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**THE EFFECT OF LIQUOR HEAT TREATMENT ON THE LIGNIN CARBOHYDRATE CONTENT**

**Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 2 March, 2016.**

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**Abstract**

This thesis had three different objectives: i) to discover different methods for kraft lignin purification that could be used alongside acid precipitation, ii) test the most suitable treatment on laboratory scale and evaluate the potentiality of this method as a kraft lignin purification method, and iii) to compare the feasibility of lignin purification alongside the acid precipitation compared to conventional acid precipitation.

Three different methods were discovered for kraft lignin purification: hydrolysis, solvent extraction and liquor heat treatment (LHT). The LHT was evaluated to be most suitable based on the existing literature. The effectiveness of the LHT was tested in laboratory scale while using cooking black liquor (CBL) and weak black liquor (WBL), which were obtained from softwood kraft pulp mill. The lignin samples were isolated from the liquors with $CO_2$ precipitation procedure. The LHT changed the precipitation behavior of the lignin, which led to a formation of pitch-like lignin. This unwanted behavior could be prevented by decreasing the precipitation temperature to 50 °C.

Both the liquors and the end product lignins were characterized. The characterized properties were dry matter content, residual alkali content, sodium sulfide content, lignin concentration, carbohydrate content and sulfur content for the liquors and purity, sodium content and elemental composition for the end product lignins. The LHT proved to be fairly effective method for lignin carbohydrate reduction. The highest carbohydrate reduction, circa 90%, was achieved with 190 °C treatment temperature, while the heat treatment at 170 °C for 45 minutes resulted to 75.3% and 65.6% carbohydrate content reduction for WBL and CBL respectively.

The feasibility of the LHT lignin precipitation process was compared to the conventional acid precipitation. This comparison was based on the operating costs of each process. The inclusion of LHT increased the operating cost by 162 - 176 €/t of lignin for WBL and 148 - 167 €/t of lignin for CBL depending on the treatment temperature. These additional operating costs increased the total operating costs by roughly 50% when compared to the conventional acid precipitation, therefore the LHT lignin should only be used for high value applications. Further research is still required in order to optimize the LHT process.

**Tekijä** Jussi Tiainen

**Työn nimi** Lipeän lämpökäsittelyn vaikutus ligniinin hiilihydraattipitoisuuteen

**Laitos** Puunjalostustekniikka

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**Tiivistelmä**
Tällä työllä oli kolme keskeistä tavoitetta: i) selvittää olemassa olevat menetelmät sulfaattiligniinin puhdistukseen, joita voidaan käyttää happosaostuksen yhteydessä, ii) tutkia soveltuvinta käsittelyä laboratoriomittakaavassa ja arvioida metodin potentiaalisuutta sulfaattiligniinin puhdistukseen, ja iii) vertailla ligniinin puhdistuksen ja happosaostuksen sekä perinteisen happosaostuksen kannattavuutta.

Kirjallisuudesta löydettiin kolme menetelmää sulfaattiligniinin puhdistukseen: hydrolyysi, liuotinuutto ja lipeän lämpökäsittely, joista lipeän lämpökäsittely todettiin soveltuvimmaksi. Lämpökäsittelyn tehokkuutta tutkittiin laboratoriomittakaavassa ja raaka-aineena käytettiin havupuusellutehtaan keittomustalipeää ja mustalipeää. Ligniininäytteet eristettiin lipeistä hiilidioksidisaostuksella. Lämpökäsittely muutti ligniinin käyttäytymistä saostuksessa, mikä johti pikimäisen ligniinin muodostumiseen. Pikimäisen ligniinin muodostuminen pystyttiin estämään laskemalla saostuslämpötila 50 °C:een.

Kaikki lipeät ja lopputuote ligniinit karakterisoitiin. Lipeiden karakterisoituja ominaisuuksia olivat kuiva-aine-, jäännösalkali-, natriumsulfidi-, hiilihydraatti- ja rikkipitoisuus. Lopputuote ligniinien karakterisoituja ominaisuuksia olivat puhtaus, natriumpitoisuus ja alkuainekoostumus. Lipeän lämpökäsittely osoittautui melko tehokkaaksi menetelmäksi lopputuote ligniinin hiilihydraattien poistoon. Noin 90 % hiilihydraateista pystyttiin poistamaan 190 °C lämpökäsittelyllä, kun taas 45 minuutin lämpökäsittely 170 °C:ssa kykeni poistamaan 75.3 % mustalipeäligniinin ja 65.6 % keittomustalipeä ligniinin hiilihydraateista.

Lämpökäsittelyavusteisen saostusprosessin kannattavuutta verrattiin perinteisen happosaostuksen kannattavuuteen. Kummankin prosessin kannattavuutta arvioitiin käyttökustannusten perusteella. Riippuen käsittelylämpötilasta, lämpökäsittely lisäsi ligniinin erotusprosessin käyttökustannuksia 162 - 176 €/t ligniiniä mustalipeäligniineille ja 148 - 167 €/t ligniiniä keittomustalipeäligniineille. Verrattuna perinteiseen happosaostukseen, lämpökäsittelyavusteisen ligniininerotuksen kokonaiskäyttökustannukset olivat noin 50 % suuremmat. Tästä syystä lämpökäsitellyt ligniinin soveltuvat ainoastaan korkean arvon tuotteisiin. Lisätutkimusta kuitenkin vielä tarvitaan lämpökäsittelyprosessin optimointiin.

**Avainsanat** ligniini, biojalostamo, lipeän lämpökäsittely, hiilihydraattien poisto

# ACKNOWLEDGEMENTS

# Table of Contents

# ABBREVIATIONS

| | |
|---|---|
| ASL | acid insoluble lignin |
| CBL | cooking black liquor |
| CFF | cross-flow filtration |
| $CO_2$ | carbon dioxide |
| DMDS | dimethyl disulfide |
| DMS | dimethyl sulfide |
| DS | dry solids |
| G | guaiacyl |
| GGM | galactoglucomannan |
| H | p-hydroxylphenol |
| HW | hardwood |
| HWT | hot water treatment |
| LCC | lignin-carbohydrate complex |
| LHT | liquor heat treatment |
| MM | methyl mercaptans |
| $M_n$ | number average molar mass |
| $M_w$ | mass average molar mass |
| PAN | polyacrylonitrile |
| PF | phenol formaldehyde |
| S | syringyl |
| SW | softwood |
| TDS | total dry solids |
| TMP | transmembrane pressure |
| WBL | weak black liquor |

# SYMBOLS

| | |
|---|---|
| $c$ | lignin concentration in the black liquor |
| $h_F$ | enthalpy of the feed |
| $h_L$ | enthalpy of the liquor stream |
| $H_S$ | enthalpy of the steam in the heating stream |
| $h_S$ | enthalpy of the water in the heating stream |
| $H_V$ | enthalpy of the vapor stream |
| $\dot{m}_F$ | mass flow in the feed |
| $\dot{m}_L$ | mass flow in the liquor stream |
| $\dot{m}_S$ | steam consumption during the LHT |
| $\dot{m}_V$ | mass flow in the vapor stream |
| $q$ | energy consumption during the LHT |
| $sf$ | 20% safety factor |
| $x_F$ | dry matter content in the feed |
| $x_L$ | dry matter content is the liquor stream |
| $\rho_{bl}$ | black liquor density |

# 1 Introduction

The awareness of the diminishing fossil resources associated with the increased concern towards environmental challenges has created a strong interest towards the development of new materials and sustainable alternatives for energy and chemical production. Lignocellulosic raw-materials are considered to be one of the most suitable feedstocks to be used as a replacement for oil and other fossil resources, as they are highly abundant, renewable and do not compete with food production.

Lignocellulosic biomass is composed of cellulose, hemicellulose, lignin and extractives. Whereas, the utilization of lignocellulosic carbohydrates (cellulose and hemicelluloses) has been moving forward, the utilization of lignin mainly consists of energy production via combustion. For a long time the lignin research was mainly focused on the improvement of the existing pulp and paper making processes, but the interest towards lignin-based products has been increasing during the recent years. The increased interest towards lignin is partly caused by the risen energy efficiency of pulp mills, which has resulted to energy surplus. Due to the energy surplus of the current modern pulp mills, lignin could be used nowadays in more high value applications. Lignin has the potential to be used in several different applications, *e.g.* materials, power, chemicals and fuels.

The lignin research is very topical issue at the moment. In June 2015 three major research projects received significant funding from European Union. The first project is UPM's Valchem project that is focused on the production of green platform chemicals and lignin based performance chemicals /1/. The second project that was funded is Innventia's project that focuses on kraft lignin based carbon fiber manufacturing /2/ and the third project is a SmartLi project that is coordinated by Finnish Bioeconomy Cluster (FIBIC). SmartLi focuses on a development of new biobased materials that can replace fossil fuels and materials based on them, *e.g.* different composites and plywood resins. /3/ This shows that the lignin valorization is very hot topic among researchers as well as in the industry at moment.

## 1.1 Objective and scope

This thesis has three different main objectives: i) to discover different methods for kraft lignin purification that could be used alongside acid precipitation, ii) test the most suitable treatment in laboratory scale and evaluate the potentiality of this method as a kraft lignin purification method, and iii) to compare the feasibility of lignin purification alongside the acid precipitation compared to conventional acid precipitation.

The scope of this thesis is focused on kraft lignin, as kraft process is the most common pulping method nowadays. In the first part of this thesis, the literature review, the structure and properties of native lignin and several different technical lignins are described. Kraft lignin and the reactions that occur during kraft cooking are described more closely. The literature review also consists of an illustration of two lignin separation techniques and an illustration on different kraft lignin purification methods. These purification methods are evaluated and the most promising method is tested in the second part of this thesis.

The second part of the thesis is experimental study, which consists of an evaluation on the effectiveness of the selected lignin purification method and a comparison between conventional lignin separation and lignin purification and separation. The experimental study is performed using two different softwood kraft black liquors. The first black liquor is taken from the digester's liquor circulation and the second is weak black liquor from the evaporators. The potential of the evaluated lignin purification method is based on the carbohydrate reduction of the separated lignin and the possible effects that the purification method might cause on the lignin separation process.

# LITERATURE REVIEW

## 2 Lignin

### 2.1 Native lignin

Lignin is the second most abundant renewable polymer in the world. The function of lignin is to give stiffness to cell wall and, hence, to contribute to the mechanical strength of the wood. Lignin also gives protection against microbial degradation by acting as a barrier and contributes to fluid transport system by making the cell wall hydrophobic. Lignin constitutes between 15% and 40% of the dry matter of woody plants and it is formed mainly from three types of monolignols./4/ Softwood lignin is mainly composed of coniferyl alcohol units, whereas, hardwood lignin contains both coniferyl and sinapyl alcohol units. The third monolignolic unit, p-coumaryl alcohol, is more commonly found from annual plants. In lignin structure, these monolignolic units are present in the form of p-hydroxylphenol (H), guaiacyl (G) and syringyl (S) residues. /5/ The monolignols and their corresponding structures in lignin are illustrated in the Figure 1 and the portions of these units in various plants are shown in the Table 1.
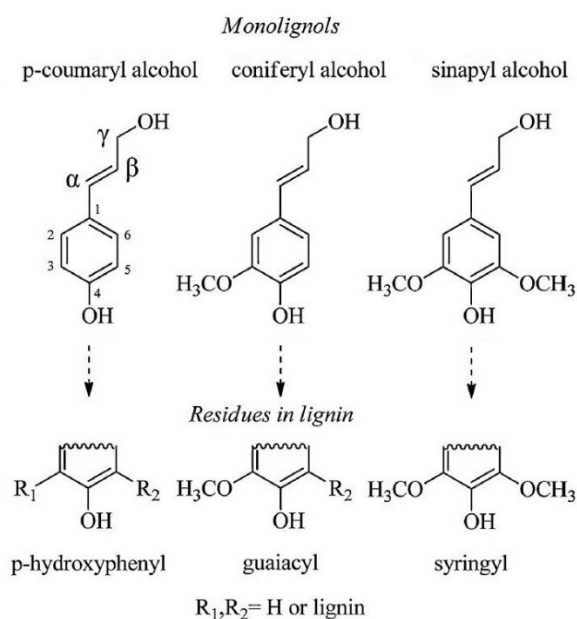


**Figure 1.** Three main precursors of lignin and their corresponding structures /6/.

**Table 1.** Portion of monolignols in various plants /7/.

| Plant type | p-Coumaryl alcohol | Coniferyl alcohol | Sinapyl alcohol |
|---|---|---|---|
| | | (%) | |
| Softwoods (SW) | <5[a] | >95 | 0[b] |
| Hardwoods (HW) | 0-8 | 25-50 | 45-75 |
| Grasses | 5-35 | 35-80 | 20-55 |

[a] Higher amount in compression wood.
[b] Some exceptions exists.

The exact structure of native lignin is still unclear, because studies have determined that the structure of lignin is modified during isolation and the isolated structure depends significantly on the isolation method. Lignin content in softwoods is known to be higher than in hardwoods, whereas, hardwoods' lignin content is higher than grasses and annual plants. /8/ Lignin compounds can be divided broadly into two different categories, ether (C-O) linked lignins and carbon-carbon (C-C) linked lignins. These two groups contain β-O-4-, 5-5-, β-5-, 4-O-5-, α-O-4-, β-1- and β-β-linkages, from which the β-O-4-linkage is the most predominant. /9/ The higher proportion of β-O-4- and β-β-linkages in hardwood lignin causes the structure to be more linear and less branched in comparison to softwood lignin. Softwood lignin has higher proportion of β-5- and 5-5-linkages, which leads to more branched and cross-linked structure. /5/ The main linkages in lignin are illustrated in the Figure 2 and the typical portions of these bonds are shown in the Table 2.

The interest in the use of lignin is partly caused by the high variety of functional groups in lignin: aliphatic and phenolic hydroxyls, carboxylic, carbonyl and methoxyl groups. The phenolic hydroxyl groups and methoxyl groups are important for the reactivity of the lignin. The abundance of these chemical sites offers a variety of possibilities for chemical modification and suggests that lignin could be used as a feedstock for range of chemicals. /5, 6/ The content of these functional groups is dependent on the origin of the lignin. Also processing, *e.g.* kraft pulping, affects the composition of the functional groups. /10/
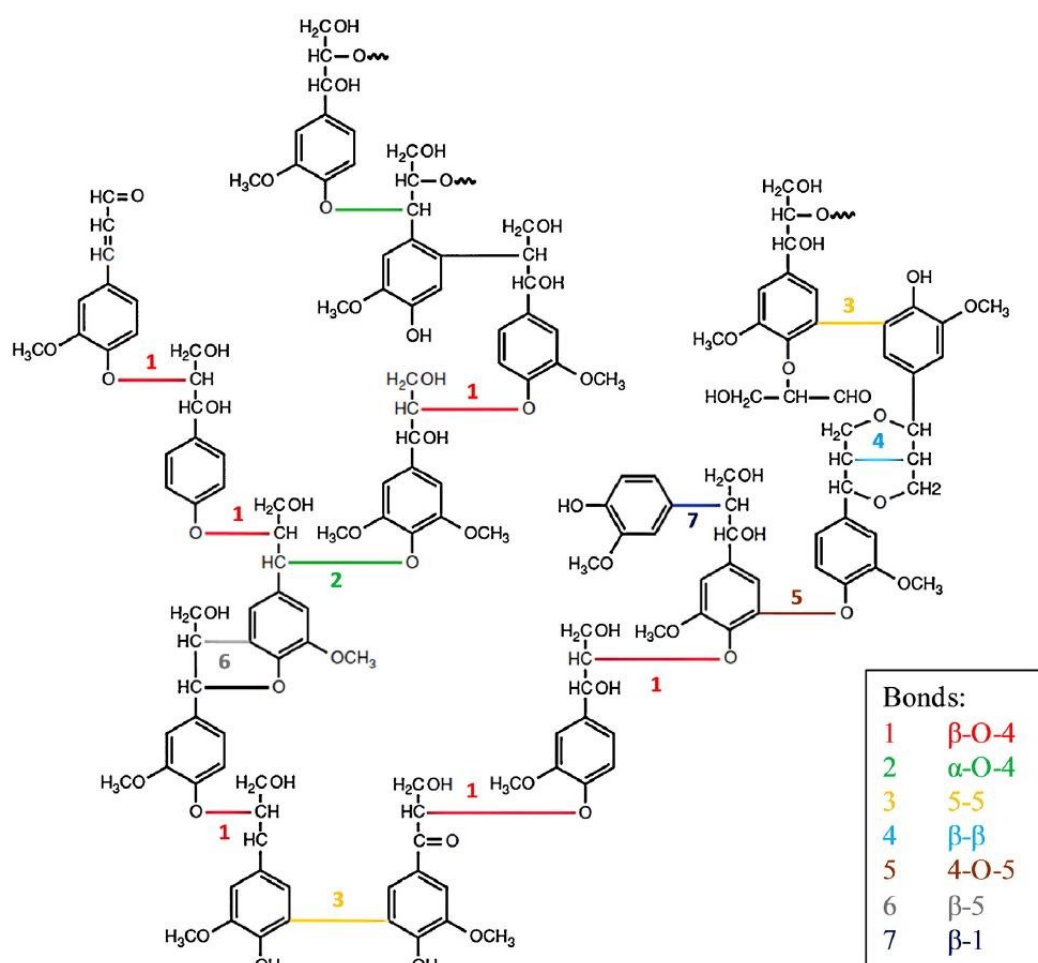
**Figure 2.** Softwood lignin's main linkages /6/.

**Table 2.** Typical proportions of major linkages in lignin /8/.

| Linkage type | SW (Spruce) (%) | HW (Birch) (%) |
|---|---|---|
| β-O-4-Aryl ether | 46 | 60 |
| α-O-4-Aryl ether | 6-8 | 6-8 |
| 4-O-5-Diaryl ether | 3.5-4 | 6.5 |
| β-5-Phenylcoumaran | 9-12 | 6 |
| 5-5-Biphenyl | 9.5-11 | 4.5 |
| β-1-(1,2-Diarylpropane) | 7 | 7 |
| β-β-(Resinol) | 2 | 3 |
| Others | 13 | 5 |

## 2.2 Technical lignins

Technical lignin is a general term for lignins that have been separated in an industrial process. The properties of these lignins vary depending on the source plant, the growth environment and the separation technique used. Generally, the end-product from the separation processes can be divided into two categories: i) sulfur lignins, and ii) sulfur-free lignins. Compared to the origin of the lignin, the separation technique used has more significant effect on the lignin properties, and as a result, each technical lignin type has to be considered individually. /6/ This division is illustrated in the Figure 3. The main properties and the separation methods of these lignins are presented in this section, apart from kraft lignin, which is presented in the next chapter in more detail.
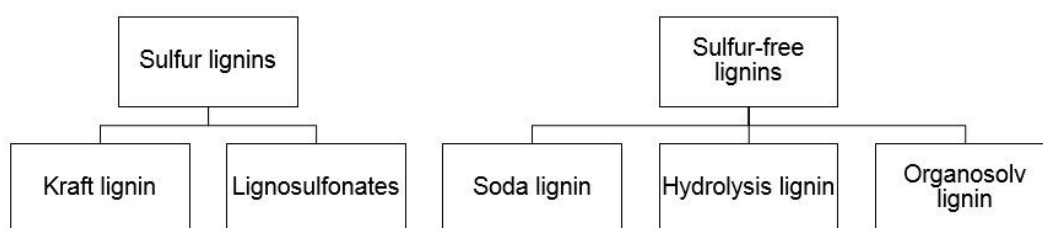


**Figure 3.** Division of technical lignins.

## 2.2.1 Lignosulfonates

Lignosulfonates are obtained from sulfite pulping process, where wood is digested at 140-170 °C with an aqueous solution of sulfite ($SO_3^{2-}$) or bisulfite ($HSO_3^-$) /11/. The most dominant sulfite processes nowadays are acid bisulfite (pH 1-2) and bisulfite processes (pH 3-5), where the base cation is $Mg^{2+}$. Sulfite pulping was originally developed around acid calcium bisulfite process, but due to the problematic chemical recovery it has been replaced with other bases. The most dominant of these bases is magnesium, as mentioned before, but also sodium and ammonium have been used in sulfite pulping. The pH of the sulfite pulping is dependent on the type of salt used in the process, *e.g.* the use of magnesium bisulfite results to acidic conditions, whereas the use of sodium sulfite results to alkaline conditions. /12/

The lignin degradation reaction during acid sulfite pulping can be divided into three categories: sulfonation, hydrolysis and sulphitolysis. The most prevalent reaction of the three is sulfonation, which renders lignin molecules hydrophilic and the hydrophilic lignin molecules are dissolved into the cooking liquor. Sulfonation reaction has a strong dependency to pH and the reaction rate is faster at lower pH values. The second reaction category, hydrolysis, mainly cleaves the linkages between lignin and carbohydrates, but to smaller extent, also inter-lignin bonds are hydrolyzed. The β-O-4 bonds that are highly dominant in both hardwoods and softwoods are rather stable at acidic conditions, hence the cleavage of these bonds can only be accomplished at a higher pH range. During neutral sulfite pulping and in a presence of strong nucleophiles ($SO_3^{2-}$ or $HSO_3^-$), the β-O-4 bonds become less stable and undergo sulphitolytic cleavage. Neutral conditions favors the reactions of phenolic lignin structures, whereas during the acidic sulfite pulping the reaction rate of the sulfonation of phenolic units is only slightly higher than the reaction rate of the nonphenolic units. Apart from degrading reactions, there is also the possibility for condensation reactions, which counteracts the delignification by forming new stable carbon-carbon linkages. Increase in acidity favors condensation reactions, but these reactions can be prevented at least to some extent by keeping the bisulfite ion concentration high enough. /12/

Lignin from sulfite pulping contains 4 - 8% sulfur depending on the source and this sulfur is mainly in sulfonate groups, although other types of sulfur compounds are also present. Due to the sulfonate groups, the lignosulfonates are water soluble and do not dissolve in organic solvents. Apart from sulfonate groups, lignosulfonates also have phenolic hydroxyl, aliphatic hydroxyl and carbonyl groups. /11/ Compared to other technical lignins the molecular weight range of the lignosulfonates is rather wide, from 200 up to 150 000 /13/. Lignosulfonates are obtained from spent sulfite liquor, which contains also carbohydrates. For industrial applications the carbohydrate content of the lignosulfonates has to be low. Low carbohydrate content lignosulfonates can be obtained via ultrafiltration /14/. Also fermentation of the spent liquor sugars and chemical degradation have been used for separation of lignosulfonates /11/. The main applications for lignosulfonates include: stabilizers in colloidal suspensions, animal feed binders and cement additives /15/.

## 2.2.2 Soda lignin

Soda lignin is a product from soda or soda-anthraquinone pulping, which are used mainly for cooking of annual crops such as flax, straws and bagasse. Compared to kraft cooking, the main difference comes from the sulfur-free cooking liquor. /15/ In the cooking process the fibrous feedstock is digested in an aqueous solution of sodium hydroxide and the cooking temperature is kept at 160 °C or lower. The cooking temperature is lower compared to kraft process, because the non-wood fibers have more accessible structure and the lignin content is lower than in wood fibers. Because the soda cooking uses mainly annual plants, one main challenge in the soda process is the high silica content of the feedstock. /11/

Lignin from soda cooking can be recovered by acid precipitation. Lignin that is degraded during soda cooking is soluble in alkaline conditions, so in order to recover the lignin, the pH of the spent liquor is reduced and the lignin starts to precipitate. Soda lignin is sulfur-free, so the chemical composition can be considered to be closer to natural lignin in comparison to kraft lignin or lignosulfonates, and it can be more readily used in applications where the manufacturing process involves heat and the production of sulfurous emissions are undesirable. Compared to lignosulfonates, soda lignin also has a low molecular weight and can be obtained with low levels of contaminants, *i.e.* sugars and ash. The main applications, at the moment, for soda lignins include: use as a component in phenol formaldehyde resin, use as dispersant and use as dietary fiber for animals. /11/

## 2.2.3 Hydrolysis lignin

Hydrolysis lignin is a product that is obtained from bioethanol production. During bioethanol production the polysaccharides in the raw material are hydrolyzed to their monomeric constituents and used for fermentation. The lignin is mainly undissolved and usually the lignin rich residue is used for energy production. /15/ Bioethanol production technologies involve typically a pretreatment, which is designed to cleave the linkages between lignin and carbohydrates. Most of these pretreatment methods rely on acids. These acids can be added mineral acids or they can be generated from the biomass during the pretreatment. The acid

pretreatment degrades lignin, although some condensation reactions may also happen. /11/

The lignin that is obtained from enzymatic hydrolysis has been reported to be more reactive than kraft lignin or lignosulfonates /16/, whereas the lignin from sulfuric acid hydrolysis has been reported to have low reactivity and have a more condensed structure /17/. Hydrolysis lignins have usually quite high carbohydrate content, up to over 20%, although the amount varies depending on the used hydrolysis method and the raw material /18, 19/. Also the enzymatic hydrolysis lignin contains protein contaminants /20/. One main application for hydrolysis lignin is sorbents, due to the good sorption properties /15/. Hydrolysis lignins have been also tested in phenol formaldehyde (PF) production /16/.

## 2.2.4 Organosolv lignin

Organosolv lignin is a co-product from organosolv pulping, where the cooking liquor is a mixture of organic solvent/solvents and water. The most common solvents used in organosolv processes include alcohols such as methanol and ethanol (usually with circa 50% of water), organic acids such as acetic and formic acid and mixed solutions consisting organic solvent and inorganic alkali chemicals. /21/ The delignification in organosolv processes is based on solubilization of lignin and this enables the production of less modified lignin in comparison to lignosulfonates and kraft lignin /15/. Also, because the delignification is based on the solubilization of lignin, the lignin can be recovered from the spent liquor by precipitation. Lignin can be precipitated by adjusting the spent liquor temperature, pH and concentration. /22/

Generally, organosolv lignins have relatively high purity, low molecular weight and low polydispersity ($M_w/M_n$) /22/. Organosolv lignins are hydrophobic and they have been used as fillers in the ink, varnish and paint formulations. However, organosolv lignins are also suitable to be used in the same applications as kraft and soda lignin, although the use in adhesives and binders is rather limited, due to the low molecular weight. /15/

# 3 Kraft lignin

Kraft lignin is produced in the sulfate (kraft) cooking process, in which, 90 to 95% of the lignin in wood is degraded and dissolved in aqueous solution of sodium hydroxide (NaOH) and sodium sulfide ($Na_2S$). Lignin is degraded into different size fragments and these fragments form major constituent of the spent cooking liquor, which is called black liquor. /12/ Kraft cooking is the most dominant pulping process at the moment and it constitutes about 85% of the world's lignin production, which is estimated to be 50 million tons of lignin annually. Nonetheless, only about 2% of the produced lignin is utilized for low-value products, *e.g.* bonding agents. The rest of the produced lignin is burned in the recovery boiler to re-generate cooking chemicals and energy, which is utilized as steam and electricity. In addition to what is needed for the recovery of cooking chemicals from black liquor, the modern pulp mill produces surplus of energy, which would allow extracting part of the dissolved lignin and its use in the production of more valuable products. /15, 23, 24/

## 3.1 Lignin reactions during kraft cooking

Several reactions take place during kraft cooking, these include the cleavage of lignin-carbohydrate linkages, lignin reactions with hydrosulfide ion, lignins condensation and depolymerization. The predominant reaction that occurs is the cleavage of the phenolic β-O-4-linkages, which produces new phenolic groups. The result of this reaction is a large decrease in the molecular weight of lignin and the degraded lignin becomes more hydrophilic, due to the new phenolic groups. The main intermediate of these reactions is quinone methide, which can react with hydrosulfide ions and produce benzyl thioalcohol structure. Thiol group in the α-carbon is strongly nucleophilic species, which displaces the aryl ether attached in the β-carbon. This reaction results to depolymerization of lignin and formation of a phenolic hydroxyl group in the displaced aryl group, which increases lignin's solubility in alkali. /11, 12, 25/

The quinone methide has also three other reaction pathways that can occur during the cooking process: elimination, side chain reduction and condensation reaction pathway /25/. During the elimination pathway, the quinone methide loses the γ-

hydroxymethyl group and is converted into alkali resistant enol ether, which may even survive the kraft cooking. In the side chain reduction pathway, the aryl ether that is attached to the β-carbon is cleaved of by the reduction of the carbon side chain. The last reaction pathway is still under debate, because the conclusive evidences of the condensation reactions are still missing, but it is thought that, during the condensation, stable carbon-carbon bonds are formed between lignin units or between lignin and polysaccharide peeling intermediates. /12, 26/ All the reaction pathways for the quinone methide are illustrated in the Figure 4.
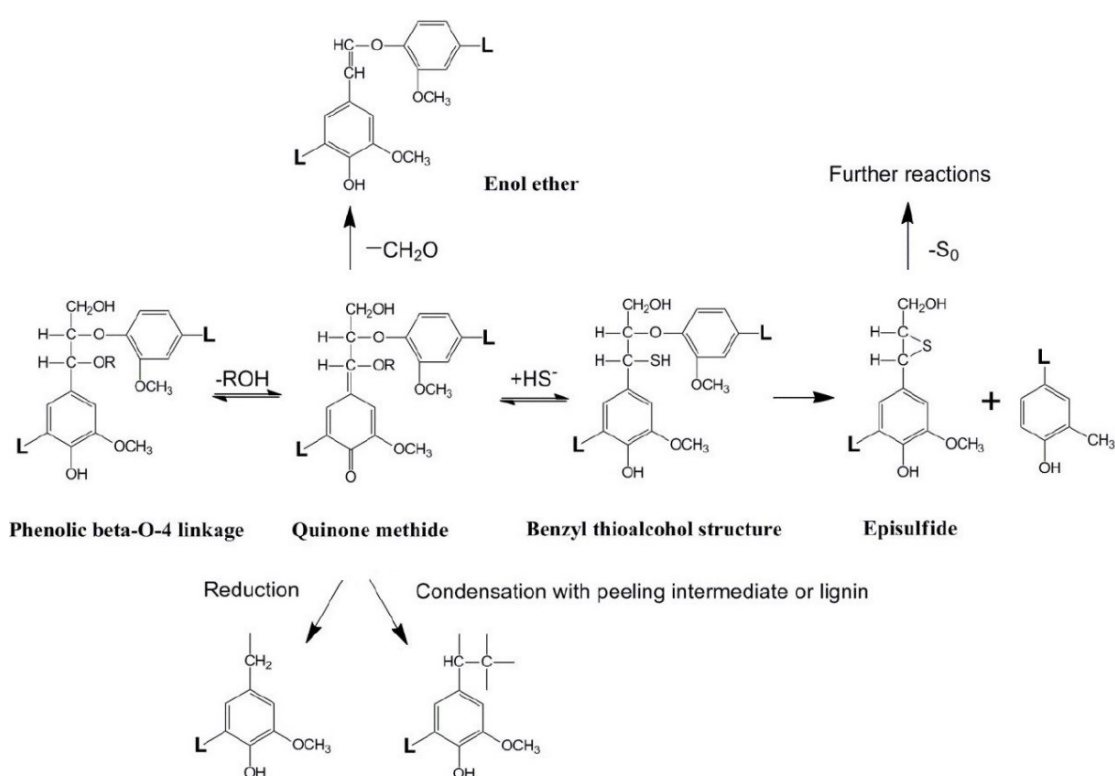


**Figure 4.** β-O-4 structure reactions during cooking. **L** denotes lignin residues./25/

The non-phenolic groups are more difficult to degrade than the units that have a free phenolic hydroxyl group. The cleavage of these non-phenolic lignin units require severe conditions, *e.g.* high temperature or alkalinity, and the cleavage involves the attack of an ionized hydroxyl present on the α- or γ-carbon. /12, 27/ The result of this reaction is the formation of an epoxide structure together with a new phenolic end-group /25/. The formed epoxide structure can react further with either hydrosulfide or hydroxyl ions. It is also possible that the epoxide structure

reacts with carbohydrate hydroxyl group, which results to formation of a new lignin-carbohydrate ether bond. /12/ These reactions are illustrated in the Figure 5 below.
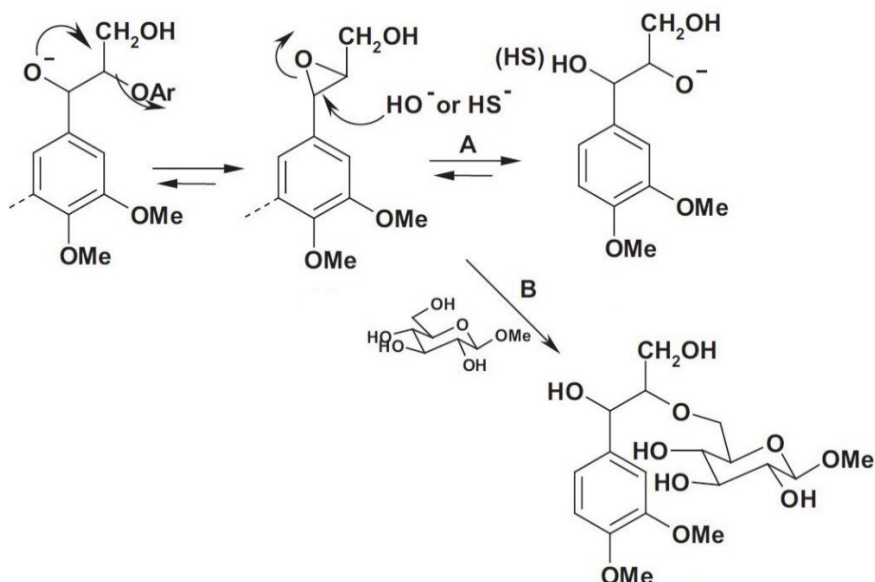


**Figure 5.** Non-phenolic lignin units' reactions during kraft cooking /12/.

### 3.2 Lignin-carbohydrate complex

In addition to lignin, carbohydrates, *i.e.* cellulose and hemicellulose, are other major constituents of wood cell wall. Carbohydrates have been reported to be chemically bonded with lignin and these covalently bonded complexes are often called as "lignin-carbohydrate complex" (LCC). The proposed connection point between lignin and carbohydrates, in most cases, is the α-position of the lignin precursor unit. /25/ Four different linkage types between native lignin and carbohydrates have been proposed and these linkages are illustrated in the Figure 6 /28/. The main hemicellulose in hardwoods is xylan and its content varies between 15 - 30% of dry wood, whereas the main hemicellulose in softwoods is galactoglucomannan (GGM). The GGM content in softwoods is usually around 20% of the dry matter. /25/
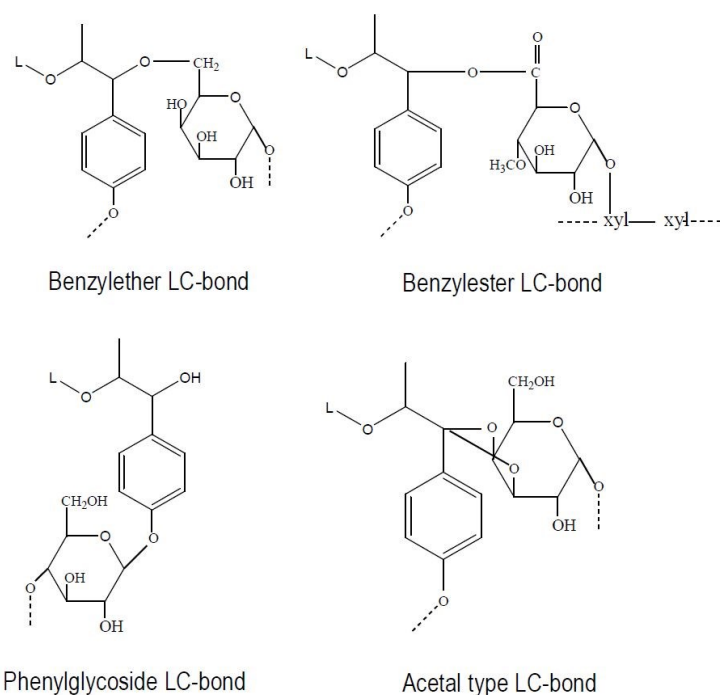
**Figure 6.** Proposed lignin-carbohydrate bonds /28/.

As mentioned before, some studies have reported that stable carbon-carbon bonds are formed between lignin units or between lignin and polysaccharide peeling intermediates during cooking /26/. However, other studies have reported the opposite results, where no new bonds between lignin and carbohydrates were found during kraft cooking. It was suspected that the bonds found in the pulp were a result of enrichment rather than a formation of new bonds. /29, 30/ Lawoko et al. (2006) found that the lignin in spruce (*Picea abies*) wood cell wall was linked through covalent bonds to all major polysaccharides, *i.e.* arabinoglucuronoxylan, galactoglucomannan, glucomannan, pectin and cellulose. Almost 90% of the lignin was found in glucomannan-lignin-xylan LCCs. Lawoko also suggested that carbohydrate-free lignin is not present in the native spruce wood. /31/ Later Lawoko et al. (2005) found out that the predominant LCC in spruce kraft pulp was also glucomannan-lignin-xylan, which could indicate that at least part of the LCCs in kraft pulp originate from native wood lignin /32/.

It is assumed that during kraft pulping the lignin and hemicellulose disintegrate, which results to formation of smaller LCC fragments. These fragments are then dissolved in black liquor. These fragments can be either branched or rather linear. It has been shown that xylan is preferentially linked with more linear type of lignin, which results to formation of a more linear LCC, whereas GGM is predominantly linked to branched lignin. Because of this behavior, the xylan-lignin bonds are more easily degraded and dissolved during kraft pulping. /33/ Nonetheless, GGM is still degraded more extensively during kraft pulping, which is partly caused by the lack of substituents that could hinder the peeling reactions /12/.

### 3.3 Characteristics of kraft lignin

Kraft lignin has few characteristics that separate it from native lignin and other technical lignins. The extended cleavage of β-aryl bonds during cooking results to an increased amount of phenolic hydroxyl groups. Also some biphenyl and other condensed structures can be found, due to the severe cooking conditions. Usually the portion of condensed structures increases with increased cooking time. /15/ The oxidative conditions during delignification can increase the amount of carboxyl groups as well as cause formation of quinone and catechol structures /27/. The unpurified kraft lignin also has high ash content, but due to the hydrophobic nature of kraft lignin, these contaminants can be removed by washing or by diluted acid treatment /11, 19/.

Although industrial kraft lignin has a relatively high degree of purity, it still contains some carbohydrates. The carbohydrate content of kraft lignin usually varies around a few percent, depending on the source of the lignin /4, 34, 35/. Recent studies indicate that the carbohydrate moieties in kraft lignin seem to be more predominant in the high molecular weight fractions /36, 37/. Kraft lignin contains also some sulfur, which is mostly present in thiol (-SH), sulfide (-S-) and disulfide bonds (-S-S-) that are formed during cooking. These sulfur units are difficult to remove as they are chemically bonded to lignin. /15, 38/ Sulfur can be also be present as inorganic (sulfate ions) or as elemental sulfur, although the amount of these forms is much lower compared to the chemically bound sulfur /38/. The major chemical properties of kraft lignin compared to other technical lignins are shown in Table 3.

**Table 3.** Comparison between various technical lignins.

| Lignin type | Ash (%) | Sugars (%) | S (%) | $M_w$ (g/mol) | $M_w/M_n$ | Reference |
|---|---|---|---|---|---|---|
| KL | <3.0 | <2.3 | 1.5-3.0 | 1500-5000 | 2.5-3.5 | /11, 15, 19/ |
| SL | 0.7-2.3 | 1.5-3.0 | 0 | 1000-3000 | 2.5-3.5 | /15, 39, 40/ |
| LS | 4.0-8.0 | - | 4.0-8.0 | 200-150000 | 4.2-7.0 | /13, 15, 19/ |
| HL | 1.0-3.0 | 10.0-22.4 | 0-1.0 | 5000-10000 | 4.0-11 | /15, 19, 39/ |
| OSL | 1.7 | 1.0-3.0 | 0 | 500-5000 | 1.5 | /15, 39, 40/ |

where, KL is Kraft lignin,
SL is Soda lignin,
LS is Lignosulfonates,
HL is Hydrolysis lignin and
OSL is Organosolv lignin

## 3.4 Applications for kraft lignin

As mentioned earlier, only a small fraction of the produced kraft lignin is utilized in other applications than cooking chemical recovery and energy production in the pulp mill. Nonetheless, kraft lignin has potential to be used in a great variety of applications, ranging from fuel applications to high value materials and chemicals. This subchapter gives a short review on the current kraft lignin application research.

### 3.4.1 Chemicals

Lignin is a very interesting material for chemical production as it is the largest renewable source of aromatics on the earth /21/. The chemicals that could be produced from lignin can be divided into two distinctive categories: i) platform chemicals and ii) fine chemicals. Platform chemicals, such as benzene, toluene and xylene, can be used in the synthesis of fine chemicals using technology already developed in the petroleum industry. In principle, the production of platform chemicals is based on lignin reduction reactions, such as cracking or catalytic reduction reactions, whereas the fine chemical production is based on catalytic oxidation reactions. /41/

Cracking is commonly used process in the modern petroleum refineries. The purpose of cracking is to convert various higher boiling hydrocarbons into more valuable products, but cracking can be also used to cleave β-O-4 aryl ether and unstable C-C bonds in lignin. During lignin cracking, lignin typically depolymerizes to a wide variety of products. /42/ The catalytic lignin reduction reactions are based on hydrogenation or hydrodeoxygenation reactions in the presence of catalyst. Compared to the reduction reactions that tend to disrupt and remove functionality in the lignin, the oxidation reactions aim to form more complex aromatic compounds with increased functionality. These chemicals can serve as platform chemicals for subsequent organic synthesis or they can serve as fine chemicals. All the above mentioned reactions are catalyst-based reactions. For lignin, a very broad range of catalysts has been researched and they can be divided into hetero- and homogenous catalysts and electrocatalysts. For more a detailed review on the catalytic valorization of lignin, one can read the review published by Zakzeski et al. /41/

Different technical barriers have been reported when concerning with lignin-based chemical production. As the chemical production methods rely on catalytic reactions, one concern is the general lack of detailed information concerning the performance of the catalysts during lignin valorization. Also the purity of the raw material lignin should be high, because different impurities, such as inorganic salts, may poison the catalysts. /41/ One major challenge is also the need to develop lignin depolymerization techniques that are more selective /43/. Based on the report by the U.S. Department of Energy, the chemical production from lignin has huge potential, but it is listed as a long-term opportunity, due to the need for further technology development and research /44/.

### 3.4.2 Activated carbon

Activated carbon is a sorbent material that has very porous structure and large internal surface area (500 - 2000 $m^2$/g). Activated carbon has been used to remove pollutant, both organic and inorganic, from liquid and gas phases. There are two main forms of activated carbon: powdered and granular. Powdered activated

carbon is composed of fine particles and it has a very high adsorption rate. Granular activated carbon, on the other hand, is composed of larger carbon particles and it is usually preferred for the adsorption of gases. Two different methods have been used for the activation of carbon-based materials: physical activation and chemical activation. Physical activation is generally performed in two steps. During the first step, carbonization, char is formed at high temperatures in inert atmosphere. In the second step, the char is put in contact with an oxidizing gas, *e.g.* $CO_2$, and the result is formation of a microporous structure. In the chemical activation, carbonization and activation happens simultaneously. Chemical activation is performed at elevated temperatures in inert atmosphere, while the material is impregnated with certain chemical, *e.g.* $H_3PO_4$, KOH or NaOH. /45/

It has been shown that the production of activated carbon from kraft lignin via physical activation /46/ and chemical activation /47/ is possible. In these experiments, the highest surface areas of the produced activated carbons were 1360 $m^2$/g and 1459 $m^2$/g respectively, which is in the range of commercial activated carbons /45, 46, 47/. Also the adsorption capacity of lignin-based activated carbons has been comparable to other activated carbons. These results have shown that the activated carbon could be one possibility for lignin valorization. Although, some issues that should be solved still exist, *e.g.* the relationship between the molecular structure of the lignin and the adsorption capacity. /45, 47/

### 3.4.3 Fuel/Energy

Lignin is currently used mainly for energy production and cooking chemical regeneration in the recovery boiler at the pulp mills, but if lignin is recovered from black liquor, it could be used also for other fuel/energy production applications. These applications can be divided into several different categories, *e.g.* solid fuels, liquid fuels, hydrogen, synthetic alcohols and Fischer-Tropsch liquid fuels. /21/ Lignin's heating value can be up to 26.6 MJ/kg, which is considerably higher than the heating value of cellulose (up to 19.0 MJ/kg) and hemicelluloses (up to 18.2 MJ/kg). The use of kraft lignin as a solid fuel is fairly simple, as it has high energy density and low ash content. Kraft lignin could be used in the pulp mill's lime kiln

as a replacement for natural gas or used as a solid fuel in a power boiler. However, as the solid lignin has a rather low price and the effect of the lignin extraction can be fairly severe on the mill's energy balance, it is important to remember that the viability of lignin separation from black liquor for solid fuel applications should be considered case-by-case. Lignin extraction is most viable when the recovery boiler is the bottleneck in the mill, *i.e.* reduction in the recovery boiler load will result to increased pulp production. /48, 49/

Liquid fuels can be produced from lignin via depolymerization. In this context, liquid fuels refers to monomeric aromatic products that can be readily blended into transport fuels with little or no further processing. Several different lignin depolymerization techniques have been experimented, *e.g.* pyrolysis, catalytic hydrogenolysis, alkaline hydrolysis, supercritical water and solvent depolymerization. /21, 50/ Hydrogen, synthetic alcohols and Fischer-Tropsch fuels are also possible to produce from lignin. All these products are manufactured from syngas, which can be produced from lignin via gasification. One technical concern of the syngas-based technologies is the need of syngas purification, which increases the production costs. /21, 44/ Due to the complex structure of lignin and lack of selectivity during lignin depolymerization, the most viable option for lignin-based fuel production will probably be integrated processes that are able to produce a variety of fuels from lignin /21/. More detailed information can be found from different reviews that focus on completely or partly on the fuel production from lignin, *e.g.* Azadi et al. and Laskar et al. /21, 50/

### 3.4.4 Carbon fiber

The main raw material for carbon fiber today is polyacrylonitrile (PAN), which is a synthetic petroleum-based polymer. The production cost of PAN accounts approximately half of the total production cost of carbon fiber, which increases the interest towards finding alternative raw materials for carbon fiber manufacturing. Several different technical lignins have been researched as a replacement for PAN, *e.g.* lignosulfonates, organosolv lignins, steam explosion lignin and kraft lignin. The best mechanical performance so far has been obtained with organosolv

lignin carbon fibers, but the abundance of kraft lignin makes it highly desirable raw material for carbon fiber manufacturing. /5, 51/

The carbon fiber manufacturing process involves spinning, oxidative stabilization at 200 - 300 °C, carbonization, which is done under inert atmosphere at 1000 - 2000 °C, surface treatment and sizing /52/. The spinning process can be wet, dry or melt spinning depending on the raw material. The melt spinning is a relatively inexpensive method, but requires that the raw material has a detectable glass transition temperature ($T_g$) and that the raw material softens upon heating. The thermal behavior and spinnability of lignin depends on the source of the lignin and the isolation method. The impurities in lignin and the large polydispersity have a negative influence on the melting ability of the lignin. High enough polydispersity may result in a non-melting lignin or a lignin that melts over a broad temperature range. /5/

Carbon fibers have been made successfully from both softwood and hardwood kraft lignin, although untreated softwood kraft lignin has shown poor processability in the spinning /51, 53/. Kraft lignin based carbon fibers do not yet have the same mechanical performance as carbon fiber made from PAN, but these new carbon fiber materials could be used for applications were the requirements for the mechanical properties are not as high /5/. One example is Oak Ridge National Laboratory's lignin-based carbon fiber insulator, which has better performance than the existing pitch based carbon fiber insulators /54/.

### 3.4.5 Composites

The use of kraft lignin in composite applications can be broadly divided into two different categories: resin/adhesives and polymer blends /44/. Lignin has been suggested as a candidate for phenol replacement in phenol formaldehyde resins and it has worked to a certain extent. The heterogeneity and the lower reactivity of the lignin has proven to cause problem in these applications. /55, 56/ Other interesting resin/adhesive application is to use kraft lignin in epoxy resins. In epoxy resin applications, the used lignin has to be impurity free, *i.e.* free from water, salts

and sugars, but the lignin-based epoxy resins have shown good performance even with relatively significant lignin fractions (up to 50 w-%). /55/

Kraft lignin has been also tested in different polymer blends, such as the incorporation of lignin into polyolefins and production of lignin-based polyurethane /57/. The incorporation of kraft lignin into polyolefins has produced varying results concerning the mechanical performance of the products, but it is certain that the lignin addition will increase the biodegradation, which is beneficial when dealing with polyolefin-based products /55/. Lignin can be used for polyurethane production without chemical modifications, but modest accessibility of the lignin's hydroxyl groups and the performance of the manufactured product has led to the use of three component systems and the use of chemically modified lignin, *e.g.* esterified lignin /58, 59/. Three component systems try to overcome these restrictions by introducing a linear polyol, such as polycaprolactone, into the manufacturing process /59/.

Several different methods for lignin modification have been researched in order to improve the usability of lignin in composite applications. These modifications aim to increase the chemical reactivity of lignin, reduce the brittleness of lignin-derived polymers, increase the solubility of lignin in organic solvents and improve the processability of lignin. These modifications can be divided into two categories: i) increasing the reactivity of the hydroxyl groups and ii) synthesis of new chemically active sites. The reactivity of the hydroxyl groups can be increased *e.g.* via esterification, etherification, phenolation and urethanization, whereas new chemically active sites can be synthesized *e.g.* via alkylation/dealkylation, hydroxyalkylation and amination. /6/

# 4 Lignin separation methods

Different techniques have been suggested for the separation and purification of kraft lignin. These techniques are based on the solubility of lignin or on the molecular weight/size of lignin. In this chapter, ultrafiltration and acid precipitation are described more closely. Both of these treatment techniques are technically available, but it has been reported that ultrafiltration would have higher capital and operational costs. /25/

## 4.1 Ultrafiltration

Ultrafiltration has been suggested as one possible method for the extraction of lignin from black liquor. The main benefits in ultrafiltration are that the liquor can be withdrawn from any position in the mill, without adjusting the pH or temperature, and the possibility to control the molecular mass of the extracted lignin by the membrane cut-off. Ultrafiltration has been used to extract lignin from the cooking liquor loop and from the evaporation unit /60/. Jönsson et al. (2007) estimated the production costs for lignin extraction from two process streams by ultrafiltration with a cut-off of 15 000 Da. The result was that the extraction from modified continues cooking (MCC) loop costs about 60 €/t of lignin and the extraction from black liquor from evaporation unit costs about 33 €/t of lignin. /61/ These two extraction points are illustrated in the Figure 7.
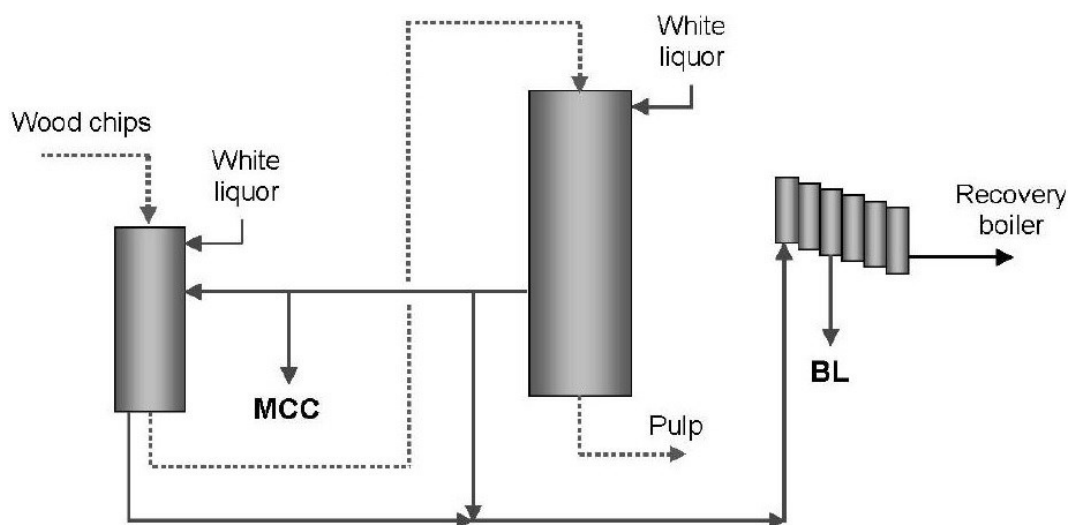


**Figure 7.** Lignin extraction points from continuous kraft cooking /61/.

Ultrafiltration is a cross-flow filtration (CFF) technique. During CFF the liquid sample flows parallel to the filter media. By creating a transmembrane pressure (TMP) across the membrane, the liquid is forced towards the membrane. Particles that are smaller than the membrane's pores will pass through the membrane as permeate and the bigger particles will be remained in the liquid sample as retentate. The pore size during ultrafiltration is about 10 - 100 nm. The cross-flow velocity, parallel to the filter media, is relatively high, and the flow is turbulent, which ensures that the feed flow will reduce the build-up of particles and molecules on the membrane surface. Ultrafiltration filter unit and filtration unit are illustrated in the Figure 8 below. /62/
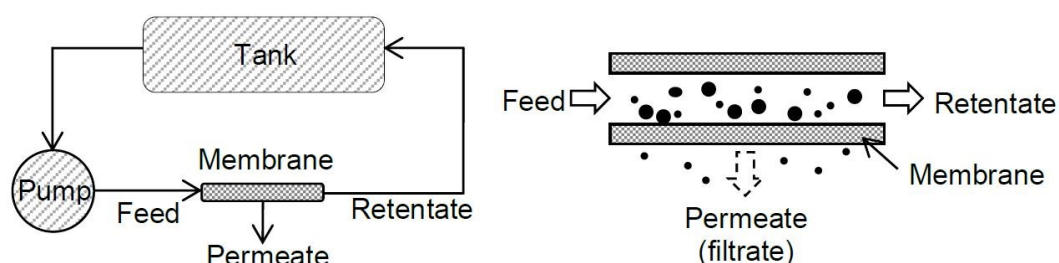
**Figure 8.** Filtration unit (on the left) and a cross-section of a tubular filter unit /62/.

The lignin obtained from ultrafiltration has smaller polydispersity compared to the original black liquor. The characteristics of the ultrafiltration retentate and permeate can differ considerably. /63/ Several studies indicate that the carbohydrates are linked to the highest molecular mass portion of the kraft lignin /37, 60, 63, 64/. These findings indicate that the production of nearly carbohydrate free lignin could be possible, if the low molecular mass fraction is recovered efficiently. Although the ultrafiltration permeate has less carbohydrate impurities, the ash content and especially the sulfur content is concentrated to the lower molecular mass portion of the lignin /37, 60/.

The product from ultrafiltration is a lignin-rich liquid stream. This stream could be used in the acid precipitation process, which is described in the next chapter, to obtain relatively high purity lignin. The produced lignin from combined ultrafiltration and acid precipitation has smaller polydispersity and carbohydrate content than

the lignin obtained from black liquor by acid precipitation. Ultrafiltration also improves the filtration properties of the lignin during the acid precipitation, which is thought to be caused by the smaller carbohydrate content. /63, 65/

## 4.2 Acid precipitation

The acid precipitation process is fairly simple. Traditionally the lignin separation is done by lowering the pH of black liquor with carbon dioxide ($CO_2$) or mineral acids. The precipitated lignin is then filtrated and washed. /64/ The traditionally separated lignin quality is not very good, it has relatively low total dry solids (TDS) and high ash content /66/. Also the separation process has some problems, due to the poorly functioning filtration and washing step. Washing has been done using displacement washing, which has resulted to partial or complete plugging of the filter cake and/or the filter media. This has led to poor washing results and the produced lignin has had very high levels of impurities. The reason for the poor results has been thought to be due to excessive pH and ionic strength gradient in the lignin cake during the washing. /67/

A new washing method was introduced by Öhman et al. (2007), where the traditional single step filtration/washing was replaced with two separate filtration steps. These two steps were separated by a re-suspension step at lower pH (2-4). The re-suspension step ensures that the pH change and most of the change in the ionic strength will not take place in the filter cake during washing, which improves the end product quality. /67/ Figure 9 illustrates an acid precipitation process, where the lignin separation is done by using two-step filtration. The process uses black liquor from the evaporation plant, which dry solids (DS) content is 30 - 45%. The black liquor is acidified with $CO_2$ and the suspension is allowed to mature, which improves the filtration properties of the precipitated lignin. After maturing the lignin suspension is filtered and the lignin precipitate is re-dispersed. The re-dispersed solids are filtered and washed with sulfuric acid or spent acid from $ClO_2$ plant. /68/
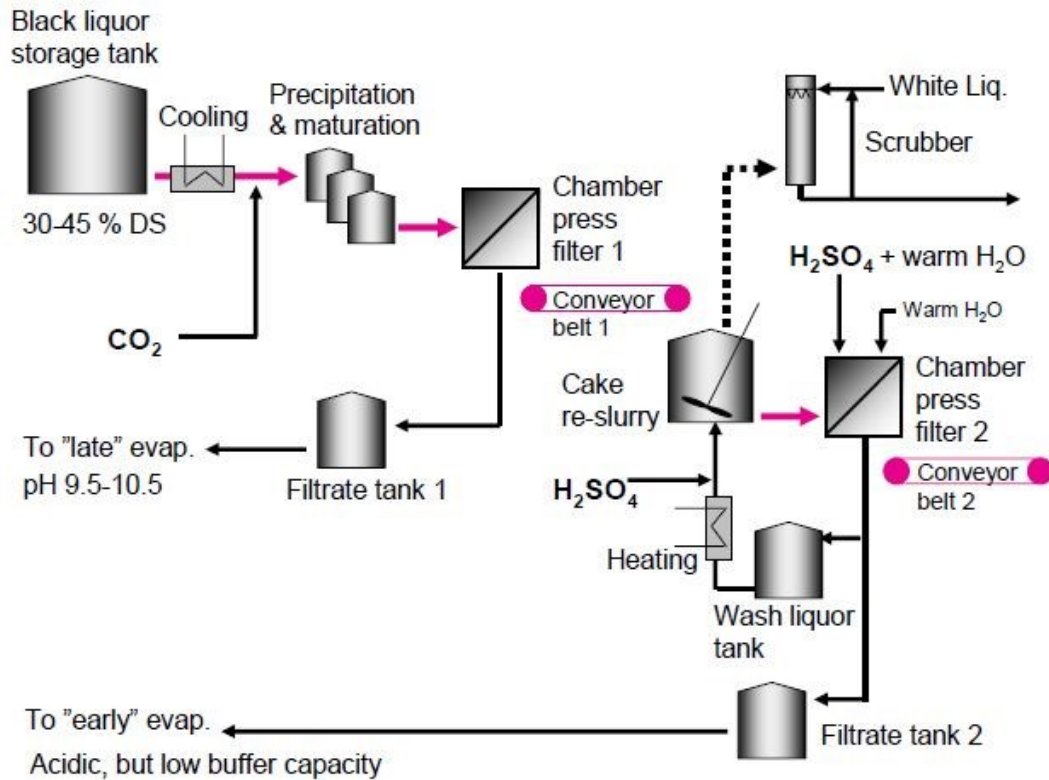
**Figure 9.** Acid precipitation process with two-step filtration /69/.

Based on the studies, lignin separation using acid precipitation costs around 78 - 317 €/t of lignin. This cost estimation takes into account the losses in the electricity production and management of mill's chemical balance. /70/ If the losses in the electricity production and the mill's chemical balance are not taken into account, the production costs drops to around 25 - 63 €/t of lignin. This estimation is based on the direct chemical costs of the precipitation process. In these calculations the biggest variable is the cost of $CO_2$. /69/ $CO_2$ should be preferred in the precipitation, because it does not disturb the chemical balance of the mill. Also the washing step should be effective, because sodium enriches in the precipitate and it has to be removed and returned to the chemical recovery cycle. If the sodium is not washed out properly it can disturb the sodium/sulfur balance at the mill and cause additional make-up chemical costs. /67/

Black liquor stability is mainly controlled by three different parameters: ionic strength, pH and temperature, of which the ionic strength and pH are the most

important /67/. Lignin starts to precipitate if the ionic strength is increased and/or the pH decreased below a certain point. The precipitation mechanism of acid precipitation can be described to be the coagulation of colloids. /35/ The dissolution of kraft lignin in alkaline conditions is due to the dissociation of carboxylic and phenolic groups, which results to negative surface charge. Dissolved lignin macromolecules are stable, *i.e.* remain in the black liquor solution, due to electrostatic repulsive forces between lignin units. Once acid is introduced, the amount of the hydrogen ions ($H^+$) increases and these ions protonate the negatively charged phenolic groups. Protonation of the phenolic groups leads to neutralization of the surface charge and decrease in the repulsive forces between lignin units. Once the repulsive forces have been reduced, the attractive forces, *e.g.* van der Waals, become dominant and lignin molecules start to aggregate and precipitate. /66/ This precipitation mechanism produces fairly pure lignin. Characteristics of acid precipitated lignin are illustrated in the Table 4.

**Table 4.** Characteristics of acid precipitated lignins.

| Lignin type | Klason lignin (%) | Ash (%) | Sugars (%) | S (%) | $M_w/M_n$ | Reference |
|---|---|---|---|---|---|---|
| SW | 97.5 | 1.0 | 1.5 | nd | 4.5 | /63/ |
| HW | 89.3 | 0.5 | 4.1 | nd | 3.6 | /63/ |
| SW | 91.0 | 0.73 | 1.2 | 2.6 | 5.9 | /10/ |
| HW | 91.0 | 0.47 | 0.67 | 2.9 | 4.3 | /10/ |

where, nd is not determined

# 5 Lignin purification treatments

Although the lignin recovered/separated from black liquor is relatively pure, especially when acid precipitation is applied, some applications, *e.g.* carbon fibers /5/, require nearly contaminant-free lignin. This has led to a need for additional lignin purification methods, which could either be implemented into the existing process or be used as a separate process. The impurities in lignin can be divided into two categories: ash and carbohydrates. In this chapter, a few different methods for lignin purification are described.

## 5.1 Ash reduction

As shown in the Table 4 earlier, acid precipitated lignin contains circa 1% of inorganic material (ash). For some applications it would be advantageous if the raw material lignin would have even lower ash content, *e.g.* in the carbon fiber manufacturing the inorganic particles can introduce voids in the spun fibers and weaken the structure /5/. Kadla et al. reported that the ash content of <0.1% would be desirable for carbon fiber manufacturing, although it is possible to produce carbon fibers with lignin that has ash content of 0.45% /53/. Typical inorganics that are found in the black liquor, are *e.g.* sodium (Na), potassium (K), aluminum (Al), barium (Ba), calcium (Ca), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn) and silicon (Si). In the precipitated lignin, Na and K have a large contribution to the ash content (approximately 75 - 80% of cations are Na and K), but also other metals and metalloids are present in some portions. /68/

One way to lower the inorganic impurities is to keep the pH low in the resuspension/washing stage in the acid precipitation process. Na and K contents in the precipitated lignin are affected by the pH of the resuspension/washing stage. By lowering the pH in this washing stage, the Na and K content of the precipitated lignin decreases. /67, 68/ Other inorganic components are virtually unaffected by the pH level in the washing, but the content of Ca, Mg, Mn, Si and Fe in lignin can be decreased by increasing the retention time of the resuspension stage. However, the increase in the retention time should be fairly high, in order to achieve a significant decrease in the ash content. The relationship between the resuspension

stage retention time and the inorganic content of lignin is illustrated in the Figure 10. /68/ Another very effective way to lower the ash content, is to use ion exchange on isolated lignin. During the ion exchange lignin is dissolved into an acetone/water solution and ran through a cation exchange column. Lignin that is recovered using evaporation has an ash content of <0.1%. /63/
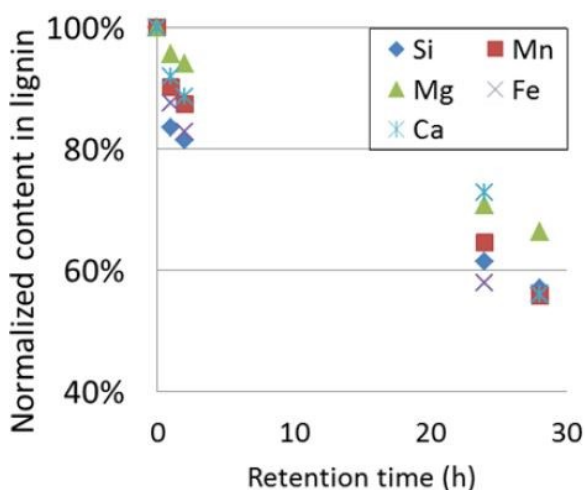


**Figure 10.** Normalized Ca, Mg, Mn, Si and Fe content of lignin as a function of resuspension stage retention time /68/.

## 5.2 Carbohydrate removal

### 5.2.1 Hydrolysis

Hydrolysis techniques can be divided into two categories: i) enzymatic hydrolysis and ii) acid hydrolysis. Although enzymatic hydrolysis has been proposed to be a potential method for hydrolysation of hemicelluloses, it is not suitable for lignin purification. Simple enzymatic hydrolysis is not able to remove all the sugars and although when using combined hydrolysis (enzymatic and acid) the sugar content is reduced to desirable level, the enzymatic hydrolysis introduces new unwanted protein contaminants into the purified lignin. /71/ Acid based hydrolysis techniques have been also used to selectively remove hemicelluloses from biomass. These hydrolysis techniques involving acids can be generally divide into three different categories: i) autohydrolysis, ii) dilute acid hydrolysis and iii) concentrated acid hydrolysis. /12/ Auto-/water hydrolysis is performed in water at 160 - 230 °C. During

autohydrolysis acetyl groups are cleaved from the wood (mainly from xylan), which results to dilute acetic acid solution that catalyzes the hydrolysis reactions. /72/ pH during autohydrolysis ranges between 3 and 4. When using added mineral acid processes (dilute acid or concentrated acid hydrolysis), the hemicellulose solubilization rate is greatly increased. The dilute acid hydrolysis is typically performed in 0.3 - 0.5% $H_2SO_4$ solution at 120 - 140 °C, whereas the concentrated acid hydrolysis is performed in 20 - 30% acid solution at 40 °C.

The dilute acid hydrolysis and auto-/water hydrolysis processes have the most promising process conditions for lignin purification. Concentrated acid hydrolysis processes suffer usually from severe corrosion problems and the chemical costs are higher than in the other techniques. /73/ One way to utilize dilute acid hydrolysis for lignin purification was proposed by Tikka. Tikka suggested in the patent application that during the acid precipitation the temperature in the resuspension stage would be kept between 100 - 140 °C at pH 1 - 3. The reaction time is calculated using P-factor at the process temperature. The resulting p-factor should be under 20 and preferably in the range of 1 - 10. /74/ The P-factor takes account the hydrolysis time and temperature and express them as a single variable /12/.

The auto-/water hydrolysis process has lower hemicellulose removal efficiency compared to the added acid processes, even when the hydrolysis is catalyzed by the acetic acid formed during the hydrolysis /73/. The water hydrolysis is still capable of removing all the sugars from precipitated lignin, if the reaction temperature is high enough. Fang et al. used hot water treatment (HWT) for lignin purification and managed to reduce the sugars nearly, when using reaction temperature over 200 °C.  The effect of the temperature on the sugar content of the precipitated lignin is illustrated in the Figure 11. Although the hot water treatment was able to reduce the amount of sugars to a desirable level, it had a sever effect on quality of the purified lignin. At 220 °C reaction temperature the polydispersity of the precipitated lignin increased from 3.5 to 25.4 and the reactive phenolic groups were eliminated to some extent. /75/
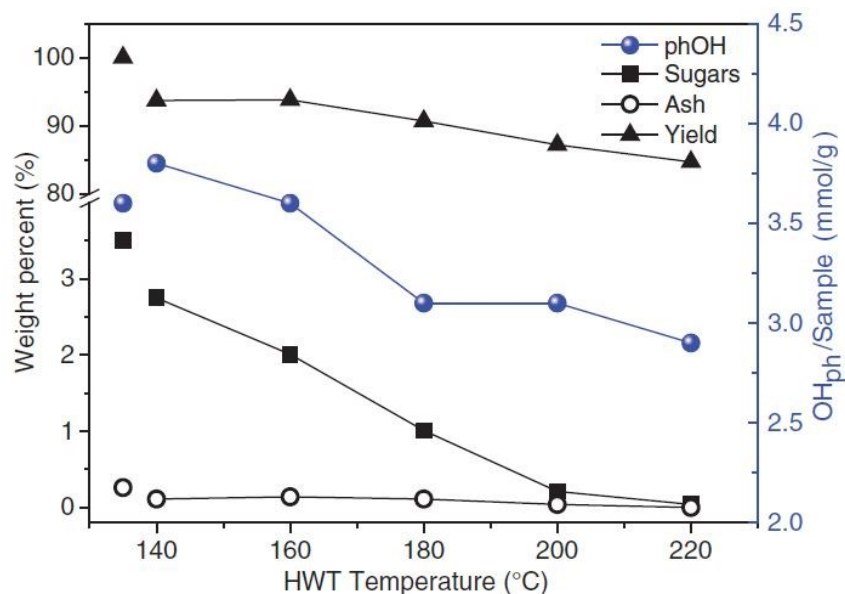
**Figure 11.** Effect of the reaction temperature during HWT /75/.

### 5.2.2 Solvent extraction

The solvent extraction relies on the solubility difference between low molecular mass lignin and high molecular mass lignin. The lignin solubility increases as the hydrogen bonding capability of the solvent increases and the Hildebrand solubility parameter approaches 11, *i.e.* weaker solvents can only dissolve the smaller molecular weight fraction of lignin. /36/ The Hildebrand solubility parameter describes the miscibility behavior of different solvents /76/. During solvent extraction, solid lignin, *e.g.* lignin from acid precipitation, is dissolved into the selected solvent and the mixture is filtrated, in order to recover the insoluble lignin. The soluble fraction of the lignin is recovered from the filtrate via evaporation. /36/ Solvent extraction can be done by using single solvent extraction /77/, where the lignin is divided into two different fractions, or with sequential extraction /78/, where the lignin is fractionated using a combination of solvents.

Solvent extraction can be done using different solvents and solvent combinations. Sequential solvent extraction can be performed with *e.g.* dichloromethane-methanol /78/, ethyl acetate-acetone/water /79/, dichloromethane-propanol-methanol-methanol/dichloromethane, /80/ and hexane-diethyl ether-dichloromethane-methanol-dioxane /81/ extractions. The solubility of lignin in

different solvents is dependent on the origin of the lignin. Softwood lignin appears to be less soluble in most solvents than hardwood lignin. /36, 81/ Although when using same solvents, the molecular mass of the dissolved fractions from softwood and hardwood are fairly similar /82/.

The polydispersity of the dissolved fractions appears to grow when using stronger hydrogen bonding capacity solvents, *i.e.* the fraction that have higher molecular mass, have higher polydispersity /82/. Also the fractions that have the highest molecular mass have the highest carbohydrate content, which is thought to be caused by the enrichment of the LCCs in the high molecular mass fraction. Although the smallest molecular weight fraction is relatively carbohydrate-free, the sulfur content is highest in this fraction. /36, 80/ Similar results have been found also with ultrafiltration, as mentioned earlier. Results from the sequential solvent extraction are presented in the Table 5 below.

**Table 5.** Characteristics of different solvent extracted lignin fraction.

| Lignin/lignin fraction | Solvent | Yield (%) | Sugars (%) | $M_w$ (g/mol) | $M_w/M_n$ | Ref |
|---|---|---|---|---|---|---|
| WY SKL | - | - | nd | 6900 | 4.6 | /36/ |
| F1 | DCM | 4 | 0 | 611 | 1.6 | /36/ |
| F2 | n-propanol | 2 | 0.5 | 1620 | 2.5 | /36/ |
| F3 | Methanol | 26 | 0.7 | 2070 | 2.8 | /36/ |
| F4 | DCM/Methanol | 26 | 0.3 | 5960 | 5.2 | /36/ |
| F5 | Residue | 42 | 0.9 | 3330 | 3.6 | /36/ |
| BY SKL | - | - | nd | 3830 | 4.0 | /36/ |
| F1 | DCM | 1 | 0 | 882 | 2.1 | /36/ |
| F2 | n-propanol | 1 | 0.9 | 2390 | 3.3 | /36/ |
| F3 | Methanol | 42 | 0.4 | 1890 | 4.1 | /36/ |
| F4 | DCM/Methanol | 37 | 0.1 | 6240 | 4.2 | /36/ |
| F5 | Residue | 19 | 5.5 | 7030 | 4.1 | /36/ |
| Indulin AT | - | - | 1.62 | nd | nd | /80/ |
| F1 | DCM | 2.5 | nd | nd | nd | /80/ |
| F2 | n-propanol | 0.9 | 0.32 | nd | nd | /80/ |
| F3 | Methanol | 43.0 | 0.32 | nd | nd | /80/ |
| F4 | DCM/Methanol | 27.3 | 0.73 | nd | nd | /80/ |
| F5 | Residue | 25.0 | 4.34 | nd | nd | /80/ |
| Curan 100 | - | - | 1.78 | nd | nd | /80/ |
| F1 | DCM | 3.1 | nd | nd | nd | /80/ |
| F2 | n-propanol | 1.0 | 0.37 | nd | nd | /80/ |
| F3 | Methanol | 29.8 | 0.83 | nd | nd | /80/ |
| F4 | DCM/Methanol | 20.0 | 0.75 | nd | nd | /80/ |
| F5 | Residue | 41.7 | 2.89 | nd | nd | /80/ |

where, nd is not determined,
WY SKL is Southern pine softwood kraft lignin,
BY SKL is Norwegian spruce softwood kraft lignin,
Indulin AT is commercial softwood kraft lignin,
Curan 100 is commercial softwood kraft lignin and
DCM is dichloromethane

*5.2.3 Liquor heat treatment*

Liquor heat treatment (LHT) is not a novel technology, Kiiskilä and Virkola applied a patent for a liquor heat treatment technology in 1985. At the time, the driving force for this technology was the interest to increase black liquor dry solids content. /83/ Raise in the black liquor dry solids content increases the capacity and the efficiency of the recovery boiler, as well as reduces sulfur dioxide emissions /84/. Once the black liquor dry solid content is increased over 60% the viscosity of the black liquor increases rapidly, which causes problems in the evaporation /83/. The high viscosity of the black liquor is caused by the carbohydrates and to some extent, the high molecular mass lignin. The basic principle of the LHT is to degrade these carbohydrate and lignin units in alkaline environment at elevated temperature. /85, 86/

It is known that the polysaccharides are degraded when they are exposed to elevated temperatures under alkaline environment. Degradation is caused by the cleavage of glycosidic bonds, which results to formation of new end groups that undergo peeling reactions. /12/ The reduction of polysaccharide content is promoted by the presence of hydroxide ions, so the LHT process works more efficiently if the residual alkali charge is sufficient. The high sulfide content promotes the fragmentation of lignin, whereas low alkali charge has been shown to increase the content of high molecular mass lignin. The increase in high molecular mass lignin is thought to be caused by polymerization of lignin fragments. /87/ Alongside the alkali reactions, also sulfide reacts with the lignin. These reactions generate dimethyl sulfide (DMS), dimethyl disulfide (DMDS) and methyl mercaptan (MM), which are malodorous gases and should be treated properly. /88/ According to the chemical suppliers Aga and Sigma-Aldrich, all of these gases are flammable and whereas DMS is only irritating to the eyes, the DMDS and MM are acutely toxic when inhaled /89, 90, 91/.

The temperature of LHT process is typically between 170 - 190°C and reaction time ranges from few minutes to several hours and the optimal conditions depend highly on characteristic of the black liquor /65, 85/. Softwood black liquor requires less sever conditions during the LHT treatment than hardwood black liquor, which

is due to lower initial carbohydrate content /87/. Higher temperature increases the carbohydrate reduction rate, *i.e.* higher the temperature, shorter the reaction time needed. Carbohydrate degradation is fast at the start of the LHT, but the reaction speed drops considerably as the heat treatment proceeds. Louhelainen et al. (2002) reached circa 50% reduction of polysaccharides with only 3.5 minutes heat treatment, but in order to reach over 90% reduction, the treatment time had to be 45 minutes. /85/

# 6 Conclusions based on the literature review

The dwindling fossil fuel resources and the increased awareness towards the environmental issues have created an interest towards renewable replacements for fossil fuels. One of the possible materials that has been under heavy research in the resent years is lignin. Lignin has a huge potential as a renewable raw material and it has been suggested to be used as a raw material for different chemicals, activated carbon and carbon fibers. It is also suggested to be used in a variety of energy and fuel applications and in different composites.

The biggest source of industrial lignin is the pulp industry, especially kraft pulping. The most predominant method for kraft lignin production is to precipitate lignin from black liquor with $CO_2$ and then wash the lignin. This method can produce fairly pure lignin, *i.e.* the end product has low ash and carbohydrate content. Other option for lignin production would be to use ultrafiltration. The resulting lignin-rich liquid stream has a lower polydispersity than the original black liquor, but it still needs to be further treated in order to get a solid end product. The lignin-rich ultrafiltration permeate has less carbohydrates than the retentate, but on the other hand permeate also has higher ash and sulfur content than the retentate.

The purity of lignin is an important factor for the lignin applications, as some impurities may worsen the quality of the end product or poison the catalysts that are used in the production process. The ash content of the lignin can be lowered by optimizing the lignin washing process, where the most important factor is the pH during the resuspension/washing stage. Low pH during the resuspension/washing stage lowers the amount of Na and K in the end product. Other inorganic impurities are virtually unaffected by the pH level during washing, but the level of these impurities can be decreased by increasing the retention time during the washing.

Carbohydrates are the second major impurity found in lignin and different techniques have been suggested for lowering the carbohydrate content in lignin.

One way is to use acid or enzymatic hydrolysis. The problem with enzymatic hydrolysis is that it introduces new protein impurities to the lignin and it is not capable of removing all the sugars from the lignin. Acid hydrolysis has been studied for the carbohydrate removal and it has suggested that the lignin washing step during lignin $CO_2$ precipitation process could be converted to acid hydrolysis step. The problem is that there is still lack of knowledge how the hydrolysis step affects the lignin, *e.g.* will the polydispersity of the lignin rise.

Second technique that has been suggested is to use solvent extraction. During solvent extraction the lower molecular mass fractions are solubilized using different solvent, while the carbohydrates found in the lignin, remain in the insoluble high molecular mass portion of the lignin. Although the solvent extraction is an interesting method, the selectivity of the process is not very high at the moment. Another concern with the solvent extraction is that the recovery of the low molecular mass lignin in a mill scale would be fairly energy intensive, as it is done via evaporation.

The last technique for the lignin carbohydrate content reduction is liquor heat treatment, which is nowadays used to lower the viscosity of black liquor. LHT is known to reduce the carbohydrate content in softwood black liquor, but it is not known how it affects the softwood lignin's carbohydrate content or how it affects the isolated softwood lignin's other properties. Based on the literature, LHT should only affect the carbohydrate content in the lignin. However, this is just an assumption, because the existing research focuses on the viscosity reduction of the black liquor, which is due to the reduction in the black liquor carbohydrate content. Since the LHT is well known technique, and widely used in evaporation, some of the additional costs could be lowered, if the steam produced during the LHT is utilized in the pulp mill, *e.g.* in evaporation plant. The objective of this literature review was to discover different methods for kraft lignin purification and choose the most suitable method for further research. Based on the findings listed above the liquor heat treatment was selected as a research subject in the experimental part of this thesis.

# EXPERIMENTAL STUDY

## 7 Materials and methods

The experimental part of this thesis consists of three different parts: (i) characterization of the LHT liquors and the lignins isolated from these liquors (ii) determination of the effect that the LHT and the $CO_2$ precipitation process have to the liquor sulfur content, and (iii) estimation of the operating costs for the LHT lignin isolation process. In this chapter, the selected materials and methods are presented. The methods for LHT liquor and lignin characterization were selected to give an overview how the heat treatment affects the liquor and isolated lignin. The methods for the liquor sulfur content determination were selected based on the reliability of the method.

### 7.1 Liquor heat treatment and lignin precipitation

Two different black liquors were used in the experimental study. Both of these black liquors were received from a commercial Nordic kraft pulp mill. First black liquor was cooking black liquor (CBL), which was taken from the digester liquor circulation. The second black liquor was weak black liquor (WBL), which was taken from the line between evaporation and cooking plant. The liquor heat treatment was done with an air bath digester, in which the heating is based on convection. The black liquor sample (circa 5 l) was divided into three metal vessels and these vessels were then locked into the digester. Once the vessels were in place, the digester was pre-heated at 200 °C for a while and after the pre-heating the temperature was set to match the treatment conditions. The LHT conditions were selected based on the experiment done by Louhelainen et al. (2002) /85/. The heat treatment time was selected to describe the time that the black liquor was kept at the heat treatment temperature. H-factor was calculated for the LHT, because the heating-up time was fairly long, compared to the actual heat treatment time. The digester and the metal vessel used during the LHT are shown in the Figure 12 and the selected treatment conditions are presented in the Table 6.

**Figure 12.** Air bath digester and the metal vessel used for the LHT.

**Table 6.** Liquor heat treatment conditions.

| Sample ID | Heat treatment conditions | |
|---|---|---|
| | Temperature (°C) | Time (min) |
| WBL Ref | Weak black liquor reference, no heat treatment | |
| WBL W1 | 170 | 15 |
| WBL W2 | 190 | 45 |
| WBL W3 | 170 | 45 |
| WBL W4 | 190 | 15 |
| WBL W5 | 180 | 30 |
| WBL W6[a] | 190 | 45 |
| CBL Ref | Cooking black liquor reference, no heat treatment | |
| CBL C1 | 170 | 15 |
| CBL C2 | 190 | 45 |
| CBL C3 | 170 | 45 |
| CBL C4 | 190 | 15 |
| CBL C5 | 180 | 30 |

[a] Same heat treatment as in W2, but different $CO_2$ precipitation conditions

Once the LHT was completed, the metal vessels were cooled in a water bath and the remaining pressure in the vessels was released. The heat treated liquor was then moved to lignin isolation. Lignin was isolated from the liquors by using $CO_2$ precipitation. This method was based on the experiment done by Tomani (2010) /69/. The $CO_2$ precipitation was performed in a 30 liter batch reactor, which was equipped with a stirrer, pH sensor, temperature controller and $CO_2$ inlet. Precipitation was done at 70 °C, under constant stirring and the black liquor was acidified to pH 9 with $CO_2$. The only exception for these conditions was the WBL W6 sample, which was acidified with $CO_2$ at 50 °C. The precipitated lignin was separated from the black liquor in a Büchner funnel with VWR qualitative filter paper 415 (pore size 12 – 15 μm). After filtration, the lignin was re-dispersed into 70 °C distilled water and acidified to pH 2 with 6 M sulfuric acid under stirring. Next the washing slurry was filtered in a Büchner funnel with VWR qualitative filter paper 415 and the resulting solid fraction was washed with 70 °C distilled water. Dilution factor 8 was used during the dilution and displacement washing. Washed lignin was then dried for 48 hours at 45 °C and grinded into powder.

## 7.2 Liquor characterization

### 7.2.1 Dry matter content

Black liquor dry matter content was determined according to SCAN-N 22:96 – standard /92/.

### 7.2.2 Residual alkali and sodium sulfide content

The residual alkali and the sodium sulfide contents were determined with an automatic titrator according to SCAN-N 33:94 /93/ and SCAN-N 31:94 – standards /94/ respectively.

### 7.2.3 Lignin concentration and carbohydrate content

The black liquor lignin concentration and carbohydrate content were determined with single-step acid hydrolysis according to NREL/TP-510-42623 – standard /95/. The lignin concentration was calculated from the amount of acid insoluble lignin,

also known as Klason lignin, and from the amount of acid soluble lignin (ASL). The amount of sulfuric acid ($H_2SO_4$) used in the standard for the hydrolysis was too small for the black liquor samples, as the standard is designed for neutral liquid samples. In these experiments, 3.00 ml and 4.00 ml of 72% sulfuric acid were used in the hydrolysis for the WBL and CBL samples respectively.

Hydrolysis was done for duplicate samples. 20 ml of the sample was measured to autoclave bottle and the corrected amount of $H_2SO_4$ (3.00 ml or 4.00 ml) was added, in order to adjust the pH to 0. The solution was mixed with a glass rod and hydrolyzed in an autoclave for 60 minutes at 121 °C. After the hydrolysis, the sample was filtered with Robu's borosilicate filter crucible (pore size 16 – 40 μm) and the filtrate was collected into a storage bottle. The filter crucible was left to dry to constant weight at 105 °C and the Klason lignin was determined gravimetrically. The carbohydrate content of the hydrolysis filtrate was determined according the NREL/TP-510-42623 – standard with a Dionex ICS-3000 high-performance anion exchange chromatograph equipped with a CarboPacPA20 column and Amperometric cell detector. Samples were diluted using dilution factor 50 and filtered into sample vials with a 0.2 μm PTFE filter.

The ASL content of the filtrate was determined according to TAPPI UM 250 – standard /96/, by diluting the sample and measuring the absorbance at 205 nm with Shimadzu UV-VIS 2550 spectrophotometer. NREL/TP-510-42618 – standard /97/ also includes a method for the ASL content determination. The difference between NREL and TAPPI – standards is that the NREL uses 320 nm wave length for the determination while the determination is done by using the 205 nm wave length in the TAPPI UM 250 – standard as mentioned above. The 320 nm wave length also often includes interfering peaks from carbohydrate degradation products /97/ and hence the TAPPI UM 250 – standard was selected for the ASL content determination. The TAPPI method uses absorptivity constant of 110 g/l cm for all lignin types, whereas the NREL method uses different absorptivity constants depending on the lignin type.

## 7.2.4 Sulfur content

The total sulfur content of the reference black liquors, the LHT liquors and the $CO_2$ liquors were determined with inductively coupled plasma atomic emission spectrometer also known as inductively coupled plasma optical emission spectrometer (ICP-AES/ICP-OES). Before the actual sulfur content determination, all the organic substances from the liquor samples were degraded with a pretreatment, in which the liquor samples were treated with concentrated nitric acid and digested in a laboratory microwave oven.

## 7.3 Lignin characterization

### 7.3.1 Lignin and carbohydrate content

Klason lignin and structural carbohydrate contents of the isolated lignin were determined according to the NREL/TP-510-42618 – standard /97/ after a two-stage acid hydrolysis. The ASL content was determined according to TAPPI UM 250 – standard /96/, for previously mentioned reasons. Two-stage hydrolysis was performed for duplicated lignin samples, by measuring 300 mg of the sample into test tube and adding 3.00 ml of 72% sulfuric acid to the test tube. Samples were first hydrolyzed in 30 °C water bath for 60 minutes. After the first hydrolysis stage samples were transferred to autoclave bottles and the sulfuric acid was diluted to 4% concentration by adding 84.00 ml of distilled water. Once the dilution was done the samples were mixed and moved to the second hydrolysis stage. The second stage was done by hydrolyzing the samples for 60 minutes at 121 °C in an autoclave. After the hydrolysis, the Klason lignin, ASL and carbohydrate content determinations followed the same procedure as in the black liquor lignin and carbohydrate content determination. The only change in this procedure was smaller dilution factor at the carbohydrate content determination. During the isolated lignin carbohydrate content determination, dilution factor 5 was used for WBL ref and WBL W1 samples and dilution factor 2 for rest of the samples.

### 7.3.2 Ash content

The ash content of lignin was determined according to ASTM D1102 – 84 (2007) – standard /98/ after incinerating the lignin at 575 °C for 4 hours.

### 7.3.3 Sodium content

The sodium content of lignin was determined according to the SCAN-CM 63:05 – standard /99/, in which the lignin is first treated with concentrated nitric acid ($HNO_3$) and digested in a laboratory microwave oven. The resulting solution is diluted and the sodium content of the solution is determined with atomic adsorption spectroscopy using flame.

### 7.3.4 Elemental analysis

The elemental analysis (CHNS) of dry lignin samples were performed with PerkinElmer Model 2400 Series II CHNS Elemental Analyzer. The oxygen content of lignin was calculated by subtracting the amount of ash, carbon, hydrogen, nitrogen and sulfur from 100%.

## 7.4 Operating costs

The operating costs of the LHT coupled with $CO_2$ lignin precipitation process are compared with a simple $CO_2$ lignin precipitation process. The capacity of the example process is 50000 t/a of dry lignin matter. The operating costs of the simple $CO_2$ lignin precipitation process are divided into six categories: (i) reduced steam production in the recovery boiler, (ii) increased evaporation costs, (iii) chemical costs ($CO_2$, $H_2SO_4$, NaOH), (iv) heat required for lignin drying, (v) increased electricity consumption and (vi) labor and maintenance. This calculation is done for the worst case scenario, *i.e.* lignin precipitation does not increase pulp production and the Na/S balance has to be re-adjusted after the lignin precipitation. These assumptions are also included in the LHT operating cost calculations. If the lignin precipitation would increase the pulp production or if the increased sulfur input would not cause problems in the mill, the result for the operating costs would be different.

The operating costs for the LHT process are divided into eight categories, of which the first six categories are the same as in the $CO_2$ lignin precipitation process. The two additional categories are: (vii) steam consumption during the LHT and (viii) additional investment costs. The operation costs for the LHT are estimated for both the WBL and CBL at three different heat treatment temperature: 170 °C, 180 °C and 190 °C. The duration of the heat treatment is not taken into account, because the energy required to maintain the temperature is assumed to be negligible compared to the energy required to increase the black liquor temperature. The energy consumption is calculated using 20% safety factor that takes into account possible heat losses and the heat required to maintain the temperature during the LHT. In addition to the energy consumption, the consumption of the heating steam is calculated. The additional operating costs and the steam consumption for the LHT process are calculated for a steady state process using assumptions that are listed below.

- Initial temperature of weak black liquor is 80 °C
- Initial temperature of cooking black liquor is 150 °C
- Yield in the lignin recovery is 60% of the lignin in the black liquor
- LHT process uses medium pressure steam (13 bar, 195 °C)
- Black liquor is flashed to atmospheric pressure after LHT
- Black liquor dry matter content increases 4.0% during flashing
- Additional investment costs caused by the LHT are 0.7 €/t of lignin

The required black liquor mass flow in the feed is calculated using the production volume, yield, lignin concentration and density. The liquor mass flow out the LHT process is calculated from the 4.0% increase in the dry matter content and the steam flow produced during the flashing is determined from the mass balance. The energy consumption during the LHT process is calculated from the energy balance. During these calculations the liquor mass flow out the LHT process is called liquor stream and the produced steam flow is called vapor stream. The lignin concentration, the black liquor density and the dry matter content used in the mass flow calculations are determined during the laboratory experiment.

The formula for the feed mass flow is shown in the Equation 1, whereas the formula for the liquor and vapor mass flows are shown in the Equations 2 - 3. The energy balance calculation is shown in the Equation 4. The additional costs caused by the LHT are calculated with the formula shown in the Equation 5. The enthalpy value for the vapor stream, which is used in the Equation 4, is taken from Keskinen's chemical engineering tables /100/. The enthalpy values for the feed and liquor stream are calculated with a model that was provided by Andritz. Other option is to use enthalpy tables that can be found from chemical engineering handbooks, *e.g.* Perry's chemical engineer's handbook /101/. The Equation 4 also includes 20% that takes into account the possible heat losses and the heat required to maintain the temperature during the LHT.

$$\dot{m}_F = \frac{\text{lignin production}}{c * \text{yield}} * \rho_{bl} \tag{1}$$

$$\dot{m}_L = \frac{\dot{m}_F * x_F}{x_L} \tag{2}$$

$$\dot{m}_V = \dot{m}_F - \dot{m}_L \tag{3}$$

$$q = (\dot{m}_L * h_L + \dot{m}_V * H_V - \dot{m}_F * h_F) * sf \tag{4}$$

$$\text{LHT steam cost} = \frac{q * \text{steam price}}{\text{lignin production}} + \text{invesment cost} \tag{5}$$

where,    $\dot{m}_F$ is mass flow in the feed,

c is lignin concentration in the black liquor,

$\rho_{bl}$ is black liquor density,

$\dot{m}_L$ is mass flow in the liquor stream,

$x_F$ is dry matter content in the feed,

$x_L$ is dry matter content is the liquor stream,

$\dot{m}_V$ is mass flow in the vapor stream,

q is energy consumption during the LHT,

$h_L$ is enthalpy of the liquor stream,

$H_V$ is enthalpy of the vapor stream,

$h_F$ is enthalpy of the feed

sf is 20% safety factor


The calculated energy consumption is used to determine the heating steam consumption during the LHT. The steam consumption is calculated from the heat exchanger's energy balance. The calculation for the steam consumption is shown in the equation 6. The enthalpy values for the steam and water that are used in the Equation 6 are taken from Keskinen's chemical engineering tables /100/

$$\dot{m}_S = \frac{\dfrac{q}{H_S - h_S}}{\text{lignin production}} \qquad (6)$$


where,    $\dot{m}_S$ is steam consumption during the LHT,

$H_S$ is enthalpy of the steam in the heating stream,

$h_S$ is enthalpy of the water in the heating stream


The Figure 13 shows an illustration of the LHT process that has been used for the operational costs estimation. The parameters used in the material and energy balance are also included in the Figure 13.
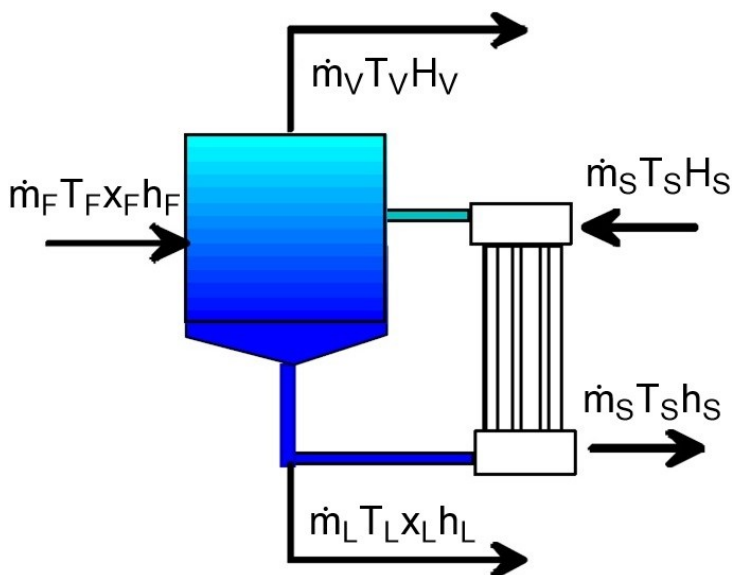


**Figure 13.** An illustration of the LHT process.

# 8 Results and discussions

The three parts that are included in the experimental part of this thesis are: (i) characterization of the LHT liquors and the lignins isolated from these liquors (ii) determination of the effect that the LHT and the $CO_2$ precipitation process have to the liquor sulfur content, and (iii) estimation of the operating costs for the LHT lignin isolation process. In this chapter, the results and possible errors for these three main parts are presented and discussed.

## 8.1 Liquor heat treatment and lignin precipitation

The liquor heat treatment was performed with an air bath digester, where the heating is based on convection. As the heating time during the LHT was fairly long, the H-factors were calculated. The H-factor fir heating was especially high for the LHT that was performed at 190 °C, as it took considerably longer to raise the temperature from 180 °C to 190 °C than from 170 °C to 180 °C. This was due to the temperature limitations in the air bath digester during the heating up period, as the maximum temperature of the digester was 200 °C. The resulting H-factors for the LHT are shown in the Table 7, divided to heat-up and overall H-factors.

**Table 7.** Liquor heat treatment H-factors.

| Sample ID | LHT conditions | | H-factor | |
|---|---|---|---|---|
| | Temperature | Time | Heat-up | Overall |
| WBL W1 | 170 | 15 | 150 | 420 |
| WBL W3 | 170 | 45 | 200 | 880 |
| WBL W5 | 180 | 30 | 640 | 1580 |
| WBL W4 | 190 | 15 | 1900 | 3200 |
| WBL W6 | 190 | 45 | 1630 | 5080 |
| WBL W2 | 190 | 45 | 1850 | 5250 |
| CBL C1 | 170 | 15 | 140 | 420 |
| CBL C3 | 170 | 45 | 150 | 890 |
| CBL C5 | 180 | 30 | 580 | 1680 |
| CBL C4 | 190 | 15 | 1650 | 3280 |
| CBL C2 | 190 | 45 | 1480 | 5060 |

The lignin precipitation with $CO_2$ to pH 9 did not result in anything unexpected when isolating the reference samples from WBL and CBL. The lignin precipitated well and it was possible to collect using filtration. The CBL resulted to a smaller amount of lignin, which was expected as the lignin concentration is lower. The first unexpected result was found during the precipitation of LHT liquors. Quite a large portion of the precipitated lignin was settled onto the bottom of the precipitation reactor and also some lignin agglomerates were stuck to $CO_2$ inlet. These agglomerated lignin portions were removed manually from the reactor and transferred to the filtration. These portions resembled highly viscous pitch, as the lignin was quite sticky and to some extend moldable. The particle size of lignin resulting from the precipitation of LHT liquors was clearly bigger than from the precipitation of the reference samples. The stirring during the $CO_2$ precipitation process was kept constant during whole experimental study. The $CO_2$ precipitation reactor and the precipitates from the LHT liquor precipitation are shown in the Figure 14.



**Figure 14.** Reactor for lignin precipitation and unwanted lignin precipitates.

The difference in the precipitation behavior between the LHT lignins and the reference lignins is thought to be due to a decreased glass transition temperature in the LHT lignins, which is caused by the fragmentation of lignin. The lower molecular weight fractions of the LHT lignins are melted at the initial precipitation temperature and the precipitating lignin is able to form much bigger agglomerates. This hypothesis was tested during $CO_2$ precipitation of the WBL W6 sample. During the precipitation of the W6 sample, the temperature was decreased from the previously used 70 °C to 50 °C. The resulting lignin behaved exactly the same as the lignin during the reference sample precipitation, which supports our hypothesis. Wallmo et al. also experienced formation of large black lignin lumps during $CO_2$ precipitation at 75 °C, while using both heat treated hardwood black liquor and ultrafiltrated hardwood black liquor. The tendency to form these black lumps was thought to be due to the occurrence of a different coagulation mechanism at higher temperatures. /65/

During the filtration step the CBL and the WBL reference samples and the WBL W6 sample had a quite low filtration resistance and filtrated easily. The LHT samples had even lower filtration resistance as the particle size of the precipitated lignin was bigger, hence the LHT samples filtrated very easily. Although, during the filtration of CBL C1 sample, the temperature of the liquor was still high enough to keep the lignin partially melted, which resulted to a partial clogging of the filter paper and partial tearing of the filter paper during the removal of the lignin. Apart from this clogging, there were no noticeable differences between the filtration properties of LHT samples or between the filtration properties of the reference samples and the WBL W6 sample. The appearance of the samples differed noticeably. The reference samples and the WBL W6 sample were brown, whereas the rest of the LTH samples were much darker. The lignins from WBL W6 and CBL C2 are shown in the Figure 15.

**Figure 15.** WBL W6 lignin (A) and CBL C2 lignin (B).

The isolated lignin fraction was washed after the filtration using two-stage washing procedure. The first stage was performed by re-slurrying the precipitated lignin to distilled water. The re-slurrying was considerably harder for the LHT lignin samples, because the melted lignin fractions were hardened. These hardened lignin fractions had to be manually crushed before re-dispersing the lignin into the hot distilled water. Apart from this problem, all the samples behaved in a similar fashion. After the re-slurrying, the pH of the suspension was decreased to 2 with sulfuric acid. During this acidification step, strong foaming occurred when the pH was between 6.5-5.0, which was due to the release of $H_2S$ and the remaining $CO_2$ /67/. The acidification was stopped until the foaming was stopped. Once the target pH of 2 was reached, the lignin suspension was filtrated. After the filtration, the resulting solid fraction was washed again with hot distilled water. The second washing was performed as displacement washing. The filtration resistance during the filtration of the washing suspension was fairly low for all the samples, although it was higher than after the $CO_2$ precipitation. During the displacement washing the filtration resistance was quite high for all the samples and the filtration was much slower.

After the displacement washing, the lignin samples were dried in an oven at 45 °C for 48 hours and crushed into powder with an electric grinder or by hand using a mortar and pestle. The color of the dried lignin samples varied between the WBL and CBL samples. The WBL lignins were brown, whereas the color of CBL lignins was darker. The color difference was noticeable in the dried lignin that was not yet grinded into powder form. After the lignin was grinded into powder the color difference was harder to notice. The color difference between WBL ref and CBL ref before grinding is shown in the Figure 16.



**Figure 16.** The color difference between WBL ref (A) and CBL ref (B).

## 8.2 Liquor characterization

Thirteen different black liquors were analyzed, from which two were reference samples, *i.e.* untreated black liquors. The summary of the results from the liquor characterization are shown in the Table 8. The detailed analysis of the results and the reliability of the results are discussed in the specific sections.

**Table 8.** Residual alkali, sodium sulfide, carbohydrate and lignin concentrations.

| Sample ID | Residual alkali (g NaOH/l) | $Na_2S$ (g/l) | Carbohydrate concentration (g/l) | Lignin concentration (g/l) |
|---|---|---|---|---|
| WBL Ref | 7.82 | 15.49 | 5.39 | 68.27 |
| WBL W1₁₇₀C, 15min, H-factor 420 | 7.13 | 15.00 | 5.04 | 68.55 |
| WBL W3₁₇₀C, 45 min, H-factor 880 | 6.24 | 15.30 | 4.58 | 68.20 |
| WBL W5₁₈₀C, 30 min, H-factor 1580 | 5.72 | 15.11 | 4.21 | 69.54 |
| WBL W4₁₉₀C, 15 min, H-factor 3200 | 4.99 | 15.45 | 3.49 | 68.36 |
| WBL W6₁₉₀C, 45 min, H-factor 5080 | 4.42 | 15.76 | 3.16 | 66.65 |
| WBL W2₁₉₀C, 45 min, H-factor 5250 | 4.96 | 15.03 | 3.14 | 66.66 |
| CBL Ref | 18.14 | 21.66 | 3.83 | 48.48 |
| CBL C1₁₇₀C, 15 min, H-factor 420 | 16.87 | 22.24 | 3.40 | 48.49 |
| CBL C3₁₇₀C, 45 min, H-factor 890 | 15.63 | 21.90 | 2.98 | 47.22 |
| CBL C5₁₈₀C, 30 min, H-factor 1680 | 15.17 | 22.59 | 2.65 | 48.34 |
| CBL C4₁₉₀C, 15 min, H-factor 3280 | 14.56 | 22.90 | 2.22 | 47.02 |
| CBL C2₁₉₀C, 45 min, H-factor 5060 | 14.29 | 22.61 | 1.94 | 45.67 |

The cooking black liquor had, as expected, higher residual alkali and $Na_2S$ content and lower carbohydrate and lignin concentration. The difference between the WBL and CBL was not huge, because the CBL was collected from the end of the cooking, but the difference is still large enough to enable the comparison between the liquors. The CBL had circa 10 g NaOH/l higher residual alkali concentration, which should give an indication whether the residual alkali concentration will affect the carbohydrate reduction at this level. The residual alkali concentration decreased during the LHT process and the harsher heat treatment resulted to

bigger decrease in the residual alkali concentration, which was expected. The $Na_2S$ concentration was roughly 6 g/l lower in the WBL. Although the $Na_2S$ concentration varied between different samples, the $Na_2S$ concentration did not change systematically in relation to H-factor.

The WBL had roughly 1.5 g/l higher carbohydrate concentration compared to the CBL. The carbohydrate content of the WBL decreased from 5.39 g/l to 3.14 g/l when the H-factor was over 5000, whereas when using the same heat treatment conditions the drop in carbohydrate content of the CBL was from 3.83 g/l to 1.94 g/l. The carbohydrate content of the sample liquors decreased fairly systematically throughout the experimental study. The difference in the lignin concentration between WBL and CBL was circa 20 g/l. This difference was noticeable during the $CO_2$ precipitation as the CBL resulted in a lower amount of lignin. The lignin concentrations of the WBL and CBL were fairly constant throughout the experimental study. Only a small decrease in the lignin concentration could be observed (circa 1.5-3.0 g/l) after the harshest LHT (H-factor over 5000).

## 8.2.1 Dry matter content

The dry matter content, also known as dry solids (DS) content, of the reference liquors and the heat treated liquors were determined. Also the dry matter contents of the $CO_2$ precipitation liquors were determined. The $CO_2$ precipitation liquor samples were taken from the reactor prior to the filtration. These values are used for the sulfur balance calculations. The results from the dry matter content determinations are shown in the Table 9.

**Table 9.** The results from the dry matter content determination.

| Sample ID | Dry solids (%) | |
|---|---|---|
| | **Ref/LHT liquors** | **CO$_2$ liquors** |
| WBL Ref | 14.08 | 15.15 |
| WBL W1$_{170C, 15min, H\text{-}factor\ 420}$ | 14.24 | 13.47 |
| WBL W3$_{170C, 45\ min, H\text{-}factor\ 880}$ | 14.77 | 14.32 |
| WBL W5$_{180C, 30\ min, H\text{-}factor\ 1580}$ | 14.02 | 15.70 |
| WBL W4$_{190C, 15\ min, H\text{-}factor\ 3200}$ | 14.20 | 14.80 |
| WBL W6$_{190C, 45\ min, H\text{-}factor\ 5080}$ | 13.78 | 14.74 |
| WBL W2$_{190C, 45\ min, H\text{-}factor\ 5250}$ | 14.53 | 13.43 |
| CBL Ref | 15.03 | 14.98 |
| CBL C1$_{170C, 15\ min, H\text{-}factor\ 420}$ | 14.62 | 14.38 |
| CBL C3$_{170C, 45\ min, H\text{-}factor\ 890}$ | 14.03 | 15.13 |
| CBL C5$_{180C, 30\ min, H\text{-}factor\ 1680}$ | 14.17 | 14.67 |
| CBL C4$_{190C, 15\ min, H\text{-}factor\ 3280}$ | 14.03 | 13.18 |
| CBL C2$_{190C, 45\ min, H\text{-}factor\ 5060}$ | 14.85 | 14.56 |

The dry matter contents of the WBL and CBL Ref/LHT liquors were fairly similar and the heat treatment did not have considerable effect on the dry matter. The CBL was collected from the end of the cooking, which shown in the similarity of the results between the WBL and CBL. The reference black liquors' and the heat treated liquors' dry matter content varied between 13.78 - 15.03%, whereas the CO$_2$ liquors' dry matter content varied between 13.18 - 15.70% The variations in the dry matter contents between the different LHT liquors is assumed to be caused by the used determination method. All determinations were made with duplicate samples and some variation existed between the duplicate samples.

The variation between the duplicate samples increased when measuring the dry matter content of the LHT CO$_2$ liquors. The only exception was the WBL W6 sample where the temperature during CO$_2$ precipitation was lowered to 50 °C. The bigger lignin particle size in the LHT CO$_2$ liquors caused problems, because the small samples taken for the dry matter content determination were fairly heterogenic. This caused bigger variations in the results between the duplicated

samples. Bigger sample size during the dry matter content determination might have given more accurate results.

In mill scale the LHT would increase the dry matter content of the black liquor, because the heat treated black liquor would be flashed after the LHT. The rapid reduction in pressure causes steam production and the produced steam could be utilized elsewhere, *e.g.* in evaporation plant. During our laboratory scale LHT process, proper flashing could not be done due to safety reasons. The metal vessels used for the LHT were cooled in a water bath before releasing the excess pressure. This procedure ensured more controlled pressure release during the experiment. The increase in the dry matter content of the black liquor is taken into account in the operating costs evaluation, because the change in the dry matter content affects the energy consumption during the LHT.

### 8.2.2 Residual alkali and sodium sulfide content

Alkali is consumed during the LHT process, as it reacts with polysaccharides and lignin. The relationship between the residual alkali and the black liquor carbohydrate content are shown in the Figure 17 as a function of H-factor.
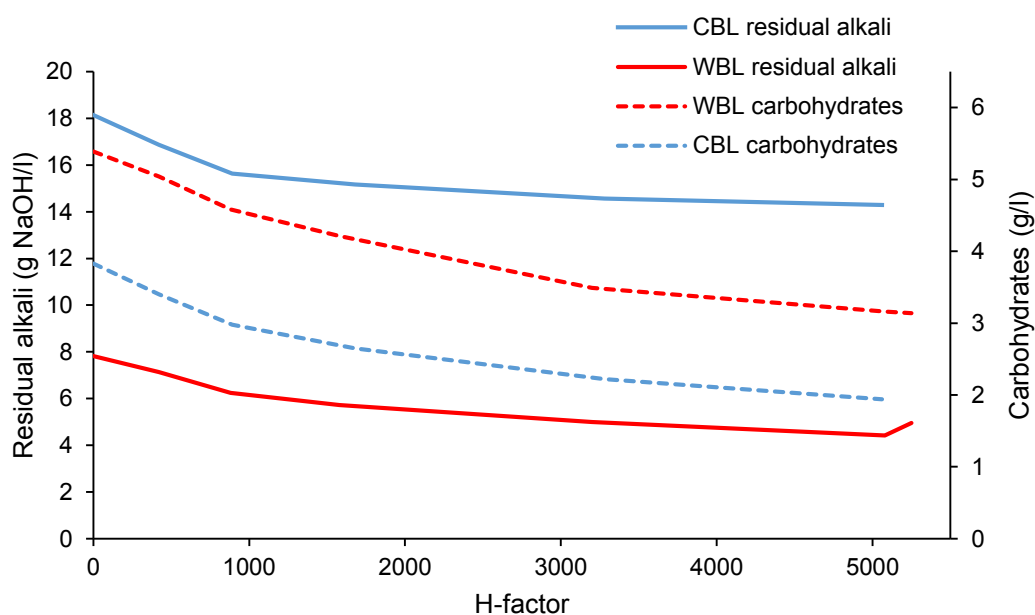


**Figure 17**. The effect of LHT to residual alkali and carbohydrate concentration.

The residual alkali is consumed at a much faster rate at the start of the LHT process. Once the H-factor reaches circa 1000, the reduction rate drops considerably for both liquors. Between the reference samples and the WBL W2 and CBL C2 samples, the drop in the residual alkali contents were 2.86 g/l and 3.85 g/l respectively, whereas the drop between the reference and the W3 and C3 samples were 1.58 g/l and 2.51 g/l respectively. The alkali reduction during the W3 and C3 heat treatments correspond to 55.24% and 65.19% of the reduction that occurred during the W2 and C2 heat treatments.

Similar trend is also seen in the black liquor carbohydrate contents, although the decrease in the reduction rate is not as severe as in the residual alkali content. The carbohydrate content reduction that occurred during the W3 and C3 heat treatments correspond to 36.00% and 44.97% of the reduction that occurred during the W2 and C2 heat treatments. Söderhjelm et al. (1999) and Louhelainen et al. (2002) achieved similar results in their experiments. In the experiment done by Louhelainen et al. circa 50% reduction in the softwood black liquor carbohydrate content was reached with only 3.5 minutes heat treatment at 185 °C, while in order to reach over 90% reduction, the heat treatment time had to be 45 minutes at 190 °C. /85, 87/

As mentioned earlier, the $Na_2S$ concentration varied between different samples, but the $Na_2S$ concentration did not appear to change systematically in relation to H-factor. The $Na_2S$ concentration of the WBL samples varied between 15.00 - 15.76 g/l, whereas in the CBL samples the $Na_2S$ concentration varied between 21.66 - 22.90 g/l. Similar results can be found in the experiment done by Louhelainen et al. (2002). They found out that the polysulfide content of the black liquor was decreased substantially, whereas the $Na_2S$ content varied only slightly during normal LHT. Louhelainen et al. also performed LHT with an oxygen addition, which resulted to a lower $Na_2S$ content, although it was believed that the sulfide was oxidized into thiosulfate. /85/

The residual alkali and sodium sulfide contents of the reference black liquors and LHT liquors were determined using automatic titrator. The results from these

determinations contain some inherent variation caused by the automatic titrator. In order to reduce the effect of the inherent variation, residual alkali was determined using 2 - 4 duplicates per sample liquor and the sodium sulfide was determined using 4 - 6 duplicate samples. Standard deviation was calculated for each sample series and the result was that the standard deviation for the residual alkali and sodium sulfide measurements varied between 0.01 - 0.30 and 0.09 - 0.45 respectively, while the averages for the standard deviation were 0.12 and 0.25 respectively.

## 8.2.3 Black liquor lignin content

The black liquor lignin content was determined alongside the carbohydrate analysis by hydrolyzing the black liquor samples after the pH of the samples was set to 0. The total lignin concentration was calculated from the amount of Klason lignin and ASL. The result and the division between Klason lignin and ASL are shown in the Table 10.

**Table 10.** Klason lignin and acid soluble lignin contents in the black liquors.

| Sample ID | Klason lignin (g/l) | ASL (g/l) | Total (g/l) |
|---|---|---|---|
| WBL Ref | 62.24 | 6.04 | 68.27 |
| WBL W1 $_{170C, 15min, H-factor 420}$ | 62.65 | 5.90 | 68.55 |
| WBL W3 $_{170C, 45 min, H-factor 880}$ | 62.24 | 5.97 | 68.20 |
| WBL W5 $_{180C, 30 min, H-factor 1580}$ | 63.38 | 6.16 | 69.54 |
| WBL W4 $_{190C, 15 min, H-factor 3200}$ | 62.21 | 6.15 | 68.36 |
| WBL W6 $_{190C, 45 min, H-factor 5080}$ | 60.09 | 6.58 | 66.65 |
| WBL W2 $_{190C, 45 min, H-factor 5250}$ | 60.09 | 6.57 | 66.66 |
| CBL Ref | 43.49 | 4.99 | 48.48 |
| CBL C1 $_{170C, 15 min, H-factor 420}$ | 43.23 | 5.26 | 48.49 |
| CBL C3 $_{170C, 45 min, H-factor 890}$ | 41.81 | 5.41 | 47.22 |
| CBL C5 $_{180C, 30 min, H-factor 1680}$ | 42.89 | 5.45 | 48.34 |
| CBL C4 $_{190C, 15 min, H-factor 3280}$ | 41.57 | 5.45 | 47.02 |
| CBL C2 $_{190C, 45 min, H-factor 5060}$ | 40.01 | 5.66 | 45.67 |

As mentioned earlier the WBL had roughly 20 g/l higher lignin concentration throughout the experimental study. The majority of the detected lignin was Klason lignin, between 60.09 - 63.38 g/l for the WBL samples and between 40.01 - 43.49 g/l for the CBL samples. The acid soluble part of the lignin contributed between 5.90 - 6.57 g/l of the WBL samples lignin concentration and between 4.99 - 5.66 g/l of the CBL samples lignin concentration. The LHT had only a slight effect on the black liquor lignin concentration, but it would seem that both the temperature and the duration of the heat treatment are factors affecting the outcome of the LHT.

When comparing the heat treatments done at the same temperature, *e.g.* W1 and W3, the longer treatment time produces lower Klason lignin contents and higher ASL contents. This trend can be found at both treatment temperatures (170 °C and 190 °C) and for both black liquors. The temperature has a similar effect, as the higher temperature results to a higher ASL content and a lower Klason lignin content. Although the ASL content increased when the temperature or the duration of the heat treatment was increased the total lignin concentration decreased slightly, indicating that a small amount of lignin was lost during the LHT.

In the LHT research done by Louhelainen et al. (2002), the lignin content was slightly increased by the heat treatment. In this study, the lignin content determination was done purely by UV/Vis spectrophotometry. This led to the conclusion that the changes in the lignin concentration indicated mainly chemical changes in the lignin fraction rather than changes in the actual content of lignin. /85/ Our results indicate that the liquor heat treatment might have a small effect on the lignin content, although this cannot be said with a full certainty, because the Klason lignin results contained fair amount of variation between duplicated samples. Standard deviation for the duplicated samples varied between 0.04 - 0.61, whereas the average for the standard deviation was 0.19. The ASL results did not contain much variation, as the average for the standard deviation was 0.04.

## 8.2.4 Liquor carbohydrate content

The carbohydrate content of the black liquor samples were determined alongside the lignin content determinations. The concentrations of the different carbohydrates found in the black liquor are shown in the Table 11.

**Table 11.** Concentration of different carbohydrates in the black liquors.

| Sample ID | Arabinose (g/l) | Rhamnose (g/l) | Galactose (g/l) | Glucose (g/l) | Xylose (g/l) | Mannose (g/l) |
|---|---|---|---|---|---|---|
| WBL Ref | 1.22 | 0.02 | 1.64 | 0.30 | 1.97 | 0.22 |
| WBL W1$_{170C, 15min, H\text{-}factor\ 420}$ | 1.13 | 0.02 | 1.60 | 0.29 | 1.79 | 0.21 |
| WBL W3$_{170C, 45\ min, H\text{-}factor\ 880}$ | 1.01 | 0.02 | 1.52 | 0.28 | 1.57 | 0.19 |
| WBL W5$_{180C, 30\ min, H\text{-}factor\ 1580}$ | 0.93 | 0.02 | 1.50 | 0.28 | 1.30 | 0.19 |
| WBL W4$_{190C, 15\ min, H\text{-}factor\ 3200}$ | 0.75 | 0.02 | 1.42 | 0.25 | 0.88 | 0.17 |
| WBL W6$_{190C, 45\ min, H\text{-}factor\ 5080}$ | 0.65 | 0.02 | 1.43 | 0.24 | 0.67 | 0.15 |
| WBL W2$_{190C, 45\ min, H\text{-}factor\ 5250}$ | 0.63 | 0.02 | 1.41 | 0.24 | 0.69 | 0.15 |
| CBL Ref | 0.85 | 0.05 | 1.34 | 0.20 | 1.20 | 0.20 |
| CBL C1$_{170C, 15\ min, H\text{-}factor\ 420}$ | 0.73 | 0.03 | 1.27 | 0.19 | 1.00 | 0.18 |
| CBL C3$_{170C, 45\ min, H\text{-}factor\ 890}$ | 0.63 | 0.02 | 1.21 | 0.18 | 0.76 | 0.16 |
| CBL C5$_{180C, 30\ min, H\text{-}factor\ 1680}$ | 0.55 | 0.02 | 1.21 | 0.18 | 0.53 | 0.15 |
| CBL C4$_{190C, 15\ min, H\text{-}factor\ 3280}$ | 0.41 | 0.02 | 1.12 | 0.16 | 0.38 | 0.13 |
| CBL C2$_{190C, 45\ min, H\text{-}factor\ 5060}$ | 0.31 | 0.01 | 1.04 | 0.14 | 0.33 | 0.11 |

The three predominant carbohydrates found in the black liquor samples were arabinose, galactose and xylose, with only small amounts of rhamnose, glucose and mannose. GGM is the most abundant hemicellulose in softwoods, which is shown in the high concentration of galactose. Although the concentration of galactose was high, interestingly the amount of mannose and glucose was fairly low. This could explained by fast degradation of GGM molecules into monomers and while galactose remains in the black liquor, glucose and mannose are degraded even further into different products /4/.

The overall carbohydrate concentration in the untreated WBL was roughly 1.5 g/l higher compared to the untreated CBL. Rhamnose was the only polysaccharide that was found in higher concentration in CBL than in WBL. However, it must be noted that the concentration of rhamnose in the samples was so small that the accuracy of the result might be affected. One interesting finding was that the concentration of galactose was higher than the concentration of xylose in the CBL reference sample, whereas in the WBL reference sample xylose has the higher concentration. This would indicate that GGM is dissolved earlier in the cooking than xylan.

The highest reduction in the polysaccharide content was achieved with the harshest heat treatment, which was expected. When comparing to the reference samples the carbohydrate content was reduced by 41.74% in the WBL W2 sample and 49.35% in the CBL C2 sample. These reductions are fairly low compared to the over 90% reduction achieved by Louhelainen et al. in their experiment. However one interesting result was found during our LHT experiment. In other research the portion of galactose from the total polysaccharide content remains fairly constant or decreases slightly, whereas in our experiment the portion of galactose increased during the LHT. /85, 102/ The reduction rate of xylose was much faster than the reduction rate of galactose, which caused the increase in the relative portion of galactose. This was not experienced in other experiments.

## 8.2.5 Sulfur content

The total sulfur content of the reference black liquors, the LHT liquors and the $CO_2$ liquors were determined from pretreated samples with ICP-AES. The results from this determination are shown in the Table 12. The sulfur content of the liquor samples are expressed as % of dry solids. The original data from the liquors' sulfur content determination is shown in the Appendix 1. The $CO_2$ liquor samples were taken from the reactor after the acidification was finished.

**Table 12.** Results from the sulfur determination.

| Sample ID | Initial (% of DS) | LHT (% of DS) | $CO_2$ (% of DS) |
|---|---|---|---|
| WBL Ref | 7.24 | - | 5.02 |
| WBL W1[170C, 15min, H-factor 420] | 7.24 | 7.16 | 6.38 |
| WBL W3[170C, 45 min, H-factor 880] | 7.24 | 7.93 | 5.26 |
| WBL W5[180C, 30 min, H-factor 1580] | 7.24 | 7.50 | 4.96 |
| WBL W4[190C, 15 min, H-factor 3200] | 7.24 | 6.86 | 5.09 |
| WBL W6[190C, 45 min, H-factor 5080] | 7.24 | 8.94 | 6.36 |
| WBL W2[190C, 45 min, H-factor 5250] | 7.24 | 6.47 | 5.88 |
| CBL Ref | 7.98 | - | 6.21 |
| CBL C1[170C, 15 min, H-factor 420] | 7.98 | 8.07 | 5.70 |
| CBL C3[170C, 45 min, H-factor 890] | 7.98 | 8.45 | 6.18 |
| CBL C5[180C, 30 min, H-factor 1680] | 7.98 | 8.96 | 5.33 |
| CBL C4[190C, 15 min, H-factor 3280] | 7.98 | 8.96 | 5.63 |
| CBL C2[190C, 45 min, H-factor 5060] | 7.98 | 8.22 | 6.04 |

The sulfur content in the reference samples were 7.24% of DS and 7.98% of DS for WBL and CBL respectively. The sulfur content in the LHT liquors varied between 6.47 - 8.96% of DS, whereas the sulfur content in the $CO_2$ liquors was between 4.96 - 6.38% of DS. The CBL samples had, on average, higher sulfur contents in all the liquors (initial, LHT and $CO_2$). Only the WBL W1 $CO_2$ liquor sample had higher sulfur content when comparing to the CBL sample with similar heat treatment. The LHT had a varying effect on the sulfur content of the WBL samples. The W1, W4 and W6 LHT liquors had lower sulfur contents than the WBL reference sample, whereas the rest of the WBL LHT liquors had higher sulfur contents. Compared to the WBL samples, the LHT had more systematic effect on the sulfur content of the CBL samples. All the CBL LHT samples had higher sulfur contents compared to the CBL reference sample.

The $CO_2$ acidification lowered the total sulfur content in all the samples, which was expected. The sulfur content was reduced between 9.12 - 33.87% and 26.52 - 40.51% for the WBL and CBL samples respectively, when comparing the LHT and

$CO_2$ liquors. On average the reduction in the sulfur content was higher in the CBL samples. This was probably due to the higher sulfur content in the CBL LHT samples. The heat treatment was also expected to decrease the sulfur content in the black liquor samples, but the decrease in the total sulfur content occurred only in three samples. The poor sulfur content reduction is thought to be caused by the unsuccessful flashing after the LHT. The reduction in the black liquor total sulfur content is caused by the formation and release of volatile sulfur compounds and it is believed that these sulfur compounds may have dissolved to the black liquor when the metal vessels were cooled in a water bath /88/.

The results shown in the Table 12 are expressed as % of DS and are calculated from the dry matter content results shown in the Table 9. While the sulfur content results shown in the Appendix 1 can be considered accurate, the dry matter content results had fair amount of variation between duplicate samples, as mentioned earlier. This increases the inaccuracy of the sulfur content results shown in the Table 12. It is also important to remember that the initial sulfur content of each sample liquor might have varied slightly from the reference sample liquors. It is clearly seen that the $CO_2$ acidification reduces the sulfur content in the black liquor, but more detailed analysis, *e.g.* did the LHT affect the sulfur content reduction during the $CO_2$ acidification, is fairly hard to do. More accurate results could be obtained if the $CO_2$ precipitation was done at a lower temperature for all the LHT samples and if the initial sulfur contents were determined for each sample liquor and not only for the reference sample liquors.

### 8.3 Lignin characterization

One of the objects in this thesis was to test the most suitable treatment on laboratory scale and evaluate the potentiality of this method as a kraft lignin purification method. The potential of the LHT was evaluated to a large extend based on the purity of the lignin that has been isolated from the LHT black liquors. The summary of the lignin characterization is shown in the Table 13. More detailed analysis of the results and the reliability of the results are discussed in the specific sections.

**Table 13.** Lignin content, impurities and mass balances of the lignin samples.

| Sample ID | Lignin content | | | | | |
|---|---|---|---|---|---|---|
| | Total (%) | Klason (%) | ASL (%) | Carbohydrates (%) | Ash (%) | Balance (%) |
| WBL Ref | 96.71 | 93.11 | 3.61 | 1.50 | 1.01 | 99.22 |
| WBL W1$_{170C, 15min, H-factor 420}$ | 95.73 | 92.93 | 2.80 | 1.07 | 1.12 | 97.92 |
| WBL W3$_{170C, 45 min, H-factor 880}$ | 96.95 | 94.96 | 1.99 | 0.38 | 2.91 | 100.24 |
| WBL W5$_{180C, 30 min, H-factor 1580}$ | 97.70 | 95.89 | 1.81 | 0.43 | 1.52 | 99.64 |
| WBL W4$_{190C, 15 min, H-factor 3200}$ | 98.69 | 96.25 | 1.70 | 0.16 | 0.57 | 98.64 |
| WBL W6$_{190C, 45 min, H-factor 5080}$ | 96.96 | 96.44 | 0.52 | 0.12 | 1.28 | 98.37 |
| WBL W2$_{190C, 45 min, H-factor 5250}$ | 97.25 | 94.42 | 2.83 | 0.46 | 1.79 | 99.51 |
| CBL Ref | 96.96 | 94.30 | 2.66 | 0.61 | 1.51 | 99.08 |
| CBL C1$_{170C, 15 min, H-factor 420}$ | 96.61 | 93.78 | 2.83 | 0.42 | 1.82 | 98.85 |
| CBL C3$_{170C, 45 min, H-factor 890}$ | 97.21 | 95.01 | 2.13 | 0.21 | 1.66 | 99.09 |
| CBL C5$_{180C, 30 min, H-factor 1680}$ | 96.41 | 94.06 | 2.35 | 0.23 | 2.37 | 99.01 |
| CBL C4$_{190C, 15 min, H-factor 3280}$ | 98.12 | 96.04 | 2.09 | 0.06 | 1.39 | 99.58 |
| CBL C2$_{190C, 45 min, H-factor 5060}$ | 96.25 | 94.22 | 2.03 | 0.10 | 2.70 | 99.05 |

The first impression of the reference lignins was that the carbohydrate content was surprisingly low. The carbohydrate content determination for the reference samples were repeated two separated times, because the first results were believed to be unreliable due to small carbohydrate content. The results from the second carbohydrate content determination are shown in Table 13, as these results were slightly higher than the previous one. The LHT lignins showed promising results, as the carbohydrate content of these lignins were systematically lower compared to the reference lignins. The WBL lignin's carbohydrate content was decreased from 1.50% to 0.12% after the harshest heat treatment (H-factor over 5000). The CBL lignin's carbohydrate content could be decreased to 0.10% from 0.61%, when applying the same heat treatment conditions.

All the lignin samples had over 92% Klason lignin content, ranging from 92.93% in the WBL W1 to 96.44% in the WBL W6 sample. The CBL lignins had even smaller variation between the different samples ranging between 93.73 - 96.04%. The ASL

content of the lignin samples varied between 0.5 - 3.61%. The ash content in the lignin samples varied between 2.91 - 0.57%, which was a reasonable result. Smaller ash contents could be possible to achieve if the displacement washing is done using a pressurized washer. Mass balances for the WBL lignin samples ranged between 97.92 - 100.24%, whereas for the CBL lignins the variation was even smaller, between 98.85 - 99.58%. Based on the mass balances, the results shown in the Table 13 can be considered to be reliable. The mass balances found in the literature for lignin characterization are usually circa 95 - 105%. The inaccuracy of the lignin characterization is partly caused by the lack of standardized lignin characterization methods, as most of the used methods are based on pulp characterization.

### 8.3.1 Lignin content

The lignin content was fairly high throughout the experimental study, as shown in the Table 13. The lowest lignin content, 95.73%, was in the WBL W1 sample, whereas the highest lignin content, 98.12%, was in the CBL C4 sample. Altogether, the lignin content of our samples was fairly constant. The lignin content in $CO_2$ precipitated kraft lignin is usually fairly high. Alekhina et al. (2015) precipitated softwood kraft lignin with $CO_2$ and found out that the precipitation pH has a major effect on the lignin content. The highest lignin content, which varied between 98.73 - 97.31%, was found when the $CO_2$ precipitation was ended at pH 10.5. In these samples the ASL content varied between 1.36 - 2.34%. /4/ The LHT process would seem to increase the Klason lignin content slightly and decrease content of the ASL. The total lignin content did not appear to change systematically during the LHT process. Although the Klason lignin and ASL contents would seem to correlate with the LHT H-factor, it is fairly hard to say how predictable this correlation is in reality due to variations between the duplicate samples.

The Klason lignin determination was done as a gravimetrical determination, so it was expected that the results between duplicate samples would vary to some degree. Most of the variation during the Klason lignin determination was caused by the material losses during the two-step hydrolysis and by the impurities in the filter crucibles. The standard deviation between the duplicated samples varied

between 0.03 - 1.46, whereas the average for the standard deviation was 0.53. The results during the ASL content determination did not vary as much as in the Klason lignin determination. During the ASL determination the average standard deviation between the duplicated samples was 0.08. Most of the variations in the ASL results was probably caused by slight differences in the two-step hydrolysis.

## 8.3.2 Carbohydrate content

The carbohydrate content of the isolated lignin was determined alongside the lignin content determination. The polysaccharide detection was done with high-performance anion exchange chromatograph from the acid hydrolysis filtrate. The proportions of the different residual carbohydrates detected in the lignin are shown in the Table 14.

**Table 14.** Proportion of different carbohydrates in the lignin samples.

| Sample ID | Arabinose (%) | Galactose (%) | Glucose (%) | Xylose (%) | Mannose (%) | Total (%) |
|---|---|---|---|---|---|---|
| WBL Ref | 0.27 | 0.72 | 0.07 | 0.39 | 0.04 | 1.50 |
| WBL W1$_{170C, 15min, H\text{-}factor\ 420}$ | 0.16 | 0.65 | 0.04 | 0.20 | 0.02 | 1.07 |
| WBL W3$_{170C, 45\ min, H\text{-}factor\ 880}$ | 0.08 | 0.14 | 0.02 | 0.12 | 0.01 | 0.37 |
| WBL W5$_{180C, 30\ min, H\text{-}factor\ 1580}$ | 0.07 | 0.16 | 0.02 | 0.13 | 0.01 | 0.39 |
| WBL W4$_{190C, 15\ min, H\text{-}factor\ 3200}$ | 0.02 | 0.05 | 0.03 | 0.04 | 0.00 | 0.15 |
| WBL W6$_{190C, 45\ min, H\text{-}factor\ 5080}$ | 0.01 | 0.05 | 0.02 | 0.04 | 0.00 | 0.12 |
| WBL W2$_{190C, 45\ min, H\text{-}factor\ 5250}$ | 0.04 | 0.24 | 0.02 | 0.14 | 0.01 | 0.46 |
| CBL Ref | 0.12 | 0.27 | 0.05 | 0.15 | 0.02 | 0.61 |
| CBL C1$_{170C, 15\ min, H\text{-}factor\ 420}$ | 0.07 | 0.17 | 0.07 | 0.10 | 0.01 | 0.42 |
| CBL C3$_{170C, 45\ min, H\text{-}factor\ 890}$ | 0.04 | 0.07 | 0.04 | 0.05 | 0.01 | 0.21 |
| CBL C5$_{180C, 30\ min, H\text{-}factor\ 1680}$ | 0.03 | 0.10 | 0.03 | 0.06 | 0.01 | 0.23 |
| CBL C4$_{190C, 15\ min, H\text{-}factor\ 3280}$ | 0.01 | 0.02 | 0.01 | 0.02 | 0.00 | 0.06 |
| CBL C2$_{190C, 45\ min, H\text{-}factor\ 5060}$ | 0.01 | 0.03 | 0.02 | 0.02 | 0.00 | 0.08 |

As mentioned earlier, the polysaccharide content in the reference lignin samples was fairly low. The initial carbohydrate contents for the WBL and CBL samples

were 1.50% and 0.61% respectively. The initial sugar content of the WBL lignin was fairly similar compared to the sugar content of the commercial softwood lignin Indulin AT, while the initial sugar content of the CBL lignin was even lower /75/. The predominant polysaccharide in the reference lignins was galactose, which was expected for a softwood lignin. 48.00% of the residual carbohydrates in the WBL reference sample was galactose, whereas in the CBL reference sample this value was 44.26%. Xylose and arabinose were both detected in moderate concentrations. Roughly 25% and 19% of the residual polysaccharides were xylose and arabinose respectively. In addition to galactose, xylose and arabinose, small concentrations of mannose and rhamnose could be detected. Rhamnose is not included in the results shown in the Table 14, because the detected concentrations were extremely low. Even the highest rhamnose content, which was found from the CBL reference sample, was only 0.0043%.

The LHT process produced fairly constant results throughout the experiment, although some inconsistencies could be found. Based on our results, it is evident that even the mildest heat treatment (H-factor 420) is able to reduce the residual carbohydrate content in the isolated lignin. The mildest heat treatment reduced the carbohydrate content in the WBL W1 and CBL C1 samples by 28.67% and 31.15% respectively, although the reduction in CBL C1 might be even higher in reality. The glucose content of the CBL C1 sample was quite high compared to the rest of the CBL samples. The high glucose concentration was thought to be originating from the filtration of the CBL C1 $CO_2$ liquor. During the filtration, the lignin stuck to the filtration paper due to the high temperature of the $CO_2$ liquor, causing clogging and tearing of the filtration paper when the lignin was collected. Thus the increase in the glucose concentration is probably caused by cellulose fibers originating from the filtration paper.

Efficient carbohydrate reduction would seem to require either high temperature (190 °C) or long treatment time (45 minutes). Although the mildest heat treatment was able to reduce the carbohydrate content in the WBL W1 and CBL C1 samples by 28.67% and 31.15% respectively, the longer treatment time in the W3 and C3 resulted to 75.33% and 65.57% reduction in the carbohydrate content respectively. The major difference between the WBL W1 and W3 samples polysaccharide

content was the galactose content. Galactose reduction increased from 9.72% to 80.56% when the treatment time was increased from 15 minutes to 45 minutes. The difference between C1 and C3 was not as major as with W1 and W3, rather the polysaccharide reduction was fairly linear when compared to the H-factor of the treatment. Interestingly the fifth heat treatment (180 °C and 30 minutes) did not reduce the carbohydrates as effectively as the third heat treatment (170 °C and 45 minutes), indicating that the polysaccharide reduction cannot be predicted purely from the LHT H-factor.

The fourth heat treatment (190 °C and 15 minutes) was able to reduce the carbohydrate content in the WBL and CBL samples by circa 90%. The increased treatment time (45 minutes) when using 190 °C temperature, did not have any significant advantages compared to the 15 minutes treatment. The differences between W4 and W6 and C4 and C2 lignins are so minimal that it is impossible to say how much of this difference is caused by the heat treatment and how much is caused by slight differences in the following precipitation and washing steps. The fairly high carbohydrate content in the WBL W2 sample was thought to be due to malfunction of the temperature controller during the $CO_2$ precipitation. The temperature of the liquor rose close to 90 °C, because the controller did not work properly. Zhu et al. (2015) found out that the higher temperature during the softwood lignin precipitation resulted to higher carbohydrate content in the isolated lignin /103/.

Based on these results it is difficult to estimate how much the higher temperature actually affected the polysaccharide reduction. The temperature increase during the LHT was fairly slow after 170 °C. While the temperature increase from 170 °C to 180 °C took slightly over 15 minutes, the temperature increase from 170 °C to 190 °C was much slower, taking up to 40 minutes. Hence, the time that the WBL W3 and W5 liquors were held at over 170 °C was nearly identical, whereas the W4 sample was kept 10 minutes longer at over 170 °C. When comparing the durations that the sample liquors were held at over 170 °C, we can see that the duration of the LHT might be the key factor affecting the result of the LHT. It is also important to remember that the results shown in Table 13 can contain slight errors resulting from the high-performance anion exchange chromatograph. Although the

equipment can detect low carbohydrate concentration, the accuracy of the result will decrease when the concentration is very low. Other problem was the high acid concentration in the samples, caused by the low dilution factor (2 - 5). The high acid concentration caused shifts in the sugar peaks and altered the shape of these peaks. The peak sifting was corrected manually in order to minimize the error, but the altered shape could not be corrected.

### 8.3.3 Ash and sodium content

The ash content in the WBL and CBL lignin samples varied between 0.57 - 2.91% and 1.39 - 2.70%, as shown in the Table 13. The LHT did not seem to have any significant effect on the ash content. The reason for the variations in the ash content between the different samples was probably due to small differences during the lignin washing. Vishtal et al. (2011) reported in their literature review that the ash content in kraft lignin varies between 0.5 - 3.0%, although as the lignin washing procedures have developed, the average ash content found in kraft lignin nowadays is probably closer to 0.5 - 1.0% /15/. Compared to these values, the ash content found in our samples can be considered fairly normal.

As mentioned earlier, the ash content could be lower if the washing equipment is different. The high ash contents in WBL W3, CBL C2 and C5 samples are probably at least partially due to poor displacement washing. The filtration resistance during the displacement washing was quite high, so the use of pressurized washer could have lowered the ash content in the lignin samples. Sodium content was also determined from two reference samples and from two LHT lignins. The selected LHT lignin samples were WBL W3 and WBL C3. These lignin samples were selected based on the effectiveness of the LHT on the lignin carbohydrate content. The results from the sodium content determination are shown in the Table 15.

**Table 15.** Results from the sodium content determination.

| Sample ID | Ash (%) | Na (mg/g) | Na/Ash (%) |
|---|---|---|---|
| WBL Ref | 1.01 | 1.50 | 14.81 |
| WBL W3[170C, 45 min, H-factor 880] | 2.91 | 6.00 | 20.61 |
| CBL Ref | 1.50 | 3.58 | 23.75 |
| CBL C3[170C, 45 min, H-factor 890] | 1.66 | 4.21 | 25.33 |

The sodium content of the selected lignin samples varied between 1.50 - 6.00 mg/g. The highest sodium content was found in the WBL W3 sample, which was expected as the W3 lignin had also the highest ash content. The sodium content of the $CO_2$ precipitated softwood lignin has been reported to vary between 1.50 - 3.50 mg/g depending on the precipitation pH and re-suspension pH /68/, although Öhman et al. (2007) reported that with a proper washing even 0.14 mg/g sodium content could be achieved /67/. These studies showed that the sodium content of the isolated lignin is heavily affected by the pH during the precipitation and washing. In our research, the sodium content was also compared to the ash content. The portion of the sodium in the ash varied between 14.81 - 25.33%. Based on these results it would seem that the CBL lignins have higher sodium content in the inorganic residue, although this cannot be said with full certainty as even the slight differences in the isolation conditions affect the sodium content of the end product lignin.

### 8.3.4 Elemental analysis

Elemental analysis for the lignin samples was done with PerkinElmer Model 2400 Series II CHNS Elemental Analyzer. The oxygen content was calculated by subtracting carbon, hydrogen, nitrogen, sulfur and ash content from 100%. The results from the elemental analysis are shown in the Table 16.

**Table 16.** Results from the elemental analysis.

| Sample ID | C (%) | H (%) | N (%) | S (%) | Ash (%) | O (%) |
|---|---|---|---|---|---|---|
| WBL Ref | 64.76 | 5.77 | 0.15 | 1.76 | 1.01 | 26.56 |
| WBL W1$_{170C, 15min, H-factor 420}$ | 64.32 | 5.86 | 0.15 | 1.96 | 1.12 | 26.61 |
| WBL W3$_{170C, 45 min, H-factor 880}$ | 64.62 | 6.07 | 0.24 | 2.39 | 2.91 | 23.78 |
| WBL W5$_{180C, 30 min, H-factor 1580}$ | 65.34 | 6.13 | 0.25 | 2.24 | 1.52 | 24.54 |
| WBL W4$_{190C, 15 min, H-factor 3200}$ | 66.63 | 6.02 | 0.27 | 1.86 | 0.57 | 24.65 |
| WBL W6$_{190C, 45 min, H-factor 5080}$ | 66.55 | 5.92 | 0.26 | 2.00 | 1.28 | 24.00 |
| WBL W2$_{190C, 45 min, H-factor 5250}$ | 64.76 | 6.02 | 0.17 | 2.26 | 1.79 | 25.01 |
| CBL Ref | 63.70 | 6.06 | 0.09 | 2.44 | 1.51 | 26.21 |
| CBL C1$_{170C, 15 min, H-factor 420}$ | 64.88 | 5.75 | 0.09 | 2.27 | 1.82 | 25.21 |
| CBL C3$_{170C, 45 min, H-factor 890}$ | 65.07 | 5.87 | 0.27 | 2.29 | 1.66 | 24.84 |
| CBL C5$_{180C, 30 min, H-factor 1680}$ | 64.70 | 5.63 | 0.29 | 2.35 | 2.37 | 24.67 |
| CBL C4$_{190C, 15 min, H-factor 3280}$ | 65.77 | 5.69 | 0.31 | 2.18 | 1.39 | 24.67 |
| CBL C2$_{190C, 45 min, H-factor 5060}$ | 65.06 | 5.78 | 0.17 | 2.46 | 2.70 | 23.84 |

The carbon content in all the samples was relatively high. The smallest carbon content was in the CBL reference sample (63.70%) and the highest carbon content was found in the WBL W4 sample (66.63%). The high carbon content is a result from the low ash and carbohydrate content. Compared to other lignin types, kraft lignin has usually relatively high carbon content /104, 105/. The nitrogen content found in the samples was very low, the highest amount of nitrogen was 0.31%. The sulfur content varied between 1.76 - 2.39% and 2.18 - 2.46% for the WBL and CBL samples respectively. The higher sulfur content found in the CBL samples is probably caused by the lower H-factor during cooking. The higher H-factor during cooking might have resulted to a higher average molecular mass for the WBL samples, *i.e.* the WBL samples have higher fraction of high molecular mass lignin compared to the CBL samples. The low molecular mass lignin has been shown to contain high amount of sulfur, whereas the high molecular mass lignin has been shown to have higher carbohydrate content /37/.

The LHT process does not appear to have any major effects on the lignin, based on the elemental analysis. Compared to the WBL reference sample, the carbon content in the WBL W4, W5 and W6 were slightly higher. All the heat treated CBL samples also had slightly higher carbon content, compared to CBL reference sample. This would indicate that the LHT slightly increases the lignin carbon content, although the effect of the heat treatment was not systematic for all the samples, as the carbon content in the WBL W1, W2 and W3 samples did not increase. The heat treatment resulted to slightly lower carbon content in the W1 and W3 samples, whereas the carbon content in the W2 sample remained the same as in the reference sample.

The sulfur content in the heat treated samples varied from the reference samples, but it is impossible to say how much the heat treatment actually affected to the varying sulfur content. If the heat treatment actually affects the sulfur content in the lignin, the effect is fairly low and inconsistent. The oxygen content in the heat treated samples changed most systematically. Excluding the WBL W1 sample, all other LHT lignin samples had lower oxygen content compared to the reference samples. The nitrogen content in the lignin samples increased slightly after the heat treatment, but the increase was fairly low. Overall only minor changes could be found from the elemental analysis results. It is important to remember that the varying ash and carbohydrate contents in different samples affected the elemental analysis results. The effects that the LHT has on the elemental composition can only be researched accurately if the lignin has uniform ash and carbohydrate contents, which not possible with our samples.

## 8.4 Operating costs

### 8.4.1 Operating costs for the lignin precipitation

The operating costs for the $CO_2$ lignin precipitation are taken from the from the lignin recovery presentation by McKeough et al. (2013) /106/. Operating costs for the lignin precipitation are shown in the Table 17. The chemical costs are divided into $CO_2$, $H_2SO_4$, and NaOH costs in the results.

**Table 17.** Operating costs for the lignin precipitation /106/.

| Operating cost | Unit price | €/t of dry lignin |
|---|---|---|
| Reduced steam production | 16 €/MWh | 115 |
| Increased evaporation costs | 21 €/MWh | 20 |
| Chemical costs: | | |
| • $CO_2$ | 125 €/t | 35 |
| • $H_2SO_4$ | 100 €/t | 20 |
| • NaOH | 350 €/t | 75 |
| Heat for lignin drying | 23 €/MWh | 10 |
| Increased electricity consumption | 50 €/MWh | 15 |
| Labor and maintenance | | 15 |
| **Total operating costs** | | **305** |

The total operating costs for lignin precipitation are 305 €/t of dry lignin. The two major individual costs are the reduced steam production and the chemical costs. These two costs form 80.32% of the total operating costs. The reduction in steam production is caused by the reduced amount of organics, mainly lignin, in black liquor. The water used in the displacement wash of the second lignin cake is recycled back to evaporation plant, and thus the evaporation demand is also increased. From the chemical costs, only 42.31% are directly from the lignin precipitation process. The $CO_2$ is used during the acidification of the black liquor and the $H_2SO_4$ is used for the washing of lignin. The remaining 57.69% of the chemical costs is caused by the NaOH consumption. The NaOH is used to re-adjust the Na/S balance, which is upset after the vast use of $H_2SO_4$ in the lignin washing.

When comparing the total direct and indirect costs of lignin precipitation, it can be seen that the direct costs during the lignin precipitation are fairly low. Only 31.15% (95 €/t of lignin) of the total costs are caused by direct costs. These direct costs are the cost of $CO_2$, $H_2SO_4$, heat for lignin drying, increased electricity consumption and labor and maintenance. The rest of the operating costs are caused indirectly by lignin precipitation. Some cost estimations found in the literature exclude the indirect costs from the cost estimation, *e.g.* the cost estimation for the ultrafiltration

done by Jönsson et al. (2007) only included the direct costs /61/. Based on the results shown in the Table 17, the exclusion of the indirect costs of the lignin isolation would produce fairly optimistic estimation of total operating costs for the lignin precipitation, because the indirect costs are 68.85% of the total costs. More realistic result is achieved when both the direct and indirect costs are taken into account.

## 8.4.2 Operating costs for LHT lignin precipitation

The results from the LHT operating cost calculations are shown in the Table 18. The liquor and temperature dependent values that have been used during the LHT lignin precipitation cost estimation are shown in the Appendix 2. The Appendix 2 also includes the steam cost and consumption calculations that are done for the WBL LHT at 170 °C. Additional investment costs that are caused by the LHT are included into the LHT costs during the calculations. The additional investment costs are taken from the McKeough et al. (2013) presentation on the lignin recovery /106/.

**Table 18.** Results from the LHT lignin precipitation cost estimation.

| LHT ID | Steam (kg/t of lignin) | LHT (€/t of lignin) | Precipitation (€/t of lignin) | Total cost (€/t of lignin) |
|---|---|---|---|---|
| WBL 170 °C | 14208 | 162 | 305 | 467 |
| WBL 180 °C | 14820 | 169 | 305 | 474 |
| WBL 190 °C | 15433 | 176 | 305 | 481 |
| CBL 170 °C | 12993 | 148 | 305 | 453 |
| CBL 180 °C | 13836 | 158 | 305 | 463 |
| CBL 190 °C | 14681 | 167 | 305 | 472 |

The total operating cost for the LHT lignin precipitation varies between 453 - 481 €/t of dry lignin. The precipitation costs for the LHT liquors are thought to be the same as in the $CO_2$ lignin precipitation shown in the previous section. The steam consumption during the LHT varied between 12993 - 15433 kg/t of lignin for the different liquors and heat treatment conditions, when the heating is done with

intermediate pressure steam (13 bar, 195 °C). The operating cost for the LHT is caused by the increased steam consumption. The steam cost for the heat treatment is thought to be the same as the steam cost for the increased evaporation caused by the lignin precipitation. When comparing to the precipitation costs, the addition of LHT increases the total operating costs by roughly 50%. The use of LHT might be viable if the isolated LHT lignin proves to be useful raw material for the high value applications mentioned in the chapter 3.4 of this thesis, otherwise the increased operational costs cannot be justified.

Based on the results shown in the Table 18, the WBL LHT is more expensive than the CBL LHT, although the difference between the WBL and CBL is not significant. The difference in the operating costs is caused by the difference in the initial liquor temperature. Although the mass flow in the feed is circa 27% smaller for the WBL LHT, the temperature difference between the initial liquor temperature and the LHT temperature is much higher than in the CBL LHT. The mass flow difference will result to different investment costs for WBL and CBL LHT, because larger mass flow requires larger equipment. This was not taken into account, because these calculations were done purely from the energy consumption perspective. The largest factors affecting the operating costs of the LHT are the lignin concentration in black liquor and the yield of the lignin isolation. If the lignin concentration is increased by 10%, the operating costs would decrease circa 9% for both liquors, regardless of the heat treatment temperature, and if yield is increased by 10%, the reduction in the operating costs is roughly 14% for both liquors. Although, it is good to remember that the increase in the lignin precipitation yield would also increase the chemical costs during the lignin precipitation.

# 9 Conclusions

This thesis had three main objectives: i) to discover different methods for kraft lignin purification that could be used alongside acid precipitation, ii) test the most suitable treatment on laboratory scale and evaluate the potentiality of this method as a kraft lignin purification method, and iii) to compare the viability of lignin purification alongside the acid precipitation compared to conventional acid precipitation. The different lignin purification methods were researched based on the existing literature and the most significant methods that were discovered were hydrolysis, solvent extraction and liquor heat treatment.

Hydrolysis, solvent extraction and liquor heat treatment are all existing methods that have been used to treat lignin or black liquor. Hydrolysis and solvent extraction have both been used for lignin purification, whereas LHT has mainly been used to reduce the carbohydrate content in black liquor. LHT has also occasionally been suggested for lignin purification, but no comprehensive studies could be found from this subject during the literature review. LHT is a well known technique, which is used in evaporation, and could be potentially integrated to existing pulp mills fairly easily. Although the solvent extraction is an interesting method, it has some negative aspects, which are mainly the poor selectivity and the energy intensive solvent recovery process. Lignin purification based on hydrolysis also has some negative aspects, because the enzymatic hydrolysis cannot remove the carbohydrates completely and it introduces new nitrogen impurities to lignin, whereas the effects of the acid hydrolysis on the lignin properties are not known. Based on these findings the LHT was selected as a research subject in the experimental part of this thesis.

The LHT was performed using both cooking black liquor and weak black liquor. The actual heat treatment was done using air bath digester and the H-factors for each heat treatment were calculated. The only problem that occurred during the LHT process was insufficient flashing after the heat treatment, which is thought to be the cause for poor sulfur reduction during the LHT process. After the LHT, the lignin was precipitated using $CO_2$ and the precipitated lignin was washed. The heat

treatment appeared to change the precipitation behavior of lignin, which led to a formation of pitch-like lignin. The change in the precipitation behavior was thought to be due to a decreased glass transition temperature in the LHT lignins and this hypothesis was tested during precipitation of WBL W6 sample, by lowering the precipitation temperature from 70 °C to 50 °C. The resulting lignin behaved exactly the same as the lignin during the reference sample precipitation, which supports the hypothesis.

The characterization of black liquors and isolated lignins was mostly successful. The largest problem was caused by the changed lignin precipitation behavior after the heat treatment, which caused a fair amount of variation between duplicate samples during the dry matter content determination. The variations in the dry matter content affected the reliability of the black liquor and the $CO_2$ liquor sulfur content determination results. Although the reliability of these results is questionable, it was evident that the $CO_2$ lignin precipitation reduced the sulfur content of the liquor fair amount. The sulfur content reduction was between 9.12 - 33.87% and 26.52 - 40.51% for the WBL and CBL samples respectively during our experiment.

The most important part of the laboratory experiment was to evaluate the potentiality of LHT as a kraft lignin purification method. The efficiency of the LHT was evaluated based on the lignin carbohydrate reduction as the modern industrial scale lignin washing equipment can produce nearly ash-free lignin. The heat treatment at 190 °C managed to reduce circa 90% of the carbohydrates, whereas the heat treatment at 170 °C for 45 minutes resulted to 75.33% and 65.57% carbohydrate content reduction for WBL and CBL respectively. There were also some indications that the duration of the LHT might be the key factor affecting the result of the LHT. The CBL lignin had initially much lower carbohydrate content than the WBL. Based on these finding, the most suitable LHT conditions was 170 °C and 45 minutes and the most suitable raw material was cooking black liquor.

The last part of this thesis was to compare the viability of the LHT lignin precipitation process and the traditional acid precipitation process. The viability

was evaluated based on the operating costs. The LHT increased the operating cost by 162 - 176 €/t of lignin for WBL and 148 - 167 €/t of lignin for CBL depending on the treatment temperature. The addition of LHT increases the total operating costs by roughly 50% compared to the conventional acid precipitation, therefore the LHT lignin should only be used for high value applications. Future research should be done in order to optimize the LHT process and to test the LHT while using black liquor that contains more carbohydrates. Also the LHT should be tested while using more concentrated black liquor, *e.g.* dry solids contents 30 - 45%, as the higher dry solids content lowers the operational costs for the LHT process. The LHT process and the use CBL for pure lignin production looks promising, but these subjects need more research.

Overall the present lignin research is still inadequate and there should be more accurate methods for lignin characterization, as many of the methods used at the moment are based on pulp characterization.

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# List of Appendices

Appendix 1: Results from the sulfur content determination

Appendix 2: Operating costs calculations for LHT lignin precipitation

## Appendix 1: Results from the sulfur content determination

| Sample ID | Initial (mg/g) | LHT (mg/g) | $CO_2$ (mg/g) |
|---|---|---|---|
| WBL Ref | 10.2 | - | 7.6 |
| WBL W1 170C, 15min, H-factor 420 | 10.2 | 10.2 | 8.6 |
| WBL W3 170C, 45 min, H-factor 880 | 10.2 | 11.7 | 7.5 |
| WBL W5 180C, 30 min, H-factor 1580 | 10.2 | 10.5 | 7.8 |
| WBL W4 190C, 15 min, H-factor 3200 | 10.2 | 9.7 | 7.5 |
| WBL W6 190C, 45 min, H-factor 5080 | 10.2 | 12.3 | 9.4 |
| WBL W2 190C, 45 min, H-factor 5250 | 10.2 | 9.4 | 7.9 |
| CBL Ref | 12.0 | - | 9.3 |
| CBL C1 170C, 15 min, H-factor 420 | 12.0 | 11.8 | 8.2 |
| CBL C3 170C, 45 min, H-factor 890 | 12.0 | 11.9 | 9.3 |
| CBL C5 180C, 30 min, H-factor 1680 | 12.0 | 12.7 | 7.8 |
| CBL C4 190C, 15 min, H-factor 3280 | 12.0 | 12.6 | 7.4 |
| CBL C2 190C, 45 min, H-factor 5060 | 12.0 | 12.2 | 8.8 |

# Appendix 2: Operating costs calculations for LHT lignin precipitation

The values used for different black liquors and heat treatment temperatures are shown in table below. Calculation example is shown after the table. This example is done for the WBL LHT at 170 °C.

| Parameters | WBL | | | CBL | | |
|---|---|---|---|---|---|---|
| | 170 °C | 180 °C | 190 °C | 170 °C | 180 °C | 190 °C |
| c (g/l) | 65 | 65 | 65 | 45 | 45 | 45 |
| $\rho_{bl}$ (kg/l) | 1.09 | 1.09 | 1.09 | 1.04 | 1.04 | 1.04 |
| $x_F$ (%) | 14 | 14 | 14 | 14 | 14 | 14 |
| $x_L$ (%) | 18 | 18 | 18 | 18 | 18 | 18 |
| $h_L$ (kJ/kg) | 658 | 698 | 738 | 658 | 698 | 738 |
| $H_V$ (kJ/kg) | 2818 | 2838 | 2858 | 2818 | 2838 | 2858 |
| $h_F$ (kJ/kg) | 311 | 311 | 311 | 589 | 589 | 589 |
| $H_S$ (kJ/kg) | 2798 | 2798 | 2798 | 2798 | 2798 | 2798 |
| $h_S$ (kJ/kg) | 852 | 852 | 852 | 852 | 852 | 852 |

Cost of steam during the LHT:

$$\dot{m}_F = \frac{50000 \text{ t/a}}{65 \text{ g/l} * 0.6} * 1.09 \frac{\text{kg}}{\text{l}} = 159022 \frac{\text{kg}}{\text{h}}$$

$$\dot{m}_L = \frac{159022 \text{ kg/h} * 0.14}{0.18} = 123684 \frac{\text{kg}}{\text{h}}$$

$$\dot{m}_V = 159022 \frac{\text{kg}}{\text{h}} - 123684 \frac{\text{kg}}{\text{h}} = 35338 \frac{\text{kg}}{\text{h}}$$

$$q = \left(123684 \frac{\text{kg}}{\text{h}} * 658 \frac{\text{kJ}}{\text{h}} + 35338 \frac{\text{kg}}{\text{h}} * 2690 \frac{\text{kJ}}{\text{h}} - 159022 \frac{\text{kg}}{\text{h}} * 311 \frac{\text{kJ}}{\text{h}}\right) * 1.20$$

$$= 157781 \frac{\text{MJ}}{\text{h}} = 44 \frac{\text{MWh}}{\text{h}}$$

$$\text{LHT steam cost} = \frac{44 \text{ MWh/h} * 21 \text{ €/MWh}}{50000 \text{ t/a}} + 0.7 \text{ €/t} = 162 \text{ €/t of lignin}$$

Steam consumed during LHT:

$$\dot{m}_S = \frac{\dfrac{126977 \text{ MJ/h}}{2798 \text{ kJ/kg} - 852 \text{ kJ/kg}}}{50000 \text{ t/a}} = 14208 \text{ kg} \Big/ \text{t of lignin}$$