Minimizing the sulphur content in Kraft lignin

Sara Svensson

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Supervisor Dr. Elisabeth Sjöholm
Examiner Dr. Sarah Angus-Dunne
Abstract

The aim of this project is to investigate the possibilities of minimizing the sulphur content in Kraft lignin. Kraft lignin contains about 1.5 to 3% sulphur. The sulphur is believed to be present in lignin as inorganic sulphur, as elemental sulphur, as adsorbed polysulphide and/or as organically bound sulphur. For the determination of these different types of sulphur components, different approaches and methods were used. For the determination of inorganic sulphur, lignin was washed with water at pH 6 and pH 2 and the wash waters were analysed with ion chromatography (IC). For the determination of total sulphur content in the lignin, two methods were used; Schöniger combustion followed by ion chromatography (IC) and wet digestion followed by inductively coupled plasma (ICP). The elemental sulphur content in water-extracted lignin was determined after n-pentane extraction. ICP analysis was performed on the washed lignin.

Calcium present in the lignin may bind polysulphides and thus be a source of the observed sulphur. The lignin was thus ion-exchanged to remove any calcium. To further investigate how the sulphur content in lignin can be decreased, two different types of reactions were performed on lignin; oxidation and reduction. The oxidation reactions were made in sodium hydroxide with oxygen at different temperatures and time on both original and water-extracted lignin. The reduction reactions were made on water-extracted lignin with Raney nickel in three different solvent systems: methanol: water, acetone: water and sodium hydroxide.

The original lignin contained 2.6% sulphur as determined by ICP. Washing lowered the content to 1.85% sulphur. By n-pentane extraction the elemental sulphur was lowered to a level of 1.82% sulphur, which was considered to be organically bound sulphur. Neither the ion exchange nor the oxidation lowered the sulphur content significantly.

The reduction reactions successfully the organically bound sulphur from 1.82% to a level of 0.54%.

The relative distribution of the sulphur content in the studied softwood lignin was as follows: about 29% as inorganic sulphur, about 1% as elemental sulphur and approximately 70% as organically bound sulphur, of which 49% could be removed by Raney nickel.
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1 Aim
The aim of this project is to investigate the possibilities of minimizing the sulphur content in softwood kraft lignin, primarily to a value below 0.5%, while keeping the structural change and mass losses low. Another aim was to investigate published information about the nature of sulphur in kraft lignin.

2 Background

2.1 Lignin
Anselme Payen observed in 1838 that wood, when treated with concentrated nitric acid, lost a piece of its substance. He named residue, a solid and fibrous material, cellulose. Much later studies proved that the fibrous material also contained other polysaccharides in addition to cellulose. The dissolved material had higher carbon content than the fibrous residue and was termed lignin, from the Latin word for wood, lignum (Sjöström 1993a).

2.1.1 Structure
Phenylpropane units build up lignin, although the exact structure is not known. In Figure 1 the three common monolignol precursors involved in the formation of lignin in different species are shown; p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.

![Figure 1. Three monolignol precursors](image)

The monolignols are generated from D-glucose through the Shikimi acid pathway including a series of enzymatic reactions. The polymerisation of lignin is formed through enzymatic dehydrogenation from α, β-unsaturated C₆C₃ precursors, regarding softwoods, of the coniferyl alcohol type (Sjöström 1993a). Although the exact biosynthesis route of lignin is not completely known, it involves radical coupling reactions rendering in a complex three-dimensional structure.
2.1.2 Linkages

Through different degradation processes, the linkages and dimeric structures of the lignin molecule have been determined and through analytical methods, functional groups have been determined. These different studies of the lignin molecule have given information about the linkages in lignin. The phenylpropane units are linked with ether bonds, which are the dominating, as well as carbon-carbon bonds. The different linkages in the lignin molecule are presented in Figure 2 and their occurrence in Table 1 (Sjöström 1993a).

![Figure 2. The common linkages present in lignin between the phenyl propane units (Sjöström, 1993)](image)

Table 1. The occurrence of the different linkages in softwood lignin (Sjöström 1993a).

<table>
<thead>
<tr>
<th>Linkage type</th>
<th>% of total linkages</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-O-4</td>
<td>50</td>
</tr>
<tr>
<td>α-O-4</td>
<td>2-8</td>
</tr>
<tr>
<td>β-5</td>
<td>9-12</td>
</tr>
<tr>
<td>5-5</td>
<td>10-11</td>
</tr>
<tr>
<td>4-O-5</td>
<td>4</td>
</tr>
<tr>
<td>β-1</td>
<td>7</td>
</tr>
<tr>
<td>β-β</td>
<td>2</td>
</tr>
</tbody>
</table>
Through the knowledge of the linkages and their occurrence the structure of lignin has been statistically determined (Figure 3). Structural understanding of lignin gives starting point information about the reactions occurring during the kraft processing of wood (Sjöström 1993a).

![Figure 3](image)

**Figure 3.** Statistical structure of lignin as proposed by Adler 1977 (Sjöström, 1993)

### 2.1.3 Lignin degradation methods

Lignin forms an insoluble residue after hydrolytic removal of polysaccharides. It can also be hydrolyzed and extracted from the wood or be degraded to soluble derivatives.

The use of dioxane, in a mixture with water and hydrochloric acid, can also extract pulp lignin, but here as well, the structure is changed. The best preparation for structural studies is the milled wood lignin, MWL, also known as Björkman lignin. Milling the wood, either dry or in the presence of a non-swelling solvent (toluene), destroys the cell structure and then lignin can then be extracted with dioxane: water. The yield of the MWL is poor, usually not more than 50%.

In the sulphite pulping, wood is treated with solutions containing sulphur dioxide and hydrogen sulphite, at low pHs and high temperatures; soluble lignin derivatives are formed, so called lignosulphonates.

The kraft lignin is dissolved when wood is treated with sodium hydroxide and sodium sulphide at a temperature of 130°C.

By the Klason method the amount of lignin can be determined gravimetrically. The Klason lignin is done on lignin, using 2.5% H₂SO₄ at 125°C, 1.3 bar for 1 hour. But the method has a serious problem since it alters the structure severely, and is thus used only for quantitative purposes.

Normal softwood contains 26-32% lignin, while compression wood contains 35-40%. In hardwood, the Klason lignin values have to be corrected for the dissolved lignin during the acid hydrolysis and normal hardwood contains 20-25% lignin (Sjöström 1993a).
2.2 Kraft pulping

2.2.1 Chemicals

In the kraft pulping process sodium hydroxide, NaOH, and sodium sulphide, Na₂S, is mixed to the so-called white liquor. Thus the active species in the defibration and delignification of the wood chips is hydroxide and hydrogen sulphide. The charge of effective alkali used is approximately 4-5 moles or 16-20% of wood (Sjöström 1993b). The equilibrium between the sodium sulphide and sodium hydroxide are as follows:

\[
\begin{align*}
S^{2-} + H_2O & \rightleftharpoons HS^- + HO^- \\
HS^- + H_2O & \rightleftharpoons H_2S + HO^-
\end{align*}
\]

In the white liquor the equilibrium strongly favours the presence of hydrogen sulphide ions whereas the sulphide ions are considered to be absent. The role of the hydroxide ions is swelling of the wood and thereby increasing the accessibility of the cooking liquor. The hydroxide ions also play an active role in the cooking reactions and by dissociating the phenol groups of the lignin, making the lignin more susceptible for degradation and increasing its dissolution in the cooking liquor (see below). Approximately 150 kg of sodium hydroxide per ton of wood is used in a kraft cook. Of this amount, 60-70% is needed to neutralize hydroxy acids formed from the monosaccharides that are peeled off from the polysaccharide chains. A part of the remaining alkali is consumed to neutralize carbohydrate derived uronic and acetic acids as well as degradation products of lignin. The spent, still very alkaline, liquor is called black liquor. Besides of low molecular mass degradation products, it contains lignin and hemicellulloses. The black liquor is evaporated, and the organic part incinerated in the soda recovery boiler to obtain energy (Sjöström 1993b).

The sulphide ions reduce lignin and yields sulphur. Sulphur then reacts with more sulphide in the black liquor and forms polysulphide. The polysulphide is not stable in alkaline solution at 170°C and rapidly disproportionates to sulphide and thiosulphate. For each mole of sulphide that reduces lignin, half a mole is subsequently regenerated by hydroxide attack on polysulphide. The resulting formation of thiosulphate eliminates some of the sulphur from the cycle (Kubes 1980).
2.2.2 Reactions in kraft pulping

Delignification reactions
The delignification process proceeds through the cleavage of ether linkages, Figures 4 and 6. The carbon-carbon bonds are essentially stable. The hydrogen sulphide ions present ease the delignification reactions, since they are more nucleophilic than hydroxyl ions. Both hydroxyl and hydrogen sulphide ions are involved in the cleavage of ether linkages. The cleavages increase the hydrophilicity of lignin, since the phenolic hydroxyl groups are formed. The degraded lignin is dissolved as sodium phenolates in the black liquor, which is the spent pulping liquor (Sjöström 1993b). The organic part of black liquor consists essentially of lignin, hemicelluloses, carbohydrate degradation products and resin and fatty acids (tall oil) (Sjöström 1993c).

![Figure 4. Cleavage of β-aryl ether bonds during alkali pulping (Gierer, 1985)](image)

During the kraft pulping, volatile sulphur containing compounds are formed. Lignin is demethylated by hydrogen sulphide ions; forming methyl mercaptan as intermediate and proceeds to dimethyl sulphide by reaction with another methoxyl group, Figure 5. Also dimethyl disulphide is formed (Sjöström 1993b).

![Figure 5. The formation of methyl sulphide (CH₃SH), dimethyl sulphide (CH₃SCH₃) and dimethyl disulphide (CH₃SSCH₃) during the kraft cook (Gierer, 1985)](image)
Lignin reactions
In the kraft pulping the hydrogen sulphide reacts with lignin, which is a step in the delignification process, Figure 6. The sulphur containing compounds produced are decomposed in later stages of the cooking, forming elemental sulphur that partly combines with hydrogen sulphide to form polysulphide. Nevertheless, the kraft lignin still contains 2 to 3% sulphur after the cook (Sjöström 1993b).

Figure 6. Delignification reactions in the Kraft pulping (Gierer, 1985).
The role of sulphide in kraft reactions
The sulphide has two benefits in kraft pulping: it promotes and accelerates the cleavage of ether linkages in phenolic units, assisting the break up of the lignin macromolecule to soluble units and it reduces the degree of undesirable condensation reactions.

In the soda pulping process, quinone methides, Figure 7, are formed by two reactions: 1) the reversible reaction of phenol groups with benzylic hydroxyl groups and 2) the irreversible reaction of aliphatic or aromatic ether groups, associated with the α-carbon (Marton 1971b).

![Figure 7. Formation of quinone methide intermediate, in acidic media and in alkaline media (Gierer, 1985)](image)

The presence of sulphide in the kraft pulping modifies the reactions of the soda process introducing a thiol group in the quinone methide structure, Figure 8. The following is the presumed alternatives due to the presence of sulphide: the quinone methide intermediates are mainly converted benzyl thiols, which decrease the opportunity for condensation reactions. The reaction path of aryl glycerol-β-ethers is greatly changed, and formaldehyde is released, by splitting of the gamma carbon. This release is decreased and the hydrolytic cleavage of the β-ether bond replaces the formation of stable enol ethers. This leads to more extensive cleavage of β-ether linkages and more reactive phenolic units are thus formed in the kraft process than in the soda process (Marton 1971b).
Only the aryl glycerol-β-ether linkages are reactive of the non-phenolic units in lignin. They form a new phenolic unit, by the conversion to a free glycerol side-chain, at high temperatures. In the primary cleavage reaction, no assistance is needed from the hydrosulphide ion, but they influence the course of reactions by the newly formed phenolic unit (Marton 1971b).

Figure 8. The nucleophilic addition of hydrosulphide ions to quinone methide intermediates (Gierer, 1985)
2.2.3 Kraft lignin

Isolation of kraft lignin
By acidification of the black liquor, most of the dissolved lignin can be isolated through precipitation, but low molecular mass lignin fragments remain in the solution. The yield from the precipitation depends on the final pH and of the ion strength of the solution. The use of carbon dioxide is beneficial for technical purposes, but the pH cannot be lowered under 8.5. More lignin can be precipitated if a strong mineral acid is used. By using carbon dioxide the weakly acidic phenolic hydroxyl groups of lignin are protonated, but not the carboxylic acid groups (Sjöström 1993d).

Intermediate thiolignins and their conversion to kraft lignin
Thiolignins have been made for studies on the intermediates formed in the lignin reactions taking place during kraft pulping (Marton 1971a). Thiolignin has been prepared with sulphur contents as high as 12 to 18% (Field 1958).
By treating wood with sodium hydrogen sulphide at pH 8 to 9 at 100°C the thiolignins are formed. When heated with sodium hydroxide at 160°C the thiolignin loses a great part of its sulphur and the product is very similar to kraft lignins with a sulphur content of 2 to 3%. Thiolignins are appropriate for studies on the sulphidation step of lignin in the kraft process, and for the decomposition of sulphur.
Several approaches have been made by sulphidation of model compounds. Treatment with mineral acid removes benzylic sulphur from several model compounds. This treatment, on thio derivatised milled wood lignin, removed two-thirds of the sulphur and gave an indication that the majority of the sulphur occupies benzylic positions (Marton 1971a).
Infrared spectroscopy of methylated thiolignin before and after oxidation indicates the presence of sulphoxide and sulphone linkages. These sulphur linkages are resistant to Raney nickel reduction. It appears that thiolignin contains minor sulphur as inorganic sulphide or in the form of thiols, thiocarbonyls, disulphides, polysulphides or dialkyl-type sulphides.

Usage of kraft lignin
Kraft lignins can be used for the same purpose as lignosulphonates, but their recovery and purification is quite expensive. Kraft lignins or their modified forms can be used as dispersing agents and as additives in rubber, resins and plastics. Kraft lignin can be condensed with formaldehyde and cross-linked with phenols to yield thermosetting polymers, which can be used for adhesives for different products. The solubility of lignins can be improved by sulphonation. Lignin can also be broken down into low molecular mass chemicals (Sjöström 1993d).
Presence of sulphur in kraft lignin
Sulphur containing lignins are a result from kraft or sulphite pulping processes. The kraft lignin contains about 1.5 to 3% of sulphur, but its nature has not fully been established (Marton 1971c). The sulphur is believed to be present in lignin as sulphate ions, as elemental sulphur, as adsorbed polysulphide and as organically bound sulphur.
In Figure 9 a possible sketch of the structure of softwood kraft lignin is shown. This has been made from proposed reactions occurring in the kraft process.

Figure 9. A sketch of possible structures in a segment of pine kraft lignin, with the sulphur marked out (Marton, 1971)
3 Project presentation

The nature of sulphur present in Kraft lignin is not fully known, nor the position or nature of the bound sulphur. The question arises as to whether it is possible to reduce the sulphur content of Kraft lignin and which treatments would be most effective. The tested treatments in this project were chosen and evaluated with respect to structural changes and mass losses.

When Kraft lignin is used as an energy source the sulphur should be removed from the combustion gases which requires expensive scrubbing. If the sulphur can be limited to approximately 0.5% the lignin can be used in smaller combustion units without any need of gas scrubbing, which will then expand the market for lignin as a fuel. In addition, limited/controlled sulphur content may also be beneficial for other lignin applications such as chemicals and materials.
4 Techniques and methods for characterisation and determination of sulphur content in Kraft lignin

The sulphur in lignin is believed to be present as both inorganic sulphur; mainly as sulphate ions (SO$_4^{2-}$), as elemental sulphur (S$_0$), as adsorbed polysulphide (S$_n$S$_2^-$), and as organically bound sulphur; thiol (-SH), sulphide bonds (-S-) and disulphide bonds (–S-S–). For the determination of these different types of sulphur different analytical methods must be used.

4.1 Analytical methods

4.1.1 Ion Chromatography

With ion chromatography (IC) sulphate concentration in water samples can be determined. In ion chromatography the principle of ion exchange is used, where a stationary phase containing ions is exchanged with ions in the eluent.

Depending on the nature of the ions in the eluent different resins in the columns can be used, cationic or anionic. Macro-molecular polymers containing many functional groups, which can bind ions, build up the resin. If the resin is cationic the functional groups are acidic, often sulphonate groups, and if the resin is anionic the functional groups are basic, often quaternary amines (Skoog 1994a).

Chromatograms are acquired after separations, where the signal (depending on detection) is plotted against elution time or elution volume. The chromatogram is useful for both qualitative and quantitative analysis, where the position of the time axis identifies the analyte and the areas of the peaks yields the amount.

Stock solutions can be used to calibrate the system by plotting the known concentration against the area obtained in the chromatogram. By using the equation for this plot, an unknown e.g. sulphate concentration in a sample can be determined provided that sufficient separation has been achieved (Skoog 1994b).

Detection can be made in using different types of detectors, such as absorbance, fluorescence, electrochemical, conductivity detectors. The method of detection depends on the nature of the analyte in the sample. Conductivity measurements are often used when analysing eluents in liquid chromatography having charged properties. Conductivity measurements are ideal, with high sensitivity, simple operations, inexpensive maintenance and are universal for charged analytes, but they have one limitation: a high concentration of analyte is needed to elute most analyte ions in a reasonable time. This causes a background noise, which can mask the signal form the analyte (Skoog 1994c).
4.1.2 Schöniger combustion

Analysis of the total amount of sulphur including covalently bound sulphur, which is not detectable with IC, can be achieved using Schöniger combustion. This method determines the total sulphur content by converting all sulphur to sulphate, and analysing the sulphate ions formed with IC. The following reaction occurs in the sample:

\[ \text{Sample (with S) + O}_2 + \text{H}_2\text{O}_2 \rightarrow \text{SO}_4^{2-} \]

The combustion takes place in an Schöniger flask (see Figure 10) by applying the sample on a sulphur free filter paper, which is put in a gasket. The platinum gasket acts as a catalyst. The sample is burned in a closed system with excess oxygen. The smoke formed dissolves in the water present in the flask (Harris 2003a). The solution is then analysed with IC.

![Figure 10. The Schöniger flask containing the platinum basket (Harris, 2003).](image)

4.1.3 Wet digestion

For analysis with inductively coupled plasma (ICP), the samples are required to be in solution since solid samples clog the instrument. Aqueous solutions are preferred over organic solvents, since the latter needs more treatment before analysis with the following ICP.

The samples are prepared through wet digestion, where the sample is usually degraded in presence of an oxidant. The hydrogen peroxide added to the solid samples ensures that no sulphur is lost during the digestion (Skoog 1994d).

The sample is put into a Teflon bomb (Figure 11) and nitric acid is added, yielding a oxidative digestion of the samples. The use of temperature and pressure sensors allows a safe, programmable control of the digestion. The Teflon bombs are put into the microwave where the digestion takes place (Harris 2003b).
4.1.4 Inductively coupled plasma, ICP

Inductively coupled plasma, ICP, is an atomic spectroscopic method, where the samples are atomised. This requires a step called atomisation where the sample is volatilised and decomposed to form an atomic gas. In ICP the typical atomisation temperature is 6000-8000°C. The nebulizer converts the sample solution to a mist or aerosol, which are fed into the plasma. The plasma is a conducting gas mixture of argon and helium containing a significant concentration of cations and electrons (Skoog 1994e).

The ICP torch (Figure 12) contains three concentric quartz tubes through which streams of argon flows, surrounded by a water-cooled induction coil, powered by a radio-frequency generator on the top.

With a spark from a Tesla coil the ionisation of the flowing argon starts. The ions and electrons produced interact with the magnetic field induced by the induction coil. Argon carries the samples, which are in aqueous form, into the hot plasma. The chemically inert environment reduces the interference between sample and noise. The emission spectra yields unique peaks form each element (Skoog 1994f). By calibrating the instrument with known amounts of elements, quantification analysis can be achieved.

Figure 11. Container for the microwave oven wet digestion step (Harris, 2003)

Figure 12. The torch in ICP apparatus (Skoog, 1994)
4.1.5 Soxhlet extraction

Elemental sulphur, which presumably is formed from polysulphides during the acidification of the black liquor, can be removed from the Kraft lignin samples by n-pentane extraction (Gellerstedt 1984).

A compound can efficiently be extracted from a solid using Soxhlet extraction. The solid is placed in a thimble, which then is put into the Soxhlet extractor (Figure 13) and attached to a round-bottled flask containing an organic solvent. The top of the extractor is fitted with a reflux condenser. The organic solvent is heated and the steam moves up via the outer tube, condenses in the cooler and drops down on the solid. In this way the extractable compounds are removed, while the other solids remain in the thimble. When the solution level reaches the top of the siphon tube it automatically empties and returns to the flask. This can be repeated several times and allows the compound extracted to be concentrated (Harwood 1999).

Figure 13. Overview of a Soxhlet extractor (Harwood, 1999)
4.2 Oxidation and reduction reactions

4.2.1 Oxidation
By mild oxidation of mercaptans and thiols, disulphides are obtained. Depending on the oxidizing agent used, different products can be produced and oxidizable functional groups can be left intact. Different sulphides can be oxidized into sulphoxides or sulphones. Depending on whether one or two equivalents of the reagent are used both products can be obtained. Also the use of different oxidizing agents, such as hydrogen peroxide and peroxy acids, can selectively oxidize sulphides to sulphoxides or sulphones. Air oxidation of sulphoxides leads to sulphones, in the presence of fine metal salts or with sodium permanganate (Hudlický 1990).

4.2.2 Reduction reactions
Lithium aluminium hydride affords a powerful means of reducing disulphides and polysulphides to thiols. The usage of potassium borohydride provides a milder reduction than lithium aluminium hydride, but still an effective reduction. Raney nickel is a good way for replacing sulphur linkages, mainly divalent ones, with hydrogen (Field, 1958). For the preparation of Raney nickel, nickel-aluminium alloy is treated with sodium hydroxide solution to yield the hydrogen active nickel. Thus, hydrogen is not added in the reaction but hydrogen is included in the reagent, which is indicated as shown below. The desulphurisation can occur in two ways depending on the freshness of catalyst and temperature.

\[
\text{R-S-R'} + \text{Raney Ni (H)} \rightarrow 1) \text{R-R} + \text{R-R'} + \text{R'-R'} + \text{NiS} \\
\rightarrow 2) \text{R-H} + \text{R'-H} + \text{NiS}
\]

Path 1 takes place when the catalyst is stored for a long time and at elevated temperatures. In fact, the hydrogen adsorption decreases when the temperature is higher than 100°C. Path 2 dominates when temperature is lower and the catalyst is fresh. It has been found that the addition of platinic chloride to the catalyst, prior to the reduction step, enhances the reactivity of desulphurisation with Raney nickel (Beigi et al. 1999). Raney nickel is used when removing ethanethiols in thioacidolysed lignin, by cleavage of sulphur-carbon bonds (Lapierre 1991). After a 12 hr reaction with Raney nickel in dilute aqueous alkali, about 74% of the sulphur was removed in the thiolignin, to a sulphur content of 1.4% (Field 1958).
5 Experimental

5.1 Lignin
The lignin used for the experiments in this project is a softwood lignin from a pilot plant in Bäckhammar where the LignoBoost concept is used for isolation of kraft lignin from black liquor. It is precipitated with CO$_2$ to pH 9-10 and then acid washed at pH 2-4. Bäckhammar only produces kraft lignin from black liquor from the cook, i.e. no oxygen is involved.

5.2 Determination of the inorganic sulphur

Extraction
For the determination of the most efficient washing to remove inorganic sulphur, two procedures were explored, one at pH 6 and the other at pH 2. Lignin (2.36 g) was washed with water (4 x 50 mL) at pH 6 and a second batch of lignin (2.40 g) was washed in the same way at pH 2. The pH was adjusted with 37% hydrochloric acid, p.a, containing maximum 0.5 ppm SO$_4^{2-}$. For every wash, the solutions were left with stirring for 20 min and then centrifugated, at 6000 rpm for 20 min. The washed lignins were then freeze-dried.

In the final washing procedure, one wash was made at pH 2 to obtain large amounts of essentially inorganic sulphur-free sample. Approximately 2 g of lignin was used for every 50 mL of water. The solutions were stirred for 20 minutes and then centrifugated at 600 rpm for 20 minutes. The sulphate content in these water extracts was not determined, only the sulphur content in the lignin was determined.

Ion Chromatography
The sulphate, SO$_4^{2-}$, content in water samples was determined by IC.

The system used was an ICS-2000 ion chromatography system, with a Dionex AS 15 column, pre-column Dionex AG 15 with a sample volume of 25 µL. The conditions chosen for conducting the separation was 30.00 mM NaOH as mobile phase, a column temperature of 30.0°C, and the conductivity detector was set on 0.070 µS and the suppressor on 90 mA. The flow rate used was 1.20 mL/min. Standard solutions of 2, 4 and 8 ppm were made. The washing water sample 1 was diluted 100 times, sample 2 was diluted 12.5 times, sample 3 was diluted 2.5 times and sample 4 was not diluted at all.

5.3 Total sulphur content

5.3.1 With Schöniger combustion
The Schöniger combustion was performed according to SCAN-N 35:96 for wet samples and SCAN-CM 57:99 for dry samples, respectively. For dissolved samples 100µL was used and 100 µL H$_2$O$_2$. Approximately 150 mg of lignin was used when analysing dry samples. Water (20 mL) and H$_2$O$_2$ (200µL) were used in the Schöniger flask irrespective of sample type.

The samples were diluted to appropriate concentration before IC analysis.
5.3.2 With ICP
The instrument used was an ICP, Perkin Elmer Instruments, Optima 2000 DV with an Optimal Emission Spectrometer.

Sample preparation- wet digestion
The dry lignin samples (0.5 to 0.9 g) were put into a tube and H₂O (5 mL) and H₂O₂ (2 mL) was added. After 10 minutes HNO₃ (4 x 2.5 mL) were added. The samples in solution (5 to 20 mL) were put into the tube and HNO₃ (5 mL) was added. The tubes were fitted with lids, placed in a container and the peg was pulled tightly. The containers were then placed into the microwave oven. Sample position tube 1 was used as a control for pressure and temperature, and the samples placed in the remaining available positions.
The program used was as follows: 0 to 20 minutes, temperature 25 to 175 °C, the temperature is held at 175 °C for 5 minutes and was then cooled down to room temperature.
The samples were collected in a retainer; the tubes were rinsed once and then the solution was diluted to a total volume of 25 mL. After this dilution a dilution series was made for each sample, see Table 2.

Table 2. Dilution series for wet digested samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dilution, units</th>
<th>Volume of sample, mL</th>
<th>Volume of H₂O, mL</th>
<th>Volume of HNO₃, mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,03</td>
<td>10</td>
<td>0</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>10,3</td>
<td>1</td>
<td>9</td>
<td>0.3</td>
</tr>
<tr>
<td>3</td>
<td>106,9</td>
<td>1 of 10,3</td>
<td>9</td>
<td>0.3</td>
</tr>
</tbody>
</table>

5.4 Elemental sulphur
The elemental sulphur in the lignin samples was extracted by Soxhlet extraction. The thimble was cleansed by refluxing with n-pentane (200 mL) for three hours. The thimble was then dried and washed dry lignin (2.27 g) was put inside. The thimble was put in the Soxhlet extractor and n-pentane (200 mL) was refluxed for 7 hrs. The solvent was concentrated to 5 mL. The lignin was then left to air-dry. The lignin was then wet digested and analysed with ICP as previously described. The solvent was analysed with Schöniger combustion followed by IC.

A second extraction was performed, with washed lignin (1.63 g). The lignin and the n-pentane extract were analysed with ICP. The n-pentane extract was applied to a filter paper, dried and then treated in the same way as for dried samples i.e. as for the lignin.

5.5 Ion exchange
In order to remove calcium ions, the lignin (2.03 g) was dissolved in 7:3 acetone: H₂O (20 mL). A column (1 cm in diameter) was filled with Amberlite IR-120 in 7:3 acetone: H₂O. The flow rate was approximately 1 to 2 drops per second.
The lignin solution was poured into the column and was collected in a round bottle flask. The acetone was removed. The sample solution was freeze-dried. The sulphur content was analysed by ICP.
5.6 Oxidation and reduction reactions

5.6.1 Oxidation

Six different reactions were performed, where both temperature and time were varied, as shown in Table 3. The first four reactions (1-4) were made on original lignin and two (5 and 6) were made on lignin washed at pH 2, one of which (6) was a dry oxidation. The lignin was dissolved in 50 mM NaOH, heated to the target temperature whilst under stirring and O₂ was bubbled through the solution. In the dry oxidation (6), lignin was impregnated with 50 mM NaOH (2 mL) and O₂ was flowed through the reaction vessel. Parafilm was put on the round bottled flask to protect the lignin from dusting out and a few extra drops of 50 mM NaOH were added to ease the stirring and to reduce dusting.

The reactions were stopped on ice with ice-cold acid; sulphuric acid in 1 and hydrochloric acid in the others (2-6). Half of the material in 1 was dialyzed for 72 hrs. The solutions were centrifuged and the pellet resolved and freeze-dried.

The obtained oxidized lignins were wet digested and analysed with ICP.

Table 3. The temperature and time used in the different oxidation reactions. Reactions 1 to 4 were done on original lignin and reactions 5 and 6 were done on washed lignin.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Temperature, °C</th>
<th>Time, minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>90</td>
</tr>
<tr>
<td>3 and 5</td>
<td>80</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>40</td>
<td>30</td>
</tr>
</tbody>
</table>
5.6.2 Raney nickel reduction

The Raney nickel slurry was stored in alkali and had been stored for 1½-2 years at room temperature.

Three different solvents were used to dissolve the lignin for the Raney nickel treatments: methanol-water, acetone-water and sodium hydroxide. In all treatments, washed lignin samples were used, and the procedure from Kuoppala (2007) was used with some modifications.

A stock solution with washed lignin (2.012 g) was made, dissolved in 6:1 MeOH: H_2O to a total volume of 50 mL. The flask was put into an ultrasonic bath for 30 minutes. The sample solution was then filtered through a pre-weighed filter paper. The filter paper was then dried along with the first flask, so that the concentration of lignin in the filtered solution could be adjusted. The filtered sample solution was diluted to 50 mL with 6:1 MeOH: H_2O.

Two different aliquots of stock solution were used, 1 mL and 2 mL. Also a zero sample, with no lignin added, and a non-reduced sample, with no Raney nickel added, was made.

After the reaction and filtration step, the MeOH was removed under reduced pressure. The solutions were then wet digested and analysed with ICP.

The other solvents used were 7:3 acetone: H_2O and 50 mM NaOH. The concentration of the lignin solutions was 52.9 mg/mL for the acetone: H_2O and 1.02 mg/mL for the NaOH.

Four different test solutions were made from each of these stock solutions. The lignin amounts varied from 25 to 100 mg.

For each solvent, a zero sample, with no lignin added, and a non-reduced sample, with no Raney nickel added, was made.

In the NaOH reaction no MeOH was used. The total volume of each reaction was 7 mL.
6 Results and discussion

6.1 The nature of sulphur in kraft lignin

In order to minimize the amount of sulphur in kraft lignin, an essential part of the project was to explore plausible forms of the sulphur present as well as determine the amount of each respective form. From the present knowledge, the plausible sulphur containing structures may be present as both inorganic sulphur, mainly as sulphate ions ($SO_4^{2-}$), as elemental sulphur ($S_0$), as adsorbed polysulphide ($S_nS_{2n}$), and as organically bound sulphur: thiol (-SH), sulphide bonds (-S-) and disulphide bonds (-S-S-).

Washing with water was done to examine the amount of inorganic sulphur present in kraft lignin. The dissolved inorganic sulphur was determined by ion chromatography (IC).

The total sulphur content was analysed by the Schöniger method, followed by IC, and with wet digestion followed by ICP.

The elemental sulphur content was calculated from the determination of the total sulphur content in the n-pentane extracts as well as in the extracted lignin samples using both the Schöniger method and the ICP-technique.

The polysulphide content was examined by studying the influence of ion exchange treatments.

6.1.1 Inorganic sulphur

Two samples of lignin were washed with H$_2$O at pH 6 and pH 2 respectively. This was done to examine the efficiency of sulphate extraction at different pH’s. The results were evaluated by analysing the sulphate content in the water extracts by IC and also by measuring the yield, i.e. estimate the mass losses.

Four consecutive water extractions were made at each pH. The water extracts were analysed for sulphate after each step. As expected, the highest sulphate concentration was obtained in the first water extract. The analysis results and corresponding calculated sulphur content in the lignin is presented in Table 4. The concentration of calculated sulphur in the lignin is also shown in Figure 14.

<table>
<thead>
<tr>
<th>pH</th>
<th>Washing step</th>
<th>Total mg SO$_4^{2-}$</th>
<th>mg SO$_4^{2-}$/g lignin</th>
<th>mg S/g lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1</td>
<td>20.5</td>
<td>9.7</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.3</td>
<td>1.1</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.36</td>
<td>0.17</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.02</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>21.1</td>
<td>8.5</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.56</td>
<td>0.63</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.15</td>
<td>0.06</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.002</td>
<td>0.001</td>
<td>0.0003</td>
</tr>
</tbody>
</table>
Sulphur content in washing steps

![Bar chart showing sulphur content in washing steps at pH 6 and pH 2.](image)

**Figure 14. The amount of inorganic sulphur, which is extracted during the consecutive washing at pH 6 and pH 2 per gram lignin.**

For both pHs the sulphate was mostly removed by the first wash, with a little being removed in the second wash as well. The final yield of the lignin after the washes was 85% for pH 6 and 97% for pH 2. The lignin is more soluble at pH 6 than pH 2, and therefore more low molecular fragments of lignin are dissolved at pH 6 than at pH 2. This can also affect the sulphur content if analysing the total sulphur content in the extract, since these low molecular fragments can contain sulphur besides of inorganic sulphur. Considering the mass losses during the washes pH 2 was applied for further analysis of the composition of the nature of kraft lignin sulphur.

### 6.1.2 Total sulphur content

**With Schöniger combustion**

By oxidation of all sulphur containing structures to sulphate by Schöniger combustion, the total sulphur content can be determined by IC. This method was applied to the lignin samples as well as to the water extracts.

The total sulphur content in the samples from the Schöniger combustion is presented in Table 5. The sulphur present in the original lignin was 13.8 mg S/g lignin. The amount of sulphur in the lignin after the washes was 12.8 mg S/g lignin and 14.6 mg S/g lignin for pH 6 and pH 2, respectively.

**Table 5. The sulphate and sulphur content in samples from Schöniger combustion analysed with IC and the percent sulphur content in the sample. Each sample was done in duplicate.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>mg SO$_4^{2-}$/g lignin</th>
<th>mg S/g lignin</th>
<th>St.dev</th>
<th>CV, %</th>
<th>Per cent S, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin, original</td>
<td>41.5</td>
<td>13.8</td>
<td>0.3</td>
<td>2.4</td>
<td>100</td>
</tr>
<tr>
<td>Lignin, washed at pH 6</td>
<td>38.3</td>
<td>12.8</td>
<td>0.9</td>
<td>7.4</td>
<td>93</td>
</tr>
<tr>
<td>Lignin, washed at pH 2</td>
<td>43.7</td>
<td>14.6</td>
<td>0.1</td>
<td>0.8</td>
<td>106</td>
</tr>
<tr>
<td>H$_2$O, step 1 at pH 6</td>
<td>9.7</td>
<td>3.2</td>
<td>1.0</td>
<td>39</td>
<td>23.2</td>
</tr>
<tr>
<td>H$_2$O, step 1 at pH 2</td>
<td>8.3</td>
<td>2.8</td>
<td>1.1</td>
<td>41</td>
<td>20.3</td>
</tr>
</tbody>
</table>
The sulphur content present in lignin, the original, and theoretically calculated from the amounts washed out, and after the four washes are presented in Figure 15.

![Sulphur content in lignin with Schöniger](image)

**Figure 15.** The sulphur content in original lignin, theoretical calculated sulphur content regarding the amounts that is in the water extract and the measured sulphur content in water extracted lignin.

For the Schöniger combustion, the results obtained were inconsistent. The achieved result on the washed lignin doesn’t compute with the content of sulphur that was removed. In the pH 2 cases the sulphur content analysed in the washed lignin is higher than in the original lignin. The mass balance doesn’t add up. One reason may be that the oxidation of the samples with H₂O₂ isn’t complete, due to insufficient H₂O₂. It can also be that the lignin isn’t enough homogeneous or that the method demands a total homogeneous sample. In addition, the filter papers used have not exactly the same weight, which also may influence the results. This can be helped by note the weight. Also, some of the SO₄²⁻ may be left on the flasks inside, so the inside of the flask should perhaps be rinsed after emptying it.

**With ICP**

After excluding the applicability of the Schöniger method for determination of the total sulphur content of lignin, the ICP method was used, which included acid degradation in wet digestion of the sample prior to the analysis by ICP.

Seven original lignin samples were analysed, and the concentration range was 23.6 to 30.6 mg S/g lignin. The mean sulphur content of original lignin was found to be 25.8 (± 2.4) mg S/g lignin, with a standard deviation of 2.6 and CV 10%.

Seven washed lignins were analysed, with a range of 14.1 to 21.1 mg S/g lignin. The mean sulphur content in lignin samples extracted once of pH 2 was 18.2 (± 3.6) mg S/g lignin, with a standard deviation of 2.9 and CV 16%.
6.1.3 Elemental sulphur

Using n-pentane elemental sulphur can be extracted from lignin. Here, water extracted lignin at pH 2 was used for the Soxhlet extraction, which were done in two individual sets.

The n-pentane extracted lignin was analysed with ICP and the n-pentane was analysed with the Schöniger method after the first extraction set. Since the Schöniger method was found not to be applicable a second n-pentane extraction set was made. The ICP method was used on both the n-pentane extracted lignin and the n-pentane after the second extraction set.

The sulphur content was found to be 23.6 mg S/g lignin in n-pentane extracted lignin, with a standard deviation of 7.2 and CV 30%. These results are unreliable. The amount of sulphur that was n-pentane extracted represents a sulphur content of 0.16 mg S/g lignin.

6.2 The distribution of sulphur

Figure 16 shows the sulphur content in original lignin, washed lignin and n-pentane extracted lignin, the latter calculated as the difference in sulphur content between the water extracted lignin and the amount removed by the pentane extraction.

The sulphur content in original lignin was found to be 25.8 (± 2.4) mg S/g lignin. By washing with water the inorganic sulphur was removed and the washed lignin contained 18.2 (± 3.6) mg S/g lignin. N-pentane extraction removes a small portion of the remaining sulphur. This consists mainly of elemental sulphur but may also include sulphur containing low molecular mass organic compounds, derived from lignin or from wood extractives, soluble in n-pentane.
The relative distribution of the different forms of sulphur in lignin is shown in Figure 17. Thus, in the studied softwood lignin sample the inorganic sulphate is about 29%, the elemental sulphur is about 1% and the rest of the sulphur, approximately 70%, remains in the lignin. These are either tightly adsorbed polysulphide and/or covalently bounded to the lignin macromolecule, presumably as thiols or sulphides.

![Overview of sulphur content](image)

**Figure 17. The sulphur distribution in kraft lignin**

### 6.3 Treatments for decreasing the sulphur content

#### 6.3.1 Ion exchange treatment

Ion exchange chromatography was performed to remove any polysulphide. The ion exchange was made to examine if removing Ca$^{2+}$ ions would reduce the sulphur content. Polysulphides are believed to bind to Ca$^{2+}$ ions and by removal of Ca$^{2+}$ the polysulphides would also be removed, yielding decreased sulphur content.

The recorded yield of lignin was 96.3%. The sample was analysed with ICP and the sulphur content was 19.9 mg S/g lignin. The sulphur content of the washed lignin used for this ion exchange treatment was 20.2 mg S/g lignin. No significant decrease in the sulphur content was thus achieved.

#### 6.3.2 Klason lignin

A Klason lignin was analysed for sulphur content for comparisons purposes. The sulphur content was 18.8 mg S/g lignin, with a standard deviation of 1.2 and CV 6.6%. This lignin did not have any lower content of sulphur than the washed lignin. So this condensation method didn’t affect the sulphur content.
6.3.3 Oxidation and reduction reactions

To remove any organically bound sulphur two treatments were performed: oxidation and reduction. The oxidation was made to remove sulphur-containing moieties. The Raney nickel reduction is normally made on thioacidolyzed lignin to remove its ethyl-S-groups. The same principle that removes these sulphur containing groups should be able to remove R-S-groups in Kraft lignin.

**Oxidation reactions**

In Table 6 the sulphur content of oxidised original unwashed lignins and oxidised washed lignins are presented. There was no obvious decrease in the sulphur content in the lignin after the oxidation reactions.

When the pH was lowered after the completed oxidation, the solution became more viscous. The longer the reaction times, the more viscous the solution became on acidification. This indicates that oxidation had occurred, since lignin normally precipitates at low pH. The shorter reaction time was chosen in hope to reduce any structural changes in lignin.

The dry oxidation was difficult to perform, the lignin easily dusted out of the reaction vessel and the O\(_2\) flow was too high.

The chosen conditions: temperature, reaction times and oxidant, were too harsh and apparently changed the lignin structure extensively. This can be concluded from the solubility of the treated lignin versus the solubility of the untreated original lignin when pH is lowered. A milder oxidation conditions may be more appropriate.

**Table 6. The sulphur content in oxidized original and washed lignins analysed with ICP.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>mg S/g lignin</th>
<th>St.Dev</th>
<th>CV, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated original lignin</td>
<td>25.8</td>
<td>2.6</td>
<td>10</td>
</tr>
<tr>
<td>60 min, 80°C on original lignin</td>
<td>9.66</td>
<td>0.9</td>
<td>9.0</td>
</tr>
<tr>
<td>90 min, 80°C on original lignin</td>
<td>15.4</td>
<td>3.9</td>
<td>25</td>
</tr>
<tr>
<td>10 min, 80°C on original lignin</td>
<td>17.9</td>
<td>0.7</td>
<td>3.8</td>
</tr>
<tr>
<td>10 min, 20°C on original lignin</td>
<td>19.1</td>
<td>2.4</td>
<td>13</td>
</tr>
<tr>
<td>Untreated washed lignin</td>
<td>18.2</td>
<td>2.9</td>
<td>16</td>
</tr>
<tr>
<td>10 min, 80°C on washed lignin</td>
<td>21.4</td>
<td>0.7</td>
<td>3.4</td>
</tr>
<tr>
<td>10 min, 40°C, dry oxidation on</td>
<td>24.7</td>
<td>0.6</td>
<td>2.4</td>
</tr>
<tr>
<td>washed lignin</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Reduction reaction
The first experiment was made according to Kuoppala (2007). But, Kraft lignin showed poor solubility in 6:1 methanol: water and therefore other solvents were explored in order to dissolve the sample. The lignin was found to be completely soluble in 7:3 acetone: water. To reduce the number of steps in the work up method, 50 mM sodium hydroxide was used, as this solvent excludes the need for an evaporation step.

Originally, three samples were made using methanol: water as a solvent. Two had a lignin concentration of 2.5 mg/mL, of these one was used as a reference without any Raney nickel added. The third had a lignin concentration of 4.4 mg/mL.

The sulphur content achieved was as follows:
For the 2.5 mg/mL sample without Raney nickel: 2.2 mg S/g lignin; for the other 2.5 mg lignin/mL sample 0.4 mg S/g lignin and; for the 4.4 mg lignin/mL sample 1.3 mg S/g lignin. Since the lignin showed poor solubility in methanol: water this may not be a representative sample, and should be kept in mind while evaluating these results.

Using acetone: water as solvent and 50 mM sodium hydroxide as solvent five different samples were prepared each and the results from ICP are presented in Table 7 and illustrated in Figure 18.

Table 7. The sulphur content in the samples from the Raney nickel desulphurisation. The amount of Raney nickel slurry was 1 mL in each sample, except in the 12.5* samples, and the total volume was 8 mL.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Sample, mg lignin/mL</th>
<th>mg S/g lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone: H₂O</td>
<td>0</td>
<td>&lt;0.05 mg total</td>
</tr>
<tr>
<td></td>
<td>12.5</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>9.4</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>6.3</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>3.1</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>12.5*</td>
<td>15</td>
</tr>
<tr>
<td>50 mM NaOH</td>
<td>0</td>
<td>&lt;0.05 mg total</td>
</tr>
<tr>
<td></td>
<td>12.5</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>9.4</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>6.3</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>3.1</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>12.5*</td>
<td>14</td>
</tr>
</tbody>
</table>

*No Raney nickel used in these samples.
Raney Nickel reduction

![Graph showing sulphur content in washed untreated lignin and different samples from Raney nickel desulphurisation.](image)

**Figure 18.** The sulphur content in washed untreated lignin and in the five different samples from the Raney nickel desulphurisation, where 12.5* is a reference without any Raney nickel.

In the acetone: water samples the specific mean sulphur content of all measurements was 5.5 mg S/g lignin, with a standard deviation of 0.5 and CV 8.4%.

In the sodium hydroxide samples the specific mean sulphur content of all measurements was 5.3 mg S/g lignin, with a standard deviation of 0.08 and CV 1.6%.

The sulphur content in washed lignin used for the Raney nickel treatments and the sample without any Raney nickel differs. This may be due to the temperature treatment of the sample without any Raney nickel used. The stem solution used for the treatments can be analysed for its sulphur content, i.e. no temperature treatment would be done.

There was also a slight mass loss achieved in the filtration step, approximately 10% in both solvents. The mass loss was determined by drying the pre-weighed filter paper after the filtration.

It appears that in spite of the different amounts of lignin used, the specific sulphur content, gram sulphur per gram lignin, is similar in each sample; thus the amount of Raney nickel used was sufficient. This also indicates that the conditions can be optimised with the respect to temperature, time, using another Raney nickel reagent and by using fresh reagent.

Since the specific amount of sulphur remaining in the sample is similar, this indicates the presence of sulphur linkages resistant to the Raney nickel reduction. As Field (1958) discussed in his report, these linkages may be sulphoxide and possibly sulphone linkages.

Investigations are needed to investigate if the sulphur content in kraft lignin can be decreased further, that is below 0.5%.
6.4 Summary on the nature of kraft lignin sulphur

Of the original sulphur, about 29% was inorganic (sulphate) and about 1% elemental (see Figure 19). Of the remaining sulphur (70%), about 70% could be removed by Raney nickel reduction, representing a 49% reduction of total sulphur content. 21% of the original sulphur is thus in the form of a sulphur, which is resistant to Raney nickel under the conditions applied.

By the use of Raney nickel, under the conditions applied, the sulphur content reached was approximately 0.5% S, which was the target concentration aimed in this project.

![Figure 19. Distribution of sulphur in lignin, where the striped area represents the amount of sulphur that is reduced with Raney nickel.](image-url)
7 Conclusions

- Of the original 2.6% total sulphur, approximately 29% of the sulphur content can be removed as inorganic sulphur by extensive acid washing of kraft lignin without any severe mass losses.
- The n-pentane extraction showed that about 1% of the sulphur present in kraft lignin is elemental sulphur.
- The remaining sulphur, 70%, in kraft lignin is in the form of organically bound sulphur.
- Oxidation with oxygen appears to degrade/change the lignin structure considerably under the test conditions.
- The Raney nickel reduction is a successful method that lowers the organically bound sulphur content with 70.3% from 1.82% to a level of 0.54%, representing a reduction in the total sulphur content by 49%.
- It appears that some of the sulphur in lignin is resistant to the Raney nickel treatment and further investigations are needed with respect to treatment conditions and characterisation regarding the nature of these possible Raney nickel resistant sulphur linkages/structures.
8 Acknowledgments

The author wish to express her sincere gratitude to Dr. Elisabeth Sjöholm, supervisor at STFI-Packforsk Stockholm, Dr. Sarah Angus-Dunne, examiner at Mälardalen University and Kristin Olander, supervisor at STFI-Packforsk. She would also like to express her gratitude to other co-workers at STFI-Packforsk, who has helped with the experimental part of this project.

Last, but not least, to my fellow master thesis students at STFI-Packforsk: Rebecka Bodin, Therese Alm and Johanna Waltersson, who made my days a little bit brighter.
9 Search route

First the main search word is given (number of hits), then search within results (number of hits) and then further limitations to a manageable amount of hits (number of hits).

Science direct
* Lignin (4835)
  And kraft lignin (950) and sulphur (166) and structure (134)
  And black liquor (280) and kraft lignin (220) and sulphur (70)
  And disulphides (19)
  And softwood (754) and sulphur (125)
* Kraft lignin (309)
  And softwood (146) and sulphur (28)
  And structure (214) and sulphur (45)
  And thio (2)
  And thiolignin (1)
  And disulphides (0)
* Softwood lignin (124)
  And sulphur (23)
* Desulphurisation (186)
  And lignin (1)
  And softwood (1)
* Raney nickel and reduction (298) and desulphurisation (5)
  * Raney nickel and organic sulphide reactions (1)

STN Easy, Chemical abstracts
*Lignin and Kraft lignin (3102)
  And structure (528) and sulphur (0)
  And structure and sulfur (9)
*Lignin and sulphur and sulfur (10)
*Kraft lignin (3102)
  And thiolignin (38) and English (13)
*Kraft lignin and English (2225)
  And thio (3)
*Black liquor lignin (1198)
  And English (540) and sulphur (1)
  And English and sulfur (33)
*Lignin and English (26770)
  And softwood (1130) and disulphide (0)
  And softwood and disulfide (1)
  And softwood and structure (284) and thiol (1)
*Raney nickel and LA: English (2352)
  And lignin (22)
  And desul? (338) and lignin (11)
  And reductive desul? (45)
  And organic sul? reactions (1)
  And hydrodesul? (9)
10 References


Sources to the figures


Figure 10: Harris D.C., 2003. Quantitative chemical analysis, 6th edition, Freeman, New York, USA, p 680.


Figure 12: Harris D.C., 2003. Quantitative chemical analysis, 6th edition, Freeman, New York, USA, p 708.