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Purification and Characterization of Lignosulphonate Side Streams from Pulp and Paper Industries

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Danksagung

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Kurzfassung

Bei der Zellstoffherstellung der Firma Sappi werden durch die Kochsäure Lignosulfonate (LS) gebildet, welche in großen Mengen in den Ablaugen der Kocherei (SSL) und den Bleicherei-Abwässern (speziell in der Sauerstoffbleiche oder Delignifizierung) anfallen. Derzeit werden diese ligninhaltigen Ablaugen eingedickt und thermisch zur Dampf- und Stromerzeugung für den Prozess genutzt. Der Gedanke der Bioraffinerie ist es, Rohstoffe höherwertig zu nutzen und so auch die LS nicht ausschließlich zu verbrennen, sondern für einen höherwertigen Zweck, zum Beispiel als oberflächenaktiver Stoff, Additiv, Binder, Klebstoffzusatz, oder Tensid einzusetzen. Da die Ablaugen sehr viele unerwünschte Bestandteile enthalten, ist es notwendig die LS zu isolieren, da die technische Weiterverwertung durch diese Begleitstoffe erschwert wird.

Ziel dieser Arbeit ist es, die LS durch verschiedene in der Literatur beschriebenen Isolierungsmethoden wie Adsorption, Extraktion, Ultrafiltration und Dialyse zu isolieren und vor allem die anorganischen Bestandteile und Restzucker abzutrennen. Die Adsorption wird an vier verschiedenen XAD Polymermaterialen sowohl für die Ablaugen (SSL) als auch für die Sauerstoffbleichen getestet. Zusätzlich werden für die Ablaugen noch eine Amin Extraktion, eine Ultrafiltration im Werk Gratkorn und eine Dialyse mit zwei verschiedenen Membranen getestet.

Die isolierten LS werden durch TGA Analyse auf die restlichen anorganischen Bestandteile vermessen, der Ligningehalt wird mittels UV-VIS Spektroskopie bestimmt. Die Leitionen, für die Ablauge Mg^{2+} und für die Sauerstoffbleiche Na^{+}, sowie der Sulfatgehalt als Richtwert für die Sulfonierung der LS werden mittels ICP-OES vermessen. Der Restzuckergehalt wird mit einem HPLC-System bestimmt und zusätzlich wird noch der Gehalt an phenolischen OH-Gruppen im Lignin, der CSB (chemischer Sauerstoff Bedarf) und der TOC (Total organische Kohlenstoff) mittels Küvetten-Schnelltest ermittelt.

Ein Vergleich der Methoden wird erstellt, wobei sich mit der Adsorptionsmethoden alle Zucker entfernen lassen, sowie der Großteil der anorganischen Bestandteile (verbleibend: 2%). Für die Ablaugen erzielte das beste Ergebnis die XAD-16, für die Sauerstoffbleichen die XAD-7 Polymerphase. Die größte Wiederfindung der LS (85%) ergab sich für die Amin Extraktion, jedoch verbleiben hier 40% der Zucker im Endprodukt. Die Ultrafiltration liefert schlechtere Ergebnisse betreffend der verbleibenden Mg^{2+} Ionen (60%) und der Restzucker (18%) verglichen mit den anderen Methoden. Die Abtrennung von anorganischen Bestandteilen und der Zucker mittels Dialyse erzielte bessere Ergebnisse als die Ultrafiltration, jedoch konnten Zuckeroligomere, die den MWCO überschreiten nicht abgetrennt werden, wodurch ein Restzuckergehalt von 5% verbleibt. Der Mg^{2+} Ionengehalt wird auf 15% reduziert. Ein höheres Oberflächen/Volumen Verhältnis der Dialysemembran liefert eine bessere Aufreinigung.

Abstract

Lignosulphonates (LS) are by-products in pulp production and are currently mainly combusted to gain thermal energy for the pulp and paper production. It is gained from digesting the wood and obtained in the spent sulphite liquor (SSL) from the cooking and in the bleaching effluents. The aim of the biorefinery is to use this renewable resource for higher value products in order to exploit the maximum potential of the highly available natural source. LS already have a variety of applications as binders, surfactants, tanning agents and used for the production of fine chemicals. To use the LS in technical applications, they need to be in a pure state. The LS obtained as spent sulphite liquor are polluted with several other components from the process.

The main challenge within this Master's thesis will be the removal of undesirable components, like inorganic salts or sugars, to obtain almost purified lignin fractions with some methods described in the literature like, adsorption, amine extraction, ultrafiltration or dialysis. The adsorption technique is tested for four different XAD polymeric resins as well for the SSL as for the bleaching effluents. Additionally, for the SSL an amine extraction, an ultrafiltration with a pilot plant at Gratkorn mill and a dialysis is tested.

The isolated LS are then characterised by several analytical techniques: the inorganic content is measured by TGA, the lignin content by UV-VIS spectroscopy. The leading ions for the samples, Mg^{2+} for the SSL and Na^{+} for the O_2-bleaching effluents, as well as SO_4^{2-} as an indicator for the sulphonation degree of the LS, is measured by ICP-OES. The residual sugar content is determined by HPLC. The phenolic OH-group value, as well as the COD (Chemical Oxygen Demand) and the TOC (Total Organic Carbon) are tested by cuvette tests.

A comparison of the different methods applied is made. The adsorption technique removes all the residual sugars and most of the inorganic components (remaining 2%). For the SSL sample the best result are achieved with a XAD-16 resin, for the O_2-bleaching effluents the XAD-7 was the best resin. The highest recovery of the LS (85%) were found to be by the amine extraction, although 40% of the sugars stayed in the isolated product. Ultrafiltration gave rather bad results concerning the inorganic ions (remaining 60%) and the residual sugars (18%) in the isolated products. The dialysis removed the sugars to 5% remaining and Mg^{2+} ions to 15%. Higher surface to volume ratio for the dialysis tubes results in better cleaning of the product.

Contents

1 Introduction

To give a smooth entry to the following Master's Thesis the origin of the lignin and its extraction is shortly described in the following sections.

1.1 Ultrastructure of Wood

Wood is generally built up of spindle-shaped cells. Each cell wall composites of three main structural components namely cellulose, hemicellulose and lignin as shown in Figure 1. Contiguous cells are fixed together by the middle lamella (M.L.), which mainly consists of lignin and a few hemicelluloses.[1] The cellulose is organised in fibrils, which contain 1,4-β-glucan chains and make up 45% of the cell wall. These are ordered parallel and packed tightly due to the intra- and intermolecular hydrogen bridging interactions. Fibrils on 4 levels form a cellulose fibre.[2] The four levels are the primary cell wall (P) and the secondary cell wall (S), split into the outer layer (S1), the middle layer (S2) and the inner layer (S3).

The lignin is described in section 1.2. The hemicellulose fraction is a heterogenous mixture of polysaccharides, which consists several pentoses (xylose, arabinose) and hexoses (glucose, galactose, fucose, mannose).[2] The backbone is linked in the same way as celluloses, but they are much shorter. However, they differ to celluloses in different side groups, which can be sugars, sugar acids or acetyl esters.[1]

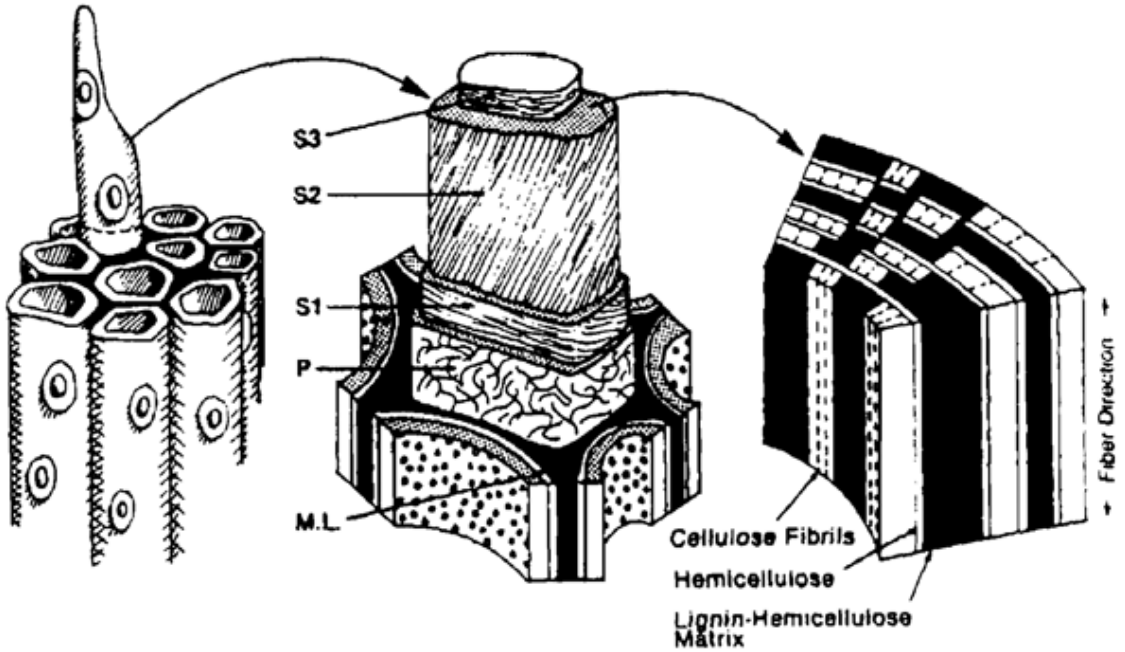

Figure 1 Schematic illustration of the contiguous plant cells (left), cell wall layers (center), and the relationship of the cellulose, hemicelluloses and lignin in the secondary wall (right). M.L., middle lamella; P, primary cell wall; S, secondary cell wall consisting of S1, outer layer; S2, middle layer and S3, inner layer (image taken from [1])

The combination of the three main components of the wood, the cellulose, hemicellulose and lignin, gives it its mechanical stability. The high compressive strength comes from the hard lignins, while its tensile strength is due to the enclosed elastic cellulose fibres. For fixing the lignin and the cellulose next to each other the hemicellulose, the “glue”, is needed. There is a covalent binding of the lignin with the hemicellulose, especially the arabinose, xylose and galactose. The cellulose binds to the hemicellulose mainly via hydrogen bonding.[2]

Additionally wood contains proteins and a fraction called extractives. These are a large number of extraordinary compounds, which are soluble in water or organic solvent. Extractives are non-structural wood constituents, almost extracellular and low molecular-weight compounds. Some examples are terpenoids, steroids, fats, fatty acids, waxes, and phenolic constituents (like stilbenes, ligans, hydrolyzable tannins, flavonoids and condensed tannins, see Figure 2.[3]

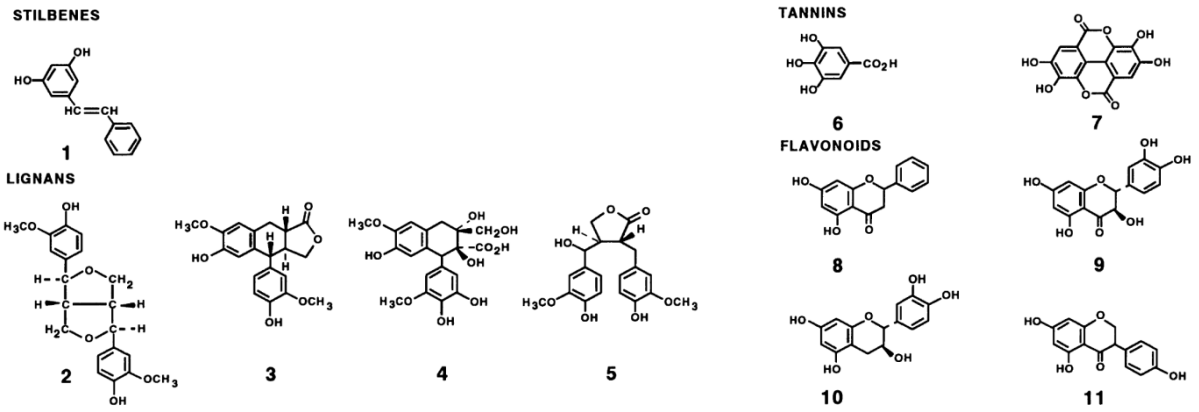

Figure 2 Phenolic extractives: Stilbenes: pinosylvin (1); Lignans: pinoresinol (2), conidendrin (3), plicatic acid (4), hydroxymatairesinol (5); Hydrolyzable tannins (hydrolysis products): gallic acid (6), ellagic acid (7); Flavonoids: chrysin (8), taxifolin (9), catechin (10), genistein (11); (image taken from [3])

Other inorganic extractives are mainly carbonates, silicates, oxalates and phosphates. Metal ions present in wood are calcium, potassium and magnesium. These metals are primary bound to the carboxyl groups of xylan (hetero-polysaccharides) and pectins. Some trace metals with concentrations up to 100 ppm are iron, manganese and cobalt. The heavy metals are bound via complexing forces to the wood constituents.[3]

1.2 The Lignin

One of the most abundant renewable raw materials is lignin. It is of great importance to drive towards the better use of lignins and using its potential for a more sustainable society. Since now, hardly any lignin is used for high added value applications.[4]

The lignin is a very complex biopolymer, built up of phenylpropanoid units, especially syringyl (S), guaiacyl (G) and p-hydroxyphenol (H) monomers, Figure 3. The phenylpropanoid units originate from the alcohols in the blue box in Figure 3, sinapyl alcohol (blue), coniferyl alcohol (green) and p-coumaryl alcohol. The ratio of these units in the polymer depends on the source of the wood, where it grew and the time it was chopped. Softwood lignin mainly consists of coniferyl alcohols, whereas hardwood lignin involves syringyl and guaiacyl monomers.[4]

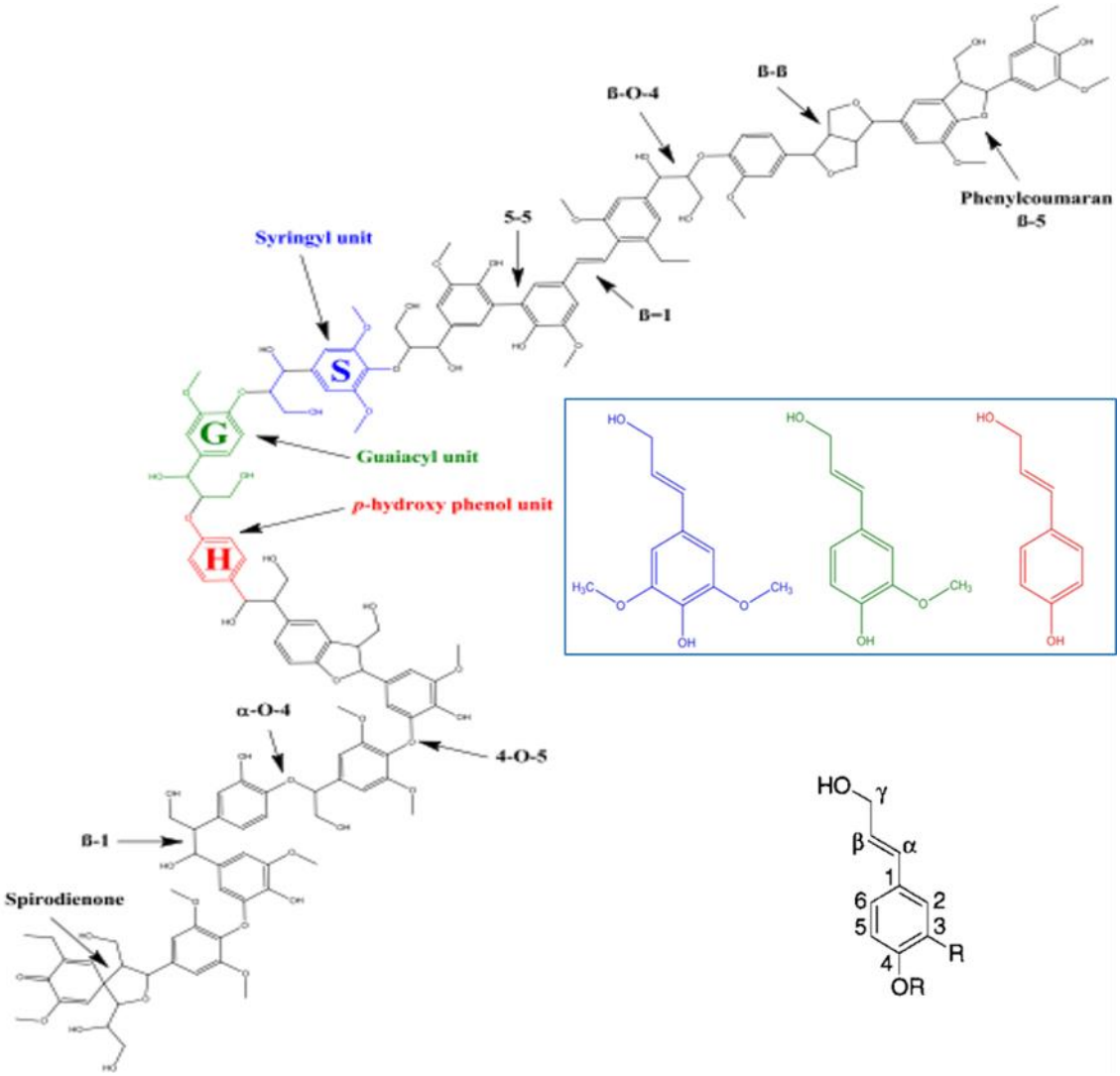

Figure 3 Schematic lignin polymer structure consisting the phenylpropanoid monomers, syringyl (S, blue), guaiacyl (G, green), p-hydroxyphenol (H, red) and the typical linkages (image taken from [5]); on the bottom to the right the general formula of a phenylpropanoid moiety with the *α, β* and *γ* position for explaining the linkages (image taken from [6])

The monomers in the lignin biopolymer are linked via dehydrogenation reactions[5] forming a radical species, which are polymerizing randomly through a radical polymerization process, Figure 4. The aryl-alkyl ether bond is the most common linkage between the monomers[6], see Figure 3.

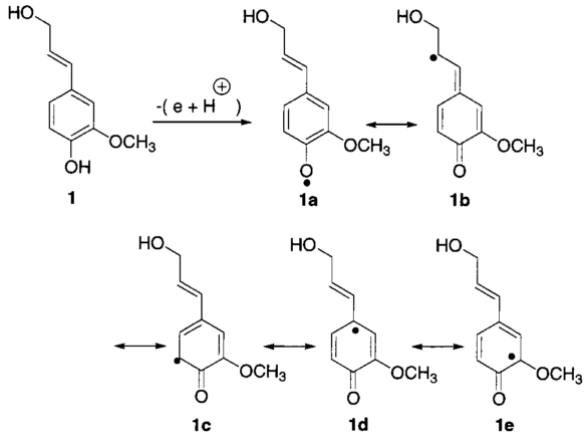

Figure 4 Exemplary radical polymerisation process of the coniferyl alcohol, starting with a dehydrogenation, yielding different radicals (image taken from [6])

1.3 The Pulping Process

Cellulose in its pure state is needed for the production of pulp, which is a basic product of wood. Thus, the lignin and other constituents of the wood have to be removed to get to the rather white cellulose fibres. The process to gain the cellulose out of wood is called pulping.

Pulp is the fibrous mixture after the digestion of wood, whereas chemical pulp describes the highly pure cellulose pulp obtained from sulphate or sufite pulping process.

Different pulping processes earn different lignins. The technical lignins obtained from the various pulping processes are listened in Figure 5.

	Sulfate process	Sulfite process	Soda process	alcohol/water process
Lignin type	Kraft-Lignin	Lignin sulfonate	alkaline Lignin	Organosolv Lignin
Molecular weight, g/mol	2.000–3.000	20.000–50.000	5.000–6.000	2.000–5.000
Poly dispersal	2–3	6–8	9–10	2,4–6,3
Sulfur content	1–2,5%	4–8%	0	0
Ash content	1–6%	up to 25%	2–4%	<0,1%
Solubility	alkaline, organic solvents	water, insoluble in organic solvents	alkaline	alkaline, organic solvents
Functional groups	numerous phenolic OH	few phenolic OH	few phenolic OH	numerous phenolic OH

Figure 5 Comparison of the properties of the technical lignins obtained from different pulping processes (image taken from [7, 8])

There are two pulping processes dominating the pulp and paper production: the sulphate or Kraft process and the sulfite process. The lignosulphonates (LS) are obtained as a by-product in the sulfite pulping process, while Kraft lignin is gained from the sulphate process. The LS

have a higher sulphur content (5%, or sometimes higher) compared to the Kraft lignins (1-2%). The sulphonation of the LS varies between 0.4 and 0.7 sulphonate groups per phenylpropane unit.[4]

The soda process and the organosolv or alcohol/water process give non sulphonated lignins. The organosolv process gives a pure lignin with a very low ash content. But solvent recovery seemed to be problematic.

The Kraft process has almost replaced the soda process. The pulp obtained from Kraft process has higher quality due to better delignification.

The general arrangement of a pulping process is shown in Figure 6.

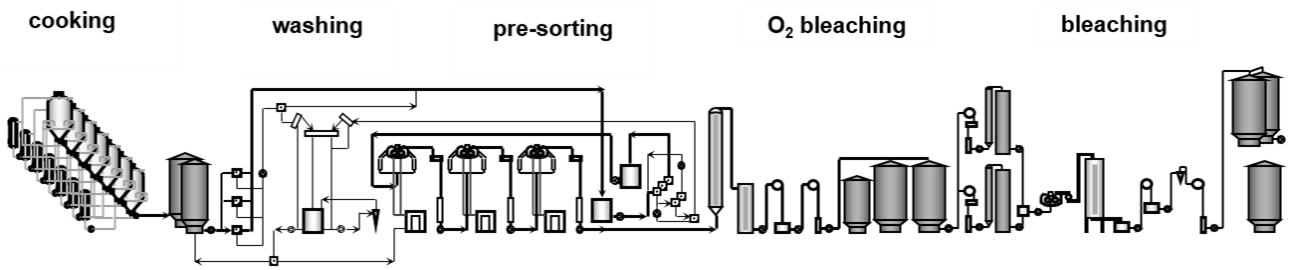

Figure 6 Pulp Process of Sappi Papier Holding GmbH (image taken from [9])

Cooking

Sappi, Gratkorn uses the magnefit process which is based on magnesium bisulfite (at pH around 4). While cooking the cellulose is digested and most of the lignin is removed, see section 1.3.1. The SSL is gained from this process step.

Washing and pre-sorting

Remaining branches and particles are removed and the pulp is washed.

O_2 bleaching

EOP-MC (Extraction-Oxygen-Peroxide Middle Consistent Step) is the first bleaching stage, where all the residual lignins are removed from the pulp to get a pulp with higher brightness. The extraction is made with NaOH to get the lignin and the degradation products out of the cellulose and to alkalify the pulp (pH 10 - 11) to get better results with the peroxide reaction in the bleaching reactor. The oxygen breaks the bonds between the lignin and the cellulose and is called delignification. The peroxide breaks down all the double bonds in the lignin to significantly recue the absorbance of the cellulose to 0 to be purely white. The bleaching takes 120 minutes at 76 °C with a matter density of 13 %.

Bleaching

To make sure to have an optimum bleaching result the main bleaching step is split into two more bleaching steps: the EP-MC (73 °C, pH = 10, matter density 13 %)and the EP-HC (High Consistent: 75 °C, pH = 10, matter density 33 %).[9]

1.3.1 The Magnesium Bisulfite Process $Mg(HSO_3)_2$

The lignosulphonates (LS) obtained from the magnesium bisulfite process are also known as spent sulphite liquor (SSL). This mixture consists of lignin fragments that contain introduced sulphite groups from the pulping process, but the overall structure is not known by now. During the sulphonation of lignin, it is released from the cellulose fibres. In the same step, the lignin is broken down and the obtained lower molecular weight fragments become water-soluble. In Figure 7, it can be seen that the benzyl ether bond of the lignin (L) is protonated and in the second step attacked by the nucleophile HSO_3^- to form the lignosulphonate (LS).

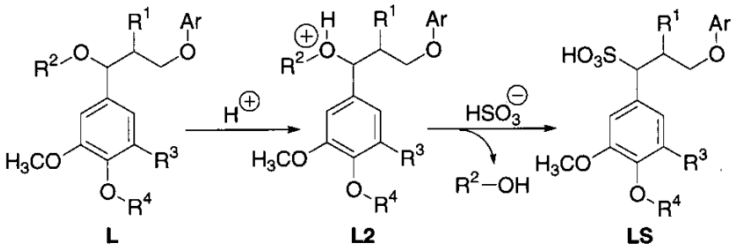

Figure 7 Sulphonation step of a lignin fragment during the magnesium bisulfite process (image taken from [6])

The magnesium bisulfite pulping processes of Sappi, Gratkorn at pH=4,0 takes 7.5 hours for digestion within a temperature of 155°C and 7.5 bar. During this process condensation reactions may occur, which are shown in Figure 8 and Figure 9.

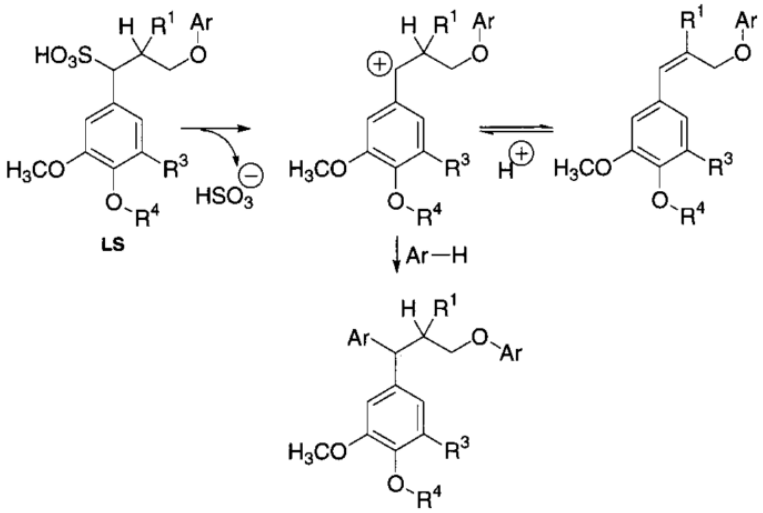

Figure 8 Friedel-Craft alkylation reaction on a lignosulphonate fragment during the magnesium bisulfite process (image taken from [6])

It is also possible that the R-carbonyl groups are sulphonated, which end up in an R-hydroxysulphonic acid, see Figure 9.[6]

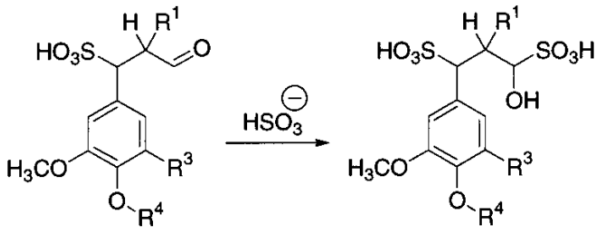

Figure 9 Sulphonation of the R-carbonyl group to give R-hydroxysulphonic acid during the magnesium bisulfite proces (image taken from [6])

The LS obtained have various molecular weights and a huge variety of aryl-aryl and aryl-alkyl linkages, which are subjected to hydrolytic and oxidative depolymerisation. Because of that a wide range of different products is obtained.[6] During the pulping process the amount of present Mg^{2+} and SO_2 are important process parameters which affect the number of obtained sulphonated lignin species.[4]

1.4 The FLIPPR Project

Flippr (Future Lignin and Pulp Processing Research) is a cooperative research project on biorefinery issues, funded by the FFG (Austrian Research Promotion Agency).

The pulp and paper mills of Austria and three Universities are involved in this project:

- Technical University of Graz
- University of Graz
- BOKU University of Natural Resources and Life Sciences
- Sappi Gratkorn
- Mondi AG
- Zellstoff Pöls AG
- Norske Skog Bruck GmbH

The focus of this project is the better use of cellulose fibres and the lignin obtained from pulping processes for higher valued products. Several subprojects deal with product innovations for the lignin, fibres and fines. The wanted target is to use these materials also outside the pulp and paper sector.

Based on existing industrial production processes, the added-value products should achieve rapid realization. Technical developments, as well as ecological and economical perspectives should be reached.

A main goal of the project is the fast and accurate analysis of industrial lignins in a reasonable time. Reliable and quick analytic techniques should be established, which can be applied by all partners.[10]

1.5 Aim and Task

The lignosulphonates (LS) are a by-product in pulp production and are currently mainly combusted to gain thermal energy for the pulp and paper production. The aim of the biorefinery is to use this renewable resource for higher value products in order to exploit the maximum potential of the highly available natural source. LS already have a variety of applications as binders, surfactants, tanning agents and used for the production of fine chemicals.[11]

To use the LS in technical applications, they need to be in a pure state. The LS obtained as spent sulphite liquor are contaminated with several other components from the process, like different sugars from the cellulose degradation, inorganic components, mainly Mg^{2+} and SO_4^{2-}, and some organic acids, see Figure 10. Constituents of the O_2-bleaching effluents of Sappi Gratkorn are shown in Figure 11.

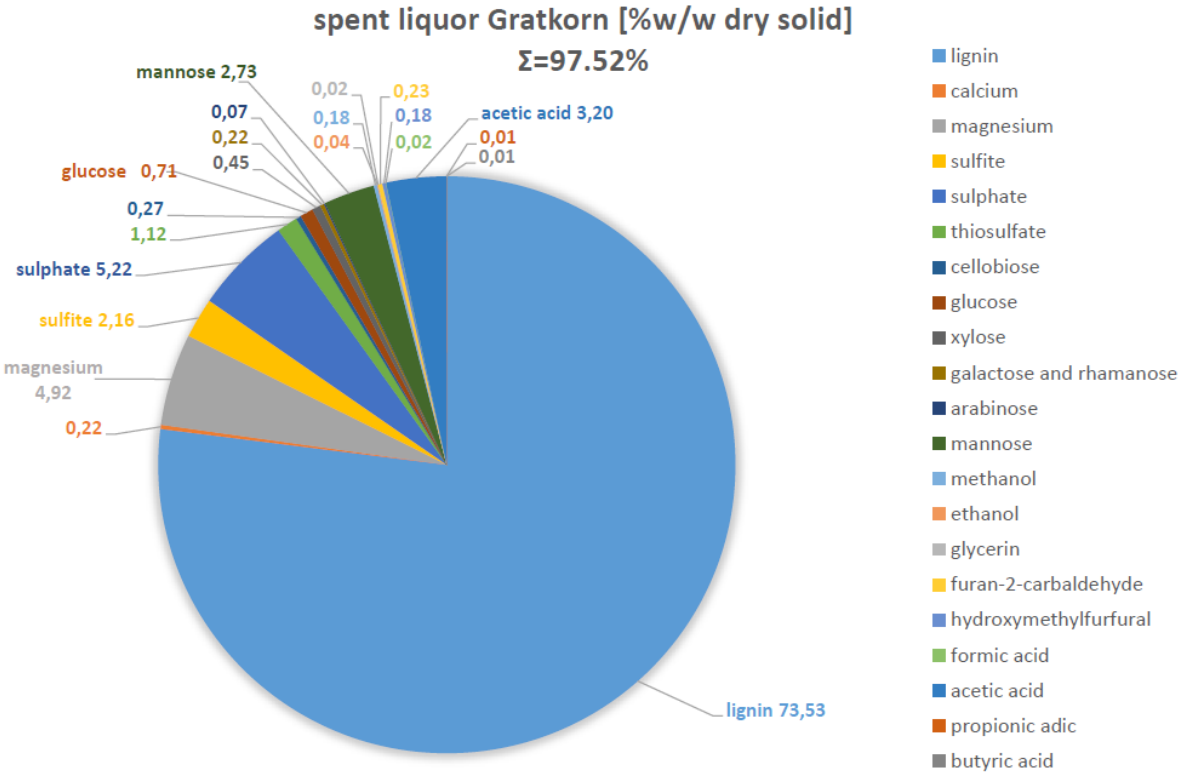

Figure 10 Compounds in the SSL and the O_2-bleaching effluents of the Sappi Gratkorn pulp and paper production plant in %weight per weight dry solid (image taken from [9]).

Moreover, it is necessary to purify the LS for analytical purpose and an easier interpretation of the obtained data. The utilization of technical lignins for added value products is currently limited due to their multi-constituent composition. The main challenge within this Master's thesis will be the removal of undesired components to obtain almost pure lignin fractions of the side steams from the pulp and paper production, the SSL and bleaching effluents after the EOP-bleaching step. Investigations of several purification techniques and an evaluation of each method are the main objectives, which is of great interest for the industrial recovery.

The results obtained during this study provide an overview of the current purification techniques and how they can be applied in the Sappi process streams.

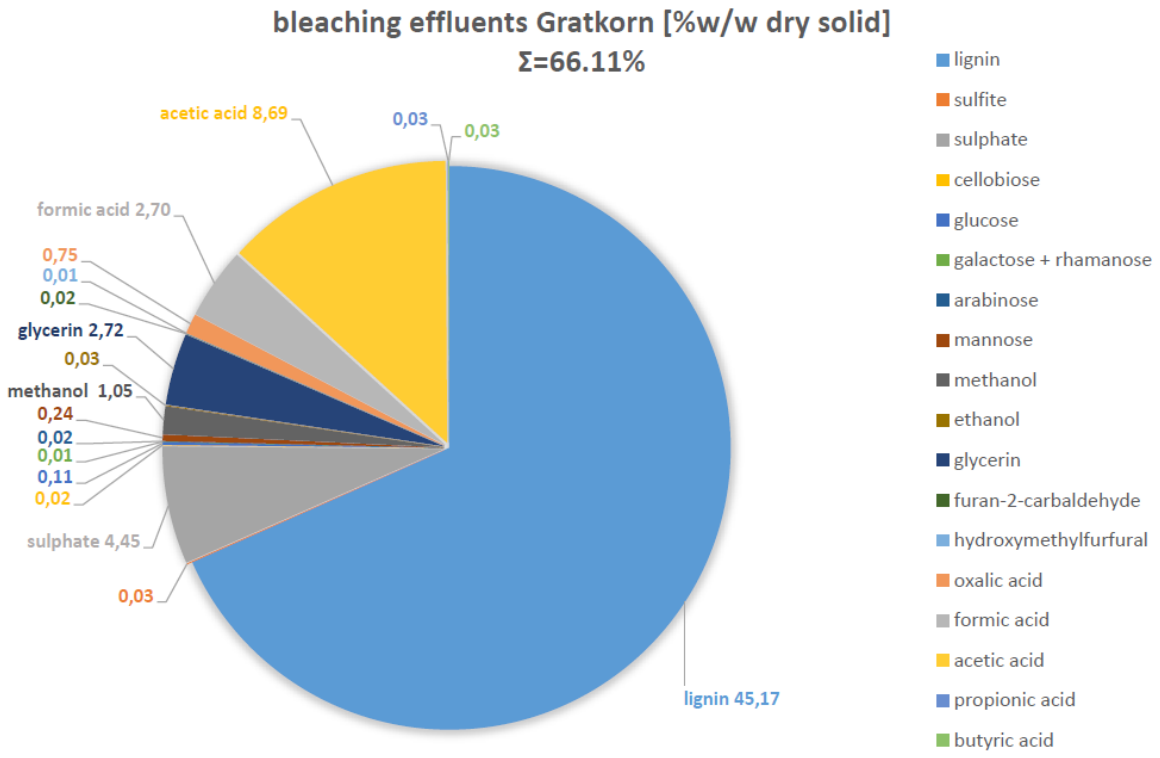

Figure 11 Compounds in the O_2-bleaching effluents of the Sappi Gratkorn pulp and paper production plant in %weight per weight dry solid (image taken from [9]).

1.6 Procedure

The main challenge of the isolation and purification of the lignosulphonates (LS) is the adsorption of these compounds on different polymeric resins, namely XAD-7, XAD-16, XAD-4 and DAX-8. A spent sulphite liquor (SSL) and an O-stage bleaching effluent are tested within an adsorption experiment. In addition, other isolation and fractionation techniques will be investigated with an SSL as an amine extraction, where the LS forms an ion pair with a nonpolar long chain aliphatic amine, which is transferred to the organic phase and extracted thereof precipitated in alkaline medium. Moreover, an ultrafiltration (UF) experiment and two dialysis experiments in laboratory scale will be investigated.

2 Theoretical Background

The theoretical background of the used techniques to isolate and purify the lignosulphonates is described in this section of the thesis.

2.1 Isolation of the Lignosulphonic Acids by Adsorption on Polymeric Resins

Precipitation of the highly polar lignosulphonates (LS) in the spent sulphite liquor solution (SSL) is not possible; therefore these compounds are adsorbed on different polymer resins to further isolate them in pure form from the other components of the water matrix.

A research group of the BOKU Vienna already successfully isolated the LS with the XAD-7 resin from a similar SSL.[11]

The macro-porous polymeric resins are more attractive to the adsorption of the phenolic LS moieties compared to other adsorbents like silica gels, activated carbon or alumina because of its chemical structure and pore structures. The XAD resins used for these trials have acrylic ester or polyaromatic backbones, which are selective towards aromatic analytes.[12]

The theoretical background of this isolation technique is the adsorption chromatography. Adsorption chromatography achieves good results for polar, multifunctional analytes as it is the case for the LS.[13]

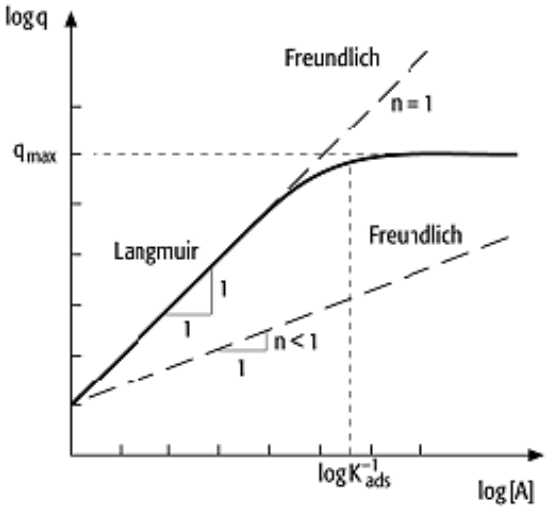

Figure 12 Schematical Langmuir adsorption isotherme in a doubble logarithmic plot in comparison with the Freundlich isotherm; maximum concentration of adsorbate, q_{max}; loading of adsorbate, q; concentration of the analyte, A (image taken from [15])

Adsorption processes always depend on an equilibrium between adsorbed and free analyte molecules. Temperature, pH and the ratio between adsorbate and adsorbent are very important variables in these kind of analyses. This method has been extensively studied by the team of the BOKU Vienna and optimum conditions for the adsorption of the LS have been described recently. The adsorption process can be described with the Langmuir model

(equation 1).[11] A schematically Langmuir plot is shown in **Fehler! Verweisquelle konnte nicht efunden werden.**.

$$q = \frac{K_L\, q_{max}\, C_{eq}}{1 + K_L\, C_{eq}} \quad (1)$$

q ..... loading of the adsorbent (mass adsorbate related to mass adsorbent)
K_L ..... Langmuir adsorption coefficient
q_{max} ..... maximum concentration of adsorbate (mass adsorbate related to mass adsorbent)
C_{eq} ..... concentration of adsorbate in solution [14]

The Langmuir model assumes that the adsorption only takes place in a single layer, that all the spaces on the surface are equal and that there are no interactions between neighbour surface spaces and the particles. [14]

After adsorption, the displacement follows with a solvent, which is more affine to the stationary phase used. Ideally the adsorbed compound should be soluble in the desorption solvent.[13]

2.1.1 Polymer resins

Three parameters, the dipole moment, the pore size and the surface area of the resin guide the capacity of a polymer resin for the binding of a particular substance. The compounds, which should be adsorbed at the adsorbing surface, have to be able to diffuse through the pores of the polymer resin. The higher the surface area of the adsorbent the higher the capacity for the adsorbate. Moreover, the smaller the pore size the higher the surface area.

The nonpolar XAD resins are generally used for adsorption and isolation of organic substances from aqueous systems and polar solvents. The substances to be adsorbed are small to medium molecular weight (up to 40 000 g/mol) for the XAD-16 resin, and relatively low molecular weight (MW<40 000 g/mol) for the XAD-4. The only available "moderately polar" resin is the XAD-7. It is used to remove organic pollutants from aqueous matrices.

The non-functionalized DAX-8 resin with strong hydrophobic organic matter is designed for the adsorption of compounds up to 150 000 g/mol. This resin is referred to as polymethylmethacrylate, commonly used for the treatment of paper and pulp mill waste. [16]

2.2 Isolation of the Lignosulphonic Acids by Amine Extraction

An amine extraction (AE) method was used to fractionate the SSL in order to isolate pure lignosulphonates (LS). The procedure was performed in analogy with Ringena et al. in 2005[17]. Primary long-chain amines form a salt pair with the anionic lignosulphonic acids. These acid-amine adducts are simply extracted into an organic phase by liquid-liquid-extraction. After alkaline treatment, the lignosulphonate sodium salts are transferred back to the aqueous phase. Following four reaction steps describe this process (equations 2 to 5).

1. Cation exchange:	$M^{n+}n(LS^{-}) \rightarrow n\,LS-H$	(2)
2. Complexation and extraction	$R_2NH + LS-H \rightarrow R_2NH_2^{+}(LS^{-})$	(3)
3. Back extraction	$R_2NH_2^{+}(LS^{-}) + NaOH \rightarrow R_2NH_2^{+}OH^{-} + Na^{+}LS^{-}$	(4)
4. Cation exchange	$Na^{+}LS^{-} \rightarrow LS-H$	(5)

The first cation exchange is an alternative to the acid catalysed amine extraction, where the amine is activated with HCl to form the ammonium chloride in the first step, and then directly mixed with the Na-LS. This procedure causes problems in the back extraction step, where NaCl is formed by adding the NaOH. The NaCl contaminates the pure lignosulphonic acids and interferes in subsequent analytical steps. The lignosulphonic acid, which is formed in the first reaction step, is adequately activated to further react with the long chain amine, and by the back extraction step, no undesired precipitation of NaCl occurs. [17, 18, 19]

2.3 Purification of the Lignosulphonic Acids by Ultrafiltration

Ultrafiltration (UF) is a low-cost method to concentrate the macromolecules in the SSL and to remove the low molecular weight pollutants.[20] The ultrafiltration, dialysis and osmose processes are part of membrane separation techniques. For osmose and dialysis the diffusion process of the particles depends on the concentration gradient (see section 2.4 Purification of the Lignosulphonic Acids by Dialysis) and for ultrafiltration a hydrostatic pressure is applied. The separation occurs in all these techniques by filtering the sample through a semipermeable membrane.[19] A general arrangement of the UF membrane is showed in Figure 13.

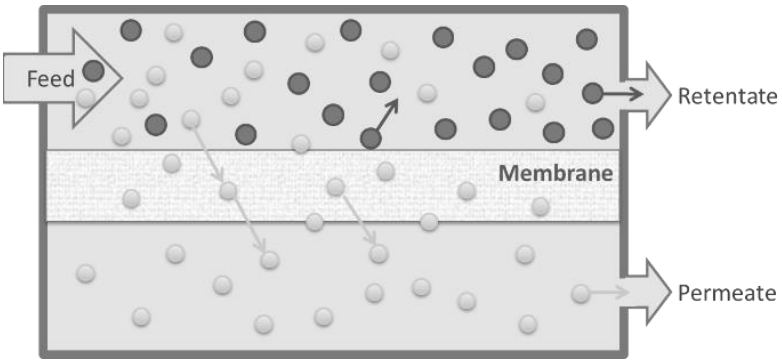

Figure 13 Schematic arrangement of an ultrafiltration

2.4 Purification of the Lignosulphonic Acids by Dialysis

To remove the inorganic matter other small pollutants of the SSL a dialysis is processed. Typical applications of dialysis membranes out of regenerated cellulose membranes (of Spectra/Por®) are desalination, buffer exchange or molecular separation. [21]

A dialysis tube has a semipermeable membrane, where the Molecular Weight Cut-Off (MWCO) gives the size of the pores. All compounds smaller than the MWCO are able to diffuse through the membrane. Outside the tube is the dialysate, which is normally deionised water. The dialysate is stirred to provide an optimum distribution. The diffusion velocity is given with the 1. Fick's law, equation (6).

$$\boldsymbol{v = D * q * \frac{dc}{dx}} \qquad \textbf{(6)}$$

D ..... diffusion coefficient
q ..... exchange surface
$\frac{dc}{dx}$ ..... concentration gradient [22]

The smaller the tubing, the faster the dialysis, because the surface area to volume ratio is higher. Longer diffusion distances in larger membrane tubing take the molecules longer time to diffuse. Thus, the dynamic equilibrium is reached later.

A dialysis process normally takes 12 to 24 hours, where the dialysate should be changed several times to enhance the diffusion process.[22] A schematic arrangement of the dialysis experiment is shown in Figure 14.

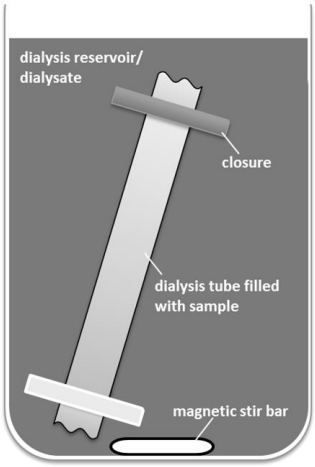

Figure 14 Schematic arrangement of a dialysis

Spectra/Por® is a versatile regenerated cellulose membrane used for laboratory dialysis. It does not adsorb most solutes and carries hardly any fixed charge. The membrane is swollen by water creating little pores, where small solute molecules are able to diffuse through the membrane.[21]

2.5 Analytical Techniques for Characterising the Purified Liquors and Isolated Lignosulphonic Acids

In order to proof the efficiency of the isolation and purification procedures, the samples are characterised by several different parameters, which were determined of the original sample and the obtained cleaner products.

2.5.1 Total Dissolved Solids (TDS)

The Total Dissolved Solids (TDS, dry solid residue after drying the sample in an oven at 105°C) in a SSL sample gives information on the suspended and dissolved components in the liquor. It is given in percent related to the weight liquid sample taken from the liquor (equation 7).

$$\boldsymbol{TDS\ in\ \%} = \frac{\boldsymbol{m_{dry}}}{\boldsymbol{m_0}} * \mathbf{100} \qquad (7)$$

m_{dry} ..... mass of the dried sample [g]
m_0 ..... mass of liquid sample used [g]

2.5.2 Density

The density was determined by a pycnometer. It is filled with sample liquid in a way, that there are no air bubbles or space left. Then it is closed and weighted. Because of the defined volume of the pycnometer, the density is calculated (equation 8)

$$\boldsymbol{\rho} = \frac{\boldsymbol{m_{total} - m_{pycno}}}{\boldsymbol{V_{pycno}}} \qquad (8)$$

ρ ..... density [g/mL]
m_{total} ..... mass of the pycnometer filled with the sample [g]
m_{pycno} .... mass of the pycnometer [g]
V_{pycno} .... volume of the pycnometer [mL]

2.5.3 UV-VIS Spectroscopy

For the determination of lignin in different samples, UV-VIS spectroscopy is used. The lignosulphonates have a characteristic absorption in the UV region from 205 to 280 nm. At 280 nm, the absorption of the lignosulphonate is interfered by furan type compounds like furfural and hydroxymethylfurfural. These degradation products of glucose and xylose strongly absorb light between 255 and 315 nm after heating in sulphuric acid. Therefore, the concentration of lignosulphonates must be determined at 208 nm, where absorption is mostly due to lignin aromatic rings, which was proven by analysis of spent sulphite liquors from a bisulphite cook with a commercial mill digester recently.[23]

The samples are measured in quartz cuvettes. The theory behind the UV measurement is the weakening of the UV light passing through a sample, which is caused by the absorption of the light of the molecules in the sample. The molecules contain different π-electron systems, which can be excited by UV radiation (*hv*). This is described by the HOMO-LUMO model (Highest Occupied Molecular Orbital- Lowest Unoccupied Molecular Orbital). The energy of the absorbed light depends on the energy gap between the HOMO and the LUMO, Figure 15.

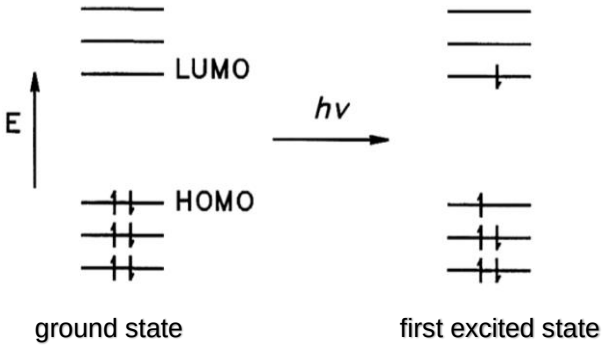

Figure 15 Energy diagram of a HOMO and LUMO (image taken from [24])

This electron transfers are characterised by the name of the molecular orbitals, which take part in this transfer. These are the binding σ- und π-orbitals, non-bonding n-orbital and the antibonding σ*- und π*-orbitals.

The wavelength of the absorbed light depends on the size of the gap between the molecular orbitals the electrons have to pass. The bigger the gap, the more energy is needed and therefore shorter wavelengths are absorbed. The typical areas of these absorptions are shown in Figure 16. However, these energies strongly depend either on functional groups in the molecules and solvent effects.

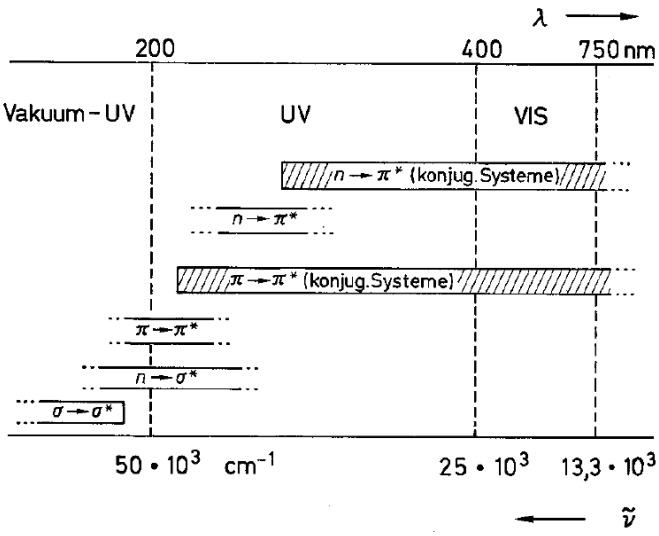

Figure 16 Some energies of the typical electron transfers (image taken from [24])

2.5.3.1 Lambert-Beer Law

The rule of Lambert-Beer describes the wavelength dependent decrease of the intensity of a light source after passing through a sample, which absorbs light. This decrease of the intensity is exponential proportional to the path length of the cuvette and the concentration of the sample (equation 9 and 10).[25, 26]

$$\boldsymbol{I = I_0 * e^{-kl}} \quad \textbf{(9)}$$

I ..... light intensity after passing through the sample
I_0 ..... initial light intensity
k ..... wavelength-dependent absorptivity coefficient [1/cm]
l ..... path length of the cuvette [cm]

$$I = I_0 * 10^{-\varepsilon cl} \qquad or \qquad E = \log\frac{I_0}{I} = \varepsilon cl \quad \textbf{(10)}$$

c ..... molar concentration [mol/L]
ε ..... wavelength-dependent molar absorptivity coefficient [L/(mol*cm)]
E ..... extinction (absorbance)

The transmittance (T) is often measured in experimental setups, which is given below. The absorption (A) is associated with T as in equation 11.

$$T = \frac{I}{I_0} \qquad and \qquad A = -\log T = -\log\frac{I}{I_0} \quad \textbf{(11)}$$

The amount of inorganic salts and sugars in the isolated and purified LS gives a hint about its purity. Although UV measuring determines lignin, its accuracy and reliability is an open question. Due to fractionation, chemical modification of the LS and pulping conditions the absorption property of the LS changes.[27]

2.5.4 Chemical Oxygen Demand (COD)

The Chemical Oxygen Demand (COD) is a direct method to determine the amount of organic components in water samples. The constituents in the liquid sample are fully oxidized and the organic become carbon dioxide and water in an acidic surrounding. The amount of oxygen, which is needed for this full oxidation is the COD given in mg/L.

The organic and inorganic compounds are oxidized by potassium dichromate in an acidic medium. Sulphuric acid is present to keep the pH of the reaction solution low. As soon as the dichromate ($Cr_2O_7^{2-}$) is reduced to Cr^{3+} (Cr_2O_3), the colour changes from orange ($Cr_2O_7^{2-}$) to green. The Cr^{3+} can be measured directly with a photometer at 602 nm, which is an indirect measurement of the oxidized organic species in the sample.[28]

The reaction is schematically shown with potassium acid phthalate in equation 12.[28]

$$2\,KC_8H_5O_4 + 10\,K_2Cr_2O_7 + 41\,H_2SO_4 \rightarrow 16\,CO_2 + 46\,H_2O + 10\,Cr_2(SO_4)_3 + 11\,K_2SO_4 \quad (12)$$

The standard reduction potential E^0(25°C)=1.36V can vary with the temperature, pH and ratio of dichromate to chromic ion concentrations according to equation 13.[28]

$$E = E^0 + \frac{0.0001983\,T}{6}\,log\frac{[H^+][Cr_2O_7^{2-}]}{[Cr^{3+}]^2} \quad (13)$$

Silver sulphate in the reaction solution is used as a catalyst, as far as it is not completely consumed for AgCl. Mercury sulphate is also present in solution to mask the chloride ions, that they do not interfere the oxidation process by consuming oxygen, as shown in equation 14.[28]

$$4\,Cl^- + O_2 + 4\,H^+ \rightarrow 2\,H_2O + 2\,Cl_2 \quad (14)$$

2.5.5 Total Organic Carbon (TOC)

As far as the lignosulphonates are the most abundant species in the SSL, the Total Organic Carbon test (TOC) is a good method for the quantification of the lignosulphonates in the samples. The determination of the TOC by expelling CO_2 is a two-staged process. In the first stage, the Total Inorganic Carbon (TIC) is expelled by adding the sample into an acidic-buffered solution of boric acid and disodium hydrogen phosphate. With the help of a shaker, the CO_2 of the sample is expelled. After that, the TOC is oxidized to CO_2 by using sodium peroxo disulphate in a digesting device, see equation 15.

$$S_2O_8^{2-} + HCOO^- \rightarrow HSO_4^- + SO_4^{2-} + CO_2 \quad (15)$$

The CO_2 passes through a gas permeable membrane into another cuvette filled with water and pH indicator (Ind), where the CO_2 is trapped in the water solution forming carbonic acid, equation 16.

$$CO_2 + H_2O \rightarrow 2\,H^+ + CO_3^{2-} \quad (16)$$

$$Ind^-\,(color\ A) + H^+ \rightarrow IndH(color\ B) \quad (17)$$

The colour changes depending on the amount of CO_2 diffusing into the indicator cuvette protonating the indicator as shown in equation 17. The colour change can be evaluated by a photometer at 435 nm and since carbon in the sample is proportional to the formed CO_2 it can be quantified.

The TOC is a sum value, which does not give any further indications where the carbon comes from. Either the dissolved and bound carbon sources are measured.[29, 30, 31]

2.5.6 Phenolic OH-Groups

The principle behind the determination of the phenolic hydroxyl groups of the lignosulphonates is the reaction of phenols with 4-nitroaniline to form an orange to reddish coloured complex. This complex is characterized by a photometer at 478 nm.

The diazotization of 4-nitroaniline is made *in situ* using NO_2^- and HCl as catalysts. The first step is the generation of a reactive nitrosyl cation NO^+, see Figure 17.

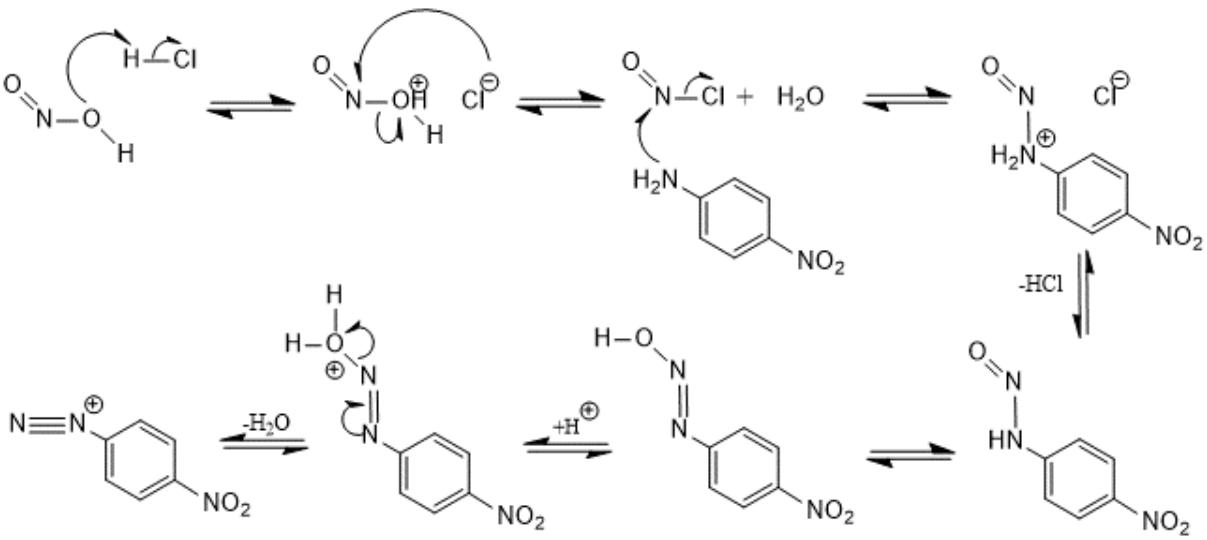

Figure 17 Formation of the reactive species ON-Cl with NO_2^- and HCl in situ and the nitrosyl binding and formation of the aromatic diazonium ion

Figure 18 shows the coupling of the diazonium ion with the phenolic OH-groups from the LS. The nitro functionality in para position of the azonium moiety enhances the electrophility of the azonium nitrogen that it can attack phenols. This results in the formation of an orange to reddish complex. The phenol is prior deprotonated by adding the Na_2CO_3 to the reaction solution.

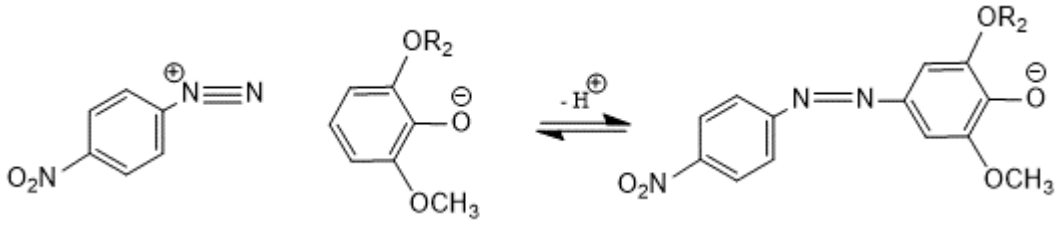

Figure 18 Azo coupling of the p-nitroazophenol and the phenolic OH-group of the LS fragment

2.5.7 Elemental Analysis of Sodium, Calcium and Sulphur by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

The ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) is a method used for the detection of trace metals in various samples, generally in a liquid state. In general, the sample is sprayed into a up to 10000 Kelvin high temperature plasma where it is converted to atoms and furthermore to excited, free ions. These excited ions emit a characteristic radiation by going back to their ground state, which is measured by an optical detector. A schematic illustration of an ICP-OES is shown in Figure 19.

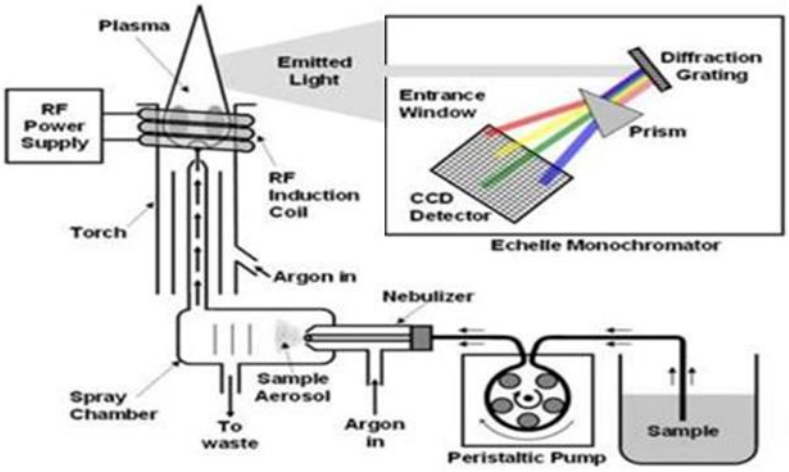

Figure 19 Schematic construction of an ICP-OES (image taken from [33])

Inductively coupled plasma is an ionized gas (freely moving electrones and ions). It is ionised by applying alternating current to generate an electromagnetic field where electrons are moving very fast (RF coil = radio freqency coil). The ignition of the plasma is made with sparks, while piezoelectric discharge or a tesla coil. The fast electrons are accelerated by the electromagnetic field and heat up the plasma due to the collisions with the atoms. Usually argon is used as a plasma gas because of its inertness, cheap compared to other noble gases and the first ionisation potential is at about 15.76eV, which is higher than the ionisation potential of other elements (exception: He, F, Ne) and lower than the second of most of the elements (exception: Ca, Sr, Ba etc). This fact makes sure that most of the analytes in the plasma are in the M^{+1} state.[34]

To get the sample to the plasma a nebulization takes place. In this first step, the sample is converted to an aerosol (finely divided droplets, see Figure 20). Therefore, pneumatic nebulizers are commonly used. Only droplets smaller than 8 µm in diameter can pass the spray chamber to the ICP torch, which is for pneumatic nebulizers less than 5 % of the injected sample.[35]

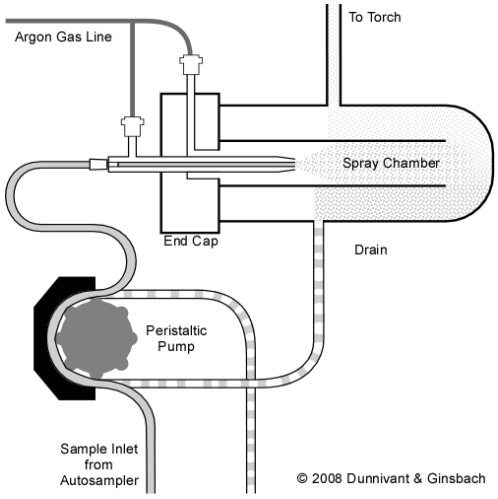

Figure 20 Nebulizer chamber of an ICP-OES, with an pneumatic concentric nebulizer (image taken from [36])

In Figure 21 a schematic torch is shown. There are three tubes, usually made out of fused silica, which are referred to as an outer, intermediate and inner gas tube. The outer one is the cooling tube to prevent the torch of getting to hot. The intermediate gas tube is the plasma tube, which directs the position of the plasma to the walls and the induction coil and supporting the monitored emission signals. The inner tube is the sample aerosol inlet.

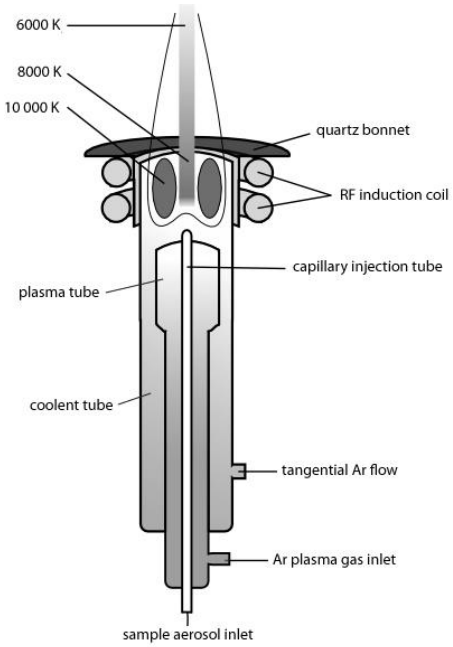

Figure 21 Schematic ICP torch (image taken from [37])

The aerosol is further transported by argon gas to the ICP torch where it passes the induction region right inside the induction coil. In the plasma, the sample droplets undergo different processes according to the temperature the plasma has it is divided into different zones, as shown in Table 1.

Table 1 Temperature, zones and processes in the plasma torch

temperature	zone	process	note
10000-8000 K	preheating zone with the plasma core	desolvation	evaporation of the solvent, dry sample particles remain
		vaporization	decomposition into gaseous state molecules
		atomization	particles are converted to atoms (preheating zone)
6000 K	normal analytical zone	excitation and ionization	excited ions emit specific radiation while relaxation to the ground state

A detector then measures the radiation, which is produced by the ions. There are two ways of detecting them: radial and axial, Figure 22. The radial detection is better for analytes in higher concentration areas and furthermore with this method the interferences are less. The axial mode achieves higher sensibility and better detection limits.

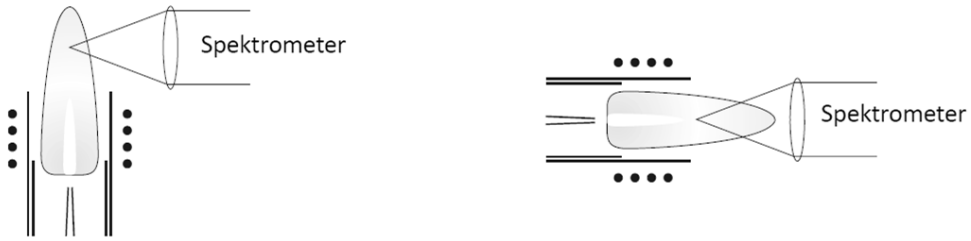

Figure 22 Radial (left) or axial detection of the radiation emitted by the ions in ICP-OES (image taken from [34])

The aim of the detector is to separate all the obtained different radiations from the desired emission wavelengths and then to quantify it. Commonly for such focusing optics, a prism or lattice is used. For the spectrometer, also two possible instruments are used: sequential or simultaneous. A sequential device only measures one specific wavelength at a time passing through a monochromator on to the detector, whereas the simultaneous instrument uses polychomators where each desired wavelength passes a slit and is detected simultaneously. [35, 34]

For the SSL samples, Mg^{2+} is measured as the main counter ion in solution, which in in the case of the O_2-bleaching effluents the Na^+.

2.5.8 Determination of the Monomeric Sugars by High Performance Liquid Chromatography (HPLC)

HPLC stands for High Performance Liquid Chromatography and is a part of the liquid-liquid column chromatography. High performance distinguishes this technique from the normal liquid chromatography in higher resolution, shorter periods to analyze and higher sensitivity. It is a common analytic technique to separate, identify and qualify components in a liquid mixture.

The basic principle of HPLC or general LC is the separation of a mixture of analytes in between two phases, a stationary and a mobile phase, due to the different molecular interactions of the analyte with both the mobile and the stationary phase. The mobile phase transports the sample or analytes trough the column which consists the stationary phase. Due to the analyte-stationary phase, interactions the analytes are retarded by adsorption and separated, Figure 23.

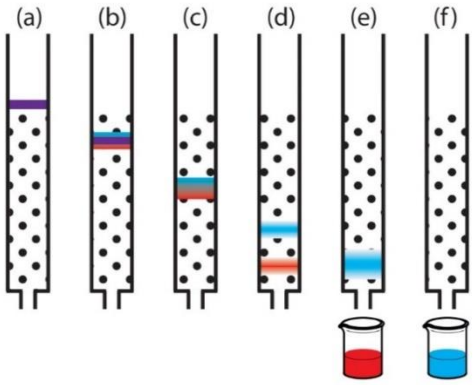

Figure 23 Schematic principle of the separation of a substance mixture by chromatography (image taken from [38])

A classic HPLC consist of the following parts, as shown in Figure 24.[39]

1. Pump: It pushes the mobile phase through the column by applying pressure. The parameter is given in millilitre per minute.
2. Injector: it introduces the liquid sample into the flow stream of the mobile phase. Usually it is used with an autosampler and injects 5-20 µL of the sample.
3. Column: It is the stationary phase, which is a tube packed tighly with fine porous particles. The fine packing caused the backpressure by moving the mobile phase through the column.
4. Detector: The separated compounds are measured, when they exit the column by a detector, which also quantifies the sample according to the integral of the peak.
5. Computer: It controls the HPLC modules and determines the elution time to create a chromatogram, Figure 25. As the sample is injected (time = 0) to the system, the time starts to count.

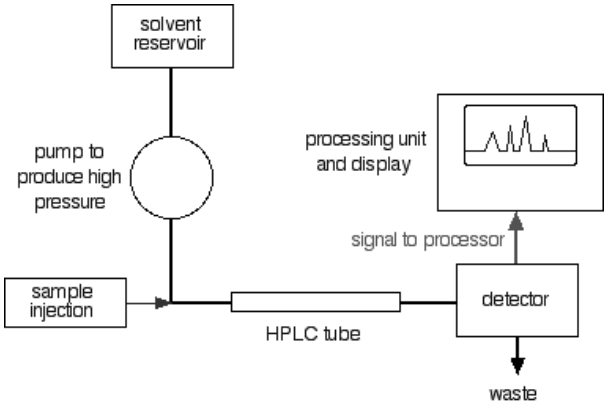

Figure 24 Schematic arrangement of an HPLC (image taken from [40])

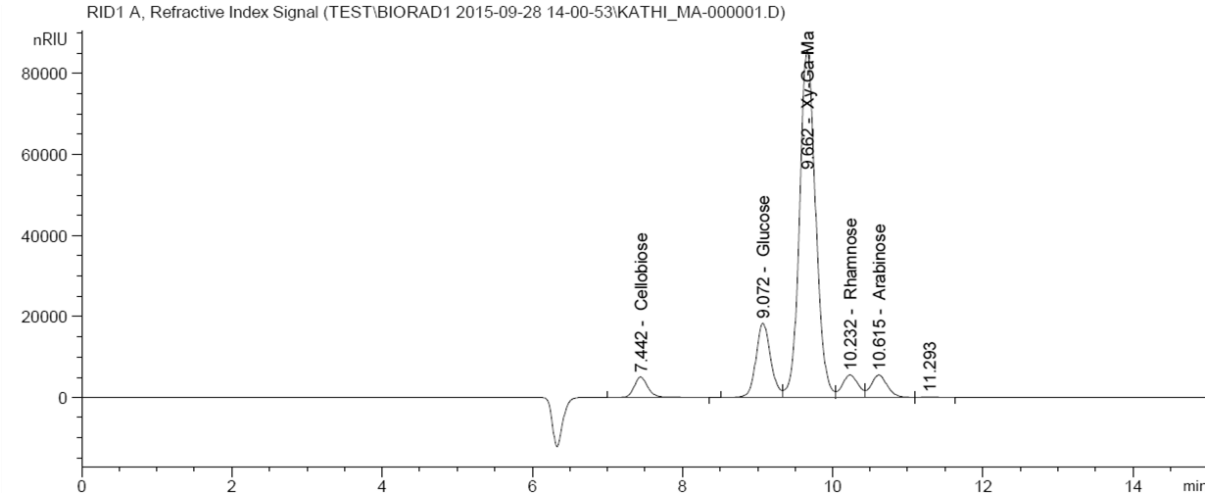

Figure 25 HPLC spectrum of a calibration standard of the monomeric sugars with their specific retention times

The identification of the detected compounds is made by the retention time t_R of the compound. t_0 describes the dead time, which is the time needed to fill the column with the mobile phase (dead volume).

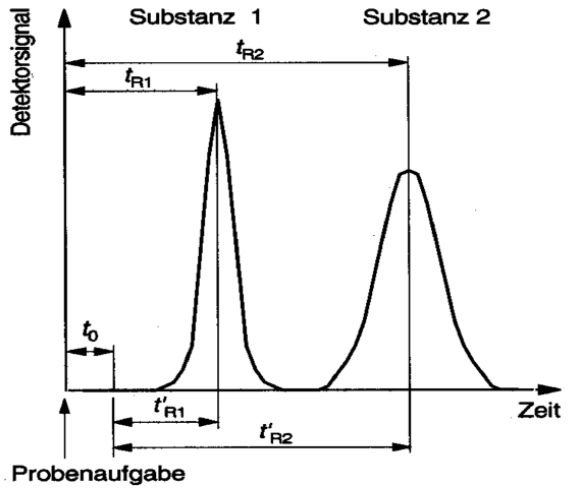

Figure 26 Chromatogram with retention times of the substances analysed (image taken from [34])

Another parameter is the distribution coefficient *K* which gives the relation of the concentration of the analyte in the stationary phase c_{stat} and the mobile phase c_{mob}, equation 18.[34]

$$K = \frac{c_{stat}}{c_{mob}} \quad (18)$$

The capacity factor *k'* is independent of the length of the column and the flow velocity. In practice *k'* should be in between one and five as an optimum, but no more than ten (equation 19).[34]

$$k' = \frac{t_R - t_0}{t_0} \quad (19)$$

The resolution *R* is important for identifying different compounds and separating the signals, see equation 20. The chromatographic peaks are approximately Gaussian curves, where *R=2* is enough for quantitative analysis, see Figure 27. The basic peak width is given with *w.* [34]

$$R = \frac{2(t_{R1} - t_{R2})}{w_1 + w_2} \quad (20)$$

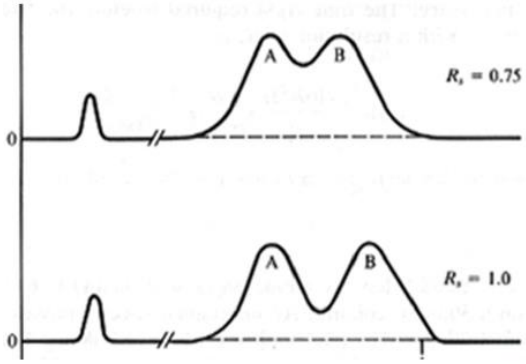

Figure 27 Chromatogram with expressing the resolution R (image taken from [34])

The selectivity *α* is given in the formula below, equation 21. If *α=1* there is no separation.[34]

$$\alpha = \frac{t_{R1}}{t_{R2}} = \frac{t_{R1} - t_0}{t_{R2} - t_0} \quad (21)$$

HPLC is performed if the analyte is not volatile, strongly polar or ionic, the MW>500g/mol or if it is thermally instable or easy decomposable.

Before performing an HPLC, it has to be ensured that the analyte, which should be detected is soluble in a liquid solvent, which should have the same matrix as the mobile phase used. Before applying the sample on the HPLC all the suspended matter should be filtered off.[34, 39]

2.5.9 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is for the investigation of the combustion and pyrolysis behavior of solid samples as well as their thermal stability and volatile components in an inert atmosphere. The sample is placed in a furnace and heat is applied in a certain programmed rate. The change of the weight of the sample is constantly recorded with a balance and plotted in a curve weight over time (black) or weight over temperature, see Figure 28. This data can give a clue about reaction processes going on during a pyrolysis process, the kinetics, reaction order and the activation energy.[41]

For a better resolution of the different processes going on hold points can be added to the sequence.

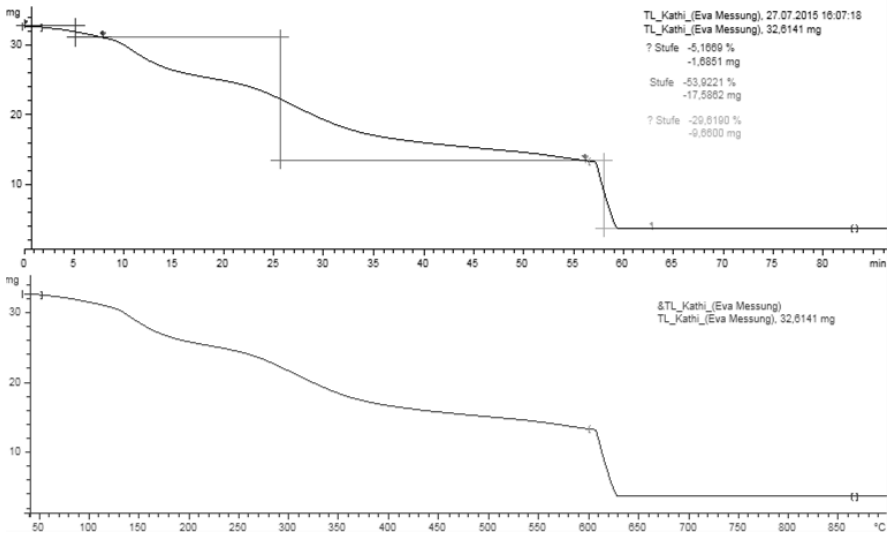

Figure 28 TGA spectrum of a spent sulphite liquor with different combustion processes; upper curve: change in weight over time; lower curve: change of weight over oven temperature

The composition of organic and inorganic components can be calculated with this information. In Figure 29 the single component units of a TGA are shown:

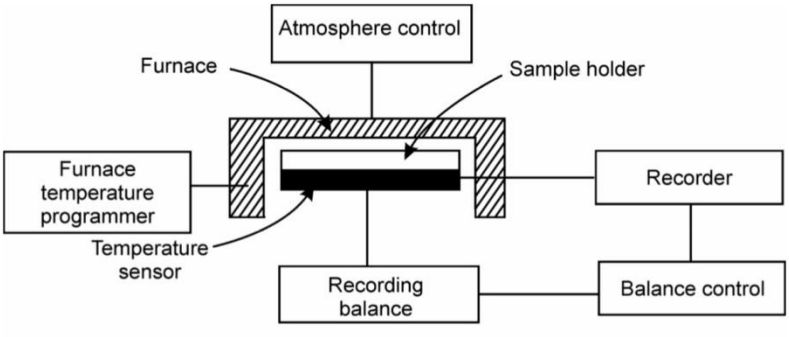

Figure 29 Schematic thermo gravimetric analyse device (image taken from [42])

3 Results and Discussion

The results of the different isolation and purification experiments are given in this section. In addition, a comparison of all the techniques used is discussed in the end of the chapter.

3.1 Isolation of the Lignosulphonic Acids by Adsorption on Polymeric Resins

The method in these experiments were performed as described in the paper of the group at BOKU Vienna[11]. Additionally to the XAD-7 resin other less polar resins were used (XAD-16, XAD-4, DAX-8) for the isolation of the LS and processed the same way as described in the paper.[11]

3.1.1 Procedure

The sample solutions used were diluted to approximately 10 % TDS. The solution of the SSL were mixed 3 to 4 hours in proportion with 4-5 g of the wet Lewatit S100G1 cation exchanger per 1g of total dissolved solids (TDS) Then the cation exchanger was filtered off and washed with deionised H_2O two to three times.

3.1.1.1 Adsorption on XAD/DAX resins

The wet resin was added to the sample solution in a ratio to the TDS 10:1, meaning 10 g of XAD/DAX resin per 1 g of TDS present in the sample. An overnight shaking of the mixture with a shaker was performed. The resin was filtered off and washed 3 times with 10 mL HCl-acidic water (pH = 2) per 10 g of wet XAD resin and 3 times with deionised water in the same proportion.

3.1.1.2 LS Desorption

Finally, to desorb the lignosulphonates from the resin, 15 mL ethanol needs to be added per 10 g of wet resin 4 to 5 times for 30 to 40 min at 50 °C, followed by one or two additional washing steps with 15 mL deionised H_2O per 10g wet resin. All the fractions obtained during the desorption were combined and the solvents were removed by the rotary evaporator. The dry content was determined and the solids were again dissolved for further analytic steps.

3.1.1.3 Observations during the experiment

After filtering off the cation exchanger resin from the O-stage bleaching effluent there was a white, sticky solid in the glass frit. This sticky substance was removed and not further processed with the residual sample.

After desorption of the LS of the resin the analytes were totally dissolved in the EtOH:water solvent (5:2). While evaporating the EtOH it was noticed, that the LS in the solution are partially precipitating. After all the EtOH was evaporated, the residual water solutions are transferred into a 250mL volumetric flask and filled up to the mark. In all the spent sulphite thick liquor

samples (TL) and the O-stage bleaching effluent (O_2) samples obtained from the different experiments with the polymer resins, a fine yellowish-white precipitate was noticed. This was maybe due to the isolation of the lower sulphonated LS, where the solubility limit was almost reached.

The determination of the lignin content, measured as LS, with an UV-VIS experiment was made with a sodium and calcium LS calibration standards. The LS in the sample solution occur in their protonated H-form (H-LS). Therefore, a calibration curve of the H-LS was additionally made of the almost pure H-LS obtained from the adsorption experiments. The TL on the XAD-16 resin was taken as the H-LS standard solution. To ensure, that the sample solution of the H-LS had the same adsorption curve as the sodium and calcium LS calibration solutions, the sodium LS was spiked with the H-LS and measured, see Figure 30.

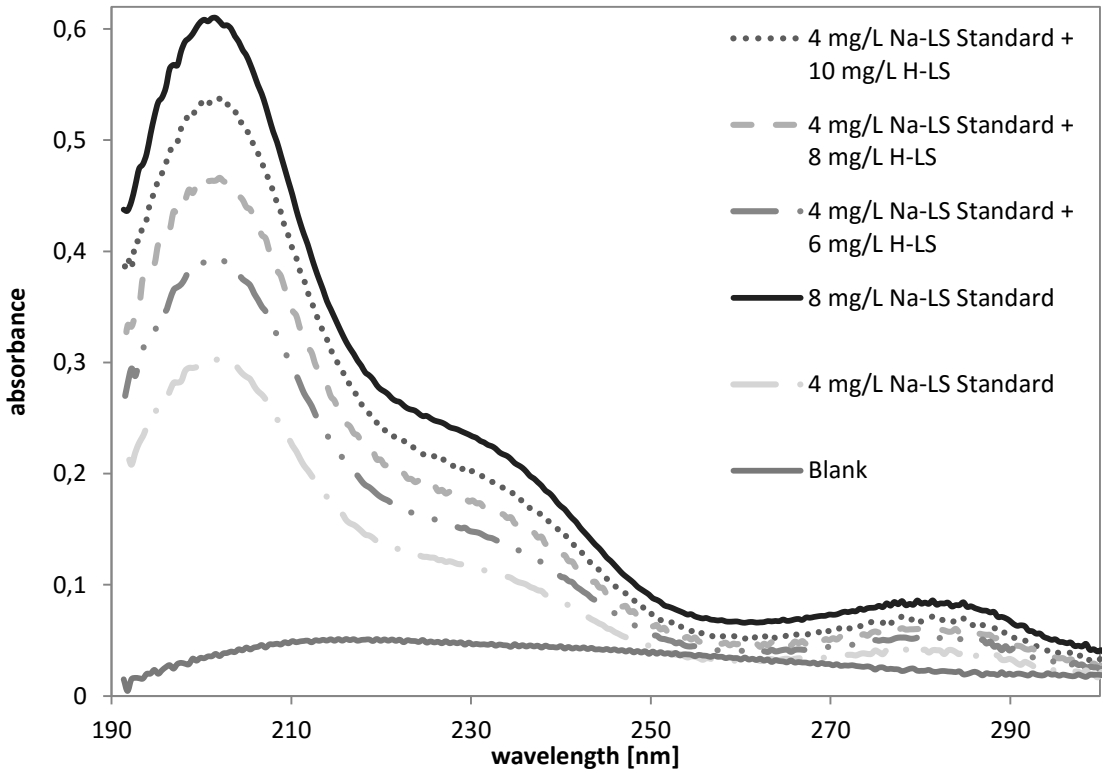

Figure 30 UV-VIS absorption spectra of the Na-LS standard solution spiked with the isolated LS of the TL adsorption on the XAD-16 resin showing the same absorption curve

3.1.2 Discussion

The adsorption experiment was tried with two different kinds of samples: a SSL, which is named Thick liquor (TL) and an effluent of an O-stage bleaching. The sample names and descriptions are shown in Table 2. Two different O-stage bleaching effluents were used, because there was not enough sample for all the experiments. Analytical data of the original samples is listened in the Appendix.

Table 2 Samples of Sappi Gratkorn used for the adsorption experiment

sample name abbreviated	sample name	type
TL	TL-EDA 2, Feed 25.9.2014	spent liquor, vaporized, thick liquor (TDS ~ 23.9 %)
O_2	O_2-bleaching effluent, 14.10.2014	O-stage bleaching effluent
O_2 new	O_2-bleaching effluent, filtered; 29.7.2015	O-stage bleaching effluent

3.1.2.1 Results

In Figure 31 a comparison of the isolated LS of the SSL are plotted. Best adsorption showed the XAD-16 resin because of its higher surface area. XAD-4 resin isolates lignosulphonates with a higher sulphonation degree than the other resins. It can be clearly seen that all the sugars in the SSL were removed by these techniques. The organic content of the original sample was 79.8 ± 1.5 % and is increased after isolation with the XAD-7 to more than ~ 97.4 ± 2.6 % , for the DAX-8 to 93.0 ± 7.0 %.

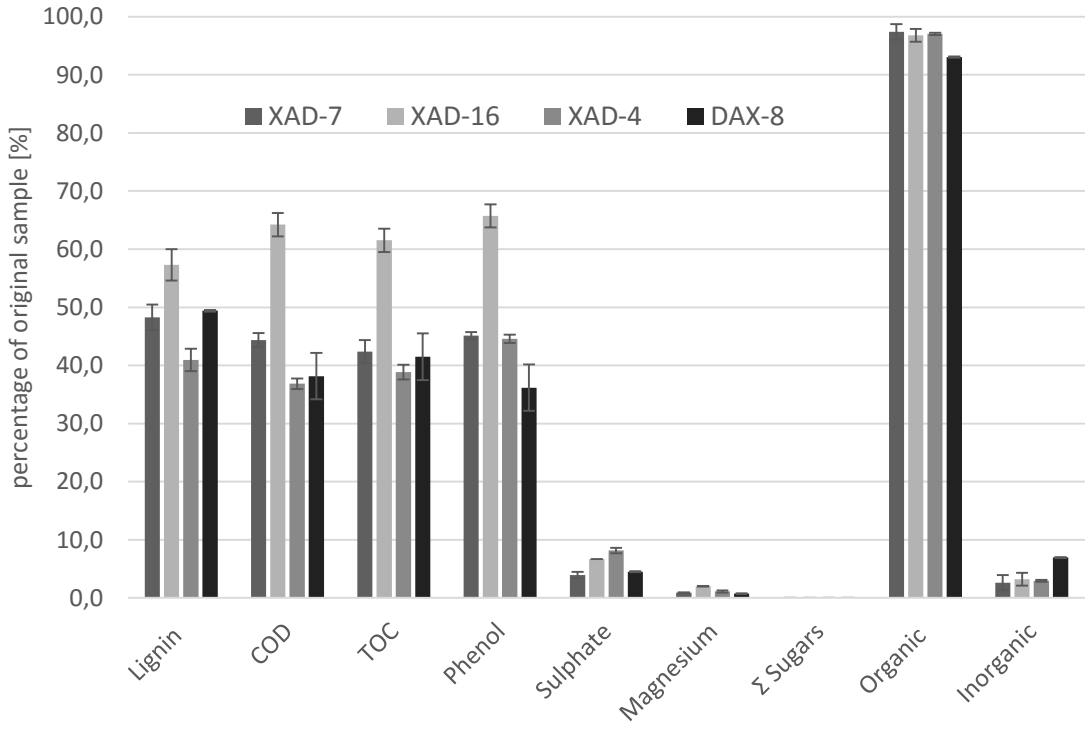

Figure 31 Comparison of the isolated LS fractions from the SSL with the adsorption polymers XAD-7, XAD-16, XAD-4 and DAX-8. Lignin content is measured as LS by an UV spectroscope. COD, TOC and Phenol content by cuvette tests. Sulphate and magnesium by ICP-OES. Sugars by HPLC and organic and inorganic content by TGA.

In Figure 32 the comparison of the isolated LS from the O_2-bleaching effluents is plotted. It clearly shows that nearly all the inorganic components are removed and an organic content of nearly 100 % is achieved (XAD-16: 99.0 ± 0.0; DAX-8 94.3 ± 0.3 %). In addition, the sugars are completely removed by this method. The XAD-4 does not isolate the LS as good as the other resins. The XAD-7 reached the highest isolated amounts of lignin (56.3 ± 2.9 %) and the DAX-8 isolated the most sulphonated LS fragments (6.7 ± 0.1 %). XAD-16 also gives good results.

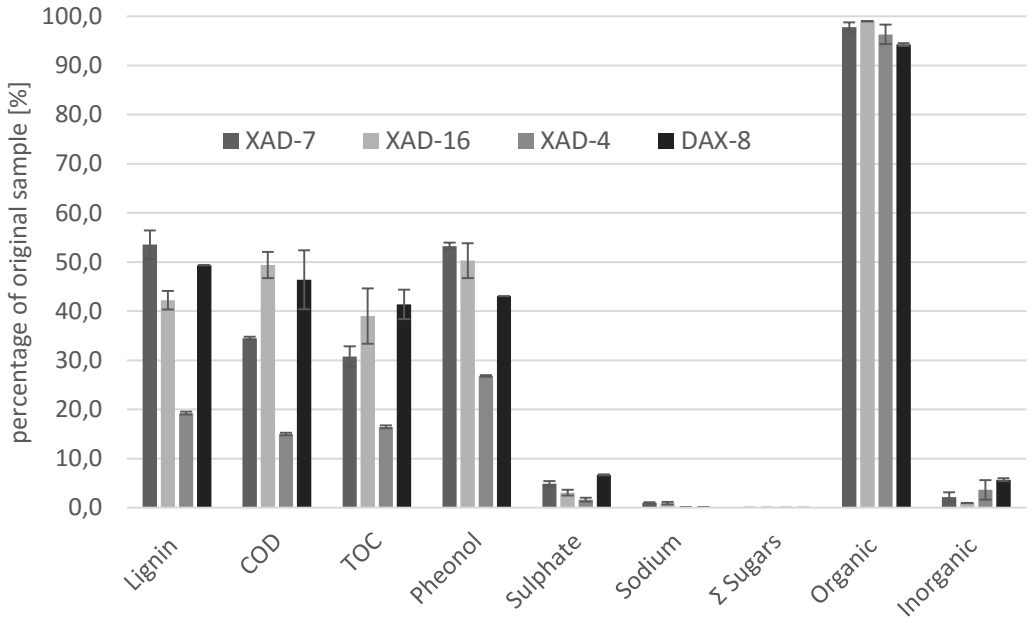

Figure 32 Comparison of the isolated LS fractions from the O_2-bleaching effluent with the different adsorption polymers XAD-7, XAD-16, XAD-4 and DAX-8. Lignin content is measured as LS by an UV spectroscope. COD, TOC and Phenol content by cuvette tests. Sulphate and sodium by ICP-OES. Sugars by HPLC and organic and inorganic content by TGA.

3.2 Isolation of the Lignosulphonic Acids by Amine Extraction

The amine extraction was performed as described in the paper of Ringena in 2005.[17] The schematic procedure is shown in Figure 33. The SSL is first converted to its acidic form by using a cation exchanger. Then the excess SO_4^{2-} ions are precipitated with $Ba(OH)_2$ and separated. For the complexation, dodecylamine in n-BuOH is added and the LS^- is extracted. The LS is regained by basic treatment and before analysis again brought to its acidic form by a cation exchanger.

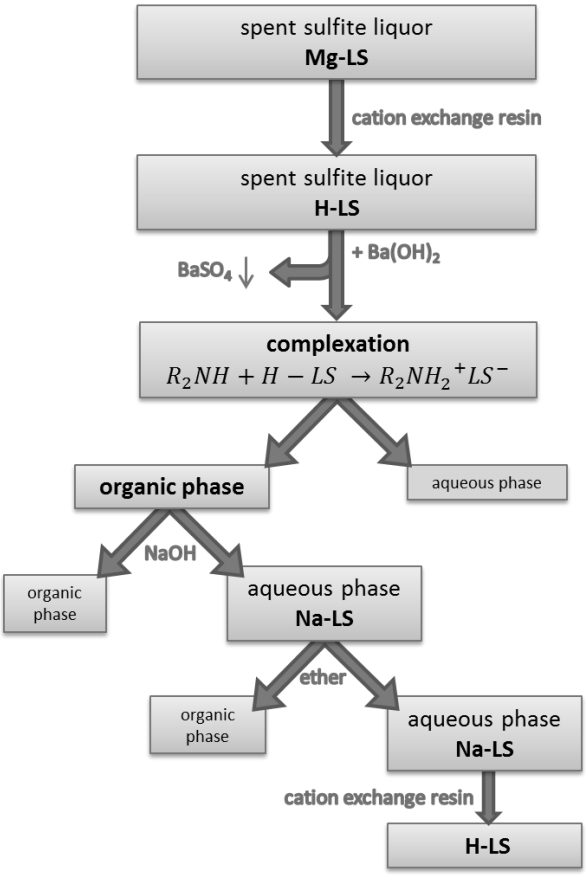

Figure 33 Procedure to isolate the LS out of the SSL by amine extraction after Ringena, 2005[17]

3.2.1 Discussion

For the amine extraction a SSL with a TDS content of 13.0 ± 0.0 %, categorised as a thin liquor (DL) was used. Analytical data of the original samples is listened in the Appendix.

The analytical data of the LS sample obtained from the amine extraction are graphically shown in Figure 34. The plotted values are the percent of the analyte in the obtained sample related to the analytical values measured in the original sample.

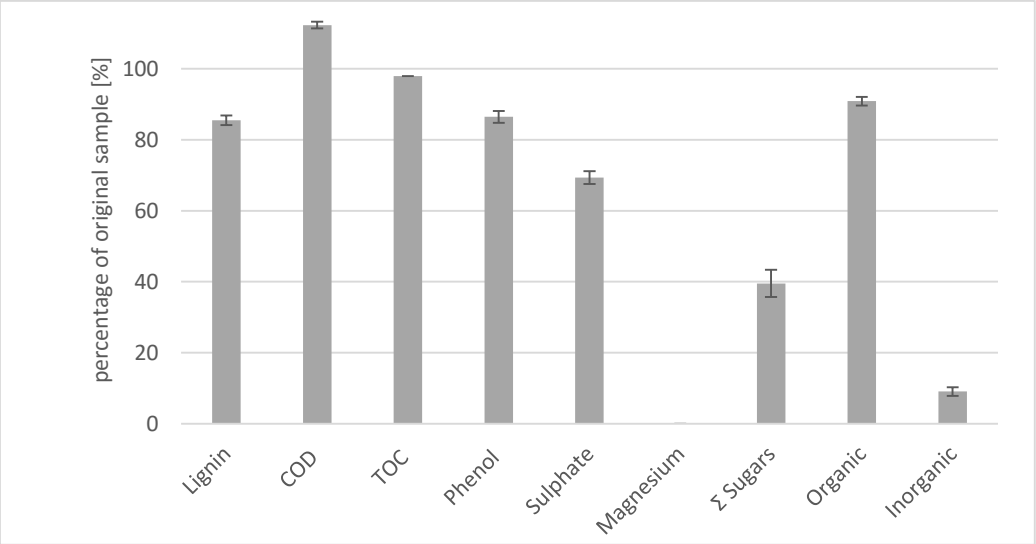

Figure 34 Amine-extracted lignosulphonates in percent related to the original sample values of the SSL. Lignin content is measured as LS by an UV spectroscope. COD, TOC and Phenol content by cuvette tests. Sulphate and magnesium by ICP-OES. Sugars by HPLC and organic and inorganic content by TGA

As it could be seen, the magnesium is completely removed during the amine extraction. This is maybe caused by the last step of the procedure: the cation exchange. The TGA analysis showed that the organic content of the sample is 90.9 ± 1.2 % and the inorganic residues were at 9.1 ± 1.2 %.

There are still 39.5 ± 3.8 % sugars measured in the sample. They extraction was processed at pH value of 3 and the pK_a of the monomeric sugars is around 12, which means that the OH groups are protonated. Because of that it is assumed that the reducing ends of the sugars form N-glycosides with the primary amine, by a Maillard reaction. [43]

The COD and TOC value are very high because not all the organic n-BuOH and the amine were removed during the extraction steps. Phenolic OH-group content is 86.5 ± 1.7 % of the original concentration, which is the same for the lignin measured in the sample. Sulphate content is at 69.4 ± 1.8 % of the original sample.

This method of extracting the LS is very time consuming, but gives better results in the lignin recovery, although 39.5 ± 3.8 % of the sugars measured in the original sample stayed in the isolated LS sample.

3.3 Purification of the Lignosulphonic Acids by Ultrafiltration

The ultrafiltration was performed with an apparatus with a MWCO 150kDa, which is categorised between micro and ultrafiltration. The pressure is applied with the membrane pump at the plant.

The Mg-SSL is filtered 5 times in a circle (Retentate 1-5). The remaining sample (Retentate 5) is then washed 3 times with the double amount of decarbonised water resulting in the end sample called Retentate end.

3.3.1 Discussion

For the ultrafiltration experiment the same sample as described for the amine extraction was used, see section 3.2.1, page 30.

After each step, a sample was taken and analysed. The TDS content should increase, as well as the COD and TOC. No significant increase of these values was noticed, it is assumed that a membrane in the ultrafiltration chamber is broken. After the washing step of the Retentate 5 is named Retentate end and analysed. After this step a concentration of all the parameters was obtained, maybe the membrane was stucked together.

All the parameters for the washing step are not optimised yet, but should be for further using of the ultrafiltration plant to earn best results. The values are listened in the Appendix.

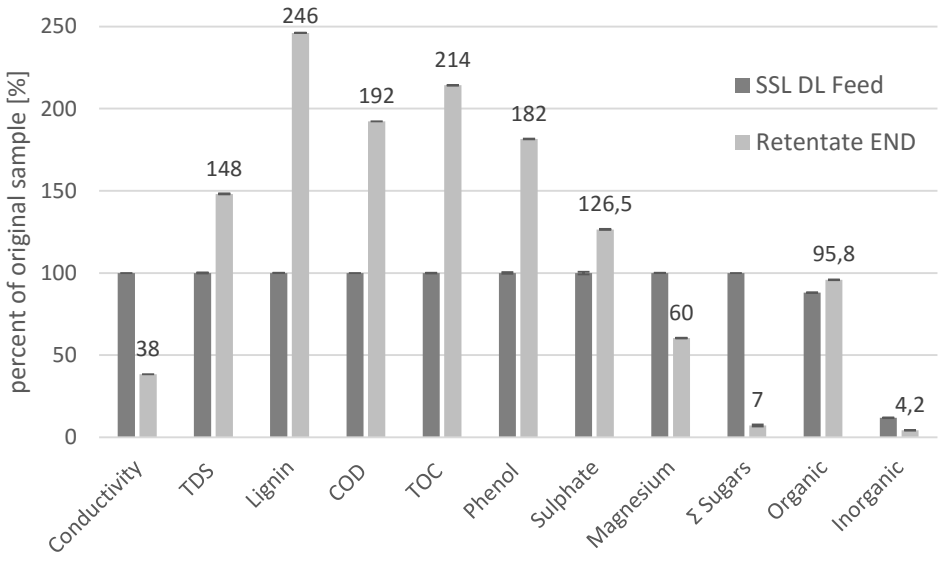

Figure 35 Comparison of the analysed parameters of the ultrafiltration sample, Retentate end with the original sample, SSL . Conductivity is measured by an electrode. TDS after total drying. Lignin content as LS by an UV spectroscope. COD, TOC and Phenol content by cuvette tests. Sulphate and magnesium by ICP-OES. Sugars by HPLC and organic and inorganic content by TGA

In Figure 35, a comparison of the analysed parameters of the Retentate end with the original SSL sample is shown in percent. The values of the SSL were determined as 100 % and the values of the Retentate end were related to them. TDS, lignin content, COD, TOC as well as the sulphate content were concentrated during the ultrafiltration. Free sulphate ions are removed during ultrafiltration, remaining sulphate content is due to the sulphonate groups on the lignin. The amount of phenolic OH-groups was increased due to the enrichment of the LS. Magnesium and sugar content were decreased by ultrafiltration. Conductivity is reduced while ultrafiltration, because small conducting species, mainly ions are removed. Due to the enrichment, also TDS content increases as well as organic content.

3.4 Purification of the Lignosulphonic Acids by Dialysis

For the dialysis, the sample is filled in the dialysis tube from Spectra/Por® and stirred in deionised water for 24 hours.

3.4.1 Discussion

For the dialysis experiment the same sample as described for the amine extraction was used, see section 3.2.1, page 30.

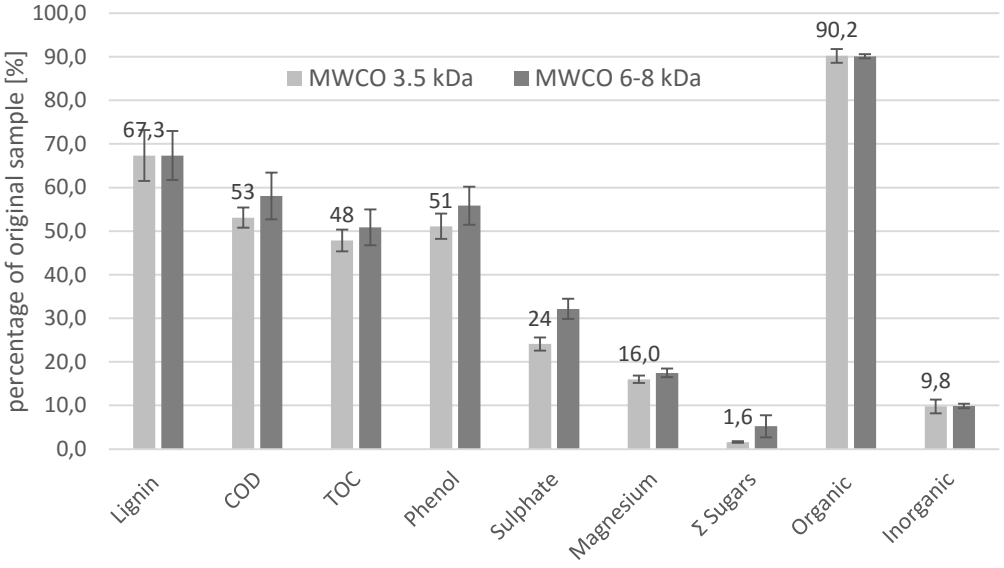

Figure 36 Comparison of the isolated lignosulphonates from the SSL obtained by dialysis with two different MWCO 3.5 and 6-8 kDa. Lignin content is measured as LS by an UV spectroscope, COD, TOC and Phenol content by cuvette tests. Sulphate and magnesium by ICP-OES. Sugars by HPLC and organic and inorganic content by TGA

As it can be seen in Figure 36 the lignin content of both dialyzed samples with the different MWCO are the same. For all the other parameters the values for the higher MWCO membrane gives higher concentration values, because the diffusion takes more time, the larger the membrane is. The sugar concentrations were measured once directly and once hydrolysed. The direct measuring did not give any concentrations, and the hydrolysed minimal ones. Monomeric sugars in the sample were removed during dialysis. Sugar oligomers or polymers, for example hemicelluloses stayed in the tube as far as their MW was bigger than the MWCO of the dialysis membrane. The organic content for the MWCO 3.5kDa was increased to 90.2 ± 1.6 %, and for MWCO 6-8 kDa to 90.1 ± 0.5 %. The original sample had an organic content of 88.2 ± 1.3 %.

3.5 Comparison of the different isolation and purification techniques

In the following illustrations, the analytic results of the isolated LS from the SSL and the O_2-bleaching effluents are shown.

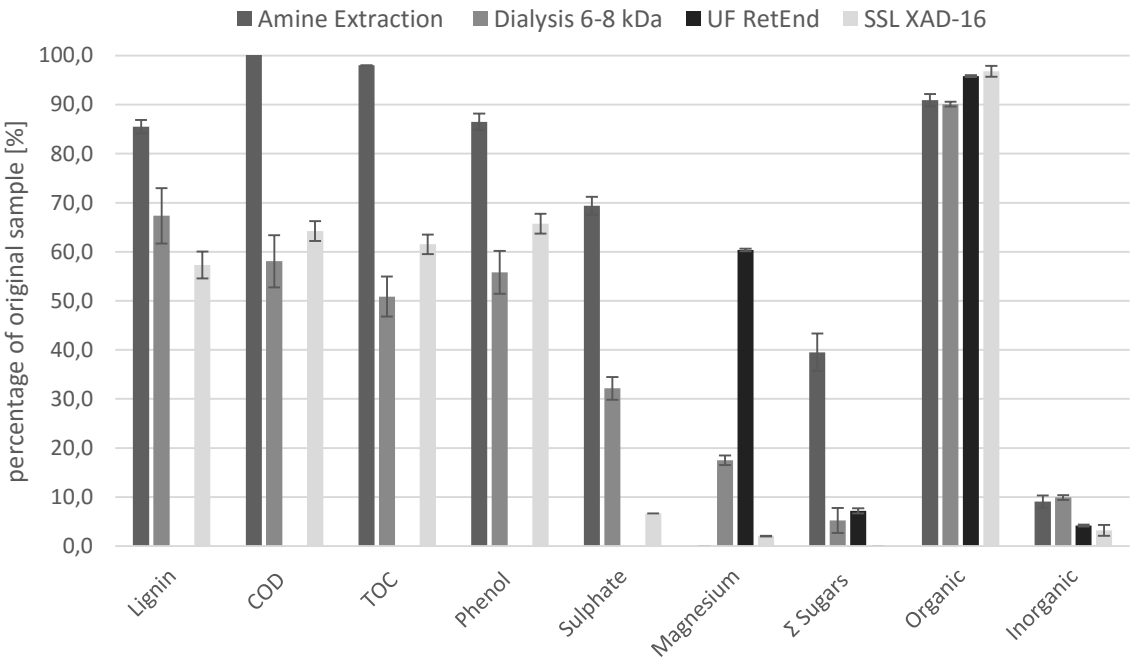

Figure 37 Comparison of the analytic results of the different isolation and purification techniques with the SSL. The UF RetEnd is just plotted for the Mg, Σ Sugars, organic and inorganic content. Lignin content is measured as LS by an UV spectroscope, COD, TOC and Phenol content by cuvette tests. Sulphate and magnesium by ICP-OES. Sugars by HPLC and organic and inorganic content by TGA

In Figure 37 there is a comparison of the obtained LS isolated from SSL samples. The amine extraction, the dialysis and the ultrafiltration were processed with the same SSL sample with a TDS content of 13.0 ± 0.0 %. The XAD-16 adsorption was examined with a different SSL with a TDS content of 23.9 ± 0.0 %. The values in the graph are the percent isolated LS related to its original sample values. The results of the Retenate end from ultrafiltration experiment is shown for the magnesium, Σ sugars, organic and inorganic content. The other parameters were concentrated during the ultrafiltration, ending up in value more than 100 %, which would confuse the diagram.

It is shown that the amine extraction does not yield the best recovery rate concerning the lignin compared to the other techniques. However, it is the technique with the most process steps and it is extremely time consuming. The adsorption on the XAD resin and the dialysis give nearly the same results, but for the XAD adsorption technique the sulphate content in the product is not that high, which means that mainly the less sulphonated lignin fragments were adsorbed. Ultrafiltration achieved the worst results in removing the inorganic Mg^{2+} ions, which were reduced to 60.4 ± 0.2 % of the initial content. Concerning sugar content in the isolated

products, definitely the XAD adsorption technique performed best. No sugars remained in the isolated LS solution. Dialysis showed to remove all the monomeric sugars, but after total hydrolysis of the oligomeric and polymeric sugars from hemicelluloses could be detected. Amine extraction only removed 60.5 ± 3.8 % of the containing sugars and the ultrafiltration more than 82.6 ± 0.1 %. The best organic to inorganic ratio was also achieved with the XAD adsorption, but it is very similar for all the samples. All the organic and inorganic rates are plotted in Figure 38. The best results were obtained with the O_2-bleaching effluent and the XAD-7 and XAD-16 resins. In general the adsorption technique removed more inorganic matter than the other procedures. Also the UF obtained good results by this category.

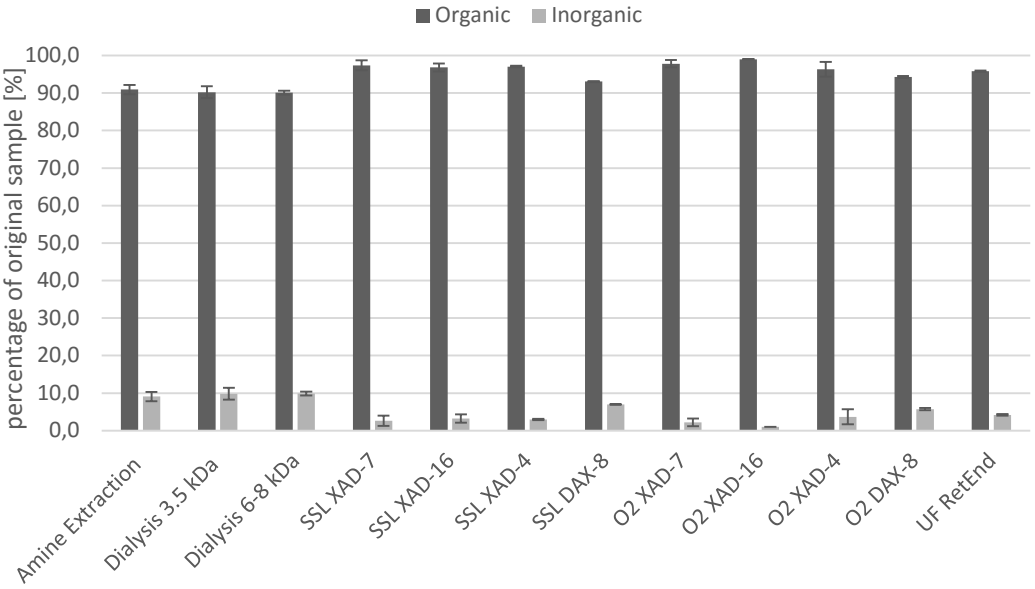

Figure 38 Organic and inorganic content of the isolated LS of the different purification processes from the SSL and the O_2-bleaching effluent. Organic and inorganic content was measured by TGA.

The comparison of the lignin contents obtained in the different isolation techniques is shown in Figure 39. As discussed before AE achieved the best lignin isolation. Dialysis recovered for MWCO 3.5 kDa 67.3 ± 5.8 % and MWCO 6-8 kDa 67.3 ± 5.6 %. The different adsorptions on the XAD resins vary between 57.3 ± 2.7 % (SSL XAD-16) and 41.0 ± 1.9 % (SSL XAD-4), where the XAD-4 obtained worse ratios than the other resins. For the O_2-bleaching effluent, the XAD-4 recovered 19.3 ± 0.3 %. The phenolic OH-groups content, Figure 40, reflects more or less the lignin content.

The comparison of the total sugar content in the purified samples clearly shows that no sugars were isolated by the adsorption technique with the XAD resins, Figure 41. Minimal sugar contents were detected in the dialysis samples, which is due to the hydrolysis of the oligomeric sugars of the hemicelluloses. Amine extraction isolated 39.5 ± 3.8 % of the original sugar content and dialysis MWCO 3.5 kDa removed 98.4 ± 0.2 % and MWCO 6-8 kDa 94.8 ± 2.5 % of the sugars of the original SSL.

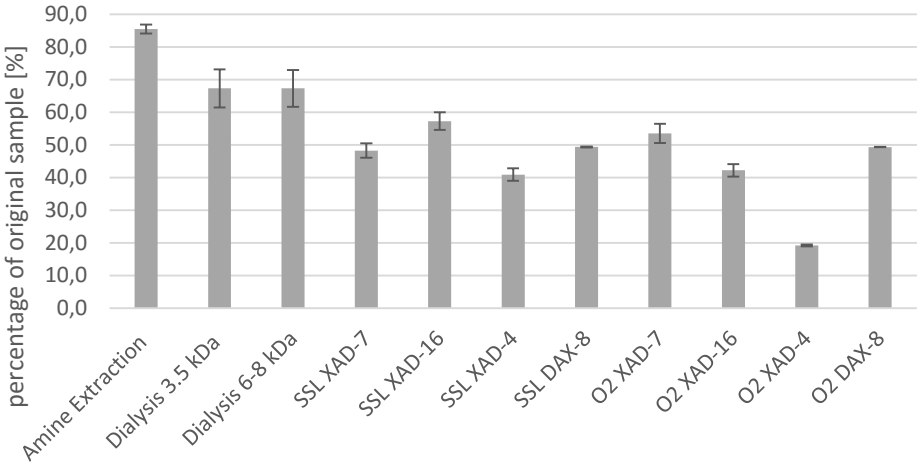

Figure 39 Lignin content of the isolated LS of the different purification processes from the SSL and the O_2-bleaching effluent. Lignin was measured as LS by UV spectroscopy.

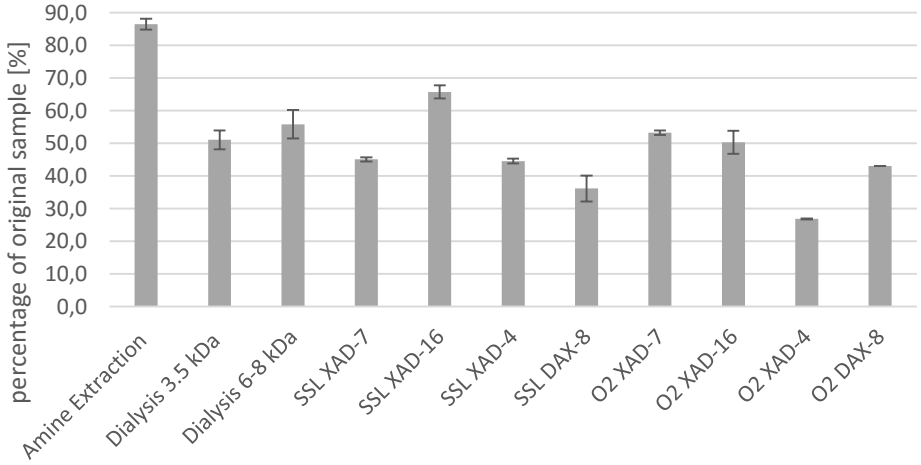

Figure 40 Phenol content of the isolated LS of the different purification processes from the SSL and the O_2-bleaching effluent determined by cuvette tests.

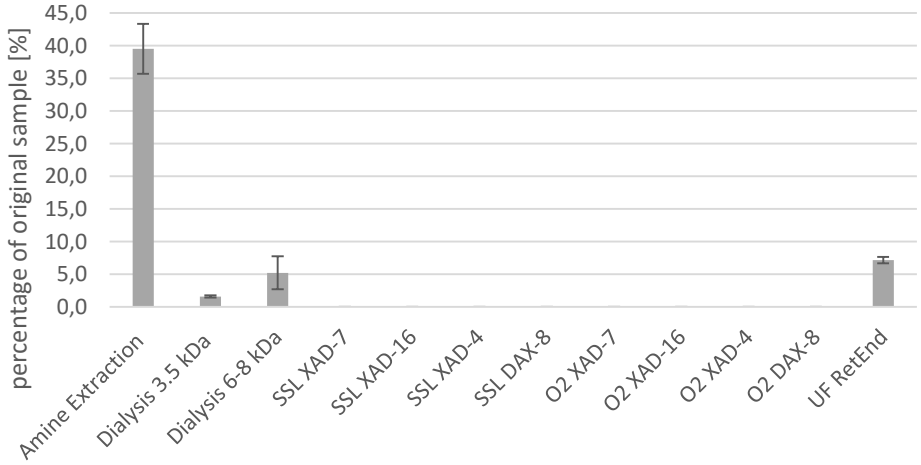

Figure 41 Total sugar content of the isolated LS of the different purification processes from the SSL and the O_2-bleaching effluent determined by HPLC

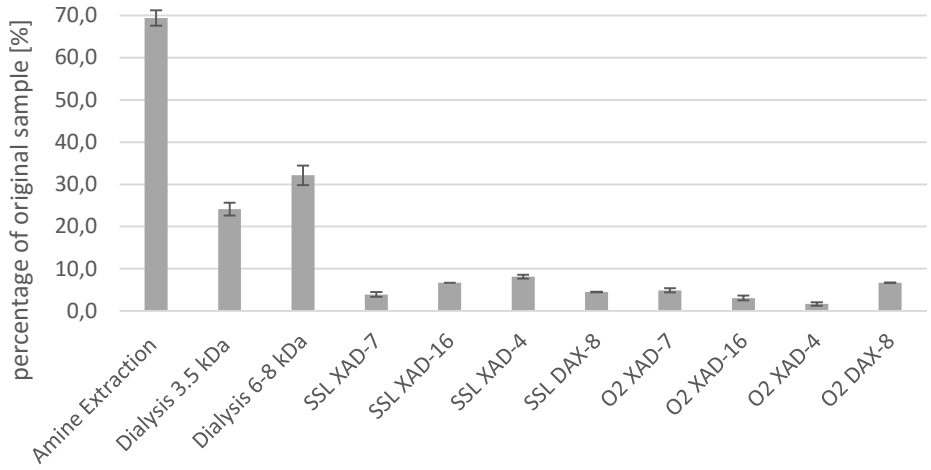

Figure 42 Sulphate content of the isolated LS of the different purification processes from the SSL and the O_2-bleaching effluent measured by ICPOES.

The sulphate content in the samples reflects on the one hand the sulphonation degree of the lignin and on the other hand, the free sulphate ions in solution, Figure 42. The highest sulphate content is detected for the AE. Although, the free sulphate ions were precipitated with barium hydroxide before the extraction, maybe not all the free sulphate ions were removed. Another reason is, that due to the ion pair formation of the sulphonate group on the lignin with the amine only the sulphonated fragments were extracted by this technique. For dialysis also all kinds of LS fragments larger than the MWCO stay inside the membrane, therefore all sulphonated lignins could be measured. In the case of the adsorption experiments, the rather non-polar XAD resins adsorb the LS fragments due to their π-π stacking and alkyl interactions and thus maybe not that much sulphonated lignin species were adsorbed.

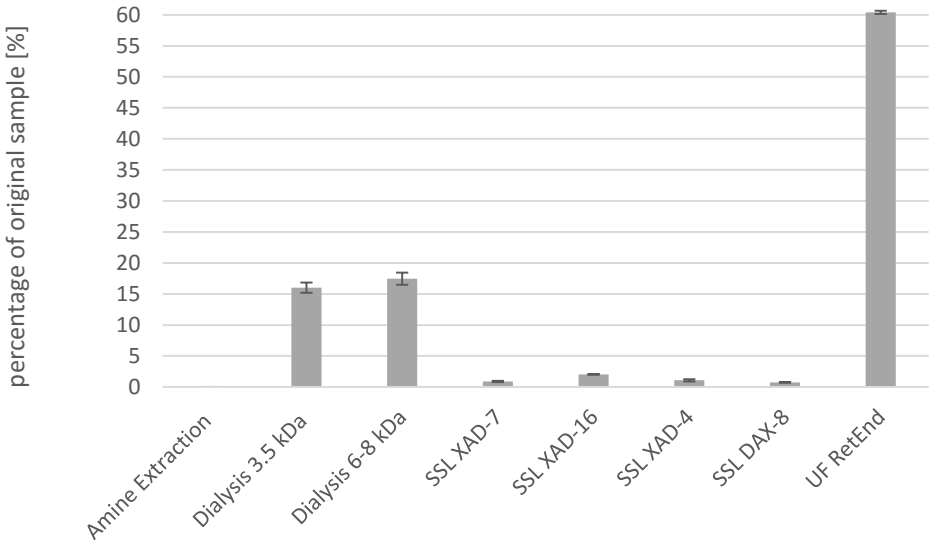

Figure 43 Magnesium content of the isolated LS of the different purification processes from the SSL measured by ICPOES.

The magnesium is the leading counter ion in the SSL samples, Figure 43. It was totally removed by the AE, and less than 2 % of the original content was detected for the adsorption

experiments. For the purification by dialysis, rather high remaining contents, MWCO 3.5 kDa 16.0 ± 0.8 % and MWCO 6-8 kDa 17.5 ± 1.0 % were measured. Maybe the ions were enclosed in the LS-coils in solution and not able to diffuse outside the membrane.

Finally, the comparison of the sodium content of the isolated LS from the O_2-bleaching effluents, Figure 44. The sodium is the leading counter ion for this kind of process effluents and is nearly removed totally by this technique. The most was removed with the XAD-4 and DAX-8 resins, for XAD-7 1.0 ± 0.14 % and for XAD-16 0.9 ± 0.25 % stayed in the solutions.

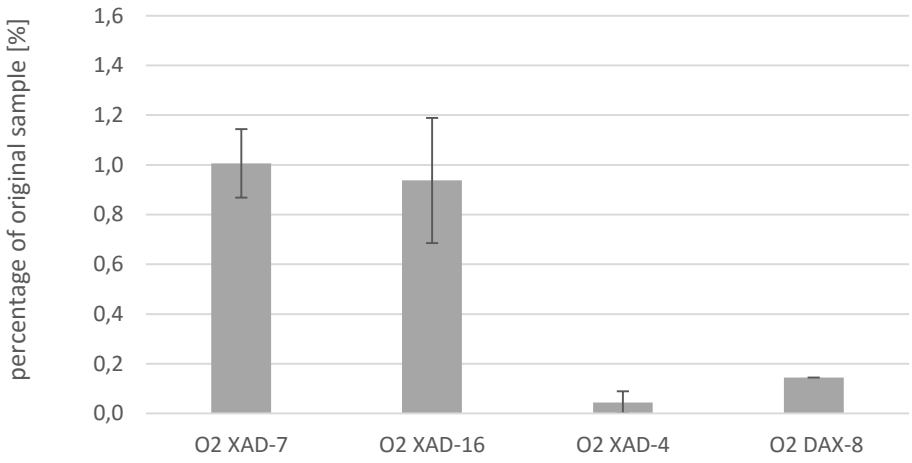

Figure 44 Sodium content of the isolated LS of the different XAD purification processes from the O_2-bleaching effluent measured by ICPOES.

4 Experimental

4.1 Materials

All the devices which were used during this thesis are now listened and briefly described.

4.1.1 Eppendorf Pipettes

Different types of Eppendorf Pipettes, head office in Hamburg, Germany, with the associated pipette tips were used for transferring different volumes of analytes or samples.

The sizes of Eppendorf Research Plus Transfer Pipettes, one-chanel, used, were: 1 – 10 mL, 0.5 – 5 mL, 100 – 1000 µL, 10 - 100 µL

4.1.2 Clear Glass Vials

Rotilabo®-srew neck ND24 vials (EPA) with a volume of 20 mL were used for different applications. The associated screw caps, PP, white, ND24 are also produced by ROTH. Rotilabo® is purchased form Carl Roth GmbH+Co. KG, head office in Karlsruhe, Germany.

4.1.3 Aluminium bowls

For the determination of the total dissolved solids the samples are dried in Rotilabo® sample bowls out of aluminium. Different sizes are purchased form Carl Roth GmbH+Co. KG, head office in Karlsruhe, Germany: 28 mL, 250 mL and 500 mL.

4.1.4 Drying Oven

The drying oven from Thermo Scientific Heraeus Kelvitron® t, head office in Waltham, Massachusetts, USA, was used for drying the samples in order to obtain the solid products in the solutions.

4.1.5 Analytical Balance

The analytical balance used was purchased from Mettler Toledo, head office in Columbus, Ohio, USA. The type used was a Mettler Toledo XS 205 Dual range.

4.1.6 IKA® Vortex shaker Genius 3

The IKA® Vortex Genius 3, 230 V, cs^{-1}, was used for de-gazing the sample vials in the TOC determination experiment. The samples were shaken for 5 minutes at level 3, approximately 1000 min^{-1} speed. The vortex is purchased from Sigma-Aldrich, head office in St. Louis, Missouri, USA.

4.1.7 Hach Lange HT 200 S

The hight temperature oven from Hach Lange, head office in Vienna, was used for the digestion of the samples for the COD, TOC and sugar measuring.

The power of the HT 200 S is 1000 watt and digestion temperatures from 40 – 170 °C are possible.

4.1.8 Hach Lange Photometer DR3900

The Photometer of Hach Lange DR 3900, head office in Vienna, was used for the measuring of the cuvette test for the determination of the COD, TOC and Phenols.

The wavelength range is from 320 to1100 nm and the scan velocity ≥ 8 nm/s (in 1 nm steps).

4.1.9 UV-VIS Spectroscope GBC Cintra 10

For the UV-VIS experiments a UV-VIS spectroscope from GBC, head office in Braeside,

Australia, Cintra 10 is used. It is a dual beam spectroscope with a deuterium light source. The wavelength range is from 190 to 1000 nm with a scan speed of 1000 nm/min and a step size of 0.427 nm.

4.1.10 FT-IR Spectroscope Bruker Equinox 55

The FT-IR spectrometer purchased from Bruker, head office in Billerica, Massachusetts, USA, uses KBr pellets for the measuring of the sample. The sample is measured by 16 scans in a wave number range of 4000 to 400 cm^{-1}. The resolution is 2 cm^{-1}.

4.1.11 Perkin Elmer Hydraulic Press and Vacuum Pump

The hydraulic pump for pressing the KBr IR pellets is from Perkin Elmer, head office in Waltham, Massachusetts, USA. The sample pellet is pressed at 10 bar. For removing the moisture and air in the pellet while pressing it, a MINNI A vacuum pump from Leybold Heraeus, head office in Köln, Germany, is applied.

4.1.12 Mettler Toledo TGA/SDTA 851^e

For the TGA analysis to determine the organic and inorganic matter in a sample the Mettler Toledo, head office in Columbus, Ohio, USA, TGA/SDTA 851^e device is used. The sample is applied to the device in platinum crucibles. The temperature range is from 25 – 1100 °C and the signal time constant 15 seconds.

4.1.13 GBC Integra XL ICP-OES

The ICP-OES device from GBC, head office in Braeside, Australia, was used for the determination of Ca, Na and S. The wavelength range is from 120 to 800 nm with a resolution of 4 pm.

4.1.14 Agilent Technologies 1260 Infinity LC

The HPLC system is purchased from Agilent Technologies, head office in Santa Clara, USA. The whole HPLC consists of a 1260 Degaser, 1260 Iso Pump, 1260 ALS Autosampler, 1290 TCC oven, 1260 RID Detector. It was used for the determination of the total sugar content after total hydrolysis.

The used HPLC column is from Bio – Rad, head office in Vienna, Austria, Aminex HPX-87H 300 x 7.8 mm. The suggested mobile phase is a 0.004 M H_2SO_4.

4.1.15 Rotilabo®-Syringe Filter, Nylon

For the preparation of the samples measured by HPLC all the suspended particles have to be removed. Therefore the nylon Rotilabo®-syringe filters, 0.2 µm, head office in Karlsruhe, Germany, are used with 2 mL single use syringes Injekt®, 2 mL from Braun Melsungen AG, head office in Germany.

4.1.16 Spectra/Por® Dialysis Membranes

For the dialysis experiment two dialysis membranes of spectrum®laboratories, head office in Rancho Dominguez, California, USA, were ordered: Spectra/Por® 1 with a MWCO of 6 - 8 kDa and Spectra/Por® 3 with a MWCO of 3.5 kDa.

4.1.17 Fridge

All the samples were stored in the fridge, at 4 °C to prevent them of being wasted. The fridge used is from Liebherr, head office in Bulle, Schweiz.

4.1.18 Ultrafiltration plant

The ultrafiltration was examined on a TRF (Turbulent Rotating Filtration) ultrafiltration plant type S5 purchased form MinerWa Umwelttechnik GmbH & Co KG, head office in Linz, Austria. A polyethersulphon membrane with a MWCO of 150 kDa is used and pressure of about 0.7 bar is applied.

4.2 Chemicals used

All the chemicals and solvents used were purchased in analytical grade from Carl Roth GmbH + Co. KG, head office in Karlsruhe, Germany. They were all used without further cleaning steps.

4.2.1 Deionised water

The deionised water used for the experiment was taken from the company intern industrial water treatment system. The Ca^{2+} and Mg^{2+} ions are exchanged by Na^{+} in a cation exchange resin.

4.2.2 Calibration Standard/Stock Solutions

All the calibration solutions for the ICP-OES and the HPLC are purchased from Carl Roth GmbH + Co. KG, head office in Karlsruhe, Germany.

4.3 Methods and Procedures

In this section the detailed information to the experiments are given, as quantities of compounds used, or detailed parameters of the sequences for the instrumental analysis.

4.3.1 Isolation of the Lignosulphonic Acids by Adsorption on Polymeric Resins

The procedure to adsorb and isolate the LS out of the samples were followed as described by the team of the BOKU Vienna. [11] The used polymer resins are generally described in Table 3.

Table 3 Physical data of the polymer resins XAD-7, XAD-16, XAD-4 and DAX-8 [16]

resin	Amberlite XAD-7	Amberlite XAD-16	Amberlite XAD-4	Superlite DAX-8
chemical nature	polyacrylic ester used to adsorb molecules up to MW 60 000; organic removal and recovery	polystyrene–divinylbenzene copolymer used to remove hydrophobic compounds up to MW 40 000; separation of large organic molecules	polystyrene–divinylbenzene copolymer used to remove small hydrophobic compounds of relatively low MW<40 000	polymethylmethacrylate resin, used for the treatment of paper and pulp mill waste, removes compounds up to MW 150 000
dipole moment	1.8	0.3	0.3	-
dry density (wet density) [g/mL]	1.24 (1.05)	1.08 (1.02)	1.08 (1.02)	- (1.09)
surface area [m^2/g]	450	900	725	160
pore diameter [Å]	90	100	50	225
mesh size [nomimal]	20-60	20-60	20-60	40-60
pore volume [mL/g]	1.14	1.82	0.98	0.79
pH range	0-14	0-14	0-14	0-14
maximal usage temperature [°C]	150	120	-	-

4.3.1.1 Preparation of XAD and Lewatit S 100 G1 (cation exchanger) resins

The resins were washed several times with deionised H_2O and filtered off the glass frit of pore size number 2. The XAD resin was kept in an ethanol solution. Before the XAD resin was used for the experiment, ethanol was removed by washing it with deionised H_2O (glass frit number 2). It is of great importance to use the wet resin, since the absorption capacity can be altered if the complete moisture is removed.

The DAX-8 resin was wetted in methanol and gently stirred for 15 minutes, then stirred in deionized water for also 15 minutes. The resin was additionally washed with water and filtered off a glass frit number 2 several times.

The Lewatit S100 G1 cation exchanger was washed with deionised H_2O several times. To regenerate the resin before usage the accumulated ions are backwashed three times with 0.5 M HCl for each 10 minutes, three times with 1 M HCl (each 10 minutes) and three times with 2 M HCl (10 minutes), respectively. After the regeneration, the resin was filtered off, put in a closed flask, and stored for later usage. Before the actual experiment, it has again been

washed with distilled H_2O until a neutral pH was reached. The used amounts of chemicals for the different experiments are listened in Table 4.

4.3.1.2 Sample solution:

For the preparative purposes, the samples used were diluted to approximately 10 % of the solid content. Therefore the SSL was diluted in ratio 1:2, approximately 12 % solid content were achieved. The O_2 bleaching effluent was used directly with an approximate 0.9 % solid content.

4.3.1.3 Sample preparation:

The solution of the SSL and the O_2 bleaching effluent were mixed 3 to 4 hours in proportion with 4 to 5 g of the wet Lewatit S100 G1 cation exchanger per 1 g of total dissolved solids (TDS) that were present in the samples. The TDS values and lignin content of the samples was determined in advance and thus, all the used amounts of chemicals were calculated. The samples were then filtered through a glass frit number 3 and washed with deionised H_2O two to three times.

4.3.1.3.1 Calculation for the example of the SSL:

The TDS content of the SSL solution is about 23.9 %. Of all the TDS, the lignin content in it is approximately 75 % (this was determined by further research). If a total lignin amount after the isolation of about 4.5 g, assumed that the yield is 100 %, 6 g of TDS is needed which gives us around 25 g of initially SSL sample.

4.3.1.4 Adsorption on XAD/DAX resins

In the next step, the filtrates were combined and the wet resin was added. The ratio between the wet resin and the TDS was 10:1, meaning 10 g of XAD/DAX resin per 1 g of TDS present in the sample. An overnight shaking of the mixture with a shaker of Edmund Bühler (KS-15 Control) at 200 rpm was performed. Followed by a vacuum filtration through a frit of pore size 3 the resin was washed 3 times with 10 mL acidic water (using HCl) with pH value of 2 per 10 g of wet XAD for 15 minutes. This step was followed by washing the wet resin 3 times with deionised water in the same proportion for each 15 minutes.

4.3.1.5 LS Desorption

Finally, to desorb the lignosulphonates from the resin, 15 mL ethanol needs to be added per 10 g of wet resin 4 to 5 times for 30 to 40 min at 50 °C, followed by one or two additional washing steps with 15 mL deionised H_2O per 10 g wet resin by the same time period and by constant temperature (50 °C). All the fractions obtained during the desorption were combined and the solvents were removed by the rotary evaporator. The dry content was determined and the solids were again dissolved for further analytic steps.

Table 4 Amount of chemicals used and original sample for the adsorption on the XAD/DAX resins

sample	Nr	used amount of sample [g]	cation exchanger [g]	XAD resin [g]	washing [mL]		LS-desorption [mL]	
					water pH=2	water	EtOH	water
TL XAD-7	1	24,41	30	60	3x 60	3x 60	5x 90	2x 90
	11	24,48	30	60	3x 60	3x 60	5x 90	2x 90
O2 XAD-7	2	987,68	44	88	3x 88	3x 88	5x 132	2x 132
	12	609,84	30	60	3x 60	3x 60	5x 90	2x 90
TL XAD-16	3	25,43	30	60	3x 60	3x 60	5x 90	2x 90
	13	24,43	30	60	3x 60	3x 60	5x 90	2x 90
O2 XAD-16	4	664,35	30	60	3x 60	3x 60	5x 90	2x 90
	14	618,27	30	60	3x 60	3x 60	5x 90	2x 90
TL XAD-4	7	25,39	30	60	3x 60	3x 60	5x 90	2x 90
	17	25,39	30	60	3x 60	3x 60	5x 90	2x 90
O2 XAD-4*	8	658,61	30	60	3x 60	3x 60	5x 90	2x 90
	18	658,59	30	60	3x 60	3x 60	5x 90	2x 90
TL DAX-8	9	25,52	30	60	3x 60	3x 60	5x 90	2x 90
	19	25,51	30	60	3x 60	3x 60	5x 90	2x 90
O2 DAX-8*	10	666,32	30	60	3x 60	3x 60	5x 90	2x 90
	20	666,32	30	60	3x 60	3x 60	5x 90	2x 90

*O_2-bleaching effluent not filtered; 29.7.2015 was used as original sample

For sample 1, 2, 3, 4, 9, 10, 19 and 20 the last process step, the evaporation of the solvent was not evaporated totally, approximately 100 mL of water was left unevaporated and the volume of it was set to 250 mL. Sample 7, 8, 17 and 18 were evaporated to maybe 10mL and set to an end volume of 250 mL. In the case of sample 8 and 18 there was a sticky yellow substance obtained in the evaporation flask, which was not able to get out of the flask.

In sample 1 a fine yellowish-white precipitate was observed. In the samples of the O_2-bleaching effluent, 2, 4, 12 and 14 there was a very fine yellowish precipitate at the bottom of the flask, which was shaken up before any analysis. Sample 3 and 13 were the only solutions where everything was totally dissolved. The problem with sample 11 was that it was not entirely re-dissoluble in water. A brown precipitate remained in the solution. It was partly soluble in EtOH and dissolved in acetone.

For all the SSL samples a brown solution with a white fine precipitate was obtained. For the samples O_2-bleaching effluents a yellowish-brown solution with a fine white precipitate was obtained.

4.3.2 Isolation of the Lignosulphonic Acids by Amine Extraction

125 mL of magnesia based spent sulphite liquor (Mg-SSL) with an total dissolved solid (TDS) value of about 13 % were de-ashed with the cation exchange resin of Lewatit S100 (1 g TDS ≈ 5 g cation exchange resin) for 3 to 4 hours. The cation exchanger was filtered off and 0.8 % $Ba(OH)_2$ was added to the solution until the pH had reached around 3. A pH of 3 was required to make sure that all the Ba^{2+} was precipitated with excess SO_4^{2-} ions, and not dissolved as $BaCl_2$ in solution, as shown by the equation below. In total 400 mL 0.8 % $Ba(OH)_2$ solution, 3 mL 1 M KOH, 6 mL 0.1 M NaOH and 31 mL 4 M KOH were added until a pH of 3 was reached.

The resulting $BaSO_4$ was centrifuged (Sigma Laboratory Centrifuges 3-15; 4651 rpm for 17 minutes) and the solution above decanted. To remove excess Ba^{2+} ions out of the reaction solution, another cation exchange step, using about 100 g of resin, was necessary. Again, the cation exchange resin was filtered off and the solvent was evaporated to reach an approximate TDS content of 5 % (~250 mL sample solution).

Meanwhile 45 mL of dodecylamine (DCA) were mixed with 300 mL n-butanol (n-BuOH). For processing the complexation step the aqueous concentrated sample solution (5 % TDS) was extracted 2 times with 100 mL , and 3 times with 50 mL of the DCA-n-BuOH mixture by putting them together into a beaker and stirring it strongly for 15 minutes at 50 °C. Then the mixture was transferred into a separatory funnel and separated into an organic and an aqueous phase. The nearly colourless aqueous phase was once more extracted with 50 mL of diethyl ether to remove the residual n-BuOH. The ether was evaporated and the obtained n-BuOH phase added to the dark brown organic phase.

For the back extraction of the isolated lignosulphonates, 1 M NaOH is added to the organic phase. This is processed by adding once 150 mL NaOH to the organic phase and stirring it strongly for 10 minutes at 50 °C in a beaker, followed by transferring it into a separatory funnel and obtaining an aqueous and an organic phase. The organic phase is again extracted in the same way with 50 mL, then 80 mL and 100 mL of NaOH and separated. The combined aqueous phases are once more extracted with 50mL of diethyl ether to remove residual n-BuOH and afterwards treated once more with a cation exchange resin (~220 g) to finally result in a pure lignosulphonic acid. The volume of the obtained aqueous solution was adjusted to 1000 mL and further analysed.

4.3.3 Purification of the Lignosulphonic Acids by Ultrafiltration

The ultrafiltration was carried out in the plant of Sappi Gratkorn. 1000 L Mg-SSL were applied to the TRF plant at room temperature. The MWCO of the polyehtersulphone membrane was 150 kDa, which is categorised between micro and ultrafiltration. The pressure is applied with the membrane pump at the plant.

The Mg-SSL is filtered 5 times, where the permeate is wasted and the retentate collected in a canister. The sample is reduced to 100 L in this way. The remaining sample is then washed 3 times with 200 L decarbonised water, which is also the water used in the pulp and paper process. Each washing step the solution is directed in a circle. After each ultrafiltration, samples were taken for analysis as well as the retentate after washing.

4.3.4 Purification of the Lignosulphonic Acids by Dialysis

For the dialysis experiment two regenerated cellulose (RC) membranes from Spectra/Por® are ordered, the properties are listened in Table 5. The RC membranes should not be used with > 25 % HCl, HNO_3, perchloric acids, 96 % H_2SO_4, 1 N KOH and 10 % phenol.

Table 5 specification of the Spectra/Por® dialysis membranes

	Spectra/Por 1	**Spectra/Por 3**
membrane type	symmetric regenerated cellulose tubing	
physical properties	transparent, flexible	
MWCO [kDa]	6-8	3.5
flat width [mm]	32	18
diameter [mm]	20.4	11.5
volume/length [mL/cm]	3.3	1.1
pH limit	2-12	
purpose	basic dialysis	
packaged	dry	
preservative	glycerin	
length of total tube [m]	5	

4.3.4.1 Preparation of the dialysis membranes

The membrane should be cut in the right length: It is recommended to use a sample volume of 10 to 15 mL. The Volume/length ratio of the used tubes is listened in Table 5. Additionally extra space for the closure (4 to 10 mm longer than the flat width of the membrane tubing on both sides) and extra tubing length (10 % of the total sample volume) for the increase of the sample volume while dialysis should be calculated.

The cut membrane tubes are soaked in deionized water for 30 minutes to remove the preservative (glycerin). Then, the membrane is washed carefully with deionized water. In this experiment, the membrane tubes were not cleaned further.

4.3.4.2 Membrane handling and use

The dialysis was carried out like described in the guide for Spectra/Por® membranes provided by the producer. It is a general protocol for basic dialysis. However, there are many parameters to consider before carrying out a dialysis of a sample. The variables, which influence a dialysis, are sample solvent, membrane compatibility, membrane MWCO, dialysate solvent, dialysate volume and temperature. The parameters for the experiment are shown in Table 6.

Table 6 Parameters for the dialysis experiment

sample solvent	water
membrane compatibility	good
membrane MWCO	6-8 kDa and 3.5 kDa
dialysate solvent	deionized water
dialysate volume	15 mL
temperature	room temperature

1. The dialysis reservoir (beaker) should be filled with a 100 times bigger volume than the sample volume (sample volume=15 mL; dialysis reservoir = 1500 mL)
2. The dialysis tubes should be cut in the correct length as described above, see Table 7.

Table 7 calculation of the tube length

	Spectra/Por 1	**Spectra/Por 3**
sample volume [mL]	15	15
volume/length [mL/cm]	3.3	1.1
extra space for the closure up and below [cm]	4.2 x 2	2.8 x 2
extra tubing length (10% of the total sample volume) [cm]	0.5	1.4
length total [cm]	**~14**	**~22**

3. Preparation of the Spectra/Por® membranes as described before
4. Closing of the tube at the lower end by inserting the dialysis tube into the closure (part of the Spectra/Por® trial kit) and clamping it that approximately 3 to 5 mm of the tube extends from the closure
5. Loading the sample into the tube at the open end and closing it afterwards in the same way that approximately 3 to 5 mm of the tube extends from the closure
6. Placing the sample in the dialysis reservoir and stirring the reservoir on a magnetic stirrer. Make sure that the stirrer speed is controlled, that it does not pull down the sample by vortex

7. The dialysis is followed by measuring the conductivity every 30 minutes. After 2 hours, the dialysate is replaced by fresh deionized water. The fourth time changing the reservoir it is stirred overnight. The next day the dialysate is changed one more time and stirred for 3 hours.
8. After the dialysis, the sample is decanted from the tube and further analysed.

4.3.5 Analytical Techniques for Characterising the Purified Liquors and Isolated Lignosulphonic Acids

4.3.5.1 Total Dissolved Solids (TDS)

For determining the TDS of a liquid sample it is weighted in an aluminium bowl and dried in an oven at 105 °C. Then the dry residue is weighted again and the TDS in % is calculated.

4.3.5.2 Density

The density is measured with a pycnometer. Therefore the samples are weighted in the pycnometer a defined volume. The density can then be calculated.

4.3.5.3 Lignin Concentration by UV-VIS Spectroscopy

For buffering the sample solutions at pH 7, 10 % phosphate buffer is added to the samples before measuring. For the buffer 3.4181 g $K(H_2PO_4)$ and 4.4723 g $Na_2(HPO_4)$ are put into a 1000 mL volumetric flask and filled up to the mark.

The calibration is made with a lignosulphonic acid sodium salt, lignosulphonic acid calcium salt and lignosulphonic acid solution (obtained from adsorption experiments), to get three different calibrations depending on the counter ion of the lignosulphonic acid. Therefore about 1.0956 g of lignosulphonic acid sodium salt and 1.3500 g of lignosulphonic acid calcium salt are put each in a 1000 mL volumetric flask and filled up to the mark. Then, these solutions are diluted 1:10 to get the stock solution, from which the calibration standards are made. Therefore defined volumes of this stock solutions are put in 100 mL volumetric flasks, then 10 mL phosphate buffer solution are added and filled up to the mark. The blank is just deionised water with 10 % buffer, see Table 8.

Table 8 Stock solution for lignosulphonic acid calibration

standard	mL of stock solution	lignosulphonic acid [mg/L]
blank	0	0
1	2	2
2	4	4
3	6	6
4	8	8
5	10	10

In the case of the lignosulphonic acid solution (obtained from adsorption experiments) directly, the obtained solution was diluted 1:100, which presents the stock solution in this case. The calibration standards are prepared the same way as seen in Table 8.

For the measuring, a dual beam UV-VIS spectrometer was used. The calibration standards/samples were put into fused silica cuvettes and measured at 208 nm. The solutions were measured triple times.

4.3.5.4 Chemical Oxygen Demand (COD)

The COD is measured with a cuvette test with LCK 014 cuvettes for a range of 1000 to 10000 mg/L. The orange Cr^{+6} solution is shook to homogenise the solution with the precipitate in the cuvettes. Then 0.5 mL of the sample (TL was diluted 1:50; O_2 was used directly) are added and the cuvettes are shook again. Then they were put into the digestion device and digested with the program 170 °C for 15 min. After that, the cuvettes were cooled down to room temperature and measured three times with the photometer at 605 nm.

4.3.5.5 Total Organic Carbon (TOC)

For the measurement of the TOC, a cuvette test (LCK 386 from the range of 30 - 300 mg/L) is used. 1 mL of the sample is given into the expel and digestion cuvette. The cuvette is containing boric acid, disodium hydrogen phosphate and sodium peroxo disulphate. For the expelling of the TIC, the vial is shaken for 5 minutes with 210 rpm. After the removal of the TIC the indicator cuvette is put onto the expel and digestion cuvette with an adapter, which is a gas permeable membrane.

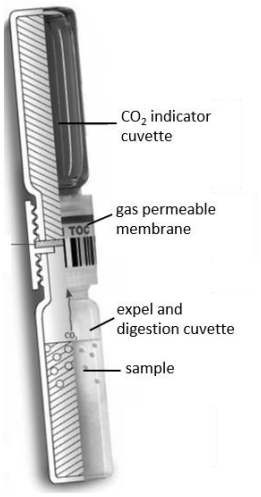

Figure 45 TOC reaction cuvettes (image taken from [45])

Care must be taken that the indicator solution is not too long opened, because the CO_2 in the air can cause high-bias results to be obtained. The combination of the two cuvettes, see Figure 45, should be vertically all the time- do not invert them. The cuvettes are then put into the digester for 2 hours at 95 °C. After the digestion, the solutions are cooled down to room temperature. The cuvette combination should be tighten once more before inverting and measuring the indicator cuvette with the photometer at 435 nm.

4.3.5.6 Phenolic OH-Groups

For the measurement of the phenols, a cuvette test (LCK 345 from the range of 0.05 - 3.00 mg/L) is used. 2 mL of the sample is pipetted into the reaction and measuring cuvette. Then 0.2 mL of solution A (LCK 345 A) are added, the cuvette is closed and inverted a few times. After two minutes (checked with a stopwatch) 0.2 mL of solution B (LCK 345 B) are given into the same cuvette. Again, it is closed and shook. After another two minutes the cuvette should be cleaned outside and measured with the photometer at 478 nm. Take care of the two minutes reaction time after adding solution A- if it is exceeded low-bias results could be obtained.

4.3.5.7 Elemental Analysis of Sodium, Calcium and Sulphur by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

The ICP-OES spectrometer is calibrated with the standard solutions and the samples are directly measured in the right dilution. The elements sodium and magnesium are directly determined out of the sample solutions. For the element sulphur, the sample is pre-oxidized with H_2O_2 in a ratio 1:1 for three hours, then, diluted to the right calibration area and measured. The appropriate setting for the different elements are listened in Table 9.

Table 9 Settings of the ICP-OES for the determination of Na, Mg and S as SO_4^{2-}

	Na	Mg	S as SO_4^{2-}
calibration standards	0, 0.1, 1, 10 mg/L	0, 10, 20, 100 mg/L	1, 5, 10, 40 mg/L
wavelength λ [nm]	589.592	293.654	182.034
height [mm]	8	6	7
nebulization gas flow [L/min]	0.5	0.5	0.6
pump [rpm]	10	20	15
PMT Volts [V]	800	620	800
power [W]	1400	1200	1250
auxiliary gas flow [L/min]	0.5	0.5	0.5
plasma gas flow [L/min]	11	11	13

4.3.5.8 Determination of the Monomeric Sugars by High Performance Liquid Chromatography (HPLC)

10 mL of the sample is pipetted into digestion cuvettes and the mass of the volume is checked gravimetrically and written down. An appropriate amount of 68 % H_2SO_4 is added, which is calculated as seen in equation 23, and shaken.

$$V(H_2SO_4) = weight\ of\ sample\ taken * 0.04 \quad (22)$$

Then, the digestion vials are put into the digestion oven and digested at 90 °C for 110 minutes. After, the solutions are cooled down and transferred into 100 mL volumetric flasks and filled up to the mark. Before measuring with the HPLC system, they are filtered through nylon syringe filters (0.2 µm), to avoid the fine particles to get into the HPLC columns.

The original samples are also all measured with the same HPLC system diluted 1:10 without digestion.

The HPLC system is calibrated with defined monomeric sugar standards, containing 4, 6, 8 and 10 mg/L of Cellobiose, Glucose, Xylose-Galactose-Mannose, Rhamnose and Arabinose, see Figure 25. The peak of Xylose-Galactose-Mannose is a common peak, because it cannot be separated with this HPLC columns. The method for the HPLC experiment is shown in Table 10.

Table 10 Method settings of the HPLC experiment

method	Sugar Biorad-H
column	Aminex HPX – 87 H 300 x 7.8 mm
injected volume	20 µL
flow	0.6 mL/min
oven temperature	50 °C
measuring time	150 minutes
mobile phase	0.004 mol/L H_2SO_4
detector	Refractive Index

4.3.5.9 Thermogravimetric Analysis (TGA)

The samples are dried before measuring in an oven at 105 °C. Approximately 10 - 20 mg are weighted into platinum crucibles and applied into to the sample holder in the furnace.

Nitrogen atmosphere	35 – 600 °C	heating rate: 10 °C/min
Oxygen atmosphere	600 – 900 °C	heating rate: 10 °C/min

4.3.5.10 IR Spectroscopy

The samples were dried in an oven at 105 °C. 2 mg of the samples and around 398 mg of KBr (purchased from Merck) were rubbed to a powder with a mortar and a pestle. The fine powder was then pressed to a pellet and measured with the FT-IR spectrometer.

5 Summary and Conclusion

The isolation and purification lignosulfonates from pulp side streams is a big research topic in biorefining processes of lignin. Main challenge of this thesis was the removal of the inorganic compounds (sulphate, magnesium, and sodium) and organics (sugars, hemicelluloses) from the spent sulphite liquor and the O-stage bleaching effluents from Sappi Gratkorn. The very complex matrix and the hydrophilicity of the sulfonated lignins obtained after bisulfite pulping are the main challenges to be addressed when analysing the side streams. Furthermore, the lignosulphonates itself have a very special and varying polymer structure, which is incompletely understood by now.

Different isolation methods were already proofed in the literature, like adsorption of polymeric resins (XAD-7, XAD-16, XAD-4, DAX-8), amine extraction, ultrafiltration and dialysis.

All the techniques tested showed the removal of inorganic matter and sugars in the samples. Best for the removal of sugars was the adsorption technique, followed by the dialysis experiments and amine extraction. With the amine extraction the removal of all the inorganic magnesium and sodium was possible. Also adsorption of the XAD resins removed nearly all the inorganic matter.

The real challenge within this master's thesis was the testing of the different techniques and the comparison of the obtained results. There is a lot of potential in the techniques for optimization. For the amine extraction other different amines and solvents could be tested to obtain better results. Furthermore the amine to lignosulphonate ratio needs to be optimized. The ultrafiltration also needs further testing for different membranes and amounts of water for the washing.

The problem with the industrial application of the amine extraction and the adsorption techniques is the extremely time consuming procedure and also the huge amounts of solvents which are used. Therefore optimization of solvents amounts need to be made. Furthermore solvent recovery is a big topic within all these techniques. Especially for ultrafiltration and dialysis a lot of water is needed, which needs to be purified in advance and after the experiments. But these two techniques just need the membranes or tubing else.

Ultrafiltration of these side steams is already done in pilot scale in Gratkorn, mainly for waste water treatment.

Generally the recovery of lignosulphonates out of the pulp side streams is a nice starting point in biorefinery, especially because lignin is such a highly abundant raw material. In future this renewable resource should be used for higher value products. Lignosulphonates already have a variety of applications as binders, surfactants, tanning agents and used for the production of fine chemicals. However, the bottle neck of these applications is the required purity of the lignosulphonates.

Nevertheless, it is a very interesting and far-reaching research area with the aim of using renewable resources for a sustainable future industry, which will be the basis for many future investigations.

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Abbreviations

AE	amine extraction
Ca-LS	lignosulphonic acid calcium salt
COD	chemical oxygen demand
DL	thin spent sulphite liquor (TDS ~13%)
EOP	extraction with sodium hydroxide, bleaching with O_2 and peroxide
EP-HC	extraction with sodium hydroxide and bleaching with peroxide– high consistence
EP-MC	extraction with sodium hydroxide and bleaching with peroxide– middle consistence
EtOH	ethanol
Flippr°	Future Lignin and Pulp Processing Research
h	Planck's quantum of action
H-LS	lignosulphonic acid
HOMO	highest occupied molecular orbital
HPLC	high performance liquid chromatography
ICP	inductively coupled plasma
K	Kelvin
LS	lignosulphonates
LUMO	lowest occupied molecular orbital
MW	molecular weight
MWCO	molecular weight cut off
Na-LS	lignosulphonic acid sodium salt
n-BuOH	n-butanol
O_2	O_2-bleaching effluent
OES	optical emission spectrometry
RC	regenerated cellulose
RI	refractive index

SSL	spent sulphite liquor
TDS	total dissolved solids
TGA	thermogravimetric analysis
TIC	total inorganic carbon
TL	thick spent sulphite liquor (TDS~30%)
TOC	total organic carbon value
UF	ultrafiltration
UV	ultraviolet
v	frequency
VIS	visible

Appendix

Appendix 1: Analytical data: original samples used for the experiments

Table 11 Analytical data of the original samples: SSL TL (thick liquor, TDS~30%), SSL DL (thin liquor, TDS~13%) and O_2-bleaching effluents (O_2)

			TDS		Lignin UV 208 nm [mg/L]						COD		TOC		Phenol	
Name	Density [g/mL]	pH	[%]	σ	NaLS	σ	H-LS	σ	CaLS	σ	[mg/L]	σ	[mg/L]	σ	[mg/L]	σ
SSL TL	1,12	7,4	23,9	0,0	191451	5990	194434	5651	184791	5065	288517	47	87667	236	4050	0
SSL DL	1,06	3,8	13,0	0,0	105990	11304	108612	10585	102327	11728	137800	20	49467	94	2187	9
O2	1,00	9,6	0,9	0,0	3878	58	4038	55	3751	45	7881	0	2900	0	53	0
O2 new	1,00	10,6	0,9	0,0	3372	74	3507	70	3224	58	7330	1	2580	0	48	0

	ICP-OES [mg/L]						Sugars [mg/L]						Σ Sugars		TGA				
Name	SO_4^{2-}	σ	Na^+	σ	Mg^{2+}	σ	Glucose	σ	Xy-Ga-Ma	σ	Arabinose	σ	[mg/L]	σ	Org. [%]	σ	Inorg. [%]	σ	[O/I]
SSL TL	231000	2000	41,7	0,5	16900	200	4464	2	18402	15	1925	6	24791	23	79,8	1,5	20,2	1,5	4,0
SSL DL	51400	400	4,4	0,1	7930	10	3212	4	10754	20	1588	6	15554	30	88,2	1,3	11,8	1,3	7,5
O2	2060	20	1490	50	119,2	0,4	-		-		-		-		45,4	1,2	54,6	1,2	0,8
O2 new	1155	20	1429	6	104,9	0,4	-		-		-		-		54,0	0,9	46,0	0,9	1,2

Appendix 2: Analytical data: adsorption on the XAD resins for the SSL (TL) and the O_2-bleaching effluent (O_2)

The values in Table 12 are given in percent related to the analytic values of the original sample used.

Table 12 Analytical data: adsorption experiment on the different XAD resins for the SSL TL and the O_2-bleaching effluent (O_2)

	TDS		Lignin UV 208 nm [mg/L]						COD		TOC		Phenol	
	[%]	σ	NaLS	σ	H-LS	σ	CaLS	σ	[mg/L]	σ	[mg/L]	σ	[mg/L]	σ
SSL TL XAD-7	0,71	0,13	48,7	2,4	47,5	2,0	48,6	2,2	44,4	1,2	42,4	2,0	45,1	0,6
O2 XAD-7	0,52	0,08	55,0	4,2	50,1	2,7	55,6	4,7	34,5	0,3	30,8	2,1	53,3	0,7
SSL TL XAD-16	0,96	0,06	60,7	1,9	50,4	4,4	60,9	1,9	64,2	2,0	61,5	2,0	65,7	2,0
O2 XAD-16	0,53	0,00	42,4	2,2	41,6	2,9	42,7	2,6	49,4	2,7	39,0	5,6	50,3	3,5
SSL TL XAD-4	0,60	0,01	40,7	1,9	41,7	2,0	40,4	1,9	36,8	0,9	38,8	1,3	44,6	0,7
O2 XAD-4	0,18	0,00	19,3	0,4	19,1	0,4	19,4	0,4	15,0	0,3	16,5	0,3	26,9	0,2
SSL TL DAX-8	0,57	0,00	49,7	0,1	48,8	0,1	49,7	0,1	38,2	4,0	41,5	4,0	36,2	4,0
O2 DAX-8	0,36	0,00	49,9	0,1	47,8	0,1	50,4	0,1	46,4	6,0	41,4	3,0	6,0	0,0

	ICP-OES [mg/L]						Sugars [mg/L]						Σ Sugars		TGA				
	SO_4^{2-}	σ	Na^+	σ	Mg^{2+}	σ	Glucose	σ	Xy-Ga-Ma	σ	Arabinose	σ	[mg/L]	σ	Org. [%]	σ	Inorg. [%]	σ	[O/I]
SSL TL XAD-7	3,9	0,6	802	322	0,9	0,1	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	97,4	1,3	2,6	1,3	37,3
O2 XAD-7	4,9	0,5	1,0	0,1	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	97,8	1,0	2,2	1,0	44,9
SSL TL XAD-16	6,7	0,0	884	201	2,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	96,8	1,1	3,2	1,1	30,3
O2 XAD-16	3,1	0,6	0,9	0,3	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	99,0	0,0	1,0	0,0	100,6
SSL TL XAD-4	8,2	0,5	65,5	3,6	1,1	0,2	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	97,0	0,2	3,0	0,2	32,9
O2 XAD-4	1,7	0,4	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	96,3	2,0	3,7	2,0	26,3
SSL TL DAX-8	4,5	0,1	200	17	0,8	0,1	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	93,0	0,1	7,0	0,1	13,4
O2 DAX-8	6,7	0,1	0,1	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	94,3	0,3	5,7	0,3	16,5

Appendix 3: Analytical data: amine extraction and the dialysis for the SSL (DL)

The values in Table 13 are given in percent related to the analytic values of the original sample used.

Table 13 Analytical data: amine extraction and the dialysis for the SSL (DL)

	TDS		Lignin UV 208 nm [mg/L]						COD		TOC		Phenol	
	[%]	σ	NaLS	σ	H-LS	σ	CaLS	σ	[mg/L]	σ	[mg/L]	σ	[mg/L]	σ
Amine Extraction	1,62	0,01	85,9	2,0	85,5	1,2	86,6	2,3	112,3	0,9	98,0	0,0	86,5	1,7

	ICP-OES [mg/L]						Sugars [mg/L]						Σ Sugars		TGA				
	SO_4^{2-}	σ	Na^+	σ	Mg^{2+}	σ	Glucose	σ	Xy-Ga-Ma	σ	Arabinose	σ	[mg/L]	σ	Org. [%]	σ	Inorg. [%]	σ	[O/I]
Amine Extraction	69,4	1,8	0,0	0,0	0,0	0,0	7,6	0,3	7,5	1,1	24,4	2,5	39,5	3,8	90,9	1,2	9,1	1,2	10,0

Dialysis	TDS		Lignin UV 208 nm [mg/L]						COD		TOC		Phenol	
	[%]	σ	NaLS	σ	H-LS	σ	CaLS	σ	[mg/L]	σ	[mg/L]	σ	[mg/L]	σ
MWCO 3.5 kDa	0,76	0,00	68,0	5,9	66,0	5,8	68,0	5,9	53,1	2,3	47,8	2,5	51,1	2,9
MWCO 6-8 kDa	0,85	0,04	68,0	5,6	66,0	5,6	68,0	5,7	58,1	5,3	50,9	4,1	55,8	4,4

Dialysis	ICP-OES [mg/L]						Sugars [mg/L]						Σ Sugars		TGA				
	SO_4^{2-}	σ	Na^+	σ	Mg^{2+}	σ	Glucose	σ	Xy-Ga-Ma	σ	Arabinose	σ	[mg/L]	σ	Org. [%]	σ	Inorg. [%]	σ	[O/I]
MWCO 3.5 kDa	24,1	1,5	240	14	16,0	0,8	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	90,2	1,6	9,8	1,6	9,2
					hydrolyzed:		0,8	0,1	0,9	0,1	0,0	0,0	1,6	0,2					
MWCO 6-8 kDa	32,2	2,3	279	32	17,5	1,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	90,1	0,5	9,9	0,5	9,1
					hydrolyzed:		2,5	1,2	2,8	1,4	0,0	0,0	5,2	2,5					

Appendix 4: Analytical data: ultrafiltration for the SSL (DL)

The values in Table 14 are given in absolute amounts. The last row gives the percent related to the analytic values of the original sample used (Feed).

Table 14 Analytical data: ultrafiltration for the SSL (DL)

	Conductivity [µS/cm]	TDS		Lignin UV 208 nm [mg/L]						COD		TOC		Phenol	
		[%]	σ	NaLS	σ	H-LS	σ	CaLS	σ	[mg/L]	σ	[mg/L]	σ	[mg/L]	σ
SSL DL Feed	17,3	13,0	0,0	117294	148	119197	158	114055	146	137800	20	49467	94	2187	9
Permeate 1	17,3	9,8	0,1	46153	25	47802	27	45122	25	79642	42	-	-	-	-
Retentate 1	16,8	12,8	0,0	87644	64	90618	68	85643	63	137967	12	-	-	-	-
Retentate 2	17,0	13,0	0,0	91151	61	94369	65	89103	60	142258	12	-	-	-	-
Retentate 3	16,9	13,1	0,0	100020	122	103856	130	97856	120	142242	42	-	-	-	-
Retentate 4	15,9	11,9	0,1	94736	85	98204	91	92641	84	135000	41	-	-	-	-
Retentate 5	16,5	13,1	0,0	109965	28	111358	30	106823	28	145050	61	-	-	-	-
Ret. END	6,7	19,2	0,1	285531	304	297596	326	279654	300	264917	12	106000	100	3970	8

	ICP-OES [mg/L]						Sugars [mg/L]						Σ Sugars		TGA				
	SO_4^{2-}	σ	Na^+	σ	Mg^{2+}	σ	Glucose	σ	Xy-Ga-Ma	σ	Arabinose	σ	[mg/L]	σ	Org. [%]	σ	Inorg. [%]	σ	[O/I]
SSL DL Feed	51400	400	4,4	0,1	7930	10	3212	4	10754	20	1588	6	15554	30	88,1	0,2	11,9	0,2	7,4
Permeate 1	-	-	-	-	-	-	-	-	determined after total hydrolysis	-	-	-	-	-	84,8	0,4	15,2	0,4	5,6
Retentate 1	-	-	-	-	-	-	-	-		-	-	-	-	-	88,7	0,5	11,3	0,5	7,8
Retentate 2	-	-	-	-	-	-	-	-		-	-	-	-	-	88,7	0,5	11,3	0,5	7,8
Retentate 3	-	-	-	-	-	-	-	-		-	-	-	-	-	88,6	0,4	11,4	0,4	7,8
Retentate 4	-	-	-	-	-	-	-	-		-	-	-	-	-	88,8	0,3	11,2	0,3	8,0
Retentate 5	-	-	-	-	-	-	-	-		-	-	-	-	-	89,1	0,4	10,9	0,4	8,2
Ret. END	65000	200	20,9	0,2	4789	12	204	1	865	3	48	2	1117	6	95,8	0,2	4,2	0,2	22,9