Aalto University
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NOVEL INDUSTRIAL SCALE APPLICATIONS OF LIGNIN

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 19 August, 2014.

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Abstract of master's thesis

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Abstract

This Master’s Thesis had three objectives, that were: (i) to elucidate the structure of 14 technical lignins and point out the differences between them, (ii) to discover novel applications of lignin which could have industrial importance and evaluate the maturity of these applications, and (iii) to evaluate the suitability of characterized technical lignins for each application. The purpose was to find potential applications for industrial scale production of novel lignin-based products. Also, the current state of lignin research was revised.

Ten of the fourteen samples were received as isolated and four samples were isolated in laboratory with CO_2 precipitation procedure. Characterization of lignin samples was performed in laboratory with known characterization methods that were adopted from previous experiments and standards. The characterized properties were purity, elemental constitution, reactivity, molecular weight distribution and the odor of samples. Softwood polysulfide kraft lignin that was isolated with CO_2 precipitation was evaluated to be the most suitable towards various applications, based on the characterization results and literature. The main problem with several lignin samples was the high amount of impurities, either carbohydrates or ash. Therefore, they require extensive purification procedures in order to be valorized.

Potential applications were divided in five categories that were: fuels, chemicals, composites, activated carbon and carbon fibers. Maturities of representing examples from each category were evaluated with modified TRL metrics alongside with three isolation technologies. The results of TRL evaluation gave a good overview about the current state and development stage of novel lignin-based fuels, chemicals, and materials.

When all the information was combined from literature, characterization results and TRL evaluation, the suitability of different lignins towards different applications was evaluated. Lignin-based carbon fiber was evaluated to be the most promising application due to the enormous market potential, after cost and strength targets are achieved. Promising innovations have been made recently in Sweden and softwood polysulfide kraft lignin could be the perfect raw material for the production of low-cost carbon fibers.

Keywords lignin, biorefinery, novel products, carbon fibers, biomaterials, biochemicals, biofuels, characterization, TRL evaluation

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Tiivistelmä

Tällä työllä oli kolme keskeistä tavoitetta, jotka olivat: (i) selvittää 14 erilaisen teknisen ligniinin ominaisuuksia sekä löytää näistä keskinäisiä eroja, (ii) löytää ligniineille uusia loppukäyttöjä, joilla on potentiaalia teollisen mittakaavan tuotantoon, sekä arvioida näiden nykyistä kehitysastetta, ja (iii) arvioida karakterisoitujen ligniini näytteiden soveltuvuutta tunnistettuihin loppukäyttöihin. Näiden tavoitteiden päämääränä oli löytää uusia teollisen mittakaavan hyödyntämismahdollisuuksia ligniinille. Työssä arvioitiin myös ligniinitutkimuksen nykytilaa.

Kymmenen neljästätoista ligniininäytteestä saatiin valmiiksi erotettuina, ja neljä näytettä erotettiin laboratoriossa hillidioksidisaostuksella. Ligniininäytteet karakterisoitiin laboratoriossa tunnetuilla menetelmillä, jotka suoritettiin aikaisempien tutkimusten ja standardien mukaisesti. Karakterisoituja ominaisuuksia olivat puhtaus, alkuainekoostumus, reaktiivisuus, moolimassajakauma sekä ominaistuoksu aiheuttajineen. Hiilidioksidisaostuksella erotettu havupuupohjainen polysulfidiligniini arvioitiin karakterisointitulosten sekä kirjallisuuden perusteella soveltuvimmaksi ligniiniksi useisiin loppukäyttökohteisiin. Joidenkin ligniinien kohdalla korkea tuhka- tai hiilihydraattipitoisuus vähensi potentiaalisten loppukäyttöjen määrää huomattavasti.

Potentiaaliset loppukäyttökohteet jaettiin viiteen kategoriaan, jotka olivat: polttoaineet, kemikaalit, komposiitit, aktiivihiili sekä hiilikuitu. Kategorioista valittiin edustavia esimerkkejä, joiden kehitysaste arvioitiin tähän työhön räätälöidyllä TRL-mittaristolla. Loppukäyttöjen lisäksi myös kolmen erotusteknologian kehitysaste arvioitiin. TRL-arvioinnin tulokset antoivat kattavan kokonaiskuvan ligniinipohjaisten polttoaineiden, kemikaalien sekä materiaalien tämänhetkisestä tilasta.

Soveltuvuusarviointi suoritettiin yhdistämällä kirjallisuudesta, karakterisointituloksista ja TRL-arvioinnista saatu informaatio, jonka perusteella ligniininäytteiden soveltuvuutta eri loppukäyttökohteisiin tarkasteltiin ja tehtiin johtopäätöksiä potentiaalisimmista vaihtoehdoista. Ligniinipohjainen hiilikuitu arvioitiin lupaavimmaksi loppukäytöksi, johtuen sen valtavasta markkinapotentiaalista, kun tuotantokustannukset ja lujuusominaisuudet saadaan oikealle tasolle. Tätä johtopäätöstä tukivat myös viime aikoina Ruotsissa tehdyt innovaatiot sekä ruotsalaisten runsas panostus hiilikuitututkimukseen.

Avainsanat ligniini, biojalostamo, uudet tuotteet, hiilikuitu, biomateriaalit, biokemikaalit, biopolttoaineet, karakterisointi, TRL arviointi

PREFACE

This thesis was written during the six-month period from the beginning of February 2014 to the end of July 2014. The work was financed by Pöyry Management Consulting Oy and Andritz Oy.

I want to thank my advisors M.Sc. Katja Salmenkivi and D.Sc. Petri Vasara from Pöyry Management Consulting Oy and M.Sc. Kari Tuominen from Andritz Oy. Thank you for providing this challenging opportunity and an interesting topic. This has been a fascinating journey, and you have provided fresh advice and strong professional opinions when needed, thank you for that. Thank you, Professor Olli Dahl and M.Sc. Kari Vanhatalo for enabling me to do this amount of work during such a short period. You two were really helpful on planning and implementing the plan B for the experimental part.

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Helsinki, 19th August 2014

Lauri Pehu-Lehtonen

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ABBREVIATIONS

G	guaiacyl
S	syringyl
H	*p*-hydroxyphenyl
SW	softwood
HW	hardwood
T_g	glass transition temperature
T_d	decomposition temperature
MWL	milled wood lignin
M_w	molecular weight
SSL	spent sulfite liquor
BL	black liquor
WBL	weak black liquor
AQ	anthraquinone
IL	ionic liquid
FT	Fischer-Tropsch
WGS	water-gas shift
PE	polyethylene
PS	polystyrene
MTG	methanol to gasoline
MAS	mixed alcohol synthesis
PF	phenol-formaldehyde

MTO	methanol to olefins
DMSO	dimethyl sulfoxide
PU	polyurethane
AC	activated carbon
CF	carbon fiber
PAN	polyacrylonitrile
HKL	hardwood kraft lignin
SKL	softwood kraft lignin
HKLP	hardwood kraft lignin permeate
SKLP	softwood kraft lignin permeate
DoE	U.S. Department of Energy
TRL	Technology Readiness Level
NASA	National Aeronautics and Space Administration
TRA	Technology Readiness Assessment
AIL	acid insoluble lignin
ASL	acid soluble lignin
NREL	National Renewable Energy Laboratory
HPLC	high performance liquid chromatography
TAPPI	Technical Association of the Pulp and Paper Industry
GPC	gel permeation chromatography
SEC	size exclusion chromatography
THF	tetrahydrofuran

DAD	diode array detector
DF	dilution factor
SPME	solid-phase micro extraction
GC	gas chromatography
MS	mass spectrometry
VOC	volatile organic compounds
NMR	nuclear magnetic resonance

1 Introduction

The dwindling of easily accessible fossil resources and the growing consciousness of environmental problems are the main driving forces for the development of more sustainable materials, chemicals and fuels from renewable resources. Lignocellulosic biomass, which consists of carbohydrates (cellulose and hemicellulose), lignin and extractives, is often considered as the most suitable and sustainable raw material for bioeconomy since it is widely available and does not interfere with food production, if not grown in farmland.

Valorization of all fractions of lignocellulosic biomass is crucial for many reasons, resource efficiency and economic feasibility being the most important ones. Carbohydrates and extractives have a good variety of end uses, but the valorization of lignin is not as developed, which is mostly due to the complexity of this material. The current applications of lignin are limited and typically low in value, and the majority of lignin is combusted for energy generation and recovery of pulping chemicals. Combustion of lignin is resource efficient in many cases but due to the development of technology the most modern pulp mills can generate vast amounts waste steam, which decreases the resource efficiency and therefore promotes the usage of lignin in other applications than combustion. Also the economic feasibility could be higher in other applications, since lignin consists of phenolic compounds that would be solely very valuable.

The complexity and potential of lignin have fascinated scientists since the discovery of this material, but major breakthroughs in high value added applications are yet to come. However, lignin and its possible novel applications have been researched with accelerating speed during the most recent years, *e.g.* over 30% of the 166 references utilized in this thesis have been published within the last two and a half years (2012-2014). Therefore, this topic is considered very relevant and current.

1.1 Objectives

This thesis has three major objectives which are: (i) to elucidate the structure of 14 technical lignins and point out the differences between them, (ii) to discover novel applications which could have industrial importance and evaluate the maturity of these applications with a tailor-made metric system, and (iii) to evaluate the suitability of the characterized technical lignins for each application. All three objectives aim at finding novel, and preferably high value added, applications for industrial scale production of new lignin-based products. Another aim of this thesis is to evaluate the current state of lignin research, suggest improvements and give recommendations for further studies.

1.2 Scope and structure

The scope of this thesis includes the most common technical lignins and novel applications that might have industrial scale potential. Applications, that are not considered as novel but can serve as a short term option for new types of technical lignins, are also presented and evaluated. Lignosulfonates are presented only in the literature review and not included in the experimental study due to their long commercial history. Characterization is performed for 14 lignin samples, of which four are isolated in laboratory. The performance of isolation process is not measured, but behavior of the samples and facility of the technology are reported. Comprehensive market and profitability analysis is not included in this thesis. However, markets and commercial potential are discussed briefly for the most promising applications and lignins.

This thesis consists of two major parts, literature review and experimental study. In the literature review, the structure and properties of native and technical lignins are illustrated and the discovered applications are presented and described. The experimental study consists of maturity evaluation of the discovered applications and isolation technologies, characterization of 14 lignin samples, and suitability evaluation based on literature review and the two other parts of experimental study.

LITERATURE REVIEW

2 Lignin

Lignin is an amorphous biopolymer that co-exists with cellulose and hemicelluloses in lignocellulosic plant tissues, where it acts as the essential glue giving structural integrity to plants./1/ In lignocellulosic biomass lignin is responsible for 15-30% of the weight and 40% of the energy content./2/ Anselme Payen, in 1838, was the first to identify the composite nature of wood. The term “lignin” which is derived from the Latin word *lignum*, meaning wood, was introduced by F. Schultze in 1865. Lignin’s relation to coniferyl alcohol was discovered by Peter Klason who also determined the linkages between coniferyl units from the alcoholic and phenolic hydroxyl groups, at the turn of the 19th and 20th centuries. Klason’s method is still widely used when determining lignin content, for example, of technical lignin samples./3/ In this chapter, the chemical structure and physical properties of lignin are elucidated based on past and current literature.

2.1 Chemical structure

The exact structure of native lignin, also known as protolignin, remains still unknown, but the central building blocks include *p*-hydroxycinnamyl alcohols: *p*-coumaryl, coniferyl, and sinapyl alcohols./1/ These three phenylpropanoids are usually referred to as monolignols which are polymerized in biosynthesis into a three-dimensional amorphous polymer./3/ The content of these monolignols in different lignins varies between the species and the different growth environments. Softwoods consist mainly of coniferyl alcohol units, hardwoods of coniferyl and sinapyl alcohol units, and non-woods of all three monolignols./4/ The monolignols and their corresponding guaiacyl (G), syringyl (S), and *p*-hydroxyphenyl structures of lignin are illustrated in Figure 1.

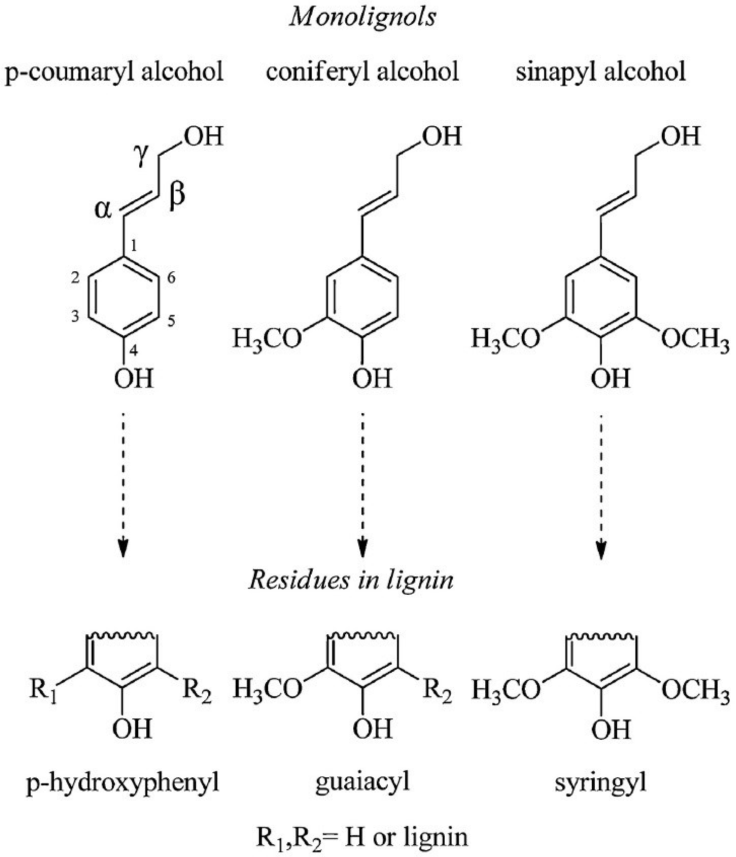

Figure 1. Monolignols and their residues in lignin./5/

The monolignols are bound together with several types of ether (β-O-4, α-O-4, and 4-O-5) and carbon-carbon linkages./6/ The most important being β-O-4, 5-5 biphenyl, β-5, β-1 and α-O-4. Also the β-β resinol units are worth mentioning due to their abundance in hardwood lignin./7/ However, the significance of the β-O-4 linkage is indisputable, since it is responsible for approximately 60% of all linkage structures in softwoods and 50% in hardwoods./8/ Lignin’s polymer network and it’s most important bonds are presented in Figure 2., and the proportions of the bonds in Table 1.

The main functional groups in lignin are hydroxyl, methoxyl, carbonyl, and carboxyl groups./5/ Both alcoholic and phenolic hydroxyl groups exist, and the methoxyl groups are attached to *ortho* position in the aromatic ring in relation to the phenolic hydroxyl group./9/ The proportions of different functional groups also depend on source and location in plant tissue, as well as the environment of origin./10/ Further processing, *e.g.* industrial separation, also has an impact on lignin structure, and the reactivity in its functional groups.

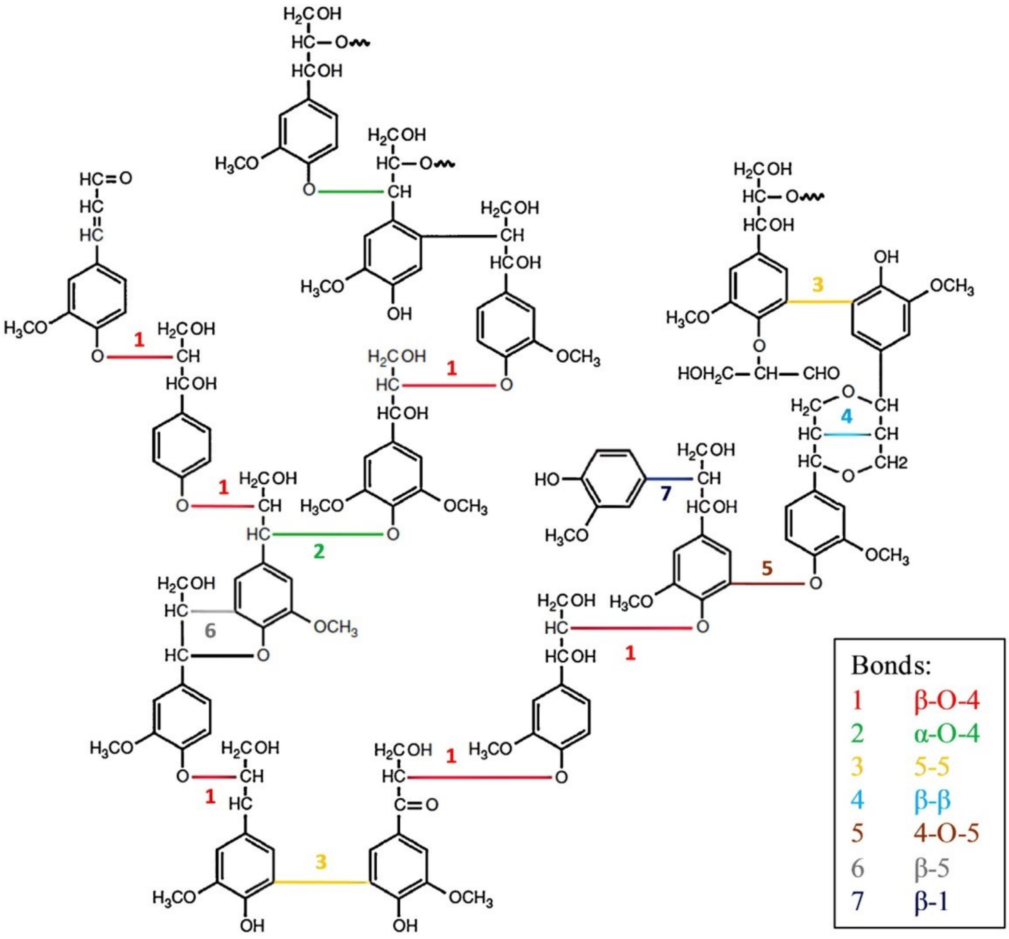

Figure 2. Main linkages in softwood lignin./5/

Table 1. Proportions of different linkages in spruce and birch./11/

Linkage type	Softwood (SW), spruce (%)	Hardwood (HW), birch (%)
β-O-4-aryl ether	46	60
α-O-4-aryl ether	7	7
4-O-5-diaryl ether	4	6.5
β-5-phenylcoumaran	11	6
5-5-biphenyl	10	4.5
β-1-(1,2.diarylpropane)	7	7
β-β-(resinol)	2	3
Others	13	5

2.2 Physical properties

Due to the random and noncrystalline network structure, the glass transition temperature T_g and the decomposition temperature T_d are the only two local mode relaxations expected in lignin. The glass transition temperature is an important factor in various applications, such as the plasticization of lignin or carbon fibers. The thermal decomposition of lignin occurs over a wide temperature range which is caused by the different thermal stabilities of the various oxygen-based functional groups./5/ The thermal properties of different technical lignins are presented in Table 2.

Lignin has several functions in plants. It protects the plants from mechanical and biochemical stresses, which are properties, required by various applications such as adhesives or complexing agents./6/ In nature, lignin is hydrophobic and its hydroxyl sites form hydrogen bonds with water./5/

Table 2. Thermal properties of different technical lignins.

Lignin type	**T_g (°C)**	**$T_{d,max}$ (°C)**	**Reference**
Kraft, acid precipitation (HCl)	144	421	/12/
Kraft, SW, Indulin AT	132	378	/13/
Kraft, SW, acid precipitation (CO_2)	134	389	/13/
Kraft, HW, acid precipitation (CO_2)	129	362	/13/
Soda, wheat straw, Protobind 2400	59	366	/13/
Soda-AQ, acid precipitation (HCl)	138	356	/12/
Organosolv	100	413	/12/
Pyrolytic, SEREX	54	234	/13/

3 Technical lignins

Technical, or industrial, lignins are co-products of chemical pulping of wood or agricultural residues, and lignocellulosic ethanol production. Worldwide, the amount of lignin separated in pulping processes is around 70 million tons per year./14/ However, only a small proportion is utilized for high-value end uses, such as chemicals, while the majority is combusted to generate heat and electricity. A non-uniform structure, unique reactivity, and various contaminants are the main factors restricting the use of technical lignins in high-value applications./15/ Although the properties of lignins differ between different plants and growth environments, the greatest differences are formed in the separation of lignin with different pulping technologies./6/

Generally, technical lignins are divided into two categories: (i) sulfur lignins, and (ii) sulfur-free lignins./5/ This categorization is visualized in Figure 3. However, distinct differences exist within these two categories, and it is preferable to treat each lignin type as a separate group.

In this chapter, the separation processes, isolation processes and characteristics of the different technical lignins are presented. These are lignosulfonates (sulfite lignin), kraft lignin, soda lignin, organosolv lignin, ethanol process lignin, and pyrolytic lignin. Laboratory lignins, such as milled wood lignin (MWL), fall beyond the scope of this thesis, and thus, are not discussed.

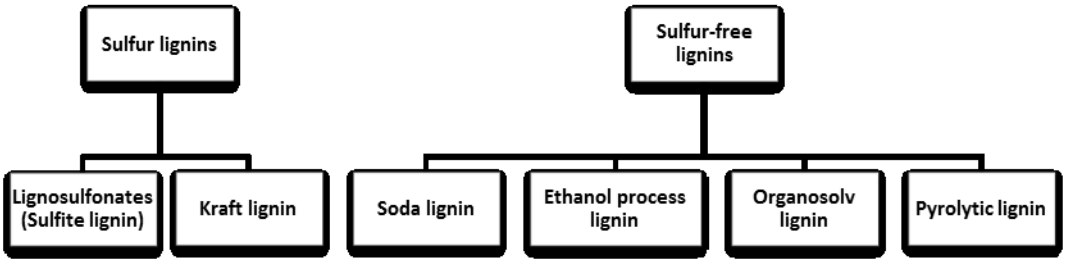

Figure 3. Categorization of technical lignins.

3.1 Lignosulfonates

Lignosulfonates, that are aliphatically sulfonated lignin oligomers, are obtained as by-products during sulfite pulping, which used to be the dominating pulping process before the kraft process. The inefficient recovery of pulping chemicals, suitability to only certain wood species, poor strength properties of the fibers, and environmental concerns were the main drivers for the declined interest for sulfite pulping in the 1950s. The inefficient recovery system is also the reason why lignosulfonates are currently the most abundant commercial lignin./14/ Approximately 1.06 million tons of lignosulfonates are produced annually worldwide./16/ Nowadays, sulfite pulping is mainly used for the production of dissolving pulp grades, with the acid sulfite process accounting for approximately 70% of the total dissolving pulp production worldwide./17/ The dominating application areas for lignosulfonates are concrete water reducers and animal feed binders. Generally, the applications of lignosulfonates are relatively low in value, with the exception of vanillin which is catalytically oxidized from softwood lignosulfonates./14/

The sulfite cooking process can be performed both as an acidic or an alkaline process with various base cations: Ca^{2+}, Mg^{2+}, Na^{+}, and NH_4^{+}. Currently, the dominating base is magnesium which is used in acid bisulfite, pH 1-2, and bisulfite, pH 3-5, processes. The main lignin reactions in acid sulfite pulping are: sulfonation, hydrolysis, and sulfitolysis./17/ Sulfonation of the aliphatic chain is the fastest of the three reactions, and the reaction that is mainly responsible for the characteristics of lignosulfonates./14/

Differing from hydrophobic natural lignin or other technical lignins, lignosulfonates are hydrophilic./9/ Lignosulfonates have higher molecular weight (M_w) and polydispersity than other lignins./15/ The sulfur content of lignosulfonates is generally between 4-8%, and the sulfur is mainly in the form of sulfonate groups./6/ The sulfonate groups are the main reason for the solubility in water, and insolubility in organic solvents. Other functional groups present in lignosulfonates are: aliphatic hydroxyl, phenolic hydroxyl, and carbonyl groups./14/ Functional group and sugar contents of two commercial lignosulfonates are presented in Table 3.

Lignosulfonates are separated from the spent sulfite liquor (SSL) that contains not only lignosulfonates, but also carbohydrates in the form of hemicellulose sugars, and further the spent pulping chemicals. Isolation can be done by diverse techniques, such as the fermentation of the residual sugars, sugar removal by chemical destruction, ultrafiltration to remove a sugar-rich permeate or by precipitation./14/ The high molecular weight has been recognized to be advantageous for ultrafiltration, since more than 80% of lignosulfonates present in SSL can be filtrated with membranes with a cut-off of 100 kDa./18/

Table 3. Characteristics of two commercial lignosulfonates./19/

Lignosulfonate type	COOH ($^{mmol}/_{g}$)	OH_{ph} ($^{mmol}/_{g}$)	Sugars (%)
Borresperse 3A, SW	3.5	1.1	1.3
Wafex P, SW	1.2	1.1	24.5

3.2 Kraft lignin

The kraft process is the most dominant pulping process worldwide, but the use of kraft lignin for other applications than combustion is rather limited. This is mainly due to the efficient recovery of pulping chemicals, which is essential from the economic point of view. However, modern kraft mills generate excess energy in the form of electricity and steam. It is usually not possible to use all of the excess energy which makes the isolation of lignin, to produce value added products and to reduce the heat value of black liquor, an interesting option./14/ The other reason leading to lignin isolation is the case where the recovery boiler is limiting pulp capacity expansion. In this case, the pulp production capacity could be increased without a large recovery boiler investment./20/

Due to the dominance of the kraft process, it is most likely the most important lignin source in the foreseeable future./8/ Lignin isolation from the kraft process is possible through acid precipitation /21/, ultrafiltration /22/ and electrolysis /23/. Kraft lignin is typically isolated from black liquor (BL) or weak black liquor (WBL) either in a multi-effect evaporation plant or in a cooking plant. Another alternative isolation medium is prehydrolyzate, which is a mixture of hemicelluloses and lignin. Prehydrolyzate is produced as a by-product of kraft-based dissolving pulp production during the autohydrolysis pretreatment./24/

3.2.1 Lignin reactions during kraft pulping

The kraft cooking of wood chips is performed in an aqueous solution consisting mainly of NaOH and Na_2S. The most important lignin reactions during kraft cooking are: (i) the desirable degradation reactions which lead to the liberation of lignin fragments and enhance their dissolution, and (ii) the less desirable condensation reactions which lead to the formation of alkali-stable linkages between the lignin fragments that, with increased molecular size, may precipitate back onto fibers./8, 25/

Delignification in kraft pulping can be divided into three stages which are: the initial delignification phase, bulk delignification phase, and residual delignification phase. Initial delignification occurs in milder conditions between 100-140°C, whereas the following delignification stages occur at the destination cooking temperature up to 170°C. In the initial phase, mainly phenolic α- and β-aryl ether linkages are cleaved. Bulk phase attacks to non-phenolic β-aryl ether linkages and to a certain amount of carbon-carbon bonds. In the residual phase, all the possible aryl ether linkages should be cleaved, and the delignification occurs mainly by the cleavage of carbon-carbon bonds in alkali-promoted retrograde aldol type of reactions./8, 25/

As mentioned, the aryl ether bonds are the main cleaved linkages in kraft pulping, whereas diaryl ether bonds are virtually stable. Some of the carbon-carbon linkages, aryl alkyl and alkyl alkyl bonds may be cleaved partially but the diaryl bonds, such as 5-5, are very refractory to delignification and are even formed in condensation reactions./25/

3.2.2 Isolation of lignin with acid precipitation

In acid precipitation, lignin is isolated from black liquor (BL) with a dry solid content typically in the range of 30-45%./26/ The precipitation of lignin begins at a pH value of approximately 11.5. In the pH range from 11.5 to 9, the yield progressively increases to about 70% of the initial lignin content in BL./21/ Acid precipitation is performed successfully with mineral acids, carbon dioxide, and waste acid from ClO_2-production./27/ After the pH is set to about 9 and most of the lignin has precipitated, the liquor is filtered, *e.g.* with a chamber press filter, followed by filtrate recycling back to the evaporation plant. After this, the filter cake is acidified, typically with sulfuric acid, or re-slurried, filtrated and washed./26/ The acid precipitation process with a re-slurrying stage is illustrated in Figure 4. Operating costs for acid precipitation with carbon dioxide are estimated to be approximately 78-317 € per ton of lignin, depending mainly on chemical costs and the price of black liquor based on the value of lost electricity production./28/

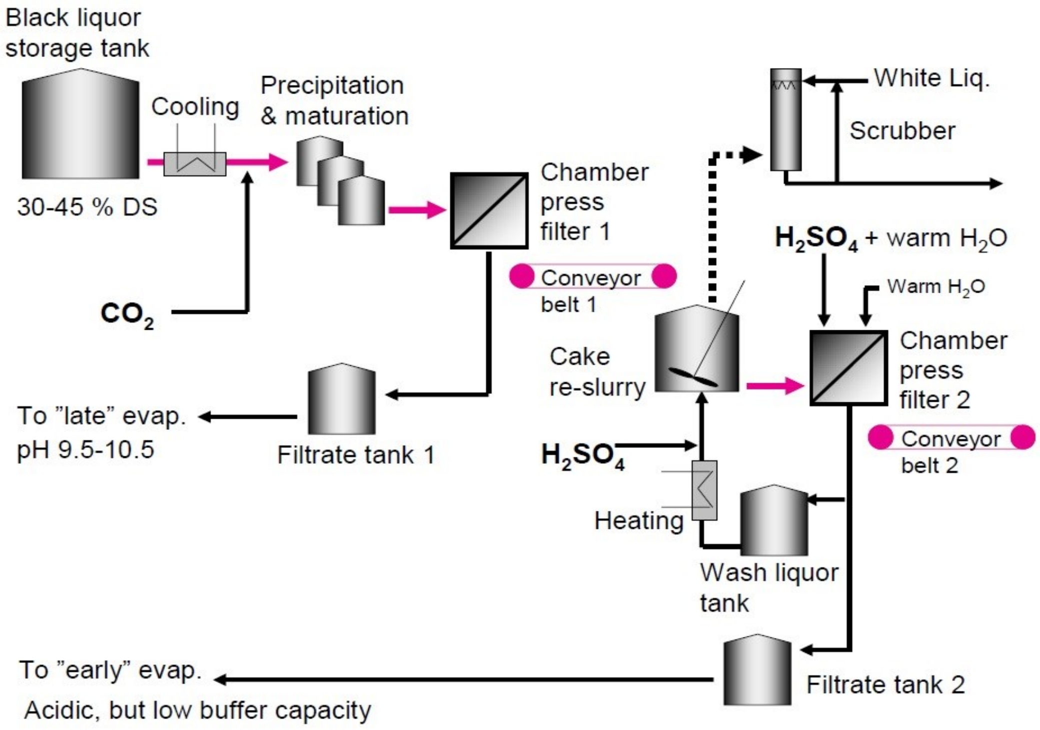

Figure 4. Acid precipitation process with a re-slurrying stage./26/

Waste acid is the cheapest of possible acidifiers, but it also increases the amount of sodium in lignin up to 10.5 wt%./27/ Sulfuric acid has shown slightly better yields than precipitation with carbon dioxide /21/, but carbon dioxide does not interfere with the sulfur balance of the mill and is, therefore, usually the preferred source of hydrogen ions. Other parameters affecting the yield and properties of precipitated lignin are: pH, temperature, and ionic strength, of which pH is the most important. In principle, lowering pH and temperature and increasing ionic strength increases yield. Also, a lower pH yields lower molecular weight lignin fractions that consequently increase methoxyl and phenolic hydroxyl group contents./29/ However, drastic precipitation conditions can influence the evaporation plant, as the residual BL is circulated back, or cause problems in the filtration process, *e.g.* by plugging the filters or by increasing the release of H_2S./21/

Plugging has been a typical problem in precipitation systems where the filter cake is washed with sulfuric acid directly after filtration. Plugging is caused by the dramatic and uneven changes in pH and ionic strength. This problem can be avoided by re-slurrying the filter cake, then filtering it again and, finally, washing it with displacement washing. This procedure evens out the conditions because the changes in pH and ionic strength are taking place in the re-slurried stage instead of in the filter cake during direct washing. Direct washing also requires very large filter areas or very high amounts of acidified wash water in order to reach a high level of lignin purity. Another upside, of the re-slurrying sub-stage, is the decrease of sodium content which has been higher in direct washing systems./26, 30/

3.2.3 *Isolation of lignin with ultrafiltration*

Lignin isolation by ultrafiltration can be done theoretically from any process stage in a pulp mill. The most studied, and possibly the most suitable, locations are the cooking /22/ and evaporation plants./31/ The possible locations for an ultrafiltration process are illustrated in Figure 5. In principle, ultrafiltration is possible to run for any lignin concentration, even in high temperatures over 100°C. No pH adjustment is required, but the yield of ultrafiltration is higher when temperature is kept below 100°C. However, the purpose is not to isolate all of the lignin because recovery of cooking chemicals and other kraft mill operations require the energy that is typically derived from lignin in the recovery boiler./20/

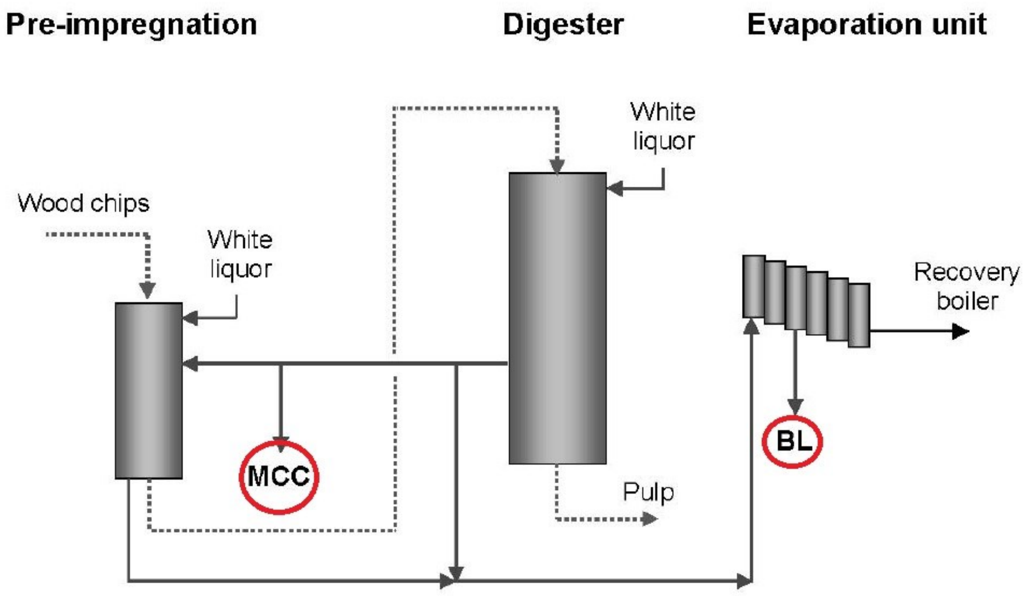

Figure 5. Possible locations for the ultrafiltration process circled with red./31/

Ultrafiltration of lignin from cooking liquor at high temperatures has been studied with ceramic membranes having cut-offs between 5-15 kDa. This system results in a filtration retentate of higher molecular lignin fractions with yields between 20-30%. Lignin recovery from cooking liquor also results in residual liquor with lower content of dissolved solids which has a positive impact on pulp quality./17/ Another advantage is that pulp production capacity could be increased without capacity expansion in the evaporation plant./22/ However, a study by Jönsson and Wallberg shows that the ultrafiltration of lignin from cooking liquor has a higher production cost (60 € per ton) than precipitation or ultrafiltration from black liquor. The higher cost is mainly due to markedly lower yield of ultrafiltration from cooking liquor compared with the others./31/

During BL ultrafiltration, the lignin permeate is recovered and the retentate is recycled back into the process. Permeate yields up to 55% have been achieved with a 15 kDa membrane. Production costs are estimated to be around 33 € per ton of lignin for BL ultrafiltration./31/ Neither cost estimate (ultrafiltration from cooking liquor or from black liquor) includes purification and concentration costs, which are essential in most of the end applications. With ultrafiltration, it is also possible to reduce the amount of sulfur in kraft lignin, since the lowest molecular weight lignin has the highest sulfur concentration./32/ However, complete sulfur removal is not possible with ultrafiltration.

3.2.4 Isolation of lignin with electrolysis

An interesting alternative for the isolation of lignin from a kraft process is the less-known precipitation by electrolysis. Electrolysis is performed for the weak black liquor stream and acidification is carried out with water electrolysis. In an actual mill operation, electrolysis is carried out in two or three steps with or without chemical acidification. The electrolysis precipitation process differs significantly from ultrafiltration and acid precipitation, since it also recovers O_2, H_2 and sodium as NaOH, whereas the residual liquor is not recycled back into the process. Therefore, it also off-loads the capacity both in the lime kiln and in the caustisizing plant by reducing both organic and inorganic loads in the recovery systems./23, 33/

An electrolysis system consists of a catholyte compartment, where aqueous NaOH is generated and recovered, and an anolyte compartment, where lignin is isolated and recovered. The precipitated lignin tends to stick on the anode and, therefore, intermediate lignin removal is preferred between electrolysis steps./23/ Lignin precipitation by electrolysis would have significantly higher production costs than the others presented, since it has an electricity requirement of over twenty times higher than acid precipitation. Current data is not available, but in 1998, the costs were estimated to be at least triple compared with acid precipitation./34/ A schematic drawing of an experimental electrolysis process is presented in Figure 6.

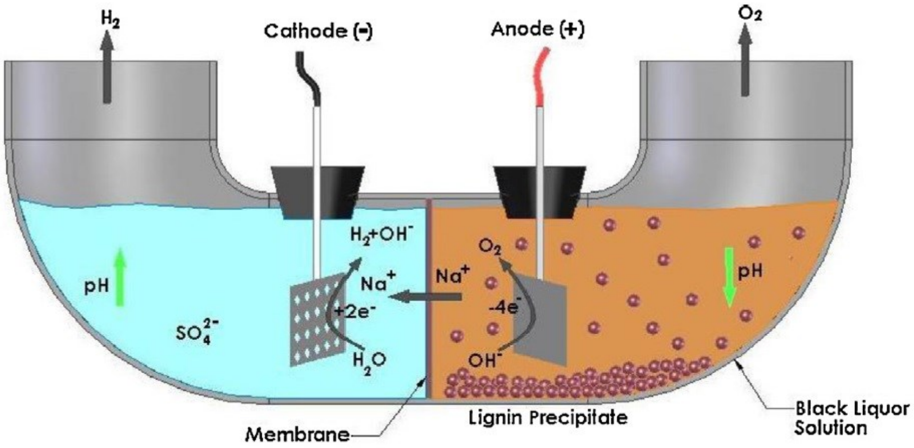

Figure 6. Experimental electrolysis setup designed by Jin et al./33/

3.2.5 *Isolation of lignin from prehydrolyzate*

Autohydrolysis with water and/or steam in temperatures from 140°C to 170°C is the prehydrolysis process typically utilized with kraft-based dissolving pulp production. This process results in an acidic solution, prehydrolyzate, of hemicelluloses and lignin./17/ Prehydrolyzate has characterized to have a lignin content of about 1%, which is about 20% of the solids content of prehydrolyzate./24/

The pH of prehydrolyzate is typically 3-4, and the lignin can be isolated by acidifying the prehydrolyzate with sulfuric acid to pH 2 which precipitates lignin./24/ Decreasing the temperature of the prehydrolyzate has also been shown to precipitate the higher molecular weight lignin compounds./35/ The main lignin reaction during autohydrolysis is the hemolytic cleavage of β-O-4 bonds, which results in a significant increase in phenolic hydroxyl content./36, 37/

3.2.6 Characteristics of kraft lignin

Even though kraft lignins contain sulfur, the sulfur content is relatively low due to the episulfide intermediate that eliminates elemental sulfur to give conjugated structures./14/ The remaining sulfur is mostly present in SH-bonds where it is difficult to remove. Sulfur is poisonous for catalysts and can cause problems in some end applications./15/ However, the presence of sulfur is not necessarily a disadvantage since sulfur is a very nucleophilic atom with good coordination properties. This can make the kraft lignin suitable for further use as a derivative without the need for a subsequent modification, such as oxidation./38/

Kraft lignin is actually characterized to have the highest purity among several technical lignins, which is mainly due to the strong hydrophobic nature that aids the removal of contaminants, such as ash and sugars, from the unpurified kraft lignin./13, 14/ As is the case with prehydrolyzate lignin, also kraft lignins have increased phenolic hydroxyl content. Kraft lignins typically have molecular weights of 3000-5000 g/mol and polydispersities of 3-6./12, 13/ Characteristics of different kraft lignins are presented in Table 4.

Table 4. Characteristics of different kraft lignins.

Kraft lignin type	**Lignin content (%)**	**Ash (%)**	**Sugars (%)**	**OH_{ph} ($^{mmol}/_{g}$)**	**S (%)**	**Reference**
SW, purified	94.1	0.44	1.58	4.50	1.25	/39/
SW, unpurified	66.1	27.1	3.28	ND*	1.68	/39/
SW, Indulin AT	96.4	3.59	1.00	3.37	2.1	/13/
SW, acid precipitation (CO_2)	96.7	0.73	1.20	4.79	2.6	/13/
HW, acid precipitation (CO_2)	98.0	0.47	0.67	3.04	2.9	/13/
SW, Indulin AT	90.0	ND*	2.06	1.8	ND*	/19/
SW, purified	96.8	ND*	0.71	2.5	ND*	/19/
SW, Curan 100	88.6	ND*	2.26	0.8	ND*	/19/
SW, Curan 2711P	80.3	ND*	2.58	1.6	ND*	/19/
HW, ultrafiltration, cooking liquor, unpurified	55.0	30.0	15.0	ND*	ND*	/31/
HW, ultrafiltration, BL, unpurified	38.0	60.0	2.00	ND*	ND*	/31/

*not defined

3.3 Soda lignin

Soda pulping has traditionally been used for non-wood raw-materials, such as straw, bagasse, and flax. It is also used in the high yield pulping of hardwood for packaging purposes. Soda pulping is done in an aqueous solution of NaOH. Anthraquinone (AQ), a redox catalyst, may also be used to enhance delignification. Non-woods have a more open structure than SW or HW and, therefore, pulping can be done at lower temperatures under 160°C. Non-wood soda pulp mills are generally very small in capacity, and the recovery processes developed for much larger operations are not economically feasible. This provides an opportunity to utilize the lignin fraction of soda black liquors./14/

Soda lignins are sulfur-free, hydrophobic, low molecular weight, and have low sugar and ash contents./14/ However, more impurities have been detected from soda lignin than from organosolv lignin./40/ Soda lignin can be separated in the same way as kraft lignin, *e.g.* with acid precipitation./15/ It is typical for non-woods to have high silicate concentrations, which responsible for the high ash contents in some cases, but silicate contents below 1% have also been reported. Due to the non-wood raw material, soda lignins can have protein residues that are recognized in the higher nitrogen contents./10/ The sulfur-free nature is an advantage in end applications where volatile sulfur compounds, such as H_2S, are causing problems. A distinct difference in non-wood soda lignin compared with wood lignins is the high presence of H-units in addition to S- and G-units./14/ This might be advantageous in some applications, such as resins and adhesives./13/ Characteristics of soda lignins from different sources are presented in Table 5.

Table 5. Characteristics of different soda lignins.

Lignin type	Lignin content (%)	Ash (%)	Sugars (%)	Reference
Soda-AQ, long fiber plant mix	96.5	0.74	2.39	/39/
Soda, Protobind 2400, wheat straw	88.0	1.30	1.61	/13/
Soda, wheat straw	87.1	1.90	2.39	/10/
Soda, hemp	85.4	4.50	3.15	/10/
Soda, flax, precipitation pH 5.5	97.6	4.60	1.74	/10/
Soda, flax, precipitation pH 2	83.3	4.90	2.09	/10/
Soda, flax, Bioplast	87.8	ND*	1.7	/19/
Soda, flax, oxidized	92.1	ND*	1.6	/19/

*not defined

3.4 Organosolv lignin

In organosolv pulping, the lignocellulose fibers are separated with organic solvents, such as ethanol, methanol, acetic acid or formic acid. The lignin from organosolv processes is less modified than in other processes because it is separated via solubilization./15/ One example of an organosolv process is the Organocell process, where delignification is performed in two-stages. Here the fibers are first dissolved in a methanol/water solution followed by addition of NaOH./41/ Disadvantages of the organosolv process include a high cost of solvent recovery which has limited commercialization./2/

In general, organosolv lignin is sulfur-free, low in molecular weight, hydrophobic, and has a high degree of chemical purity. In comparison with soda lignin, organosolv lignin possesses higher phenolic hydroxyl and lower carboxyl contents./10/ Organosolv lignin can be extracted, *e.g.* by evaporating the solvent resulting in precipitated lignin /41/, and purified, *e.g.* with ionic liquids (IL)./40/ Characteristics of two organosolv lignins are presented in Table 6.

Table 6. Characteristics of two organosolv lignins.

Organosolv lignin	**Lignin content (%)**	**Ash (%)**	**Sugars (%)**	**OH_{ph} ($^{mmol}/_{g}$)**	**Reference**
Formasolv, eulalia grass	94.2	1.71	1.16	2.66	/39/
Alcell, mixed HW	96.5	0.10	0.32	2.90	/10/

3.5 Ethanol process lignin

The production of lignocellulosic ethanol, or so called second generation (2G) biofuels, is an emerging route for replacing both fossil fuels and biofuels derived from processes (first generation biofuels, 1G) that might use food crops. A biochemical platform, where biomass is pretreated, enzymatically hydrolyzed and then fermented, is claimed to be the most promising route to produce lignocellulosic biofuels./42/ Of course, this generates a vast lignin rich process stream that should be utilized in order to make the process economically viable./4, 43/

Lignin separated with enzymatic hydrolysis appears in a solid form and can be isolated from the residual process stream simply by filtering through a fine mesh. It contains high amounts of unhydrolyzed cellulose residues, up to 15% by weight./15/ Due to the use of enzymes in the hydrolysis process, the ethanol process lignin has a high nitrogen content which is an indication of protein contamination. Phenolic hydroxyl contents similar to lignosulfonates and significantly lower than kraft lignin have been characterized for the ethanol process lignin./39/

3.6 Pyrolytic lignin

The pyrolysis, either fast or slow, of biomass is a zero-waste process that results in three products: bio-oil, char, and syngas. In the fall of 2013, the world's first commercial fast pyrolysis demo plant started in Joensuu, Finland./44/ Pyrolytic lignin is the water-insoluble fraction in bio-oil, and it is thought to be responsible for the poor storage stability of bio-oil due to its high reactivity./45/ At laboratory scale, pyrolytic lignin is isolated from bio-oil by pouring the bio-oil in iced water under stirring./46/ Separated pyrolysis lignin is in the form of brown powder. The yield of pyrolytic lignin obtained from bio-oil can be as high as 28% by weight./47/

Pyrolytic lignin is similar to other technical lignins in terms of its chemical structure and composition. However, pyrolytic lignin has higher carbon content, lower molecular weight and is sulfur-free. Pyrolysis induces depolymerization which explains the lower molecular weight. Also the cleavage of methoxyl groups, the reduction of phenolic hydroxyl groups and condensation reactions between the aromatic carbons have been detected during pyrolysis./46, 47/ The yields and elemental composition of several pyrolytic lignins are presented in Table 7.

Table 7. Yields and elemental composition of pyrolytic lignins from different sources./47/

Bio-oil producer, source	Lignin yield from bio-oil (%)	C (%)	H (%)	N (%)	O (%)
IWC, beech	13.5	66.91	6.19	0.27	26.63
ENSYN, mixed HW	24.1	66.18	6.02	0.23	27.57
FENOSA, eucalyptus	25.0	63.68	5.79	0.19	30.34
FENOSA, wheat straw	16.5	65.22	6.13	1.02	27.63
ASTON, poplar	24.0	66.03	6.11	0.21	27.65
NREL, poplar	23.0	66.60	6.24	0.34	26.82
BTG, mixed SW	27.7	67.43	6.19	0.24	26.14
VTT, pine	19.0	70.56	6.64	0.15	22.65

4 Applications

Due to the unique properties, different technical lignins hold the potential to be used in various end applications that are high in value, such as carbon fibers. Being regarded as the major aromatic resource of the bio-based economy, lignin could be an important raw material, *e.g.* for a variety of bulk and fine chemicals. However, the unique structure and complexity are challenges that have to be overcome before high value-added products can be produced cost competitively from lignin. It is essential for biorefineries to valorize all components of lignocellulosic biomass in order to reach the best possible economic performance. Thus, receiving extra revenues from lignin is in most cases a prerequisite for economic feasibility./2, 6, 15/

In this chapter, the most promising novel applications of technical lignins are presented and discussed. The possible production technologies and the most suitable raw materials for each application will be reviewed. The applications are divided into five categories: fuels, chemicals, composites, activated carbon and carbon fibers, as illustrated in Figure 7. The current applications of lignin, typically low in value, are only touched upon briefly. These include applications in *e.g.* concrete admixtures, animal feed binders and dust control. The current commercial applications are presented in Table 8.

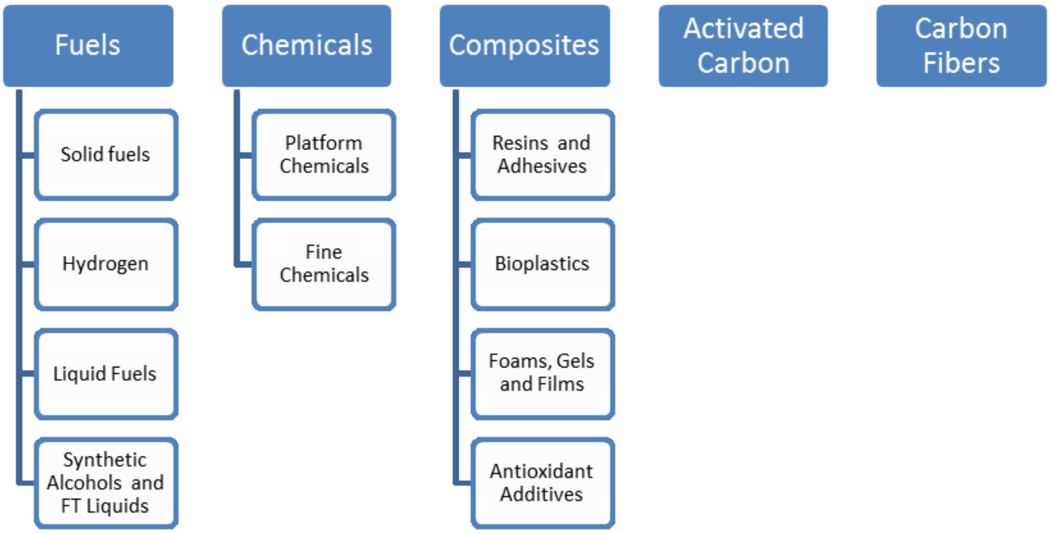

Figure 7. Categorization of lignin applications

Table 8. Current commercial applications of lignin.

Application	**Raw material**	**Reference**
Concrete Admixtures	Lignosulfonates	/16/
Animal Feed Binders	Lignosulfonates	/16/
Road Binders, Dust Control	Lignosulfonates	/16/
Pesticide Dispersants	Lignosulfonates	/16/
Oil Well Drilling Muds	Lignosulfonates	/16/
Dye Dispersants	Lignosulfonates	/16/
Animal Feed Additives	Lignosulfonates	/16/
Chelants	Lignosulfonates	/16/
Vanillin	Lignosulfonates	/16/
DMSO	Lignosulfonates	/16/
Adhesives, Resins, Binders	Lignosulfonates, Soda lignin	/48, 49/
Carbon Black	Lignosulfonates	/48/
Water Treatment	Lignosulfonates	/48/
Battery Expanders	Lignosulfonates	/48/
Emulsifiers	Lignosulfonates	/48/
Cleaning chemicals	Lignosulfonates	/48/
Micronutrients	Lignosulfonates	/48/
Leather Tannin	Lignosulfonates	/48/
Rubber additive	Lignosulfonates	/48/
Thermoplastic fiber composite	Soda lignin	/49/
Solid fuel	Kraft lignin	/50/
Process Heat & Power	Kraft black liquor	/16/

4.1 Fuels

The lignin-based fuels are one promising application of isolated lignin. Lignin is currently used as a fuel in the recovery boilers of kraft mills in the form of black liquor. This application will remain because the economically viable recovery cycle is an essential part of kraft pulping. However, the isolation of the excess lignin from black liquor might be logical, since black liquor with a dry solids content of 80% has a heating value of 12.6 GJ per ton of BL while the heating value of lignin is 26.9 GJ per ton of air dry lignin./51/ The lignin based fuels can be divided into four categories: (i) solid fuels, (ii) hydrogen, (iii) liquid fuels, and (iv) synthetic alcohols and Fischer-Tropsch (FT) liquids./52/ The possible routes from lignin to fuels are illustrated in Figure 8.

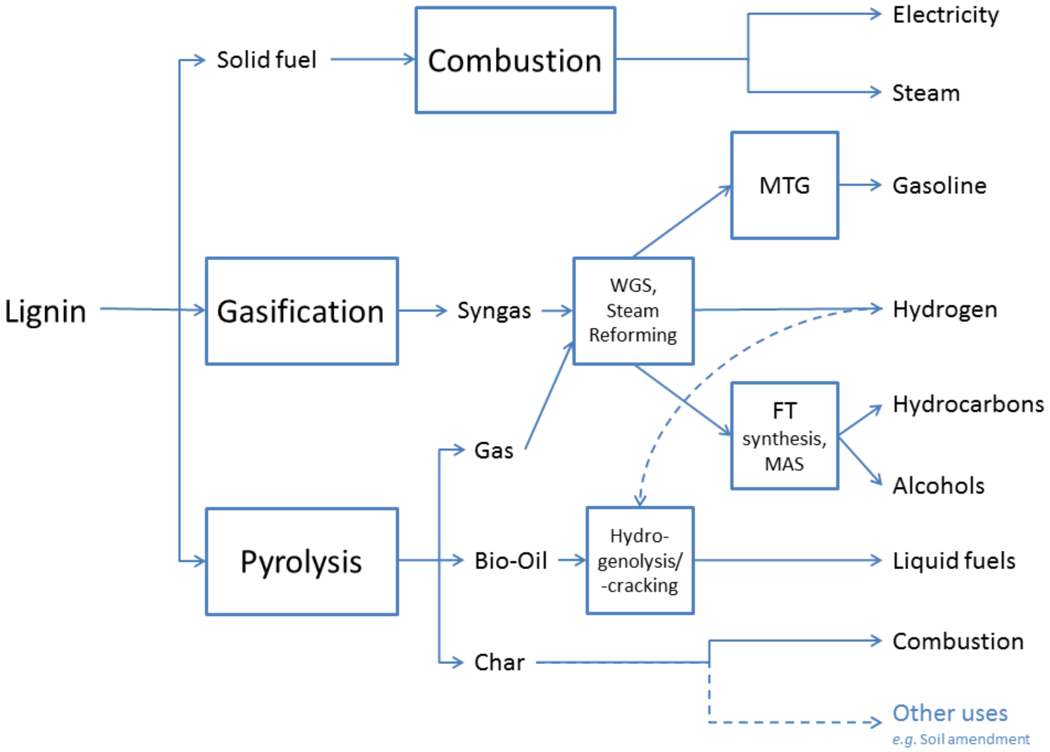

Figure 8. The possible routes from isolated lignin to fuels.

4.1.1 Solid fuels

The lignin-based solid fuels are quite low in value. Generally, solid fuels from lignin are untreated isolated lignin that is either completely or partially dewatered. They are either combusted on site, *e.g.* in a lime kiln, or sold out to be combusted, *e.g.* in a multi-fuel boiler. The feasibility of isolation and drying of lignin versus energy generation from spent liquor is mainly dependent on the cost of the isolation process and the price of electricity. In the case of a kraft mill where the recovery boiler limits pulp capacity, the isolation of lignin could be profitable even when the costs of lignin precipitation are high if the isolation of lignin debottlenecks the recovery boiler, which makes pulp capacity increase possible and, thus, increases revenues. From an environmental point of view, using isolated lignin as a solid fuel in lime kiln reduces the dependence on fossil fuels as the lime kiln, in modern mills, is the only place where fossil fuels are used during normal operations./20, 53, 54/

4.1.2 Hydrogen

Pure hydrogen can be obtained from lignin via thermal treatment, such as gasification or pyrolysis. Black liquor gasification has been studied widely, but corrosion problems exist mainly due to the vast amount of alkali and other inorganics present in black liquor./55/ Many isolated lignins, especially purified ones, have low inorganics and could serve as good gasification fuels. Gasification of lignin produces syngas which consists of H_2, CO, CO_2 and CH_4 with varying ratios, and residues, such as H_2S, depending on the lignin source and purity./52, 56/ Pure hydrogen can be obtained from syngas through the water-gas shift (WGS) reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{1}$$

and through steam reforming

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{2}$$

Lignin pyrolysis is another possible hydrogen source, since the resulting gas fraction is very rich in hydrogen. The yields of gas products from lignin pyrolysis compared with hemicellulose and cellulose pyrolysis are presented in Table 9. The hydrogen derived from lignin can be used in fuel cell applications or for hydrogenation and hydrogenolysis, which are hydrogen mediated upgrading procedures for bio-oil./16/

Table 9. Gas product yields from pyrolysis of hemicellulose, cellulose and lignin./57/

Sample (all values $^{mmol}/_{g\text{-}biomass}$)	**H_2**	**CO**	**CH_4**	**CO_2**	**C_2H_4**	**C_2H_6**
Hemicellulose	8.75	5.37	1.57	9.72	0.05	0.37
Cellulose	5.48	9.91	1.84	6.58	0.08	0.17
Lignin	20.84	8.46	3.98	7.81	0.03	0.42

4.1.3 Liquid fuels

The most prominent process for converting biomass into liquids is pyrolysis, which can be applied also to lignin or lignin rich residues, *e.g.* from biochemical ethanol production./4, 16/ Pyrolysis of lignin results in products in three phases: solid char, liquid bio-oil, and gas products. Decomposition of lignin during pyrolysis is complex as it occurs in a wide temperature range /58/, is dependent on the amount of lignin condensation /59/, and results in high solid residue. However, higher selectivity towards liquid products can be achieved by using catalysts and high hydrogen pressures./52/ Pyrolysis oil from lignin is highly oxygenated and unstable and, therefore, needs to be upgraded, *e.g.* with the hydrogen derived from the gas fraction./11/

Pyrolysis of lignin can be performed through slow pyrolysis /60/, fast pyrolysis /61/, co-pyrolysis with polymers /62/ or in a hydrogen donating medium /63/. The usage of $ZnCl_2$ and $AlCl_3$ catalysts has been proven to reduce the char residue in the slow pyrolysis of kraft lignin from 54.56 wt% to 38.10 wt% and 27.02 wt%, respectively./64/ Zeolites have been shown to promote selectivity to aromatic hydrocarbons and increased yield of liquid products, when used as catalysts in fast pyrolysis./65/ Co-pyrolysis of CO_2 precipitated kraft lignin and different polymers (1:1 mix) have been shown to lower solid residues./62/ Examples of the results from lignin co-pyrolysis with polyethylene (PE) and polystyrene (PS) are presented in Table 10. The upgrading of pyrolysis oils could be avoided by applying pyrolysis to lignin in hydrogen donating medium, *e.g.* formic acid/alcohol, which would eliminate the need for deoxygenation and result in liquid bio-oil which could then be blended with conventional motor fuels./63/

Table 10. Co-pyrolysis of CO_2 precipitated kraft lignin and polymers at 500°C./62/

Sample	Gas (%)	Water (%)	Oil (%)	Tar (%)	Char (%)
Lignin	12.7	23.7	14.5	4.5	44.6
PE	11.8	0	85.4	0	2.8
PE/Lignin	16.8	15.9	43.6	2.6	21.1
PS	0.3	0	81.2	0	18.5
PS/Lignin	8.2	6.4	51.6	4.7	29.1

Pyrolysis is not a source sensitive process and it can be applied to all technical lignins. However, distinct differences exist within the products from different sources of lignin. The fast pyrolysis of kraft lignin results in a bio-oil with a high content of aromatics, whereas organosolv lignin generates more alkyl hydrocarbons./66/ Raw material content has an effect on end-product composition. Pyrolysis of hardwood lignin typically results in formation of more methanol than pyrolysis of softwood lignin./67/ This is because variations in molecular weight distributions and functional groups have a substantial influence on formation of pyrolysis products. Hence, the lignin to be used in a certain pyrolysis process should be characterized thoroughly before designing pyrolysis and upgrading procedures.

Pyrolysis upgrading of bio-oil can be done with hydrogen mediated reactions, such as hydrogenolysis and hydrogenation, which reduce or saturate lignin compounds in the presence of a catalyst. Liquid transportations fuels can be obtained also from syngas formed during lignin gasification using known technologies, such as the methanol to gasoline (MTG) process./11, 16/

4.1.4 Synthetic alcohols and Fischer-Tropsch liquids

Fischer-Tropsch liquids and synthetic alcohols are catalytically synthesized from syngas. Generally, hydrocarbons are produced via FT-synthesis with the following reaction

$$2_n\, H_2 + n\, CO \rightarrow C_nH_{2n} + n\, H_2O \qquad (3)$$

and, more specifically, alkanes with the following reaction

$$(2_n + 1)H_2 + n\,CO \rightarrow C_nH_{(2n+2)} + n\,H_2O \qquad (4)$$

A wide range of hydrocarbons can be obtained from FT-synthesis depending on the process conditions and the catalyst used. Well known FT-synthesis catalysts are cobalt and iron based./68/ FT-synthesis requires a certain ratio of H_2 and CO which can be achieved with the water-gas shift reaction. The CH_4, typically present in lignin syngas, can be steam reformed to CO and H_2. The gasification of wheat straw residual lignin from biochemical ethanol production has yielded H_2/CO ratios between 0.54 and 0.63./56/

Synthetic alcohols can be obtained from the mixed alcohol synthesis (MAS), which is similar to FT-synthesis and could be used for syngas conversion to mixed alcohols, such as *n*-propanol and *n*-butanol. The main reaction in MAS is the alcohol formation reaction

$$2_n\,H_2 + n\,CO \rightarrow C_nH_{(2n+1)}OH + n\,H_2O \qquad (5)$$

However, MAS is not applied at industrial scale. This is mainly due to challenges with catalysts. The alcohol formation reaction is more complicated than reactions in FT-synthesis which generates problems with space time yields (kg of product/kg of catalyst/h). Also catalysts applied to MAS have a tendency to become contaminated quite easily by impurities in the syngas./16, 69/ Although FT-synthesis is a proven technology, it also has some obstacles regarding the use of lignin or other biomass. For example, the economic scale in the petrochemical industry is somewhere between 10,000 and 20,000 tons of FT liquids per day /51/, whereas the lignin that can be isolated from a kraft mill is around 0.15 tons per air dry ton (ADt) of pulp /20/, which in a mill producing 2000 ADt/d of pulp is 300 tons of lignin per day. However, larger lignin streams might be available in the future, *e.g.* from the lignin rich residues of lignocellulosic ethanol production.

4.2 Chemicals

Lignin is a major source of aromatics which is why it could be an interesting source for various high value aromatic chemicals. Several ways to divide the lignin derived chemicals into categories exist. In this thesis, the chemicals are divided into two categories: (i) platform chemicals, which are used as precursors in petrochemical technologies, including phenol and BTX (benzene, toluene, and xylene) chemicals, and

(ii) fine chemicals, which consist of high value chemicals, such as vanillin and syringaldehyde. Platform chemicals are typically high volume chemicals, whereas fine chemicals are niche products. The possible routes from lignin to chemicals are illustrated in Figure 9.

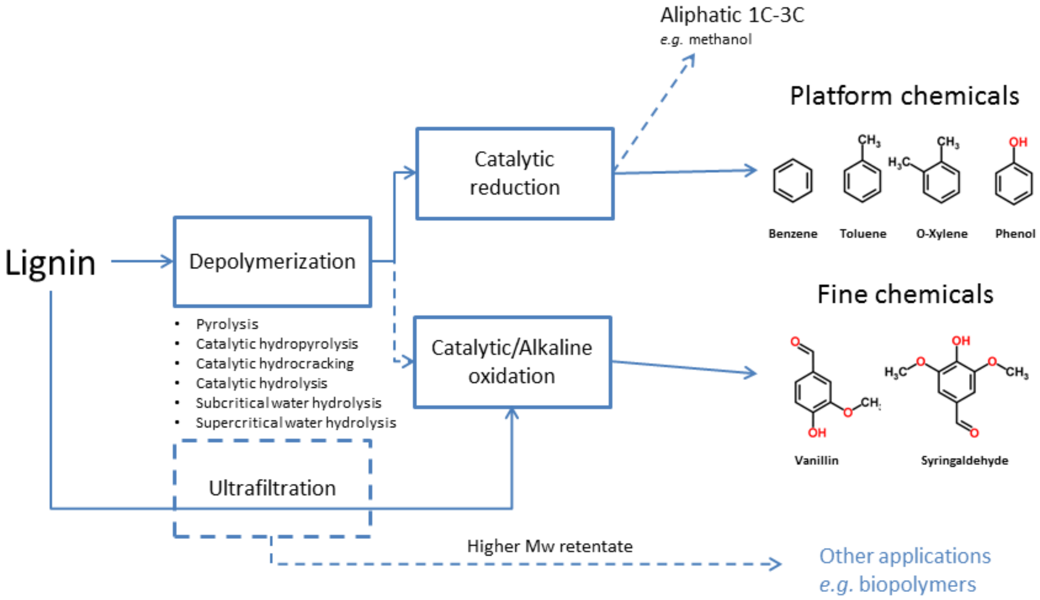

Figure 9. The possible routes from isolated lignin to chemicals.

4.2.1 Platform chemicals

The first stage towards platform chemicals is the depolymerization of lignin into aromatic monomers. After depolymerization, these aromatic monomers include various functional groups. Aromatics, such as phenol and BTX chemicals, can then be produced by selectively cleaving the functional groups./11/ A catalytic route is seen as the most promising option for selective reduction of alcohol, aldehyde, ether and acid substituents from the monomeric aromatics. However, the optimal catalysts have not been found yet./2/

The depolymerization of lignin results in a mixture of monomeric, dimeric and oligomeric substances. The yield of each fraction depends on the depolymerization method and the raw material. Hardwoods contribute to higher yields of monomers than softwoods, and technical lignins with lower molecular weights and polydispersities are less recalcitrant to depolymerization than the ones with high molecular weights. Depolymerization can be done with several methods, such as pyrolysis, catalytic hydropyrolysis or -cracking /70/, catalytic hydrolysis, and sub- and supercritical water treatment./2, 52/

The selective reduction of the functionalities from the aromatic monomers could be achieved via selective catalytic hydrogenation. The monomeric depolymerization products of lignin are a complex mixture of different monomers that are hard to recover without further modification./52/ In order to yield considerable amounts of certain products is the reductive route preferred because it yields the simple aromatics mentioned earlier. The cleavage of functionalities also yields valuable side products, such as methanol from methoxy groups. Although optimal catalysts are yet to be found, the cobalt- and nickel-promoted molybdenum catalysts with various support catalysts have yielded promising selectivity./2/ However, the general problem with catalysts is their intolerance of certain impurities, especially sulfur, which makes the sulfur-free lignins more suitable raw material for catalytic systems.

The production of phenol and BTX chemicals from lignin, if performed in an efficient and viable manner, is supported by three motives: (i) these chemical building blocks can be easily converted in conventional petrochemical processes /16/, (ii) substantial yields could be achieved with the effective catalytic reduction of functional groups /2/, and (iii) these products have existing markets /16/, which significantly reduce the risk in producing such components. One major disadvantage of producing platform chemicals from lignin is the need for complete depolymerization, which is currently very challenging./5/ This is one of the key facts why most of the previous studies suggest production of aromatic chemicals from lignin is a long-term option./16, 52/

4.2.2 Fine chemicals

Whereas the reductive route produces simple aromatics that can be utilized as platform chemicals, the oxidative route results in more complex fine chemicals with increased functionality. A plethora of complex molecules, that are not readily available from conventional petrochemical routes, could be produced with the catalytic oxidation of isolated lignin./2/ Vanillin, which currently is produced from SSL /71/, and syringaldehyde are good examples of the high value-added chemicals obtainable from lignin./72/ Depolymerization is not necessarily needed in all oxidation routes, *e.g.* vanillin can be extracted directly via alkaline oxidation. The common lignin oxidants are nitrobenzene, oxygen and some metal oxides. These all are mild oxidants that preserve the aromatic ring of lignin monomers. With nitrobenzene, total phenolic aldehyde yields of 14% have been achieved from hardwood kraft lignin./73/ Yields of different aldehydes depend on the lignin precursors present, *e.g.* vanillin which is mainly yielded from G units and syringaldehyde from S units./71/

Traditionally, vanillin production from SSL has caused environmental problems due to the huge amount of caustic liquids generated. Up to 160 kg per kg of vanillin has been reported./71/ One solution to reduce the amount of waste could be the fractionation of the lignin stream with ultrafiltration into higher molecular weight retentate, which could be used in different applications, and lower molecular weight permeate, which would be oxidized into fine chemicals./74/

Methyltrioxorhenium has been found to be a good catalyst in catalytic oxidation of different technical lignins with H_2O_2 as oxidant. It has been used as a catalyst in the oxidation of phenolic, non-phenolic, monomeric and dimeric lignin compounds into acids, aldehydes and quinones with yields up to 49%./75, 76/ Homogeneous catalysts, that selectively attack specific linkages and leave other groups untouched, represent a catalyst group that could maximize the valorization potential of lignin./2/ The selective catalysts designed for the total chlorine-free (TCF) bleaching of kraft pulps, such as iron tetraamido macrocyclic ligand /77/, could be a good starting point for the design of selective and robust lignin oxidation catalysts.

4.3 Composites

Researchers have studied whether lignin could function as an additive or act as a base material in a wide range of composite applications. Lignin could act as an alternative to synthetic phenols and olefins, or act as an antioxidant additive. With the addition of lignin, mechanical properties of natural fiber composites can be enhanced since the irregular shape of lignin fragments provides mechanical interlocking in the composite matrix. However, the heterogeneous nature of technical lignins creates challenges in applications where low polydispersities are desired./78, 79/

There are as many ways to categorize lignin-based composite material applications as there are applications. In this thesis, composites are classified, based on their end uses and functionalities, into four categories: (i) resins and adhesives, (ii) bioplastics, (iii) foams, gels and films, and (iv) antioxidant additives. Various lignin routes to composites and composite building blocks are illustrated in Figure 10.

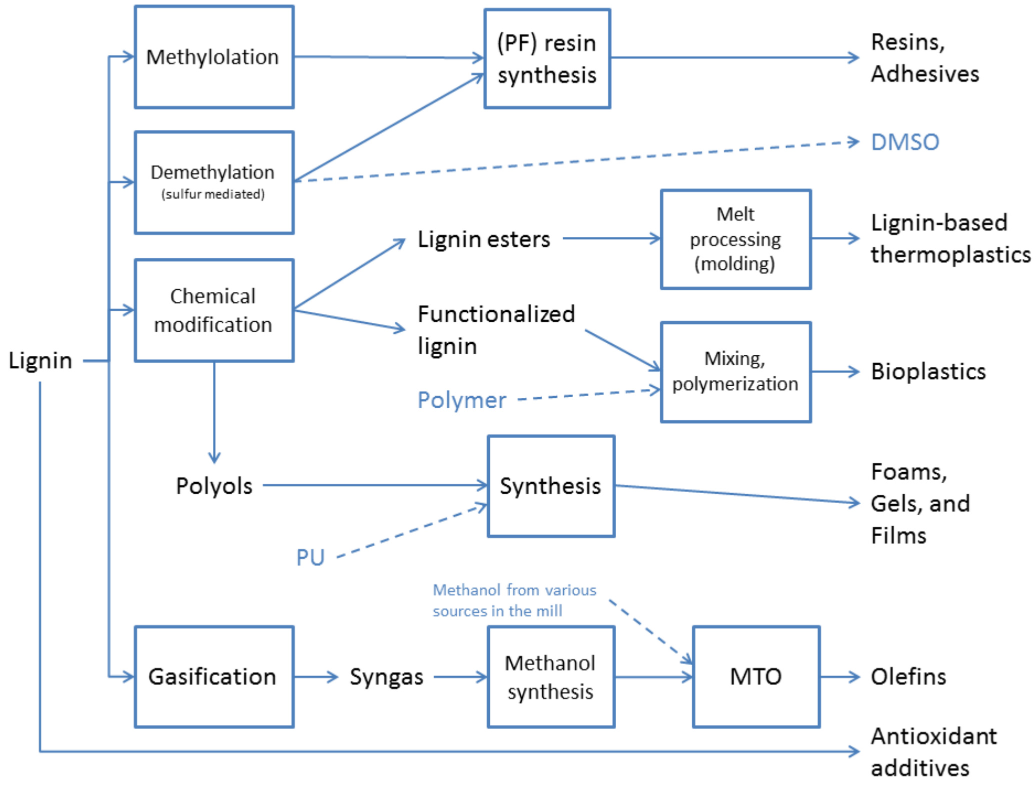

Figure 10. Various routes from lignin to composites and composite building blocks.

4.3.1 Resins and adhesives

Resins and adhesives offer a good opportunity for the use of isolated lignin. Lignin has been suggested as a substitute for phenol in phenolic resins. Two types of phenolic resins exist: resol and novolac. Resol is synthesized under alkaline and novolac under acidic conditions./80/ Phenol-formaldehyde (PF) resins are a noteworthy group because technical lignins, with modifications to their reactivity, can be quite simply polymerized with formaldehyde. PF resins are commonly used in wood adhesive applications./81/ Here, lignin could increase the degree of renewability. Lignin could also be used as a phenol substitute in other resin and adhesive applications, *e.g.* in epoxy resin blends, chelating resins and ion exchange resins./39, 82/

In wood adhesives, the cost savings achieved by using lignin as phenol substitutes have typically been lost due to the lengthening of pressing times./83/ Therefore, the reactivity has to be modified prior to the PF resin synthesis. Methylolation, or hydroxymethylation, has been used to increase reactivity of lignin to the extent that it can be incorporated directly into PF resol resin in alkaline medium. Another adequate reactivity enhancer is sulfur mediated demethylation, which can be used in dimethyl sulfoxide (DMSO) production./84/ The polymerization of PF resins occurs via electrophilic substitution of formaldehyde. This takes place at a free position in the phenyl ring which elucidates the need for demethylation./12/

As is the case in many other lignin applications, a lower molecular weight is preferred also in PF resins. The amount of free phenolic hydroxyl groups and unblocked *ortho* positions in the phenyl rings are important factors when determining the suitability of technical lignins for PF resin applications. Kraft and soda-AQ lignins have been characterized with high hydroxyl group and low methoxy group concentrations and would therefore be suitable phenol substitutes in PF resins./39/

4.3.2 Bioplastics

Today, the vast majority of plastic material is produced from petroleum. A small share of the commercial plastic products originates from different bio-based materials. These enable the production of *e.g.* various cellulose based acetates. Lignin could substitute a portion of the petroleum based raw materials, and not only decrease the carbon footprint of the plastics production but also add new functionalities, such as antioxidant activity and biodegradability./13/ Unmodified technical lignins can be directly blended as additives or fillers in various polymers. This will reduce the costs of production, but often results in decreased physical properties. Thus, the properties of lignin should be enhanced via chemical modification. The chemical modification of lignin can be performed in three ways: (i) fragmentation/depolymerization, (ii) creating new chemically active sites, and (iii) chemical modification of hydroxyl groups./5/

The global market for polyolefins is very significant. Polyolefins are currently recalcitrant to biodegradation /79/, but this could significantly be improved by the addition of lignin./85/ It is also possible to produce olefins solely from lignin via a gasification followed by methanol synthesis and a petrochemical methanol-to-olefins (MTO) process./16/ This route would also enable the use of excess methanol derived from other sources, such as digestion or evaporation plants /86/, in a pulp mill.

Thermoplastics, with comparable flexural properties with polypropylene and polyethyleneterephthalate, can be produced from lignin esters, such as acetate, propionate and butyrate. These esters are synthesized through a one-step esterification process in acetic, propionoic, or butyric acid anhydride. The resulting lignin esters can be molded into products./87/

4.3.3 Foams, gels and films

Lignin can be utilized mainly in the production of, polyurethane (PU) based foams /88/, hydrogels /89/, and films /90/. In these applications, lignin improves the mechanical properties and the biodegradability of the product. Lignin adds rigidity to the film and foam applications with additions between 5-10%. In films, improvements in rigidity are achieved at the cost of a detriment to elasticity. Film properties can be further improved with the addition of other bio-based products, such as cellulose nanowhiskers./91/ The brown color of technical lignins can be a problem in all material applications but especially in films, where high optical properties are required./15/

Oxopropylation, which stands for the chain extension of lignin with propylene oxide, has been found to be a suitable preparation for lignin-based PU applications. Oxopropylation enables adding a higher content of lignin into PU applications without the loss of mechanical properties, but rather enhancing them./88/ Chemical crosslinking of lignin with isocyanate group-terminated polyurethane ionomers was previously used to prepare lignin-PU materials./90/

4.3.4 Antioxidant additives

An interesting functionality of lignin is the antioxidant activity it bears. This ability comes from the radical scavenging capacity of lignin and is potentially applicable in the protection of light and oxygen sensitive goods, *e.g.* in active packaging solutions. The antioxidant activity can be advantageous in various composite materials also with low concentrations of lignin blended, so that the mechanical properties are not weakened./92/ The antioxidant abilities of different lignins have been measured by determining the rate of generation of linoleic acid peroxide during an inhibited peroxidation of linoleic acid initiated by azo-compounds with a known rate of initiation. The best antioxidant effects were found in hardwood organosolv and softwood soda lignins./19/

4.4 Activated carbon

Activated carbons (ACs) are well known adsorbents that have a very porous structure and large internal surface area from 500 to 2000 m^2/g. These properties give ACs good adsorption capacities toward various inorganic and organic substances. Lignin is an interesting precursor to AC production due to the high carbon content and the molecular structure which is similar to bituminous coal./93/ The elemental composition of various technical lignins is presented in Table 11.

Table 11. The elemental composition of different technical lignins.

Lignin type	C (%)	H (%)	N (%)	O (%)	S (%)	Reference
Kraft, SW, CO_2 precipitation	65.4	5.70	0.11	26.2	2.60	/13/
Kraft, HW, CO_2 precipitation	62.5	5.70	0.25	29.0	2.90	/13/
Lignosulfonate, Ca	44.8	5.15	0.02	44.1	5.85	/39/
Enz. Hydrolysis, poplar	58.3	6.01	1.26	34.4	0.00	/39/
Acetocell, monterey pine	66.5	5.07	<0.50	26.6	<0.05	/94/
Soda, Protobind 2400, wheat straw	61.2	6.30	0.93	24.2	2.00	/13/
Pyrolytic, FENOSA, eucalyptus	63.7	5.79	0.19	30.3	0.00	/47/
Pyrolytic, VTT, pine	70.6	6.64	0.15	22.7	0.00	/47/
Kraft, Indulin AT, pine	64.5	5.42	1.01	24.7	1.85	/94/

As the reactivity of lignin is naturally quite low, so is also the adsorption capacity. Thus, activation is needed to enhance these properties. The activation can be performed via two routes: (i) physical, and (ii) chemical. The two routes and their typical process conditions are illustrated in Figure 11. Physical activation is typically done in two-stages, carbonization and activation. During carbonization, 600-900°C in inert atmosphere, the non-porous char is formed. The char is then activated with an oxidizing gas, such as CO_2, in the temperature range of 600-1200°C. The activation removes the more disorganized carbon and results in well-developed micropore structure. In chemical activation, carbonization and activation are occurring simultaneously. Lignin is first impregnated with chemicals such as H_3PO_4, KOH or NaOH, and then followed by heating up to 450-900°C under nitrogen flow./93/

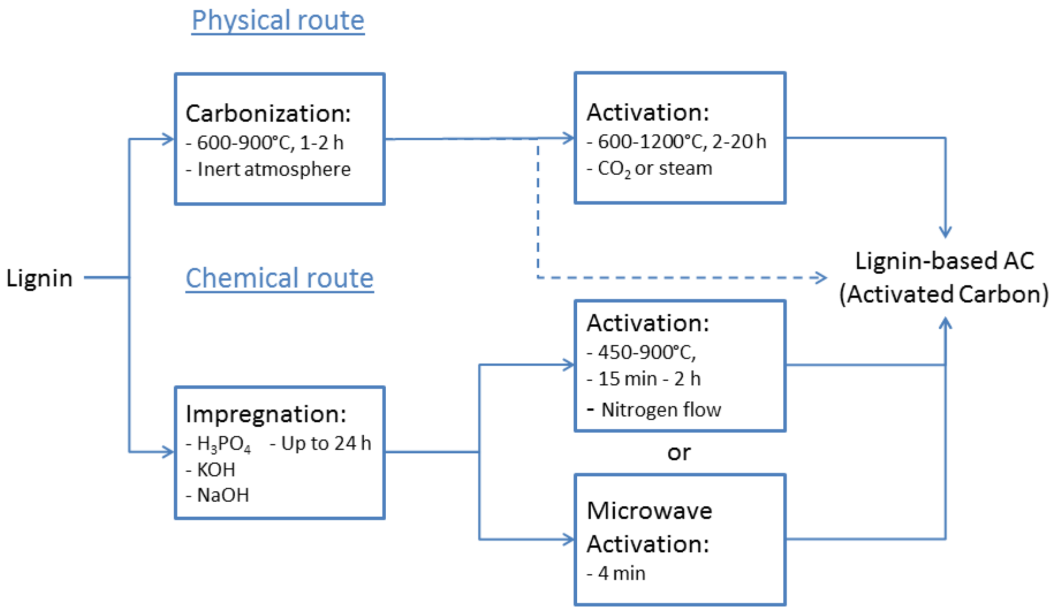

Figure 11. Routes to lignin-based ACs (data adopted from /93, 95/).

Chemical activation gives higher micropore volumes and wider micropore sizes and is, therefore, preferred in liquid phase applications./93/ H_3PO_4 has been shown to be the best impregnation chemical resulting in high micropore volumes and a high carbonization yield of almost 60% under an activation temperature of 600°C./96/ AC prepared with chemical microwave treatment results in higher micropore volumes and better adsorption capacity of endosulfan and Cu(II) than AC prepared with traditional chemical treatment./95, 97/

Long activation times, up to 20 hours, are needed in the physical route which is mainly due to the comparatively low reactivity of lignin./93/ Another challenge here is the thermoplastic nature of lignin which can cause the melting of the smallest lignin particles in high temperatures. The latter can, however, be avoided with oxidative thermal stabilization or by lower heating rates. Sulfur containing lignins can cause odor problems during carbonization, which promotes the use of sulfur-free lignins./98/ Other than the sulfur problem, no limitations have been presented for suitable technical lignins for AC production. Of course, high carbon content is preferable which encourages using pyrolytic lignin as a raw material for AC.

4.5 Carbon fibers

Carbon fibers (CFs) are used in a wide-range of high performance applications in aerospace, military, construction, medical and sporting goods industries. They are lightweight, have high strength, flexibility, and fatigue resistance due to the high orientation of the fibers. Currently, CFs are mainly produced from polyacrylonitrile (PAN), and of smaller quantities from petrochemical pitch rayon. However, PAN-based CFs are expensive (13-19 € per kg) which reduces the use of CFs in large volume applications, such as replacing steel parts in automotive industry. The target price of low-cost CFs, for steel replacement, has been estimated to be around 8 € per kg. Since PAN is responsible for approximately 50% of the costs of CFs, are new cheaper precursors needed. Lignin could be an inexpensive precursor to low-cost CF production./99, 100/

4.5.1 Production of lignin-based carbon fibers

The production of lignin-based CFs consists of four steps: (i) purification, (ii) spinning, (iii) thermal stabilization, and (iv) carbonization. Purification, *e.g.* with dilute HCl, is needed to remove hemicelluloses, salts, volatiles and other contaminants./101/ Unpurified lignins have exhibited very poor spinnability due to the foaming and crosslinking that occurs during spinning./99/ Lignin can be either melt spun or dry spun /102/, but the melt spinning is more widely researched. Melt spinning is performed with a thermal extrusion process in temperatures typically between 140°C and 230°C. The melt spinning temperature is closely related to the molten viscosity of lignin and principally is between T_g and T_d./103/

To prevent the fusion of fibers during carbonization a thermal stabilization stage is needed./104/ Thermal stabilization is typically performed at a temperature of 250°C in an air, nitrogen or oxygen atmosphere with quite slow heating rates. In principle, the heating rate follows the rule $T_g>T$ in order for the fibers to stay in a glassy state./103/ Essentially, the T_g will disappear indicating that completely stabilized fibers are formed due to the oxidation reactions occurred./99/ In literature, the heating rate of thermal stabilization has typically varied from 0.06°C/min to 2°C/min./103, 105/ However, Nordberg et al. have been able to successfully stabilize lignin-based fibers with heating rates of 4°C/min in nitrogen and 15°C/min in air atmosphere. They have also been able to combine the thermal stabilization and carbonization stages./106/

In the carbonization stage the thermally stabilized fibers are treated in a nitrogen atmosphere typically between 800°C and 1400°C with heating rates between 1°C/min and 5°C/min./91, 101/ During carbonization the cyclized polymer structure crosslinks at lower temperatures followed by condensation reactions at higher temperatures. These reactions are responsible for the well-oriented structure of the CFs./99/ A few routes from different technical lignins to CFs are illustrated in Figure 12.

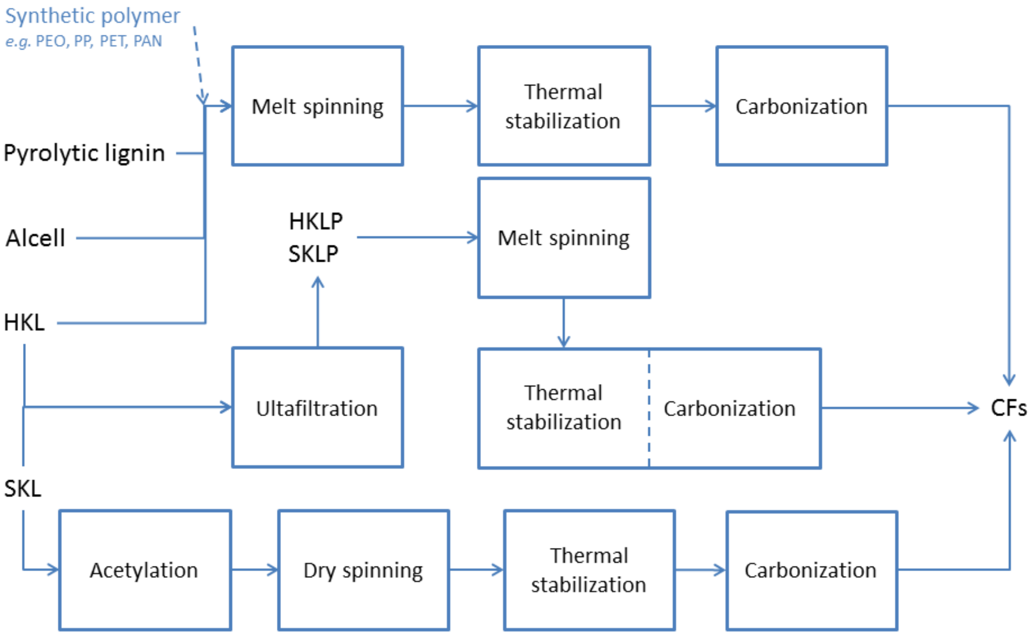

Figure 12. Routes to lignin-based CFs.

4.5.2 Suitable raw materials

CFs with various qualities have been successfully made from: hardwood kraft lignin (HKL) /103/, softwood kraft lignin (SKL) /107/, Alcell organosolv lignin /103/ and pyrolytic lignin /108/. Pyrolytic lignin could be interesting due to its high carbon content that increases the yield of carbon fibers. However, it contains a great deal of volatiles that have to be removed in a pretreatment stage prior to spinning in order to prevent the fibers from fusing during thermal stabilization. Carrying out the pretreatment itself is challenging as there is only a narrow operational window where suitable properties can be achieved./108/ From Alcell lignin, CFs have been manufactured with yields around 40% which is lower than for HKL (45%) but higher than for petroleum pitch (33.4%)./103/

The yield of CFs from raw material is an important factor when aiming at cost reduction in CF production, especially for lower quality CFs. Synthesizing HKL with PAN by using free radical polymerization and producing CFs from this copolymer has resulted in an overall yield of 56% with 16% PAN addition./101/ The addition of other synthetic polymers, such as polyethylene oxide (PEO), polypropylene (PP) and polyethylene terephthalate (PET), has generally decreased the yield since these polymers are not carbonized. However, with the addition of a synthetic polymer spinnability can be increased./109/

Whereas HKL shows good spinning properties both as pure and in mixtures with a synthetic polymer, the spinning of SKL has been proven to be problematic due to the more highly cross-linked structure compared with HKL./103/ Different softening agents have failed to mobilize SKL. However, the utilization of hardwood kraft lignin permeate (HKLP) as an additive or the spinning of pure softwood kraft lignin permeate (SKLP) seems to have overcome this problem./107/ The production of CFs from SKLP has also been the fastest process, approximately 26 times faster than the previous methods for HKL /106/, which could have significant industrial importance. In a recent study by Zhang and Ogale, CFs were also produced successfully with the dry spinning of acetylated SKL./102/

The success of SKLP-based CFs suggests that the low polydispersity and probably the low molecular weight are desirable characteristics when selecting the raw material for the lignin-based CF production. The kraft lignin permeates were obtained from the ultrafiltration of CO_2 precipitated kraft lignins with a ceramic membrane with a cut-off of 15 kDa./106, 107/ As the ultrafiltration can be performed directly from BL /31/, it would be interesting to obtain results from the production of CFs from SKLP isolated directly from BL, since this would be economically preferable as the costs of CO_2 precipitation would be eliminated.

4.5.3 Properties of lignin-based carbon fibers

The U.S. Department of Energy (DoE) has set targets for the properties of low-cost CFs: tensile strength at least 1.72 GPa, tensile modulus at least 172 GPa, elongation preferably above 1%, and target diameter of 10 µm./110/ The mechanical properties of different lignin-based CFs are presented in Table 12.

Table 12. The mechanical properties of lignin-based and conventional CFs.

Sample (%)	Diameter (µm)	Tensile strength (GPa)	Tensile Modulus (GPa)	Elongation (%)	Reference
PAN (100)	5-10	3.5-6.3	200-500	0.8-2.2	/111/
HKL (100)	46±8	0.42±0.08	40±11	1.12±0.22	/103/
HKL-PEO (97/3)	34±4	0.45±0.07	51±13	0.92±0.21	/103/
Alcell	31±3	0.39±0.12	40±14	1.00±0.23	/103/
HKL-PP (88/12)	44±5	0.44	54	0.85	/109/
HKL-PET (75/25)	34±5	0.70	94	1.06	/109/
Pitch (100)		0.6-0.7	61		/109/
Pyrolytic lignin	49±2	0.37±0.04	36±1		/108/
Acetylated SKL	12±1	1.04±0.1	52±2	2.0±0.2	/102/

So far, the dry spun acetylated SKL CFs have the best mechanical properties, but one of the lignin-based CFs has achieved the criteria set by DoE as of yet. However, lignin-based CFs could be also utilized in applications that do not require high performance quality, such as interior details in automotive industry or casing of electronic appliances. No public data is available about the properties of SKLP-based CFs, which is a regrettable pity since they have the greatest potential from the ease-of-production point of view.

EXPERIMENTAL STUDY

5 Materials and methods

The experimental study consists of three parts: (i) technology readiness evaluation of lignin applications and isolation technologies, (ii) isolation and characterization of technical lignins in laboratory, and (iii) suitability evaluation of the characterized lignins towards certain applications. In this chapter, the applied materials and methods are presented. Lignosulfonates and their applications are not discussed in the experimental study because they cannot be considered as “novel” due to their long commercial history. However, the current applications for lignosulfonates were presented in Chapter 4 (Table 8).

5.1 Technology Readiness Levels

The readiness and the development phase of a certain technology can be assessed by using the Technology Readiness Level (TRL) metric system developed by the National Aeronautics and Space Administration (NASA) in the late 1980s. TRLs have been adopted and applied in many areas mostly by U.S. government agencies, such as the Department of Energy /112/, the Department of Defense /113/ and the Department of Homeland Security /114/. For example, the Department of Energy has conducted a TRL scale to measure the readiness of carbon capture technologies./112/ Other than in government agencies, TRLs have also been applied in consumer goods and services to measure consumers’ perception of technology readiness and ability to embrace new products./115/

Technology Readiness Assessment (TRA) is an expansion of TRL which also identifies the risks associated with technologies and investment requirements, the potential problems early when solutions are less expensive to execute, and the gaps in testing, demonstration and knowledge. This means that the TRA is a complete process that aids the development process to stay on schedule and within budget./114/ The original TRLs from NASA are presented in Table 13.

Table 13. The original TRLs as presented by NASA./116/

Level	Definition	Description
1	Basic principles observed and reported	Scientific research begins to be translated into applied research and development.
2	Technology concept and/or application formulated	Practical applications invented, identified and defined. The application is still speculative: there is not experimental proof or detailed analysis to support the conjecture.
3	Analytical and experimental critical function and/or characteristic proof-of-concept	Analytical studies to set the technology into an appropriate context and laboratory-based studies to physically validate that the analytical predictions are correct.
4	Component and/or breadboard validation in laboratory environment	Basic technological elements are integrated to establish that the "pieces" will work together to achieve concept-enabling levels of performance for a component and/or breadboard.
5	Component and/or breadboard validation in relevant environment	The basic technological elements must be integrated with reasonably realistic supporting elements so that the total applications can be tested in a simulated or somewhat realistic environment.
6	System/subsystem model or prototype demonstration in a relevant environment (ground or space)	A representative model or prototype system/subsystem is tested in a relevant environment. The demonstration has to be successful to achieve this level.
7	System prototype demonstration in a space environment	An actual system prototype demonstration in space environment. The prototype should be near or at the scale of the planned operational system.
8	Actual system completed and "flight qualified" through test and demonstration (ground or space)	The end of true "system development" for most technology elements. The actual system tested in space. Might be integrated into an existing system.
9	Actual system "flight proven" through successful mission operations	The end of last "bug fixing" aspects of true "system development". Technology included in real mission operations.

In this thesis, the TRL scale will be used for the evaluation of the lignin-based applications and isolation technologies. The original TRLs defined by NASA are tailored to better describe the development process of biorefining technologies. The TRLs for lignin-based applications and isolation technologies are presented in Table 14.

Table 14. The TRLs for lignin-based applications and isolation technologies.

Level	Definition	Description
1	Basic principles observed and reported	Published research that identifies the principles that underlie this technology.
2	Formulation of application and technology concept	Commercial potential detected. Speculative practical applications invented, identified and defined. Targets and tolerances defined. Examples are limited to analytical studies or experiments with model compounds.
3	Analytical and experimental proof-of-concept	The analytical predictions are physically validated by experimental laboratory studies. Individual experiments for critical subsystems/unit processes and parameters.
4	Laboratory scale operation, integration of subsystems/unit processes	Basic technological components are integrated at laboratory scale to establish that they will work together.
5	Laboratory scale operation, optimization of parameters	Parameters are optimized at laboratory scale to achieve the targets and tolerances defined earlier. Successful production of products that meet the targets required in order to scale-up.
6	Scale-up to pilot scale, test runs	Pilot scale prototype built. Test runs performed to achieve the required quality for commercial production at pilot scale.
7	Commercial operation at pilot scale	Products of commercial quality produced at pilot scale for reasonable period. Minor “bug fixing” and preparation for scale-up.
8	Scale-up to industrial scale, test runs	Industrial scale prototype built. Test runs performed to achieve the required quality for commercial production at industrial scale.
9	Commercial operation at industrial scale	Products of commercial quality produced at industrial scale for reasonable period. Continuous improvement of process capabilities and performance.

It is good to note that the TRL scale does not evaluate the potential of a certain technology but rather the maturity of it. Of course, a comprehensive TRA would give a more detailed picture about lignin technologies than the simplified TRL scale, but the scope of this thesis is limited and a complete TRA would require a whole study dedicated to it. However, even the simplified TRL scale gives a proper and understandable illustration of the current state of lignin-based applications and isolation technologies.

5.2 Lignins for characterization

Fourteen lignin samples were characterized in this thesis. Ten lignin samples were received as isolated and four lignin samples were isolated in a laboratory from two weak black liquors (WBL) received from commercial kraft pulp mills. The two WBLs were collected from Nordic kraft pulp mills. The lignin samples used for characterization are presented in Table 15.

Table 15. Lignin samples used for characterization.

Sample ID	Raw-material	Description
WBL1	SW	CO_2 precipitated kraft lignin, polysulfide cooking
WBL2	HW	CO_2 precipitated kraft lignin
KRA1	SW	Kraft lignin
KRA2	HW, euca	Kraft lignin, modified continuous cooking
KRA3	HW, euca	Kraft lignin, conventional cooking
PRE1	SW	Prehydrolysis kraft lignin
PRE2	Non-wood	Prehydrolysis non-wood lignin
ORG	Non-wood	Organosolv lignin (acetic acid/formic acid/water)
HYD1		Ethanol by-product hydrolysis lignin
HYD2		Ethanol by-product hydrolysis lignin
LIG1		
LIG2		
LIG3		
LIG4		

5.2.1 Isolation of lignins from weak black liquor

The lignins were isolated from WBLs according to the CO_2 precipitation approach./26, 117/ The precipitation was performed in a 30 liter reactor specifically built for this purpose. The reactor was equipped with a stirrer, temperature control, pH sensor and CO_2 inlet. The yield of CO_2 precipitation was not measured since it does not fall in the scope of this thesis.

5 liters of each WBL was preheated to 70°C for softwood and 60°C for hardwood, and acidified with CO_2 to pH 9. After the desired pH was reached, the acidified liquors were centrifuged (15 min, 4500 rpm) and the solid fraction was collected. Then the solid fractions were re-slurried in distilled water and acidified to pH 2 with 1 M sulfuric acid under stirring. The resulting sludges were filtered in a Buchner funnel with VWR qualitative filter paper 415 (pore size 12-15 µm) and subsequently washed two times with 300 ml of distilled water. The washed samples were dried at 45°C for 48 hours and crushed into powder with an electric mixer.

5.3 Characterization of lignins

A set of characterization experiments was applied for all of the lignin samples. Literature review and its references were used as selection criteria for the applied test methods. The methods were selected to give a comprehensive overview on the properties of the different lignin samples. The facility of the methods was also an important criterion since there were a lot of samples and the time to perform these experiments was limited.

5.3.1 Dry matter content

Dry matter contents were determined gravimetrically, according to ISO 638:1978 – standard /118/, after drying duplicate samples to constant weight at 105°C.

5.3.2 Ash content

Ash contents were determined gravimetrically, according to ASTM-D1102-84 – standard /119/, after in-furnace calcinations for 4 hours at 575°C.

5.3.3 Lignin and structural carbohydrate contents

Acid insoluble lignin (AIL) which is also known as Klason lignin, acid soluble lignin (ASL) and structural carbohydrate contents were determined with the conventional two-step acid hydrolysis method according to National Renewable Energy Laboratory (NREL)./120/

The two-step acid hydrolysis was performed for duplicate samples. 300.0 mg of each sample was weighed in separate test tubes and 3.00 ml of sulfuric acid was added to each tube. After the sulfuric acid addition, the tubes were placed in a water bath set at 30°C and incubated for 60 minutes while stirring the samples with a glass rod every five minutes. After the first hydrolysis step was completed, the samples were transferred from the test tubes to autoclave bottles and 84 ml of distilled water was added to each sample to dilute the acid to a 4% concentration. The bottles were then mixed by inverting the bottles several times, followed by the second hydrolysis step in an autoclave for 60 minutes at 121°C.

When the two-step acid hydrolysis was completed, the samples were filtrated with formerly weighed filtering crucibles, and 50 ml of each filtrate was collected into sample storage bottles. The storage bottles containing the filtrates were then stored in a freezer prior to the analysis of ASL and structural carbohydrates. The filtering crucibles containing the AIL were dried to constant weight at 105°C and the AIL was determined gravimetrically.

Carbohydrate analysis was performed with high performance liquid chromatography (HPLC) equipment equipped with a Dionex CarboPac PA20 column. Duplicate injections were done for each sample. The samples for HPLC were prepared by diluting the hydrolysis filtrate tenfold and filtering the diluted samples into sample vials with a 0.2 µm PTFE filter.

The ASL analysis was performed with a Shimadzu UV-VIS 2550 spectrophotometer for diluted filtrate samples. Duplicates were analyzed from each sample. The ASL calculations were done with two different methods, and results from both methods are presented in Chapter 6. The first method, according to NREL /120/, was based on the average UV-Vis absorbance for the sample at 320 nm with absorptivity constants of 12 l/g cm for softwood, 25 l/g cm for hardwood, and 30 l/g cm for non-wood lignins. The second method, according to Technical Association of the Pulp and Paper Industry (TAPPI) /121/, was based on the average UV-Vis absorbance for the sample at 205 nm with absorptivity constant of 110 g/l cm for all lignin types.

5.3.4 Elemental analysis

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

5.3.5 Phenolic hydroxyl group content

Content of free phenolic hydroxyl groups was determined with a modified Δε UV-method. The method is based on the difference in absorption between lignin in alkaline solution and lignin in neutral solution. Ionization of phenolic hydroxyl groups in lignin with alkali causes a bathochromic shift and a hyperchromic effect in the absorption spectrum, which can be measured by subtracting the neutral spectra from the alkaline spectra./122/

The original method, introduced in 1954 /123/, required calibration with lignin model compounds for each lignin type, whereas the modified Δε UV-method is calibrated with model compounds representing typical phenolic structures present in lignin. The procedure used in this thesis was developed by Zakis /124/ and gives not only the amount of free phenolic hydroxyl groups but also the proportions of different phenolic structures. Zakis identified four different phenolic structures that have been expanded to six different structural types by Gärtner and Gellerstedt /125/. These six structural types of phenolic lignin are presented in Figure 13.

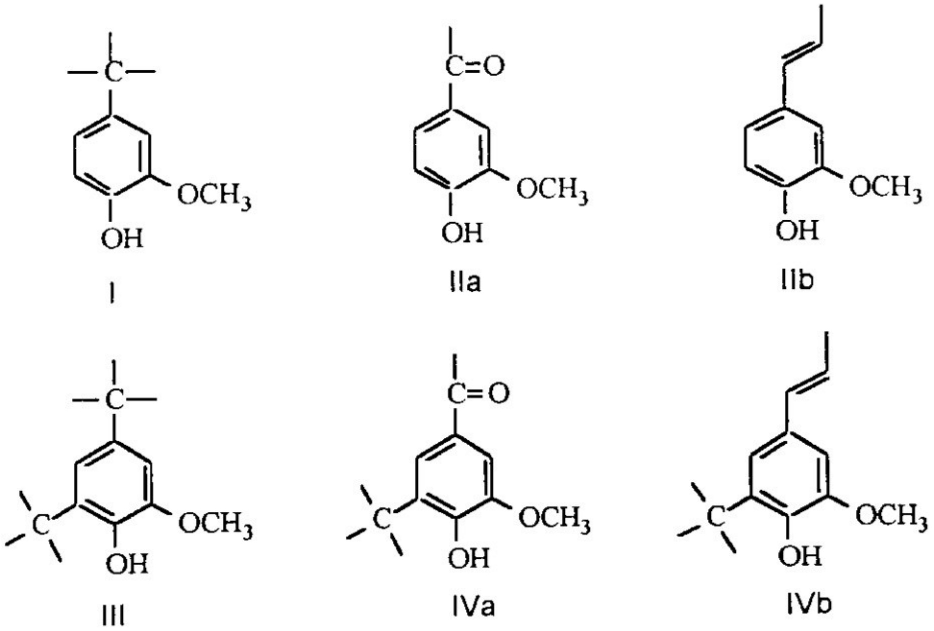

Figure 13. Types of phenolic structures in lignin./125/

The samples were prepared by dissolving 10 mg of each lignin in 5 ml of 0.2 M NaOH and 5 ml of dioxane. Three of the solutions (LIG4, HYD1 and HYD2) were not quite clear and these were filtered through a 0.45 µm PTFE membrane filter prior to further preparations. LIG3 did not dissolve at all in the NaOH-dioxane solution and it was thus not analyzed. 2 ml of each dissolved lignin was further diluted to 25 ml with either pH 6 buffer solution, pH 12 buffer solution or 0.2 M NaOH.

UV-spectra was then recorded for these three solutions with Shimadzu UV-VIS 2550 spectrophotometer, with the pH 6 solution as reference and the two alkaline solutions measured against it. Three scans were performed for both alkaline solutions, which results in six scans per lignin. The calculations were performed according to Equations 1-5./125/ The absorbance peaks used for calculations were within 290-300 nm and 350-370 nm.

$$Total\ amount\ of\ phenolic\ hydroxyl\ groups:$$

$$OH(tot) = OH(I + II + III + IV) =$$

$$= [0.250 * A_{300\,nm}(NaOH) + 0.107 * A_{300\,nm}(NaOH)] * \frac{1}{c*l}\ mmol/g \qquad \text{Eq. 1}$$

$Non - conjugated\ phenolic\ structures\ (I + III)$:

$$OH(I + III) =$$

$$= [0.250 * A_{300\,nm}(NaOH) + 0.0595 * A_{350\,nm}(NaOH)] * \frac{1}{c*l}\ mmol/g \qquad \text{Eq. 2}$$

$Conjugated\ phenolic\ structures\ (II + IV)$:

$$OH(II + IV) = 0.0476 * A_{350nm}(NaOH) * \frac{1}{c*l}\ mmol/g \qquad \text{Eq. 3}$$

$Phenolic\ structures\ ionized\ in\ the\ pH\ 12\ solution\ (I, II)$:

$$OH(I) = [0.250 * A_{300\,nm}(pH12) + 0.0595 * A_{350\,nm}(pH12)] * \frac{1}{c*l}\ mmol/g \qquad \text{Eq. 4}$$

$$OH(II) = 0.0476 * A_{350\,nm}(pH12) * \frac{1}{c*l}\ mmol/g \qquad \text{Eq. 5}$$

Where (Eqs. 1 to 5):	A is absorbance
	c is concentration in g/l
	l is path length through the sample in cm

5.3.6 SPME-GC-MS

Technical lignins have typically a distinctive odor which is said to originate from the compounds, mainly sulfur containing, formed during fractionation and isolation processes./15/ These odors can be harmful in some applications, *e.g.* in biocomposites. In this thesis, solid-phase micro extraction - gas chromatography - mass spectrometry (SPME-GC-MS) analysis aims at resolving the culprit of odor for each lignin. SPME-GC-MS also provides important information about the different valuable chemical compounds, *e.g.* vanillin, found from the samples.

SPME is a sample preparation technique that is fast, simple, and does not require solvent extraction. In SPME-GC-MS, a fused silica fiber that has been coated with a stationary phase is exposed to volatile compounds that have been collected at certain temperature for certain time. The compounds partition into the stationary phase and are further thermally desorbed in the gas chromatograph and mass spectrometer./126/

Volatile compounds were analyzed in duplicate from 50 mg samples using a HS-SPME injector (combiPAL, CTC Analytics, USA) with a DVB/CAR/PDMS-fiber (50/30 µm film thickness). The SPME was coupled to an Agilent HP 6890 series GC with an Agilent 5973 MS detector. The GC was equipped with a capillary column SPB-624 (30 m x 0.25 mm, 1.4 µm film thickness). Sample vials were first incubated for 20 min at 80°C prior to extraction of the volatile compounds at the same temperature for 30 min. During incubation and extraction, the samples were agitated at 250 rpm. Volatile compounds adsorbed to the fiber were desorbed for 10 min at 250°C in the injection port of GC.

The GC operating conditions were the following: helium flow 0.7 ml/min; oven temperature 40°C for 5 min, then increased by 5°C/min to 200°C and held there for 10 min. The ionization energy of MS was 70 eV and the scan range was from 50 to 300 amu. Identification of compounds was performed by matching their mass spectra with the database Wiley 7N.

5.3.7 Odor panel

Odors of lignin samples were determined with olfactometric techniques by an odor panel. The measured parameters were intensity and pleasantness, and the panelists were also instructed to describe each sample with 1-3 words if they noticed something that they recognize or were able to describe. The parameters are presented in Table 16. Two identical panels were held with a total of 13 participants. Similar panels have been applied in automotive industry for car interiors./127/

SPME-GC-MS does not give information about the human perception of odor./128/ Therefore, an odor panel combined with SPME-GC-MS results can give valuable information about the origin of odors. In this thesis, these two methods are used for complete odor analysis to solve the compounds causing the odor of each lignin and to clarify the suitability of lignins for material applications. The possible toxicity of the odorous compounds is also investigated.

Table 16. Parameters for odor panel.

Rating	Intensity	Pleasantness
1	No noticeable odor	Very pleasant
2	Slight, but noticeable odor	Pleasant
3	Definite odor, but not strong enough to be offensive	Neutral
4	Strong offensive odor	Unpleasant
5	Very strong offensive odor	Very unpleasant

5.3.8 Molecular weight distribution

Molecular weight distribution was determined with gel permeation chromatography (GPC) which is also known as size exclusion chromatography (SEC). The method is based on the different retention times of different sized molecules in a column filled with porous particles. A small molecule that can penetrate most pores will travel a longer distance in the column than a large molecule that cannot penetrate into any pores./129/

The used solvent was tetrahydrofuran (THF), which is an organic solvent commonly used in GPC analysis of lignin. GPC analyses were performed with an HPLC Agilent 1260 series at room temperature. The columns used were 50 Å and 1000 Å Phenogel (300 x 7.8 cm) 5 µm particle size and the detector was a diode array detector (DAD). THF was used as eluent with a flow rate of 1 ml/min and the injection volume was 50 µm. The calibration was performed with two standards containing seven polystyrenes with molecular weights ranging between 208-76600 g/mol, toluene 92 g/mol, syringol 154 g/mol and 2,2-dihydroxybiphenyl 186 g/mol.

The samples were prepared by dissolving lignin in THF where they were kept overnight, and after that they were filtered through a 0.45 µm PTFE membrane filter into GPC sample vials. Due to the large amount of samples no prior acetylation was done, which means that the results are only for the THF soluble fraction of each lignin.

Lignin has been characterized to be soluble in solvents having Hildebrand's solubility parameter between 9 and 11 with increasing solubility of higher molecular weight fractions as the solubility parameter of the solvent decreases, and *vice versa*. However, low molecular weight lignin fractions dissolve in solvents with a wider range of solubility parameters. Another factor contributing to solvent properties is hydrocarbon chain length. The solubility of lignin decreases with increasing hydrocarbon chain lengths even when the solubility parameter is close to eleven./130/ THF has a Hildebrand's solubility parameter of 9.52, and can thus be considered as a good solvent for lignin in general. However, the solubility of different lignins in THF is depending on plant origin, isolation procedure, functionality and molecular weight distribution./129/ This issue and findings based on it are discussed more widely in Chapter 6.

5.4 Suitability evaluation

Suitability of the characterized lignins for certain applications was evaluated with a suitability matrix. The purpose was to find the most suitable lignins for each application, and *vice versa*. The selected applications were the same that were evaluated with TRL metrics. The evaluation was based on the characterization results obtained in this thesis and known properties of technical lignins, *e.g.* hardwood lignins are more thermoplastic and softwood lignins thermosetting. The lignins were evaluated primarily against each other with H, L, or empty, where H is high suitability, L is low suitability and empty is very low or not suitable. The main criteria, desired properties of lignins, for each application are presented in Table 17. The criteria were defined based on literature review and its sources.

Table 17. Evaluation criteria for the suitability matrix.

Application	Desired properties
Solid fuel	High carbon content, low ash content
Hydrogen	High lignin content, low ash content
Liquid fuels	Low ash content
FT-liquids	High carbon content, high lignin content, low ash content
BTX-chemicals	Low sulfur content, high overall purity
Vanillin	High vanillin content in VOC, SW
Syringaldehyde	High syringaldehyde content in VOC, HW
PF-resin	High phenolic OH content, high amount of free C3/C5 positions (HW<SW<non-wood), low apparent M_w
Thermoplastics	High thermoplastic behavior (HW>SW), low odor intensity, high molecular weight, low polydispersity
PU-foam	No toxic volatiles, high reactivity, low odor intensity
Antioxidant additive	High reactivity (phenolic hydroxyl groups), high antioxidant activity (not measured, might be very structure dependent, which means that the suitability values can be wrong)
Activated carbon	High carbon content, high thermosetting behavior (SW>HW), low sulfur content (not critical -> causes odor problems during activation)
Carbon fibers	High purity, high crosslinking ability (softwood kraft), low polydispersity

6 Results and discussion

First, the maturity of representative examples from each application category, presented in Chapter 4, and the most interesting isolation technologies were evaluated with the TRL scale tailored for this specific purpose. Secondly, several technical lignins were characterized to study their properties. And finally, the suitability of the characterized lignins for certain applications was evaluated with the suitability matrix. In this chapter, the obtained results and possible sources of error are presented and discussed.

6.1 TRL evaluation

TRL evaluation was performed based on isolation technologies and applications presented in the literature review part of this thesis. The evaluation criteria and TRLs used are presented in Table 14. The evaluated isolation technologies were: CO_2 precipitation, ultrafiltration and electrolysis. All of these are primarily designed for the kraft process and were selected for this evaluation due to the current dominance of the kraft process. The applications that were evaluated have a broader scale of applicable lignins and processes. The evaluated applications were: solid fuel, hydrogen, liquid fuels, FT-liquids, BTX-chemicals, vanillin, syringaldehyde, PF-resin, thermoplastics, PU-foam, antioxidant additive, activated carbon and carbon fiber.

TRL evaluation is considered to be a more informative way to identify the development status of a novel technology than trying to estimate years to commercialization, since the TRL rating clearly points out the required steps left to achieve industrial scale commercial production. The TRLs are presented solely for each technology with a brief description of current situation including possible challenges and opportunities. A summary of this TRL evaluation is presented in Table 18.

Table 18. Summary of TRL evaluation for isolation technologies and applications.

Name	**Category**	**TRL**
CO_2 precipitation	Isolation technology	8
Ultrafiltration	Isolation technology	5 (9)
Electrolysis	Isolation technology	4
Solid fuel	Application	8
Hydrogen	Application	6
Liquid fuels	Application	4
FT-liquids	Application	6
BTX-chemicals	Application	2
Vanillin	Application	5
Syringaldehyde	Application	5
PF-resin	Application	5 (9)
Thermoplastics	Application	4
PU-foam	Application	5
Antioxidant additive	Application	3
Activated carbon	Application	5
Carbon fibers	Application	5

As can be seen from the summary table, many applications are in the verge of scaling-up to pilot scale (TRL 5). The gap between TRL 5 and TRL 6 is the biggest leap within the different TRLs since it is the first real capacity expansion, which typically requires significant financial investment. TRLs 6-9 are quite easy to assign since they are mainly capacity related. The assignment of TRLs 1-5 is much harder since some data about the state of current development is most likely not publicly available, and thus there is an estimated ±1 level error tolerance in the technologies evaluated to have TRL 1-5.

6.1.1 CO_2 precipitation, TRL 8

Precipitation of lignin with CO_2 is currently the most developed lignin isolation technology. Demonstration plant in Bäckhammar, Sweden, started operation in 2007, and the first full-scale prototype started production in 2013 in Plymouth, NC, USA. The second full-scale plant is currently being built in Kotka, Finland, and it is expected to start operation during 2015./131/ CO_2 precipitation is evaluated to fulfill TRL 8 requirements, and it will most likely reach TRL 9 during 2015 when the second full-scale plant starts operation.

6.1.2 Ultrafiltration, TRL 5 (9)

Lignin isolation with ultrafiltration is evaluated to fulfill TRL 5 requirements. The parameters for efficient operation have been optimized in laboratory scale for industrial black and cooking liquors /132/, and the operation costs have been estimated./31, 133/ Scale-up to pilot scale is required in order to reach TRL 6. Ultrafiltration research is currently related to the development of lignin-based carbon fibers because ultrafiltration can produce lignin with specific molecular and thermo-mechanical properties /32/ that are desired in the production of CFs from lignin./107/ Therefore, it is probable that scale-up to pilot scale will not happen until the development of lignin-based carbon fibers from ultrafiltrated lignin advances.

As a curiosity, ultrafiltrated kraft lignin has been produced industrially in the late 1970s in Äänekoski, Finland./134/ However, the exact process technology is not known and it could have been markedly different in comparison with ultrafiltration technology presented in this thesis. Thus, this was not considered in the TRL evaluation, but is presented in parenthesis after the current TRL rating.

6.1.3 Electrolysis, TRL 4

Electrochemical isolation of lignin is ranked to have TRL 4. Even though the concept is demonstrated at laboratory scale, the resulting lignin has not been characterized thoroughly yet. Some characteristics have been published /135/ but more comprehensive studies are needed in order to achieve TRL 5. It is also debatable whether the technology is suitable for current kraft mills since it interferes with the chemical balances more than the other technologies presented in this thesis.

An interesting process step to recover lignin with electrolysis could be the effluent treatment plant. Recovery of organics from wastewater has been demonstrated successfully with electrochemical acidification./136/ Therefore, electrolysis might have potential to be applied for the simultaneous purification and lignin recovery from either wastewater or bio-sludge.

6.1.4 Solid fuel, TRL 8

Using isolated lignin as a solid fuel, *e.g.* in a lime kiln, is probably the least novel application in this thesis. However, it is an important one since it is also the easiest one to implement and can reduce the use of fossil fuels in a pulp mill. Another upside is that this application does not require external market demand but can be used at the isolation site. The dependence of profitability on energy prices is counted as a disadvantage./137/ TRL 8 requirements are fulfilled since the application has been demonstrated at industrial scale in Sweden./138/ The next level will be achieved after the lime kiln in Kotka, Finland, has been operating with isolated lignin for reasonable period.

6.1.5 Hydrogen, TRL 6

Hydrogen can be produced from lignin via gasification or pyrolysis. In theory, conventional gasification of isolated lignin has TRL 9, since it is a proven technology for biomass./139/ However, it is not practiced commercially for lignin and only pilot scale gasification of isolated lignin has been performed./56/ Therefore, the gasification route from isolated lignin to hydrogen fulfills the criteria for TRL 6. The pyrolysis route for this application is more widely researched, but the optimization of process parameters has been investigated only at laboratory scale./140/ This results in TRL 5 rating for the pyrolysis route of isolated lignin to hydrogen, but it is good to note that hydrogen is not the main product of pyrolysis. Thus, the higher TRL for gasification can be considered as more representative for this application.

6.1.6 Liquid fuels, TRL 4

Due to the complexity of pyrolysis oils, the upgrading procedure into a final product can be challenging. The upgrading procedure is not as mature as the isolation of hydrogen from the gas phase products, and therefore the TRL is decreased to TRL 4 in the case of liquid fuels from pyrolysis of isolated lignin. However, promising one-step processes are being developed as new catalysts for pyrolysis are invented./63/

6.1.7 FT-liquids, TRL 6

FT-liquids from lignin are evaluated to have TRL 6, even though they have never been produced from lignin. This is due to the TRL 6 of lignin gasification and the fact that syngas can be used in FT-synthesis despite its origin, as long as it is conditioned to have a certain H_2 to CO ratio. The main challenge in utilizing FT-synthesis for lignin is the economic scale of the process, which is much larger than the typical capacity of biorefinery operations./51/

6.1.8 BTX-chemicals, TRL 2

The production of BTX chemicals from lignin is possible through various catalytic routes, but the optimal catalysts are yet to be found. The current research in this area studies the catalysts mostly by experiments with lignin model compounds, but also with technical lignins./141/ This means that the application is in the verge of TRL 3, but has not quite achieved it. The main challenges are the depolymerization process and the yield of catalytic reduction of functionalities.

6.1.9 Vanillin, TRL 5

Synthetic vanillin has been traditionally produced either from oil derived guaiacyl or from sulfite spent liquors, which of neither is very sustainable since the former is from fossil resources and the latter has caused environmental problems./71/ Research for a more sustainable source of vanillin is concentrated on the catalytic oxidation of technical softwood lignins. Vanillin from these resources is assessed to TRL 5, since laboratory scale optimization of process parameters for yield optimization have been reported./142/ Compared with bulk chemicals, the higher price of vanillin makes it more likely to be commercialized, *e.g.* from kraft lignin, since the yield does not have to be really high in order to run profitable operations.

6.1.10 Syringaldehyde, TRL 5

Syringaldehyde can be produced from lignin with the same technologies as vanillin /143/, and thus has the same TRL 5. The only significant difference is that syringaldehyde is derived from the syringyl units of hardwood lignin whereas vanillin is from guaiacyl units. Hardwood lignin has both syringyl and guaiacyl units, and therefore both vanillin and syringaldehyde can be produced from hardwood lignin.

6.1.11 PF-resin, TRL 5 (9)

Phenol-formaldehyde resins are used as adhesives for various wood products. They have been produced industrially from lignin, since Karatex, a kraft black liquor based plywood adhesive was manufactured industrially in the late 1970s./144/ Its production was shut down in 1984 as the mill producing the lignin was closed./134/ This means that there is a technology that fulfills TRL 9 requirements for producing PF-resin from kraft lignin. The current research, however, is operating still at laboratory scale and searching the most suitable technical lignin to optimize the properties of PF-resin./145/ Therefore, TRL 5 describes the current situation of this application the best.

6.1.12 Thermoplastics, TRL 4

Lignin-based thermoplastics are evaluated to fulfill TRL 4 requirements. In current research, they are approached with few different routes, such as lignin esters /87/, nanoparticles /146/ and lignin modification by selective masking of phenolic OH-groups /147, 148/, that enhance polymerization properties of lignin. Main challenge in lignin-based thermoplastics lays on the previously mentioned polymerization properties that need to be enhanced by modifying either the reactivity or thermal properties of lignin.

There is an existing lignin-based commercial thermoplastic product Arboform, which is so called “liquid wood” /149/, but it was not included in this evaluation because its manufacturing technology is not entirely known. However, its existence is worth mentioning and should not be overlooked.

6.1.13 PU-foam, TRL 5

PU-foams produced from lignin derived polyols are actually shown to have better mechanical properties than their commercial counterpart./88/ They have been produced at laboratory scale and the research is well developed because real products possessing commercial potential have been made. Therefore, TRL 5 rating is well justified. Reduction of isocyanate by addition of lignin and nanofibrillar cellulose has surprisingly resulted in decreased odor of PU-foams./150/

6.1.14 Antioxidant additive, TRL 3

Antioxidant activity of lignin is well known but the development of products is fragmented. Different lignins have been characterized for their antioxidant capabilities /151, 152/ but these studies have not considered the utilization of this feature in commercial applications. However, promising results have been published, *e.g.* in comparison of lignins with commercial antioxidants./151/ Therefore, the maturity of this application was evaluated to be TRL 3.

6.1.15 Activated carbon, TRL 5

Production of activated carbon from lignin is evaluated to have TRL 5. Recent study by Li et al. /153/ considered the preparation conditions, surface area, pore volume and yield of AC production from kraft lignin. The study was conducted at laboratory scale, but the results were promising in comparison with ACs from fossil-based raw materials.

6.1.16 Carbon fibers, TRL 5

Currently, the lignin-based carbon fibers are the single most researched lignin application./154/ This is mainly due to the massive market potential after the required properties and production costs have been achieved. The research is considered to be still at laboratory scale, even though the DoE facilities at Oak Ridge could be considered as pilot scale. The required strength properties of lignin-based CFs are not reached yet but the production costs might be within acceptable tolerances, especially with the carbon fibers produced from SKLP./106/ Thus, the evaluation resulted in TRL 5. However, the rating might soon upgrade to TRL 6, since Innventia is planning to build a joint demonstration plant with Swerea SICOMP./155/

6.2 *Isolation of lignins from weak black liquor*

The CO_2 precipitation process with a re-slurrying stage proved to be an effective and facile technology to isolate lignin from WBL, especially for WBL1 from polysulfide kraft cooking, since it was characterized with the highest lignin and the lowest ash contents.

Precipitation with CO_2 to pH 9 did not result in anything unexpected, and neither did the centrifugation. After re-slurrying the precipitated lignin samples in distilled water they were acidified to pH 2 with sulfuric acid. During this second acidification, strong foaming was detected between pH 6.3-5.0 with WBL1 and between pH 6.6-5.5 with WBL2. During foaming, the acid addition was stopped until the solution settled and the foam disappeared. The foaming problem is believed to occur due to the release of H_2S and CO_2 during the second acidification./30/

The lignin samples were filtrated and washed after the second acidification in a Buchner funnel. WBL1 was filtrated quite easily, but WBL2 had much higher filtration resistance and the filtration was much slower. This different filtration resistance has also been detected by Tomani /26/ and Öhman /30/ when comparing lignins precipitated from different mills. Possible reasons are believed to be a change in particle structure during the re-slurrying step, or electrostatic effects from approaching the pK_a of the carboxylic groups in lignin./30/ Also, the different raw-material, WBL1 from SW and WBL2 from HW, might have caused the difference in filtration resistance. This assumption is supported by the fact that pK_a values of different phenolic lignin structures have been characterized to have large variation./156/

After filtration, the lignins were dried in an oven at 45°C for 48 hours and crushed into powder with an electric mixer. The dry WBL1 powder was easy to handle and to move from the mixer into sample containers, but the handling of WBL2 was more difficult. The dry WBL2 powder had a strong electrostatic charge and it agglomerated quickly. The reason for this is assumed to be the same that caused the difference in filtration resistances. WBL1 and WBL2 in different stages of isolation are presented in Figure 14.

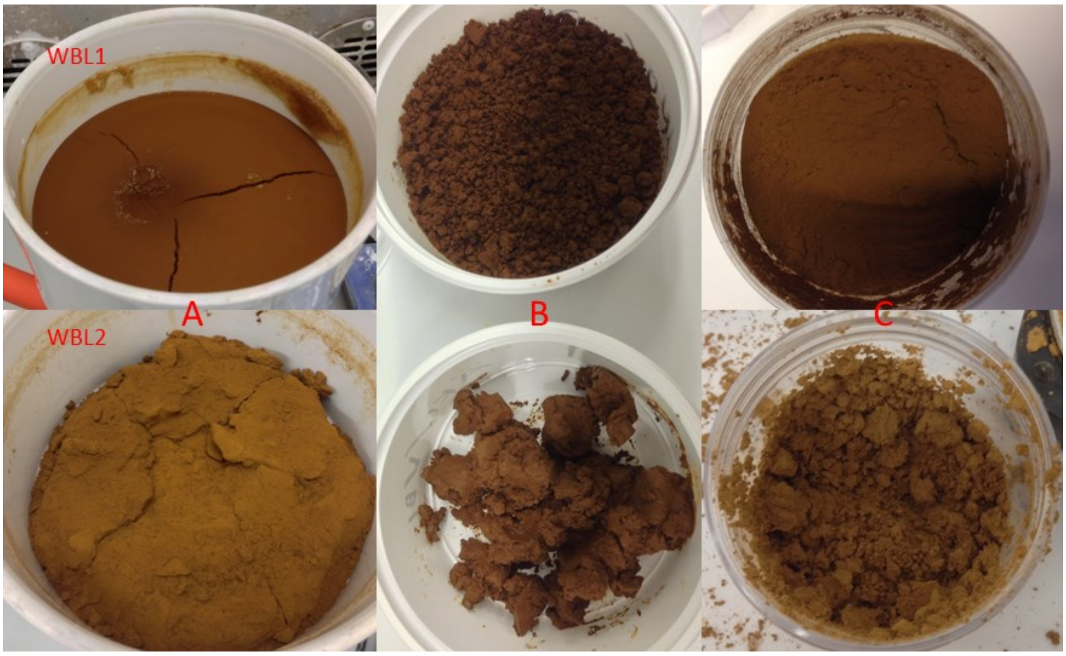

Figure 14. WBL1 and WBL2 after filtration at pH 2 (A), after washing with distilled water (B), and as dry powder (C).

6.3 Characterization of lignins

Fourteen different technical lignins were characterized to get a comprehensive overview about their properties. All experiments could not be completed for all lignin samples due to various reasons, which are discussed more widely in the specific sections. Twelve of the fourteen lignin samples characterized are presented in Figure 15. WBL1 and WBL2, which are not included in Figure 15, are presented in Figure 14.

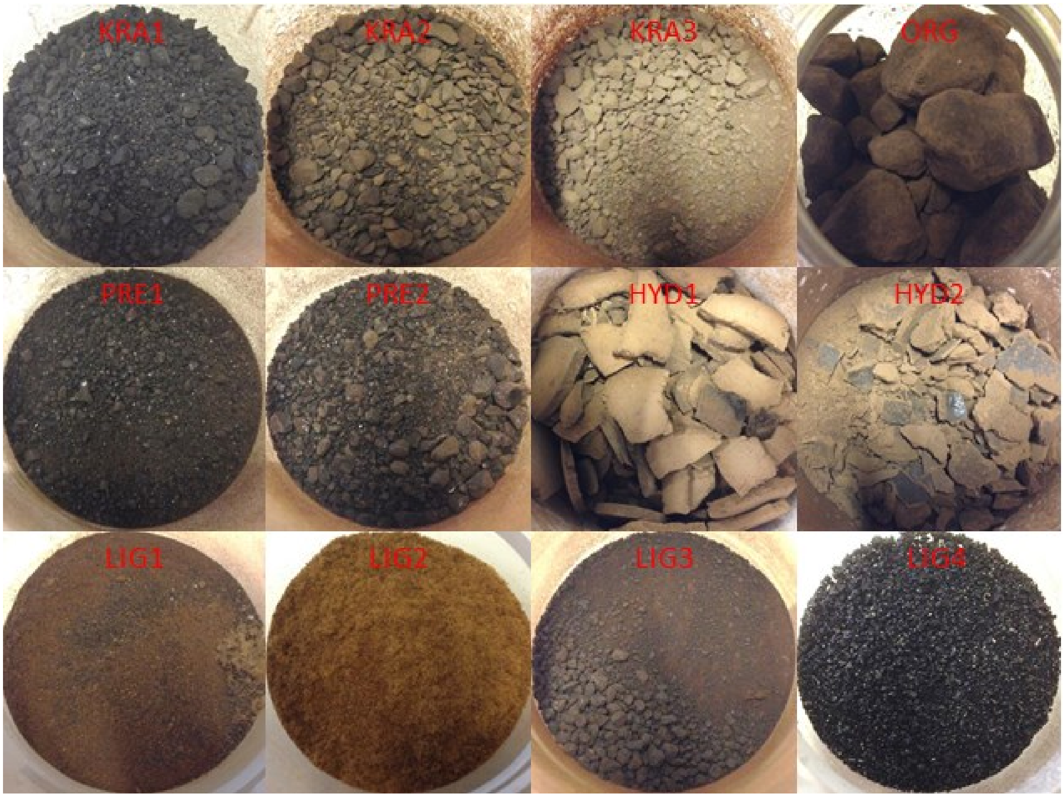

Figure 15. Twelve of the fourteen lignin samples characterized.

6.3.1 Mass balances and sources of error

Two mass balances were calculated for all lignin samples due to the two different methods for ASL calculations. The mass balances are presented together with moisture, lignin, carbohydrate and ash contents in Table 19. The TAPPI calculation method for ASL seems to result in more accurate mass balances (closer to 100%) than the NREL calculation method.

Notable variation can be detected from the total mass balances but this is quite typical. For example, lignin characterizations performed by Brodin et al. /157/ have resulted in mass balance variation between 98-105% with the TAPPI calculation method of ASL. However, their lignins were all isolated with the same procedure. Therefore, the total mass balance (TAPPI) variation between 95.01-105.55% (HYD1, HYD2 and LIG4 excluded) obtained in this thesis can be considered to be good, since the fractionation and isolation procedures vary a lot among the samples. The variation is expected to come mainly from acid soluble lignin (ASL) analysis with UV-spectroscopy and carbohydrate analysis with HPLC.

The shapes of UV-spectra obtained from the hydrolysis filtrates varied, as can be seen from Figure 16. This might cause errors especially for the more exotic lignin samples. The errors might also originate from the calculation methods, since the absorbances used were from specific wavelengths (205 nm and 320 nm) and not from a peak or a low point within some range, which means that even slight shifts of peaks can cause errors.

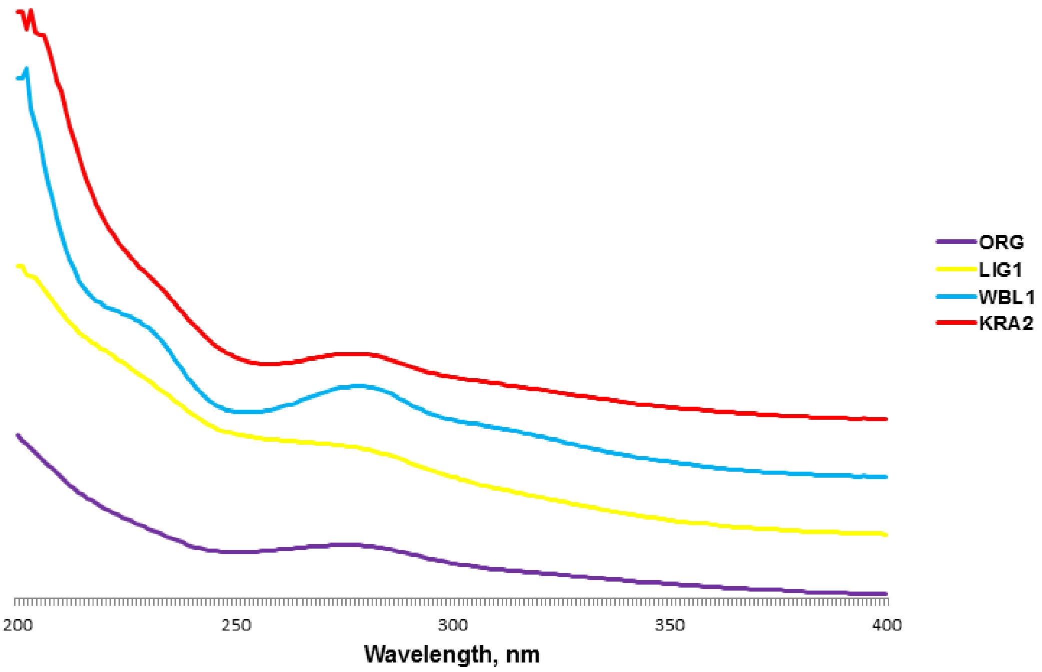

Figure 16. ASL UV-spectra of four different samples.

HPLC is another possible source of error, since only one set of standards was used for all lignin samples. This can cause variation in results especially for the samples that have really high carbohydrate contents. Dilution factor (DF) of 10 in HPLC might have also caused some errors, since the acid concentration is a lot higher than with the typical DF 100. The high acid concentration caused slight shifts in sugar peaks but these were manually assigned afterwards to minimize the possible errors. HPLC analysis was first done with DF 100 but the sugar concentrations were too low to be recognized by the detector.

Table 19. Moisture, lignin contents, impurities and mass balances of the lignin samples.

Sample	Moisture (%)	AIL (%)	ASL (NREL) (%)	ASL (TAPPI) (%)	Carbohydrates (%)	Ash (%)	Total (NREL) (%)	Total (TAPPI) (%)
WBL1	4.91	94.77	3.97	3.32	3.32	0.25	102.31	101.66
WBL2	5.24	79.51	3.24	9.40	15.60	1.04	99.39	105.55
KRA1	5.80	79.02	1.84	1.48	2.99	11.52	95.37	95.01
KRA2	5.40	84.36	3.54	8.79	2.45	3.49	93.84	99.09
KRA3	4.17	83.34	3.27	8.54	3.00	4.42	94.02	99.29
PRE1	5.47	79.82	4.46	3.21	0.32	13.17	97.77	96.52
PRE2	7.28	70.52	2.78	7.09	1.15	21.99	96.44	100.75
ORG	40.11	89.96	1.70	2.54	3.11	1.11	95.88	96.72
HYD1	8.19	33.39[a]	1.75	2.74	50.27	2.99	88.40	89.39
HYD2	5.28	66.19[a]	1.43	4.43	9.31	10.77	87.73	90.70
LIG1	11.05	90.45	3.82	2.46	5.99	0,93	101.19	99.83
LIG2	6.84	85.95	2.22	3.16	6.60	0.79	95.56	96.50
LIG3	2.39	36.64	0.76	0.35	59.04	0.51	96.95	96.54
LIG4	1.90	78.93[a]	5.85	6.75	2.58	1.69	89.05	89.95

[a]result is suggestive

6.3.2 Lignin content

Lignin content is a good estimator of lignin purity, and it tells much about the performance and efficiency of fractionation and isolation technologies. Higher lignin contents are preferred, naturally, and it is even better if they are achieved without extensive purification procedures. The highest lignin contents were determined in descending order for WBL1, KRA2, LIG1, ORG and KRA3. The high lignin content of WBL1 (98.09%, TAPPI) is assumed to be mainly due to the applied polysulfide cooking, which increases the carbohydrate yield of kraft process and, therefore, reduces the amount of carbohydrates in black liquor./158/

The analysis for gravimetric determination of acid insoluble lignin (AIL) did not turn out to be successful for HYD1, HYD2 and LIG4, which means that the results for these samples can be considered only as suggestive. There was a variation between 4-36%

in AIL content between duplicate samples. The source of error is believed to relate to the crucibles used, since this error occurred again when the experiment was repeated. The crucibles might have been either impure or moist even after drying at 105°C, of which the latter is more likely since no visible impurities were detected. The AIL contents were confirmed to be at least 72.10% for LIG4, 31.06% for HYD1 and 65.29% for HYD2 by weighing the dry lignin powder that could be poured from the crucibles. However, substantial amount of lignin was still attached to the crucibles and was not quantified. The suggestive AIL contents presented in Table 19 present the higher values from the gravimetric determination of AIL but are still believed to be lower than the real values since the mass balances were much lower in comparison with the other lignins.

ASL was determined with two different calculation methods from two different wavelengths. The results varied quite much between the two methods, but only for hardwood lignins. The NREL method uses different absorption constants for different wood species in contrast to the TAPPI method that uses only one constant for all lignin types. Observing the mass balances in Table 19 shows that the TAPPI method results in values that are closer to 100% than the values obtained with the NREL method. On the other hand, the lignin that exceeds the mass balance most of all (WBL2, 105.55% TAPPI) is from hardwood, which indicates that some kind of correction factor between lignins from different botanical sources would be useful.

6.3.3 Ash content

The highest ash contents were determined for PRE2, PRE1, HYD2 and KRA1, all over 10%. These lignins require better purification procedures in order to gain valorization opportunities. KRA2, KRA3 and HYD2 also had quite high ash contents between 3-5%, thus, further purification is recommended. The lowest ash content of 0.25% was determined for WBL1. This indicates that the CO_2 precipitation procedure with a re-slurrying stage results in really pure lignin without the need for extensive purification stages. Also the polysulfide cooking could have an effect on the low ash content, since the ash content of WBL2, which was isolated with the same procedure, was four times higher.

The ashes of the characterized samples were mostly greyish or white with few exceptions that were ORG, LIG3 and LIG4. ORG resulted in black ash with some yellow residues and the ash from LIG3 was also black. The most interesting was the ash from LIG4 which was brownish red. This is expected to be a result from presumably high iron content in the inorganics of LIG4. The ashes of six lignins are presented in Figure 17.

Figure 17. The ashes of six different lignins.

6.3.4 Carbohydrate analysis

The proportions of different residual carbohydrates detected by HPLC are presented in Table 20. They represent the botanical source of the lignin quite well. This can be identified by comparing the hemicellulose compositions of different wood species, since most hemicelluloses are easily degraded during kraft pulping.

For example, hardwood kraft lignins WBL2, KRA2 and KRA3 have over 70% xylose content of the residual carbohydrates. Hardwood xylan is dissolved easily in alkaline conditions, and the xylan content of hardwoods is also high./17/ Dissolved xylan is typically reprecipitaded onto the fiber matrix as the kraft cooking proceeds but it can also form lignin-carbohydrate complexes that are hard to degrade./159/ These lignin-carbohydrate complexes could also explain the high total carbohydrate content of WBL2 compared with WBL1, which was isolated and purified with the exact same procedure, since almost 90% of the residual carbohydrates in WBL2 is xylose.

The main hemicellulose in softwood is galactoglucomannan which is even more unstable than xylan, and dissolves more easily during kraft cook./17/ Therefore, softwood kraft lignins are easily identified from the presence of mannose and higher proportion of galactose. The big difference in galactose contents between WBL1 and KRA1 is believed to be caused by the applied polysulfide cooking for WBL1, and possibly from different isolation methods between the two lignins.

The hydrolysis lignins HYD1 and HYD2 both have really high glucose contents which is typical to hydrolysis lignins recovered as by-products from ethanol production, since the lignin is isolated as a solid residue that contains also the unhydrolyzed carbohydrates. The yield of hydrolysis, and the purity of lignin, can be improved with efficient pretreatments./160/ Therefore, the difference in total carbohydrate contents between HYD1 and HYD2 is expected to be due to different purification procedures or different pretreatments.

Table 20. Proportions of different carbohydrates from total carbohydrates in lignin.

Sample	Arabinose (%)	Galactose (%)	Glucose (%)	Xylose (%)	Mannose (%)	Total in lignin (%)
WBL1	12.05	70.18	3.31	12.95	1.51	3.32
WBL2	2.24	2.05	6.99	88.72	0.00	15.60
KRA1	23.41	20.40	7.69	47.49	1.01	2.99
KRA2	8.57	14.69	2.45	74.29	0.00	2.45
KRA3	8.00	14.00	3.67	74.33	0.00	3.00
PRE1	3.13	25.00	15.62	43.75	12.50	0.32
PRE2	2.61	0.87	15.65	80.87	0.00	1.15
ORG	9.65	6.75	40.19	38.91	4.50	3.11
HYD1	0.50	0.16	89.44	9.49	0.41	50.27
HYD2	2.15	1.83	79.16	11.60	5.26	9.31
LIG1	13.86	37.56	31.22	15.03	2.33	5.99
LIG2	7.42	5.46	57.73	29.39	0.00	6.60
LIG3	0.00	0.00	98.02	0.30	1.68	59.04
LIG4	8.14	21.71	32.95	18.21	18.99	2.58

6.3.5 Elemental analysis

The results from elemental analysis are presented in Table 21. The elemental constitutions of PRE2 and LIG4 are not defined. PRE2 was characterized but the variation between the duplicate samples was larger than is accepted. This was assumed to result from a possibly heterogenic sample, since the test was run several times for the duplicates. LIG4 was not characterized at all, since it was received after the tests had already been performed.

Carbon, hydrogen and oxygen contents give indications about the different phenylpropane units present in lignins. WBL1 has higher carbon and lower oxygen contents than the hardwood kraft lignins (WBL2, KRA2 and KRA3) which refers to higher proportion of guaiacyl structures in WBL1 and higher proportion of syringyl structures in WBL2, KRA2 and KRA3. This also means higher methoxyl content for WBL2, KRA2 and KRA3. KRA1 is harder to analyze based on carbon, hydrogen and oxygen contents due to the high amount of ash present. LIG2 has the highest carbon and hydrogen contents which indicate that most of the methoxyl groups have been cleaved during fractionation or isolation. HYD1 and LIG3 have the highest carbohydrate contents and were therefore characterized with the lowest carbon contents.

Sulfur is believed to originate mainly from the fractionation process, and to some extent from the plant resource./161/ Lignins with really low sulfur content, such as ORG, HYD1, HYD2 and LIG3, are considered sulfur-free. The highest sulfur contents were characterized for KRA1, KRA2, KRA3, WBL1 and WBL2. For kraft lignins, sulfur contents of 1.85-2.90% have been characterized in previous studies /13, 66, 94/, and the results obtained in this thesis were all within that range. Notable is, that WBL1 from polysulfide cooking had the lowest amount of sulfur within the kraft lignins.

Nitrogen contents varied between 0.18-3.49% and the variation is mainly due to different raw-materials used./161/ Non-wood lignin, such as ORG, has typically higher nitrogen content than lignins from SW or HW. Eucalyptus (KRA2 and KRA3) seems to also have higher nitrogen content than birch (WBL2). This might result from the different cultivation methods as eucalyptus is cultivated in plantations and birch in regular forests. HYD2 was characterized with the highest nitrogen content of 3.49%, and this is assumed to result not only from the botanical source but also possible protein contamination during the hydrolysis. This assumption is supported by the similar findings by El Mansouri and Salvado./39/

Table 21. Elemental analysis of lignins.

Sample	C (%)	H (%)	N (%)	S (%)	Ash (%)	O (%)
WBL1	65.35	6.25	0.30	2.01	0.25	25.86
WBL2	60.53	6.46	0.39	2.39	1.04	29.20
KRA1	56.99	5.50	0.28	2.49	11.52	23.23
KRA2	58.38	5.55	1.18	2.67	3.49	28.73
KRA3	57.58	5.63	0.68	2.75	4.42	28.95
PRE1	56.16	5.09	0.24	1.77	13.17	23.57
PRE2	nd[a]	nd	nd	nd	21.99	nd
ORG	60.13	5.60	1.88	0.43	1.11	30.86
HYD1	47.56	6.25	0.80	0.45	2.99	41.96
HYD2	52.34	5.90	3.49	0.60	10.77	26.92
LIG1	62.81	6.63	0.27	1.32	0.93	28.06
LIG2	68.80	8.99	0.37	1.27	0.79	19.80
LIG3	48.22	6.38	0.18	0.48	0.51	44.23
LIG4	nd	nd	nd	nd	1.69	nd

[a] not defined

6.3.6 Phenolic hydroxyl group content

The amount of phenolic hydroxyl groups is often considered as the most important parameter of lignin reactivity. For example, high phenolic hydroxyl group content promotes base-catalyzed cleavage of interunit ether linkages, oxidative degradation of lignin and reactivity towards formaldehyde. It also causes the poor brightness stability of lignin containing pulps./162/ Total phenolic hydroxyl groups and phenolic hydroxyl groups in different phenolic structures were determined with UV-spectroscopy by using the $\Delta\varepsilon$ method. The results are presented in Table 22.

The highest total phenolic hydroxyl groups where characterized for lignins isolated from kraft process. Sulfur-free lignins HYD1, HYD2 and ORG had lower amounts of phenolic hydroxyl groups. Similar trend has also been recognized in previous studies by El-Mansouri and Salvado /39/, Schorr et al. /13/, and Monteil-Rivera et al. /163/. This indicates that fractionation and isolation processes contribute more to the amount of phenolic hydroxyl groups than the botanical source of lignins.

Table 21. The amount of different phenolic structures in characterized lignins.

Sample	Total phenolic OH-groups (mmol/g)	Non-conjugated phenolic OH-groups (mmol/g)	Conjugated phenolic OH-groups (mmol/g)	Weakly acidic phenolic structures (mmol/g)
WBL1	2.12	1.82	0.30	0.15
WBL2	2.14	1.88	0.26	0.37
KRA1	2.71	2.35	0.36	0.33
KRA2	2.70	2.34	0.36	0.58
KRA3	2.76	2.39	0.37	0.87
PRE1	2.69	2.34	0.35	0.71
PRE2	2.46	2.14	0.32	0.35
ORG	1.77	1.52	0.25	0.38
HYD1	0.66	0.29	0.37	0.41
HYD2	0.78	0.54	0.24	0.21
LIG1	0.68	0.50	0.18	0.12
LIG2	-0.32	-0.35	0.03	0.05
LIG3	nd[a]	nd	nd	Nd
LIG4	0.81	0.69	0.12	0.24

[a]not defined

Phenolic hydroxyl group content was not defined for LIG3 since it was almost insoluble in 0.2 M NaOH-dioxane solution. The result obtained for LIG2 is not reliable because phenolic hydroxyl group content cannot be negative. Absorbance in the Δε-spectrum was negative for LIG2 except in wavelengths between 340-390 nm as can be seen in Figure 19. This means that in the negative regions the absorbance was stronger for the neutral solution in comparison to the alkaline solution. The origin of this phenomenon is not known since similar occurrence was not found in previous studies. However, the characteristic peaks at 250 nm and 350 nm were detected, which means that some ionization must have occurred.

Gärtner and Gellerstedt have compared the Δε UV-method to aminolysis, and discovered a good correlation between the results. However, the results from aminolysis were systematically 15-20% higher than the ones obtained with the Δε UV-method./125/ Therefore, the results presented in this thesis cannot be considered absolute but highly comparable with each other.

Variations between the shapes of Δε-spectra were detected especially for the more exotic lignins such as LIG1, LIG4 and HYD2. These lignins might have phenolic structures that are not included in the model, which is likely to decrease the reliability of the obtained results for those lignins since the method is calibrated for more conventional types of lignins. The Δε-spectra of the analyzed samples are presented in Figure 18, Figure 19 and Figure 20.

Figure 20 also shows the difference in absorbance between the two alkaline solutions. The two lignins (WBL1 and KRA3) were selected in this figure since they have the biggest differences in weakly acidic phenolic structures. The weakly acidic structures (types III and IV in Figure 13) are not ionized in the pH 12 solution and they can thus be quantified by comparing absorbances of the two alkaline solutions./125/

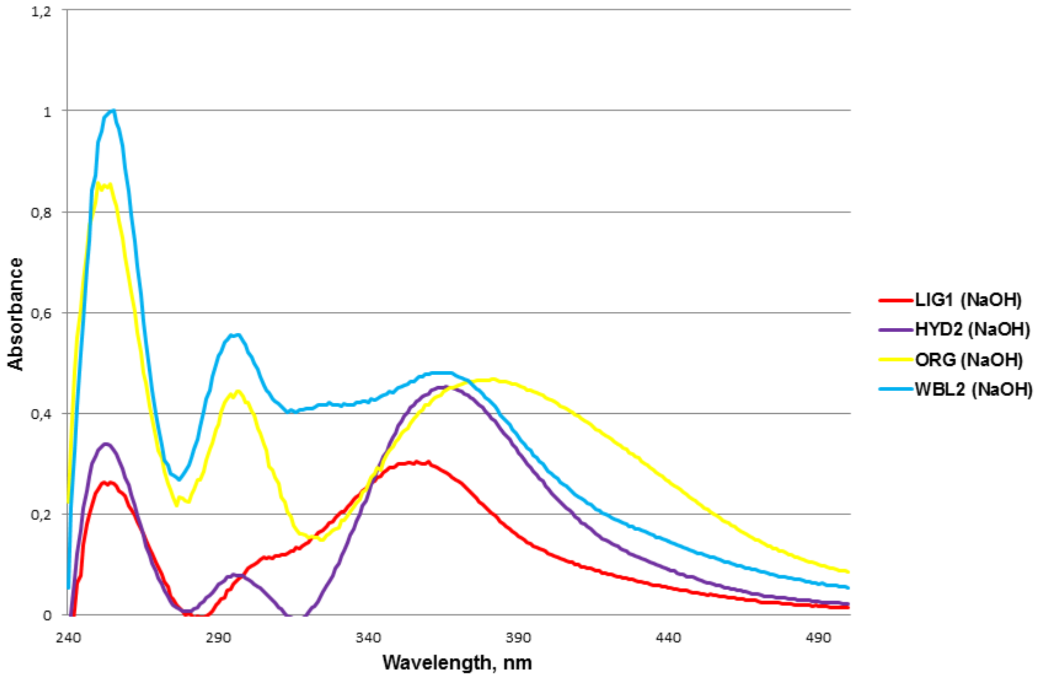

Figure 18. Ionization difference spectra of LIG1, HYD2, ORG and WBL2.

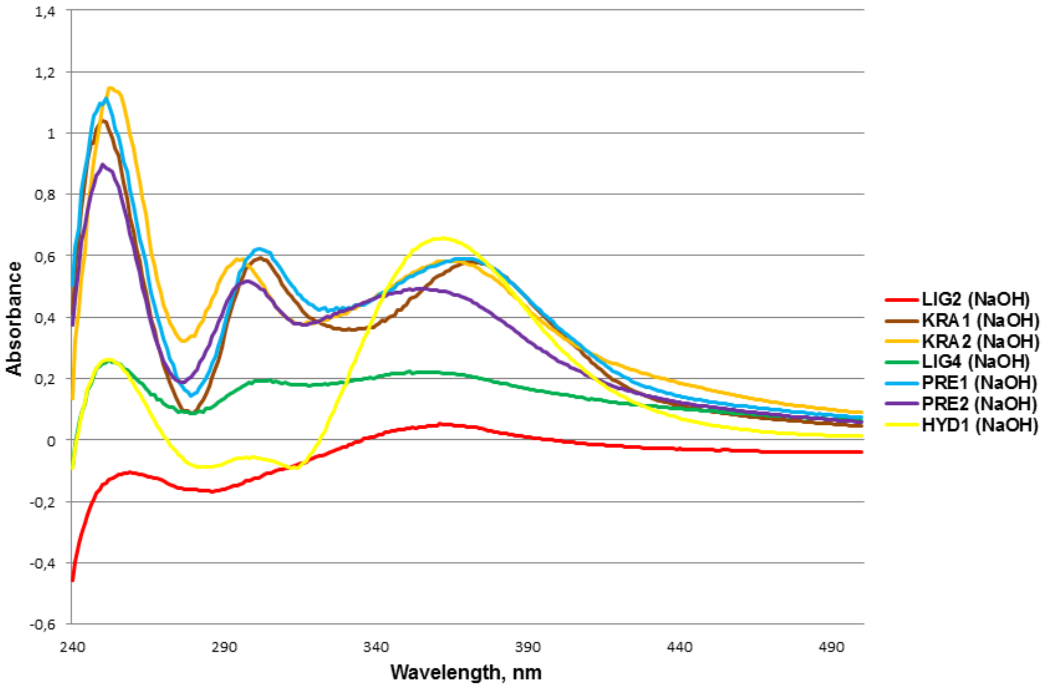

Figure 19. Ionization difference spectra of LIG2, KRA1, KRA2, LIG4, PRE1, PRE2 and HYD1.

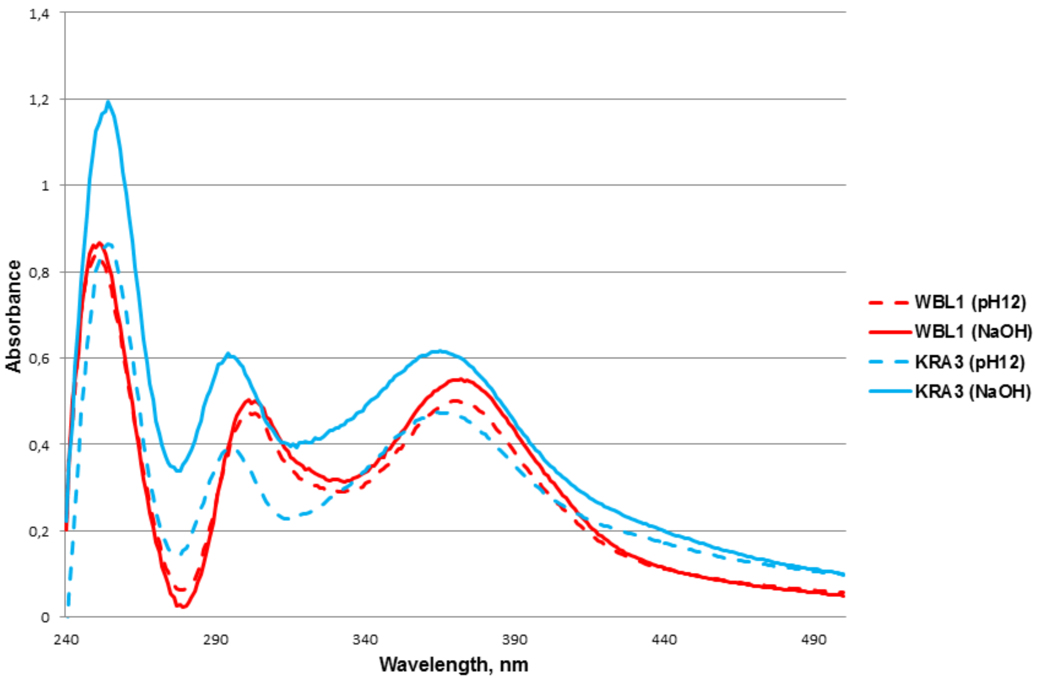

Figure 20. The difference in ionization between pH 12 and 0.2 M NaOH solutions of WBL1 and KRA3.

6.3.7 Odor analysis

The odor of lignin samples was characterized with two methods: odor panel and SPME-GC-MS. Volatile organic compounds (VOC) were analyzed with SPME-GC-MS. Extraction temperature was selected to be at 80°C, since lignin-based materials can be exposed for such temperature *e.g.* in car interiors during a hot weather./164/ The odor intensities of lignins obtained from odor panel and the number of different VOC detected with SPME-GC-MS are presented in Table 22. These results can be considered good, since clear differences between the different lignin were found, even though the scale from 1 to 5 is quite narrow.

Table 22. Odor intensity of lignins and the number of different VOC.

Sample	Average	Standard deviation	Median	Number of VOC (SPME-GC-MS)
WBL1	2.85	0.66	3	76
WBL2	2.46	0.84	2	87
KRA1	2.23	0.58	2	71
KRA2	3.62	0.74	4	113
KRA3	3.27	0.97	3	95
PRE1	2.85	0.77	3	79
PRE2	3.92	0.62	4	101
ORG	4.62	0.62	5	93
HYD1	3.08	0.83	3	87
HYD2	2.46	0.50	2	103
LIG1	2.35	0.77	2	107
LIG2	2.27	1.01	2	113
LIG3	1.23	0.42	1	25
LIG4	3.00	0.78	3	65

Certain correlation was also detected between the SPME-GC-MS results and the odor intensity results from the odor panel. If the number of VOC is really low, lignin most likely has low odor intensity as is the case with LIG3. However, high number of VOC does not guarantee that the odor intensity will be high, since different compounds have different odor intensities or can even be odorless. Also, the number of different VOC does not express the quantity of a single compound. For example, ORG was characterized to have the most intensive and also the most unpleasant odor, even though it did not have the highest number of VOC. This can be explained with acetic acid which was characterized to be the major compound with SPME-GC-MS. It is also well in line with the descriptions received from odor panel, where adjectives “pungent” and “vinegar” were repeating for ORG. The repeating descriptions from odor panel and the major compounds detected in SPME-GC-MS analysis are presented in Appendix 1.

Table 23. Odor pleasantness.

Sample	Average	Standard deviation	Median
WBL1	2.67	0.85	2
WBL2	2.75	0.72	3
KRA1	2.29	0.66	2
KRA2	3.79	0.56	4
KRA3	3.50	0.74	3.5
PRE1	2.83	0.90	3
PRE2	3.88	0.51	4
ORG	4.17	0.90	4
HYD1	3.58	0.49	4
HYD2	2.50	0.76	2.5
LIG1	2.25	0.83	2
LIG2	2.67	1.03	2.5
LIG3	2.08	0.95	2.5
LIG4	3.08	0.86	3

The odor pleasantness results obtained from odor panel are presented in Table 23. The odor pleasantness did not result in as clear differences as the odor intensity. The median answer is not 1 or 5 for any of the samples. This might be due to the different taste of people, since pleasantness is quite personal parameter to measure. However, the standard deviations are not significantly greater compared with odor intensity, which suggests that the scale from 1 to 5 could be too narrow to result in clear differences for odor pleasantness.

LIG2 had the largest standard deviation in both odor intensity and odor pleasantness. This could be due to the high number of VOC, which can cause variation in answers due to the different perception of odor within the participants of odor panel. Another explanation might be the main component, 2-nonenal, found in LIG2 with SPME-GC-MS. 2-nonenal is more commonly known as the “old people smell”, and its secretion from humans increases with aging./165/ This might cause variation in answers between the participants of different ages, when some find the smell familiar or not even notice it at all and the others find it unfamiliar, which can be described either as pleasant or unpleasant depending on the preferences of an individual.

Quite surprisingly, sulfur containing compounds were found from only one of the samples, when one of the other major compounds in KRA2 was characterized to be dimethyltrisulfide. Elemental analysis proved that all of the samples contained sulfur but it seems that sulfur containing compounds are not released at 80°C or under. The absence of sulfur is a good sign, since sulfur restricts the utilization of lignin in demanding application such as synthesis of polymers and low-molecular substances. Sulfur is also poisonous for catalysts and can cause odor problems./15/ Besides dimethyltrisulfide, KRA2 was also characterized to release chloroform which is really toxic.

Based on the results obtained from odor panel, the most suitable lignins for applications where odor is a critical parameter are LIG3, LIG1 and KRA1. The highest combined odor intensity and unpleasantness was characterized for ORG. KRA2 and PRE2 were also characterized with high intensity and unpleasant odor. However, the odor of a certain lignin can be reduced with further processing. Vishtal and Kraslawski /15/ have suggested further purification and addition of oxidizing chemicals such as hydrogen peroxide for possible methods to deodorize technical lignins. Kalliola et al. /164/ have also investigated this subject. They discovered that oxygen oxidation at alkaline pH would be the most straightforward deodorizing method to apply at industrial scale.

Another objective of the odor analysis was to find valuable compounds, such as vanillin and syringaldehyde, from the samples. Vanillin was detected from 10 samples but in only one sample (WBL1) it was within the three major compounds. Syringaldehyde was detected only in LIG2.

6.3.8 Molecular weight distribution

Molecular weight distributions were analyzed for the THF soluble lignin fractions. The results are expressed as the number average molar mass (M_n), the mass average molar mass (M_w) and polydispersity, which is the ratio of M_w to M_n. The results are presented in Table 24.

Table 24. Molecular weight distributions of characterized lignins.

Sample	M_n (g/mol)	M_w (g/mol)	Polydispersity (M_w/M_n)
WBL1	773.2	1844	2.38
WBL2	556.9	1021	1.83
KRA1	665.8	1467	2.20
KRA2	371.6	1047	2.82
KRA3	560.7	1024	1.83
PRE1	832.3	2613	3.14
PRE2	575.1	1203	2.09
ORG	479.8	1378	2.87
HYD1	663.6	1544	2.33
HYD2	631.1	1547	2.45
LIG1	478.4	882.7	1.85
LIG2	414.1	648.0	1.56
LIG3	241.2	661.3	2.74
LIG4	467.7	807.6	1.73

The lignins characterized in this thesis had a varying solubility in THF which has an effect on molecular weight distribution, and is therefore discussed more broadly. The solubility of the characterized lignins was estimated visually. The best solubility was detected for KRA1, KRA2, KRA3, PRE1, PRE2, WBL1 and WBL2. All of these were almost completely dissolved, they were all more or less cloudy but no solid particles were visible. ORG, HYD1 and HYD2 were mostly dissolved in THF but had some visible dregs that did not dissolve. The poorest solubility was detected for LIG1, LIG2, LIG3 and LIG4, of which the solubility of LIG3 was clearly the worst. LIG3 was almost completely insoluble in THF and visible solid particles were left in clear solution. Even though the solubility for some lignins seemed almost complete, it is good to take account for the fact that only 90-94% solubility of lignin in THF has been characterized by Baumberger et al. /166/ for acetylated samples. The solubility of different lignins in THF is visualized in Figure 21.

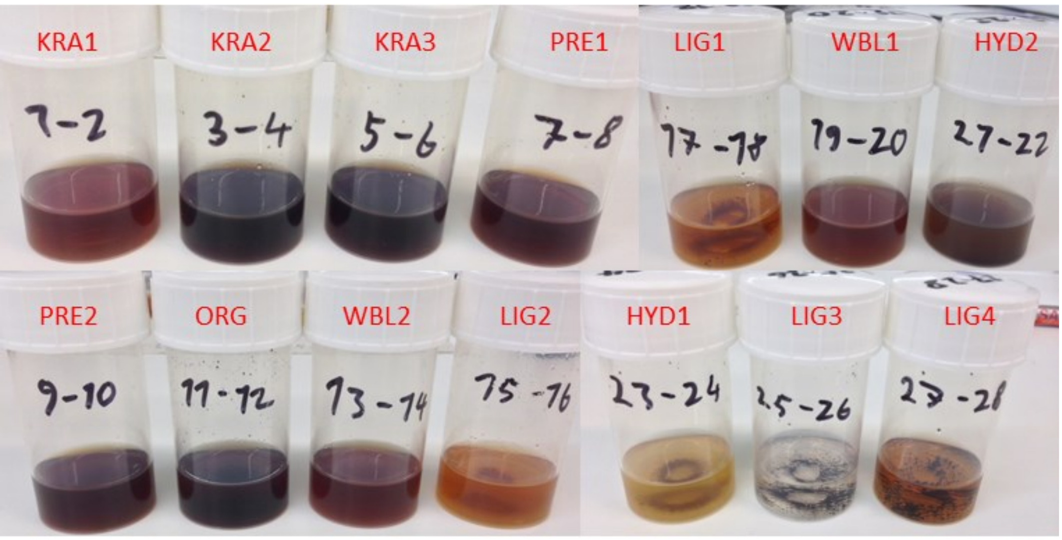

Figure 21. Lignins dissolved in THF.

Based on the different solubility of the different lignins in THF it can be assumed that there are structural differences between the characterized lignins. The three-dimensional structure of lignin has been recognized to be the most obvious explanation of lignin insolubility because these kinds of complex structures require fragmentation by chemical reaction in order to dissolve./130/

Despite the limited solubility, certain trends can be detected from these results. Softwood lignins WBL1, KRA1 and PRE1 have higher M_n and M_w than hardwood lignins WBL2, KRA2 and KRA3. Similar results have been obtained by Brodin et al. /157/ for acetylated samples in THF. The biggest difference between non-acetylated and acetylated samples is in M_w, which indicates that the high molar mass fraction does not dissolve well in THF. This can be further supported by analysis results showing systematically lower amounts of polydispersities compared to results obtained by Brodin et al./157/ The high molar mass fraction of lignins has been showed to be the main source of intra- and interlaboratory variations /166/, and therefore single values from different studies should not be compared with each other but rather the overall trends detected. These trends mean that at least the results of the lignins that had the same visually detected solubility in THF can be compared with each other.

An interesting phenomenon occurred, when the GPC analysis was performed for the duplicate samples that were analyzed one day after the first sample. The duplicates showed 9-50% increase in M_w and 4-66% increase in M_n. This was thought to be caused by some kind of repolymerization reaction. The duplicate samples were filtrated into vials at the same time with the first samples, which gave them an extra day to repolymerize. The smallest increases in M_w and M_n were detected for PRE2 and the biggest M_w for KRA1 and M_n for KRA2. However, no clear trends were detected about which types of lignins had the largest or the smallest increases, and thus another study would be needed to confirm this phenomenon and its cause.

6.4 Suitability evaluation

The results from suitability evaluation are presented in the suitability matrix in Table 25. The suitability was evaluated based on the data and findings obtained during this thesis from characterization results and literature. Since all the possible properties and functionalities were not characterized, suitabilities of certain lignins towards certain applications detected in previous studies were used as supporting information alongside with the defined criteria described in Chapter 5.

This evaluation indicates that the kraft lignins isolated with CO_2 precipitation (WBL1 and WBL2) and the organosolv lignin ORG have the best suitability towards various applications. Other notable lignins were LIG1 and LIG2 that were also evaluated highly suitable towards various applications. The main problem with lignins that did not perform well in this evaluation was the purity, which is important in many applications. Especially ash can be a huge dead load or even corrosive in some applications. Therefore, extensive purification should be done to increase the purity and the value of those lignins.

Table 25. The suitability matrix.

	WBL1	WBL2	KRA1	KRA2	KRA3	PRE1	PRE2	ORG	HYD1	HYD2	LIG1	LIG2	LIG3	LIG4
Solid fuel	H	H	L	L	L	L		H	L	L	H	H	L	L
Hydrogen	H	L		H	H			H			H	H		L
Liquid fuels	H	H		L	L			H	L		H	H	H	H
FT-Liquids	H	H	L	H	H	L		H			H	H		L
BTX-chemicals								H	L	H	L	L	L	
Vanillin	H	L	H		L	H	L		L				L	
Syringaldehyde		L		L	L		L					H		
PF-resin	H	L	H	H	H	H	L	L						L
Thermoplastics	L	H		L	L						L	H	L	L
PU-foam	H	L	H	L	H	H	L	L						L
Antioxidant additive	H	L	H	H	H	H	H	H						
Activated carbon	H	L	L	L	L	L		H			H	H		L
Carbon fibers	H	L	H	L	L	L		L			H	H		L

H = High suitability

L = Low suitability

Empty = Very low suitability / not suitable

7 Conclusions

The ultimate goal of this thesis was to find potential candidates for industrial scale production of novel lignin-based products. This was done by combining the information gathered from literature and experimental work. Five categories of lignin applications were identified from previous experiments and the maturity of these applications was evaluated, four lignin samples were isolated and fourteen characterized in laboratory, and suitability of the characterized lignins towards various applications was evaluated.

Characterization of the lignin samples was mostly successful and provided valuable information about the differences and properties of the samples. However, the reliability of the results for the more exotic lignins is questionable, which was discussed earlier. Determination of molecular weight distributions was not very successful, since the solubility of the lignin samples in THF varied a lot. However, this occurrence provided valuable information about the solubility of different lignins. It also suggests that there are significant structural differences between the samples that should be verified with a more advanced characterization method, such as nuclear magnetic resonance (NMR) spectroscopy.

Of the lignin samples, the polysulfide kraft lignin (WBL1) is the most suitable sample towards various applications. This might be due to the efficient isolation technology, but also to the different composition of black liquor in polysulfide cooking in comparison with conventional kraft cooking. One very interesting fact was that the WBL1 had the lowest sulfur content among kraft lignins. This should be verified and clarified in future studies. Also an investigation of the facility of sulfur removal from polysulfide kraft lignin is highly recommended.

Also ORG seems to be widely applicable in various kinds of applications, even though it does not possess any superior properties except the low sulfur content. Only problem with ORG is the strong odor. The least promising lignin samples were HYD1 and HYD2 which both had a really high level of impurities.

Lignin-based carbon fibers are clearly the most promising novel application for technical lignins. The main reasons are the undisputed and almost infinite market potential and the high value of the end product. Also the recent announcement of expanding lignin-based carbon fiber research in Sweden supports this. Kraft lignin is currently the most promising raw material for lignin-based CF production. Based on the results obtained in this thesis, softwood polysulfide kraft lignin could be even more suitable raw material than regular kraft lignin. Although, it might require adjustments to molecular weights to be suitable for melt spinning, as is the case with regular softwood kraft lignin. LIG1 and LIG2 could also be very potential raw materials for lignin-based carbon fibers, since they possess very high carbon contents and low polydispersities. Especially the carbon contents are surprisingly high, even though both have carbohydrate contents around 6%. This means, that after purification to suitable level they could result in very good yields when converted into carbon fibers.

Another valuable application category with existing markets is platform chemicals, such as phenol and BTX-chemicals. However, their production from lignin was evaluated as least developed. This is mainly due to the heterogeneity of the raw material and the lack of ideal catalysts. Production of fine chemicals from lignin is not as complicated, but it requires development of applications for the residual lignin that is not converted into fine chemicals in order to achieve efficient use of material. These applications would not need to be very high in value because the price of the extracted fine chemicals might be self-sufficient to provide enough revenues.

Lignin-based fuels are considered as a short-term option due to the low-price of the products in comparison with chemicals and materials. This is eminently true for solid fuels, which serve as a good option until the markets for other lignin-based products develop. Some of the other fuels, such as FT-liquids, have an economy-of-scale problem, which makes them unfeasible in most cases.

7.1 Reliability and validity of the work

The vast majority of the references used in this thesis were adopted from peer-reviewed scientific publications. The TRL evaluation was performed with a modified version of widely used metric system, and the evaluation and its assumptions were made based on literature review and additional references. The suitability matrix was created for this specific purpose and it served as a tool to make justified conclusions about all the data and information presented in this thesis.

The characterization methods that were used in the experimental study of this thesis were adopted from previous studies or standards. Therefore, their repeatability should be as good as it can be for as complex and heterogeneous material as lignin. The experiments were performed carefully, and all noticed errors and possible error sources were presented and discussed in conjunction with the results. Storage times of the samples, that were isolated beforehand, were not known. Thus, the effects it might have had for the results are not known and were not discussed earlier. However, it is good to note that the properties of lignin can alter depending on the storage time and conditions. The characterization methods were selected to give an overview on the properties of the characterized samples in order to evaluate their suitability towards certain applications.

7.2 Recommendations for further studies

Characterization of lignins is recommended to be done for a large variety of lignin samples, *e.g.* 8 and up. This is due to the fact that the different characterization methods do not result in absolute values and interlaboratory comparison might be since difficult. Large variety of different samples clearly points out the differences between the different lignins even if the results are not absolutely right, which is assumed due to the complexity of this material. However, large quantity of samples can create schedule problems since characterization of lignin is very time consuming, especially if the characterization methods require modifications such as acetylation.

Several brilliant ideas and inventions were found from literature for production of the optimal raw-material for lignin-based carbon fibers. The best ideas are combined in a schematic drawing of combined ultrafiltration and CO_2 precipitation process which is presented in Figure 22. It is designed to produce rather homogenous softwood kraft or softwood polysulfide kraft lignin with a low polydispersity and tailored thermal properties for the production of lignin-based carbon fibers. It consists of two consecutive ultrafiltration units to narrow down the molecular range and a CO_2 precipitation process to yield lignin with maximum purity. The process is based on the data and references presented earlier in this thesis. It is highly recommended to be further tested at laboratory scale to find out the optimal molecular weight range for melt spinning kraft lignin into lignin-based carbon fibers with enhanced properties. It could be possible to tailor the properties of kraft lignin with this process also for other applications than carbon fibers, and it is therefore also equipped with options to recover different fractions from the ultrafiltration units.

Of other applications than CFs, lignin-based composites and other materials could be a promising area but the research seems to be quite fragmented. Therefore, future research should set systematic goals to develop products that will replace the old fossil-based ones and discover market opportunities for products with completely new functionalities. The carbon fiber research led by DoE at Oak Ridge National Laboratory and Innventia in Sweden should be a role model and used as an example also for other areas of lignin research.

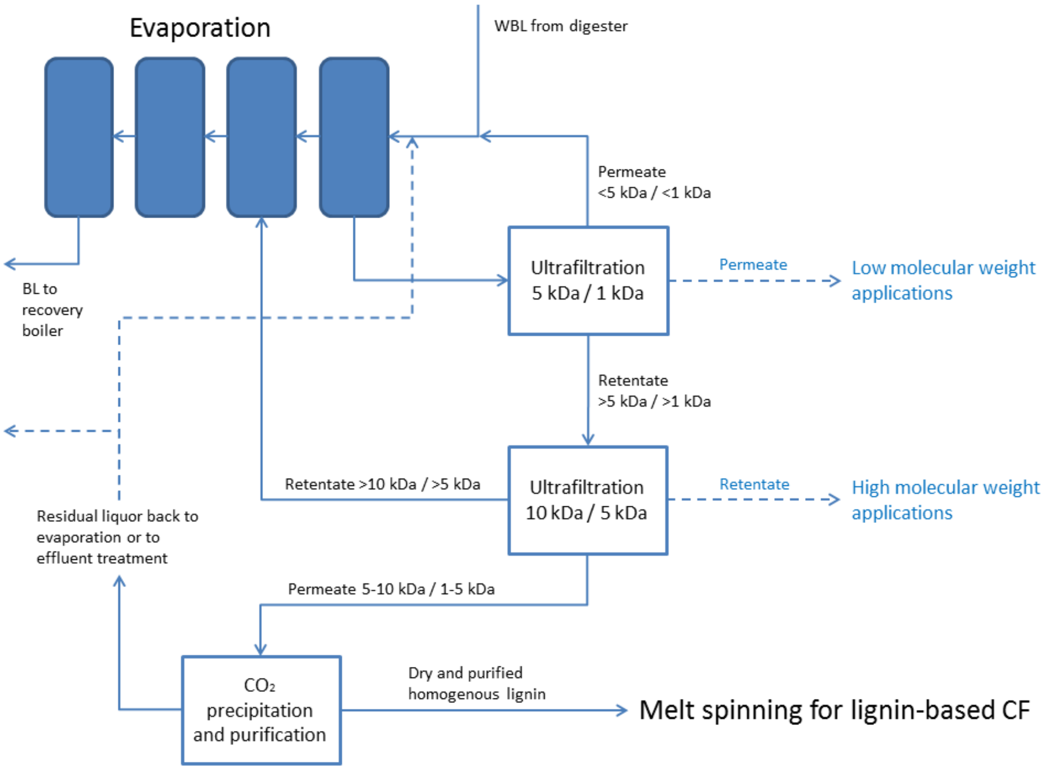

Figure 22. Combined ultrafiltration and CO_2 precipitation for homogenous lignin production.

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Repeating descriptions and major compounds detected in odor analysis

APPENDIX 1

Sample	Repeating descriptions (Odor panel)	Three major compounds (SPME-GC-MS)	Other major compounds (SPME-GC-MS)
WBL1	Pulp mill Wood Soil	Guaiacol *p*-Ethylguaiacol Vanillin	α-Terpineol
WBL2		Guaiacol Syringol *p*-Ethylguaiacol	Vanillin Acetic acid
KRA1	Pulp mill Stone	Guaiacol Nonanoic acid Hexanoic acid	Vanillin Acetic acid Acetovanillone
KRA2	Pulp mill	Syringol Guaiacol Unidentified hydrocarbon	Vanillin Acetic acid Chloroform Furfural Dimethyltrisulfide
KRA3	Pulp mill	Guaiacol Syringol	Vanillin Acetic acid Dodecane
PRE1	Pulp mill Roasted	Nonanoic acid Guaiacol	Vanillin Acetic acid Acetovanillone
PRE2	Tar Roasted	Syringol Guaiacol *p*-Ethylphenol	Vanillin Acetic acid Furfural
ORG	Pungent Tar Vinegar	Acetic acid Furfural Unidentified solvent	Vanillin Benzaldehyde 5-Methylfurfural
HYD1	Acidic Pungent	Furfural Acetic acid Nonanoic acid	Vanillin Hexanoic acid *p*-Vinylguaiacol
HYD2	Wood Graham flour Malts	Acetic acid Hexanal Furfural	Furfuryl alcohol α-Muurolene
LIG1	Pulp mill Wood Soil	α-Muurolene δ-Cadinene Hexanal	α-Cadinene
LIG2	Fusty Wood Soil	2-Nonenal Tricycloheptane α-Muurolene	Hexanal Syringol Syringaldehyde
LIG3		Cembrene Nonanal	Hexanal Vanillin
LIG4	Plastic Swamp	α-Muurolene α-Cadinene δ-Cadinene	Caprolactam Junipene cis-Calamenene