org/10.1515/9783110487282-014

Tadros, T. F. 2017b. *Suspension concentrates: preparation, stability and industrial applications*. Walter de Gruyter GmbH & Co KG. Tadros, T.F., 2016. Formulations: In Cosmetic and Personal Care. Walter de Gruyter GmbH, Berlin/Boston, GERMANY.

Tadros, T.F., 2015. Interfacial Phenomena and Colloid Stability: Industrial Applications. Walter de Gruyter GmbH, Berlin/Boston, GERMANY.

Tadros, T. F. (2014). *An introduction to surfactants*. Walter de Gruyter. Tiwari, S., Mall, C., Prakash Solanki, P., 2018. Surfactant and its applications: A review. Int J Eng Res Appl 8, 61–66.

Uner, A., Yilmaz, F., 2015. Efficiency of Laundry Polymers Containing Liquid Detergents for Hard Surface Cleaning. J. Surfactants Deterg. 18, 213–224. https://doi.org/10.1007/s11743-014-1634-x

Veeramanoharan, A., Kim, S.-C., 2024. A comprehensive review on sustainable surfactants from CNSL: chemistry, key applications and research perspectives. RSC Adv. 14, 25429–25471. https://doi.org/10.1039/D4RA04684F

Verardi, A., De, I., Ricca, E., Calabr, V., 2012. Hydrolysis of Lignocellulosic Biomass: Current Status of Processes and Technologies and Future Perspectives, in: Pinheiro Lima, M.A. (Ed.), Bioethanol. InTech. https://doi.org/10.5772/23987

Verma, C., Goni, L.K.M.O., Yaagoob, I.Y., Vashisht, H., Mazumder, M.A.J., Alfantazi, A., 2023. Polymeric surfactants as ideal substitutes for sustainable corrosion protection: A perspective on colloidal and interface properties. Adv. Colloid Interface Sci. 318, 102966. https://doi.org/10.1016/j.cis.2023.102966

Wang, F., Nithianandam, S., Pylypchuk, I., Sipponen, M.H., 2025. Lignin gel emulsions for environmentally benign hair conditioning. Sci. Adv. 11, eadr8372. https://doi.org/10.1126/sciadv.adr8372

Witten, T.A., 2004. Structured Fluids: Polymers, Colloids, Surfactants. Oxford University Press, Incorporated, Oxford, UNITED KINGDOM.

Xu, J., Li, C., Dai, L., Xu, C., Zhong, Y., Yu, F., Si, C., 2020. Biomass Fractionation and Lignin Fractionation towards Lignin Valorization. ChemSusChem 13, 4284–4295. https://doi.org/10.1002/cssc.202001491

Xu, Q., Bai, Y., Zhao, X., Ren, M., Wang, S., Kong, F., 2021. Synthesis and characterization of an amphiphilic lignin-based cationic surfactant. Ind. Crops Prod. 164, 113376. https://doi.org/10.1016/j.indcrop.2021.113376

Yue, F., Lu, F., Ralph, S., Ralph, J., 2016. Identification of 4–O–5-Units in Softwood Lignins via Definitive Lignin Models and NMR. Biomacromolecules 17, 1909–1920. https://doi.org/10.1021/acs.biomac.6b00256

Zhang, J., Chen, Y., Sewell, P., Brook, M.A., 2015. Utilization of softwood lignin as both crosslinker and reinforcing agent in silicone elastomers. Green Chem. 17, 1811–1819. https://doi.org/10.1039/C4GC02409E

Zhou, N., Thilakarathna, W.P.D.W., He, Q.S., Rupasinghe, H.P.V., 2022. A Review: Depolymerization of Lignin to Generate High-Value Bio-Products: Opportunities, Challenges, and Prospects. Front. Energy Res. 9. https://doi.org/10.3389/fenrg.2021.758744

Appendix 1. CMC derivation of samples from surface tension graph

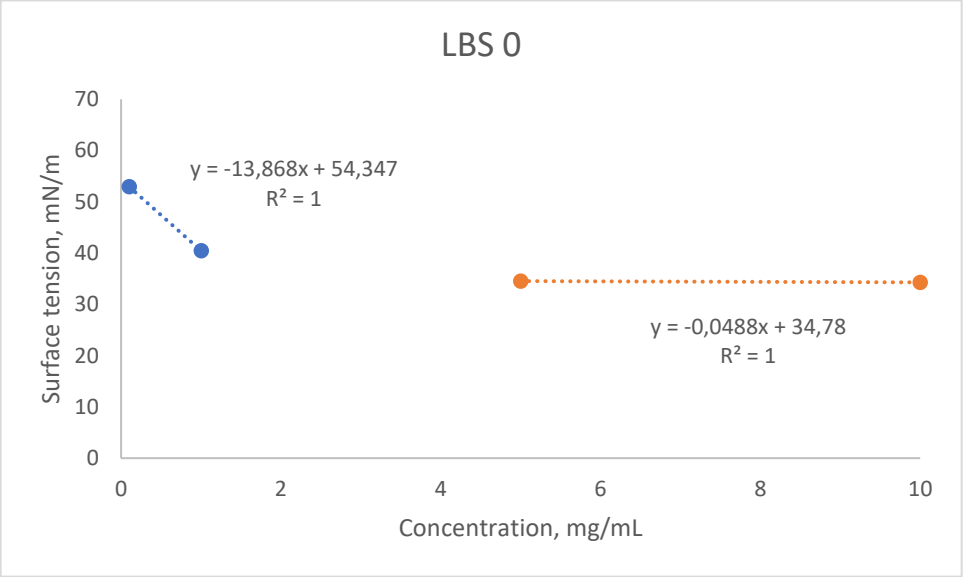


Figure 1. Derivation of CMC of LBS 0

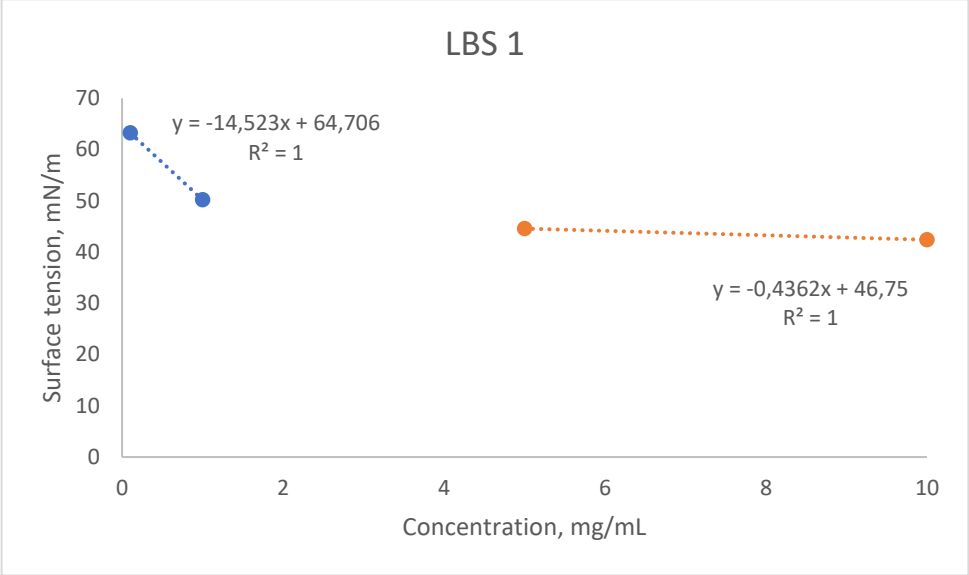


Figure 2. Derivation of CMC of LBS 1

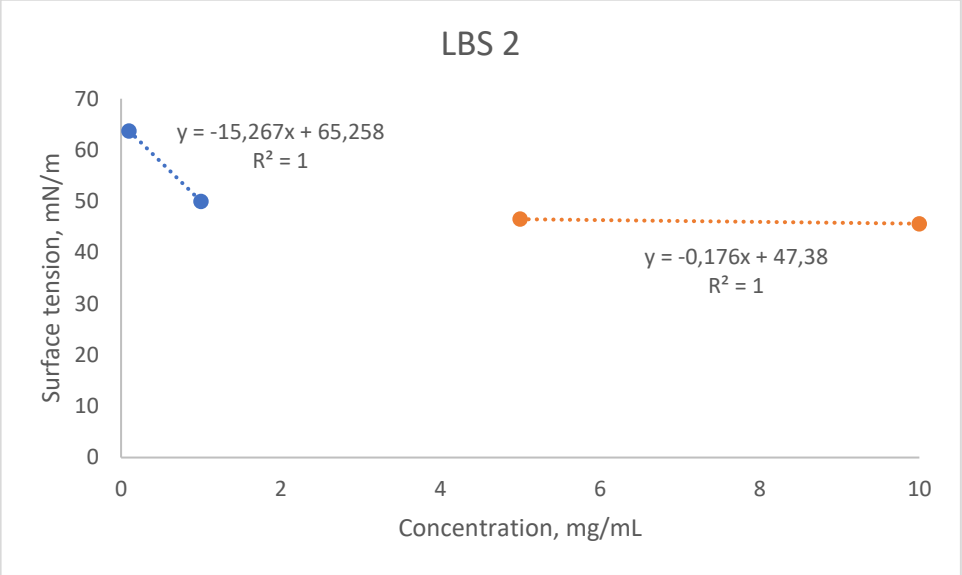


Figure 3. Derivation of CMC of LBS 2

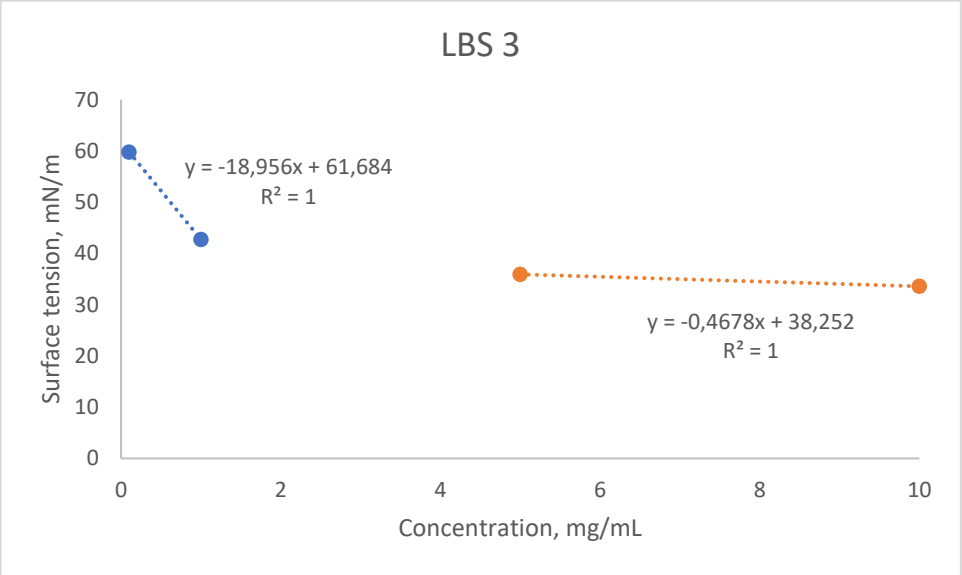


Figure 4. Derivation of CMC of LBS 3

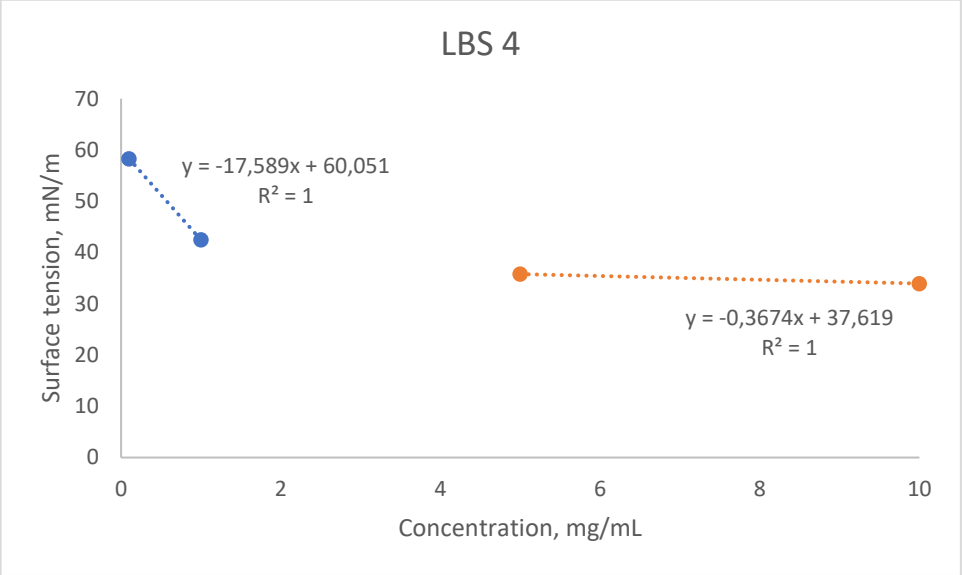


Figure 5. Derivation of CMC of LBS 4

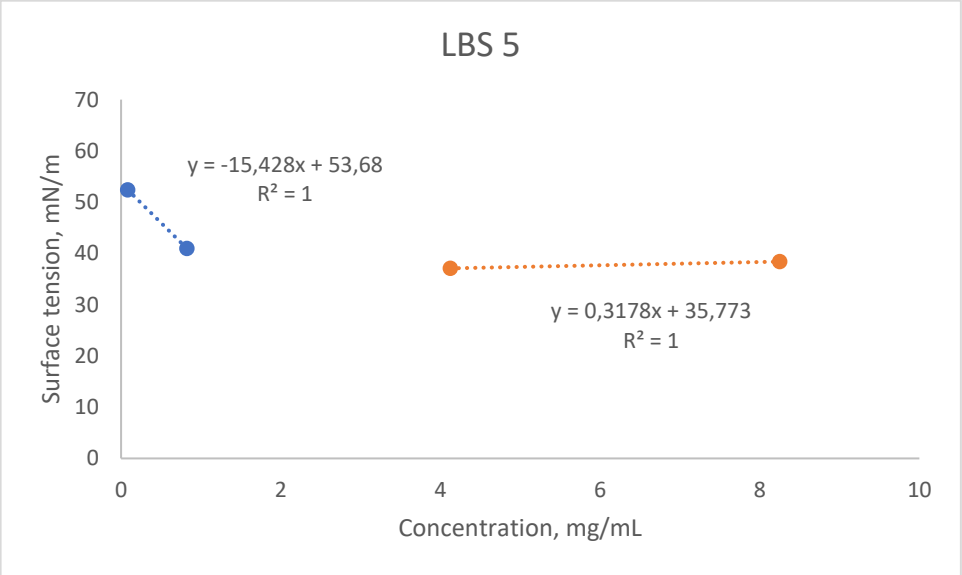


Figure 6. Derivation of CMC of LBS 5

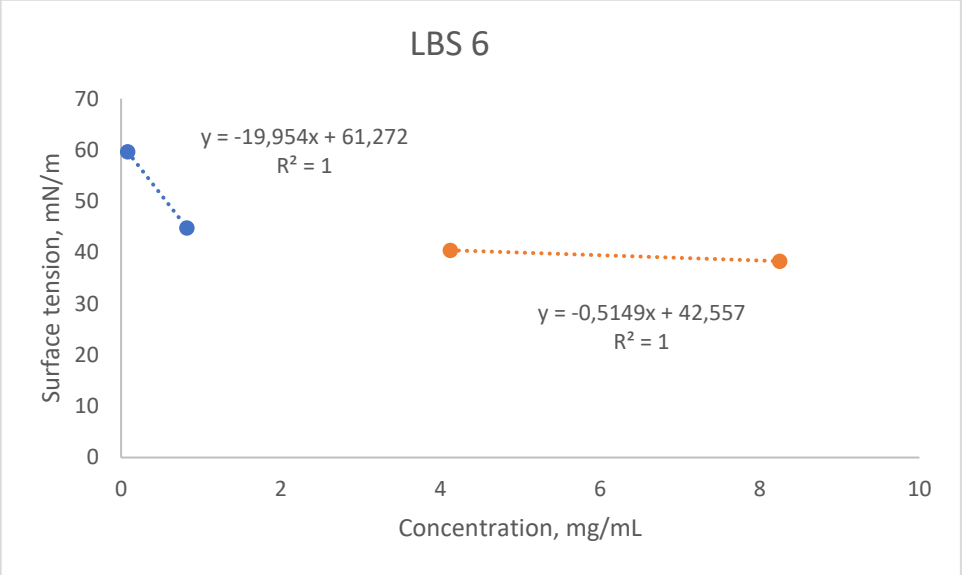


Figure 7. Derivation of CMC of LBS 6

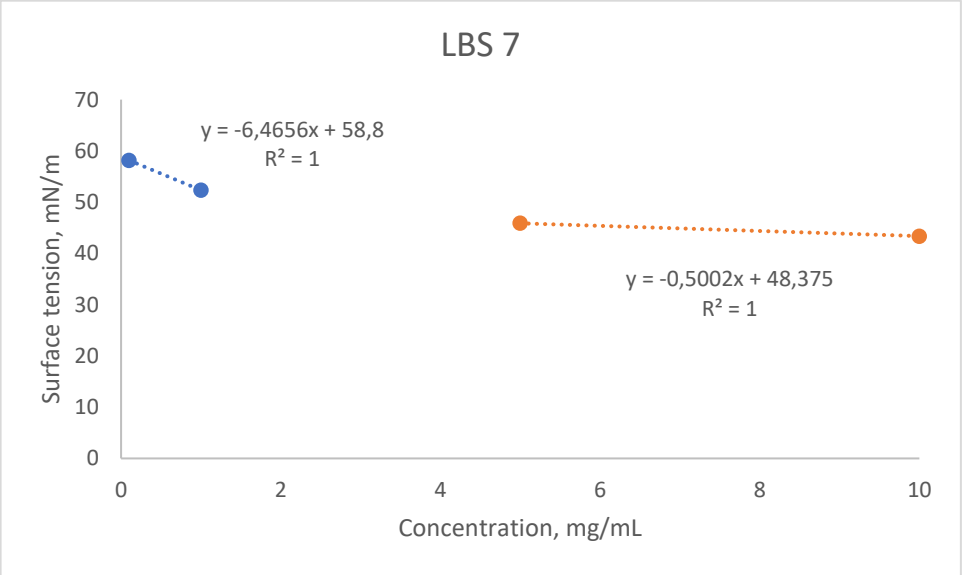


Figure 8. Derivation of CMC of LBS 7

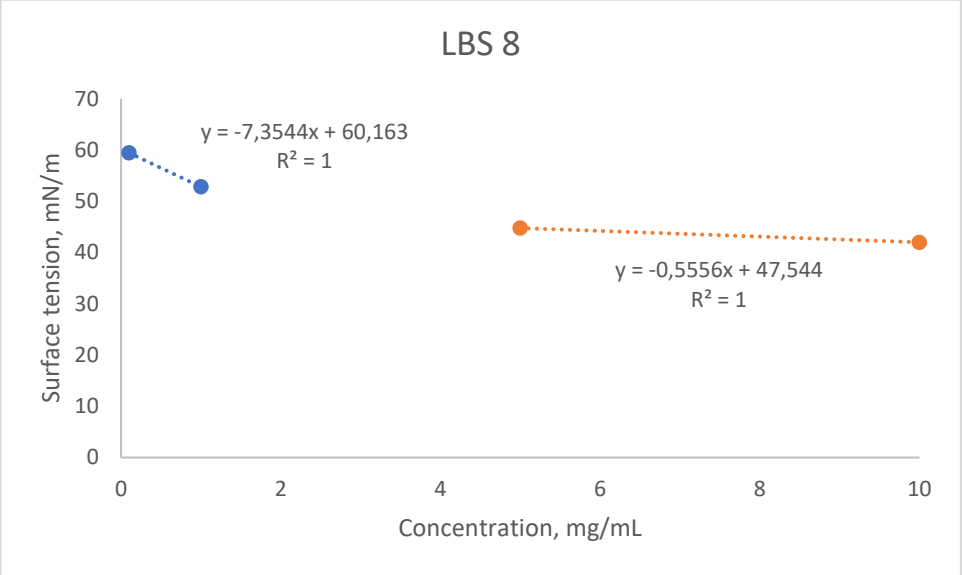


Figure 9. Derivation of CMC of LBS 8

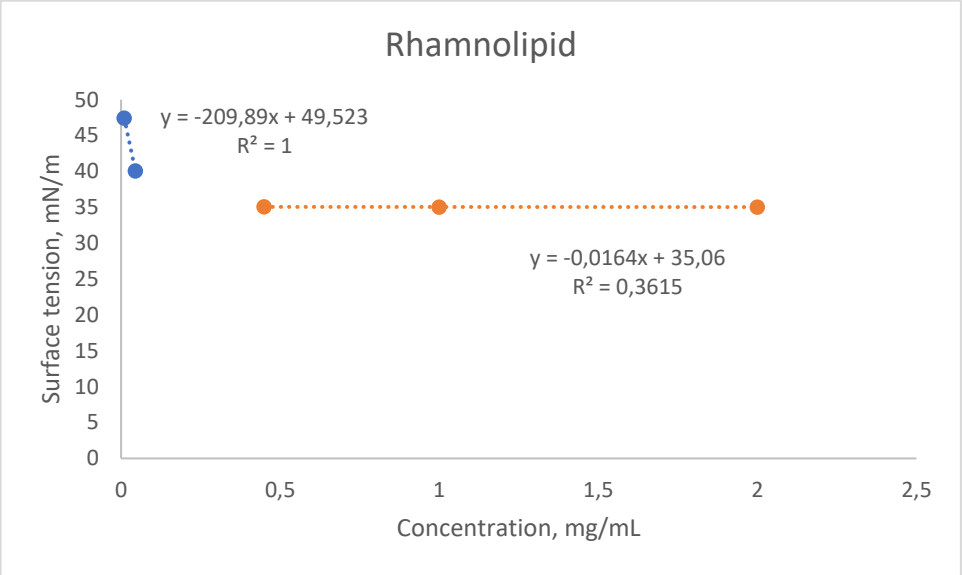


Figure 10. Derivation of CMC of Rhamnolipid