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CARBON FIBRES FROM KRAFT LIGNIN

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Doctoral Thesis

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"A pessimist sees the difficulty in every opportunity;
an optimist sees the opportunity in every difficulty"

W. Churchill

ABSTRACT

Kraft lignin has a high potential for use in more valuable applications than its current use as fuel in pulp mills and integrated pulp and paper mills. The possibility of using kraft lignin, a green material with a carbon content of more than 60 %, for the manufacturing of carbon fibres was investigated in this thesis. The strong and lightweight carbon fibre material has many potential application areas, e.g. in cars; the main obstacle limiting its demand is the high production cost, with the raw material (petroleum pitch and polyactrylonitrile) and fibre spinning constituting approximately 50 % of the cost.

Industrial kraft lignins originating from both softwood (spruce/pine) and hardwood (birch/aspen) were isolated with the LignoBoost technique and then purified and characterized to determine the best suitable lignin for the production of carbon fibre. Using ultrafiltration of the black liquor before isolation using the LignoBoost technique, a kraft lignin with satisfactory high purity was obtained. The fractionated kraft lignin can be used either as such or as a softening agent during melt spinning to obtain continuously spun kraft lignin fibres.

The behaviour during thermal treatment was found to differ depending on the type of kraft lignin used. After oxidative stabilisation, the studied lignins became more stable, and thus, the final yield after carbonisation was increased by 10-20 % in comparison to stabilisation in absence of oxygen. The identified products indicate that the main reactions during oxidative stabilisation are radical, oxidation, condensation and rearrangement reactions.

The structural differences between softwood and hardwood kraft lignins facilitated the stabilisation of the softwood lignin fibre as compared with the hardwood lignin fibres. Thermal stabilisation in an inert atmosphere using only heat was successfully achieved for the softwood kraft lignin fibres. Stabilisation and carbonisation was successfully performed in a one-step operation on softwood kraft lignin fibres. Thus, it seems possible that the separate stabilisation step can be omitted, which may reduce the processing costs of softwood kraft lignin-based carbon fibres.

SAMMANFATTNING

Sulfatlignin har hög potential för att kunna användas i mer värdefulla applikationer jämfört med idag då det främst används som bränsle i massabruk och integrerade massa/pappersbruk. I egenskap av ett grönt material med en kolhalt på mer än 60 %, har möjligheterna att använda kraftlignin vid kolfibertillverkning undersöks i den här avhandlingen. Kolfiber är lätt och starkt med många olika potentiella användningsområden. Det som idag huvudsakligen begränsar efterfrågan är den höga produktionskostnaden, där råmaterialet (petroleum pitch och polyakrylonitril) och fiberspinningen står för ca 50 % av kostnaden.

Industriella sulfatligniner från både barrved (gran/tall) och lövved (björk/asp) har framställts enligt LignoBoost-processen och har därefter renats och karaktäriserats med syfte att hitta det mest lämpliga råmaterialet för tillverkning av kolfiber. Genom att använda ultrafiltrering av svartlut innan isolering med LignoBoost-tekniken, kan man få ett kraftlignin som är tillräckligt rent. Det fraktionerade kraftligninet kan användas antingen rent eller som mjukgörare under smältspinning, för att få fram kontinuerligt spunna sulfatligninfibrer.

Sulfatligniner från olika vedslag beter sig olika under termisk behandling. Efter oxidativ stabilisering blir ligninerna mer stabila jämfört med stabilisering i frånvaro av syre, vilket medför ett högre utbyte med 10-20 % av den slutgiltiga kolfibern efter karbonisering. De viktigaste reaktionerna som sker under oxidativ stabilisering av fibrer från sulfatlignin är radikal-, oxiderings- och omlagringsreaktioner.

De strukturella skillnaderna mellan sulfatlignin från barrved och lövved gör det möjligt att stabilisera barrvedslignin mycket fortare. Termisk stabilisering i inert atmosfär med endast värme har lyckats med sulfatligninfibrer från barrved. Vidare har även stabilisering och karbonisering i ett enda steg lyckats med sulfatligninfibrer från barrved. Detta kan göra det möjligt att utesluta stabiliseringssteget, vilket förhoppningsvis kan reducera processkostnaderna för kolfiber från barrvedssulfatlignin.

LIST OF PUBLICATIONS

This thesis is based on five papers. Paper I-IV consists of the experimental results and is presented in the Results and Discussion. Paper V is a review paper, which is a part of Introduction. The papers are appended at the end of the thesis.

I. *Kraft Lignin as Feedstock for Chemical Products. The Effects of Membrane Filtration*
Ida Brodin, Göran Gellerstedt and Elisabeth Sjöholm
Holzforschung 63:290-297, 2009

II. *The Behaviour of Kraft Lignin during Thermal Treatment*
Ida Brodin, Göran Gellerstedt and Elisabeth Sjöholm
Journal of Analytical and Applied Pyrolysis 87:70-77, 2010

III. *Oxidative Stabilisation of Kraft Lignin for Carbon Fibre Production*
Ida Brodin, Marie Ernstsson, Göran Gellerstedt and Elisabeth Sjöholm
Holzforschung 66:141-147, 2012

IV. *A new Method for Stabilization of Softwood Kraft Lignin Fibers for Carbon Fiber Production*
Ida Norberg, Ylva Nordström, Rickard Drougge, Göran Gellerstedt and Elisabeth Sjöholm
Submitted to Journal of Applied Polymer Science

V. *The Wood-Based Biorefinery: A source of Carbon Fiber?*
Göran Gellerstedt, Elisabeth Sjöholm and Ida Brodin
The Open Agriculture Journal 3:119-124, 2010

AUTHOR'S CONTRIBUTION TO THE PAPERS

Paper I	Performed the experimental work except from the ultrafiltrations.
	Contributed to the writing.
Paper II	Performed the experimental work, contributed to the interpretation and the writing.
Paper III	Principal author. Planned and performed the experimental work except from the XPS analysis.
Paper IV	Principal author. Planned and performed the experimental work except from the NMR, FTIR and ESEM analysis.
Paper V	Contributed with information and to the writing.

OTHER RELATED PUBLICATIONS

A new Softening Agent for Melt Spinning of Softwood Kraft Lignin
Nordström, Y., Sjöholm, E., Norberg, I. and Drougge, R.
Manuscript

Method for Stabilizing Lignin Fiber for Further Conversion to Carbon Fiber
Norberg, I., Drougge, R., Sjöholm, E. and Gellerstedt, G.
Patent application 2012, No. P41105208US00

Method for Producing Lignin Fiber for Further Conversion to Carbon Fiber
Nordström, Y., Norberg, I., Drougge, R., Sjöholm, E. and Gellerstedt, G.
Patent application 2012, No. P41002726PCT00

Carbon fibre – a new application for lignin
Sjöholm E., Brodin I., Drougge R. and Gellerstedt G.
European Workshop on Lignocellulosics and Pulp (EWLP), August 16-19, Hamburg, Germany, 2010.

Carbon fibre from kraft lignin
Brodin, I.
Forest-Based Sector Technology Platform (FTP) Conference, November 9-11, Stockholm, Sweden 2009. Oral presentation.

Characterisation of Fractionated Kraft Lignins by Pyrolysis-GC/MS
Brodin, I., Gellerstedt, G. and Sjöholm, E.
14th ISWFPC: International Symposium on Wood, Fibre and Pulping Chemistry, June 15-18, Oslo, Norway 2009. Poster presentation.

Characteristics of Lignin Blends Intended for Carbon Fibre Production
Brodin, I., Gellerstedt, G. and Sjöholm, E.
10thEWLP: European Workshop on Lignocellulosics and Pulp, August 25-28, Stockholm, Sweden 2008. Poster presentation.

Kraft Lignin as Feedstock for Chemical Products. The Effects of Membrane Filtration
Brodin, I., Gellerstedt, G. and Sjöholm, E.
NWBC: Nordic Wood Biorefinery Conference, March 11-13, Stockholm, Sweden 2008. Poster presentation.

Kraft Lignin as Feedstock for Chemical Products
Brodin, I., Gellerstedt, G. and Sjöholm, E.
14th ISWFPC: International Symposium on Wood, Fibre and Pulping Chemistry, June 25-28, Durban, South Africa 2007. Oral presentation.

Initial Study of the Relation between the Thermal Properties of Kraft Lignin and its Chemical Composition
Brodin, I., Uhlin, A. and Sjöholm, E.
9th EWLP: European Workshop on Lignocellulosics and Pulp, August 27-30, Vienna, Austria 2006. Poster Presentation.

TABLE OF CONTENTS

ABBREVIATIONS

C1	carbon with no bond to oxygen in XPS analysis
C2	carbon with one bond to oxygen in XPS analysis
C3	carbon with two bonds to oxygen in XPS analysis
C4	carbon with three bonds to oxygen in XPS analysis
CF	carbon fibre
CP/MAS ^{13}C-NMR	cross polarized/magic angle spinning ^{13}C nuclear magnetic resonance
DSC	differential scanning calorimetry
EDS	energy dispersive spectroscopy
ESCA	electron spectroscopy for chemical analysis
ESEM	environmental scanning electron microscopy
FTIR	fourier transformation infrared spectroscopy
GC	gas chromatography
GP	general performance (carbon fibre quality)
GPa	giga Pascal
HP	high performance (carbon fibre quality)
HKL	hardwood kraft lignin
HKLP15	hardwood kraft lignin permeate after fractionation through a 15 kDa membrane
HKLP5	hardwood kraft lignin permeate after fractionation through a 5 kDa membrane
HKLR15	hardwood kraft lignin retentate after fractionation through a 15 kDa membrane
HKLR5	hardwood kraft lignin retentate after fractionation through a 5 kDa membrane
HW	hardwood (birch/aspen)
IC	ion chromatography
kDa	kilo Dalton
LCC	lignin-carbohydrate complex
MOE	Modulus of elasticity
MMD	molecular mass distribution
M_n	number-averaged molecular mass
MPa	mega Pascal
MS	mass spectrometry
M_w	weight-averaged molecular mass
MWL	milled wood lignin
^{31}P-NMR	^{31}Phosphorus-nuclear magnetic resonance spectroscopy
PAN	polyacrylonitrile
PEO	polyethylene oxide
PET	polyehylene terephthalate
Py-GC/MS	pyrolysis-gas chromatography/mass spectrometry
SEC	size exclusion chromatography
SKL	softwood kraft lignin
SKLP15	softwood kraft lignin permeate after fractionation through a 15 kDa membrane
SKLP5	softwood kraft lignin permeate after fractionation through a 5 kDa membrane
SKLR15	softwood kraft lignin retentate after fractionation through a 15 kDa membrane
SKLR5	softwood kraft lignin retentate after fractionation through a 5 kDa membrane

SW	softwood (spruce/pine)
T_d	decomposition temperature
T_g	glass-transition temperature
TGA	thermal gravimetric analysis
THF	tetrahydrofuran
T_m	melting temperature
XPS	x-ray photoelectron spectroscopy

1 INTRODUCTION

The focus on more environmentally friendly materials and processes has promoted interest in lignin as a source for fuel and new materials. Kraft pulping is the most common pulping process in the world, giving of large quantities of kraft lignin that is burnt in the recovery boiler. Partial isolation of the kraft lignin would be of benefit for the mill, which gains in both a new kraft lignin raw material and the possibility of increasing pulp production. Of the carbon fibres (CFs) produced today, over 90 % originates from the oil-based synthetic polymer polyacrylonitrile, which is expensive to produce (1). This thesis focuses on the possibilities of producing carbon fibre from kraft lignin. Although, the thesis highlights the work on kraft lignins from softwood (spruce/pine) and hardwood (birch/aspen), in the papers *Eucalyptus globulus* and lignin obtained from the high-yield kraft pulping of softwood (liner) are also discussed.

1.1 OBJECTIVE

The aim of this thesis was to investigate the possibility of using kraft lignin as a precursor for the manufacturing of carbon fibre. The work was performed by studying the chemical properties and thermal behaviour of hardwood and softwood kraft lignins as well as the stabilisation of kraft lignin fibres.

1.2 BACKGROUND

1.2.1 Wood Components

The three main components in wood are cellulose, hemicellulose and lignin with the proportions differing depending on the source of the wood (see Table 1). Another component group in wood is extractives, which constitutes of 1-5 % of the wood depending on source of wood.

Table 1. The cellulose, hemicellulose and lignin content of different types of wood (2).

Wood type	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Temperate Softwood	40-45	25-30	25-30
Temperate Hardwood	40-45	30-35	20-25
Eucalypt	45	20	30

Lignin

Second to cellulose, lignin is one of the most abundant biomacromolecule in the world. In trees, lignin gives stiffness to the cell wall and, hence, contributes to the mechanical strength of the wood. Moreover, lignin protects the tree against microbial degradation by acting as a barrier and contributes to an efficient water and nutrition transportation system by making the cell wall hydrophobic (3). In contrast to cellulose, which is a linear polymer, the lignin structure is complex and forms a three-dimensional network (see Figure 1). To form the network, mainly three types of monolignols (see

Figure 2) are linked together by different ether and carbon-carbon bonds. Hardwood lignins are mainly composed of two monolignolic units; coniferyl alcohol and sinapyl alcohol, whereas softwood lignins only contain the coniferyl alcohol units. The third monolignol, p-coumaryl alcohol, is usually found in very low amounts in softwoods and hardwoods but is more commonly present in grass and annual plants. In the lignin structure, the monolignols are present in the form of p-hydroxylphenol, guaiacyl and syringyl residues (see Figure 2).

To use lignin as a material, it must be removed from the wood, commonly by dissolution that leads to a change in the chemical structure as compared with native lignin. The structure of lignin differs depending on the source of the wood, the process used to dissolve the lignin from the wood and the isolation process. The dissolution of lignin is often performed using pulping, and kraft pulping is the most common pulping process. Lignin is then dissolved in black liquor and used as a fuel in the recovery boiler (see section 1.2.2).

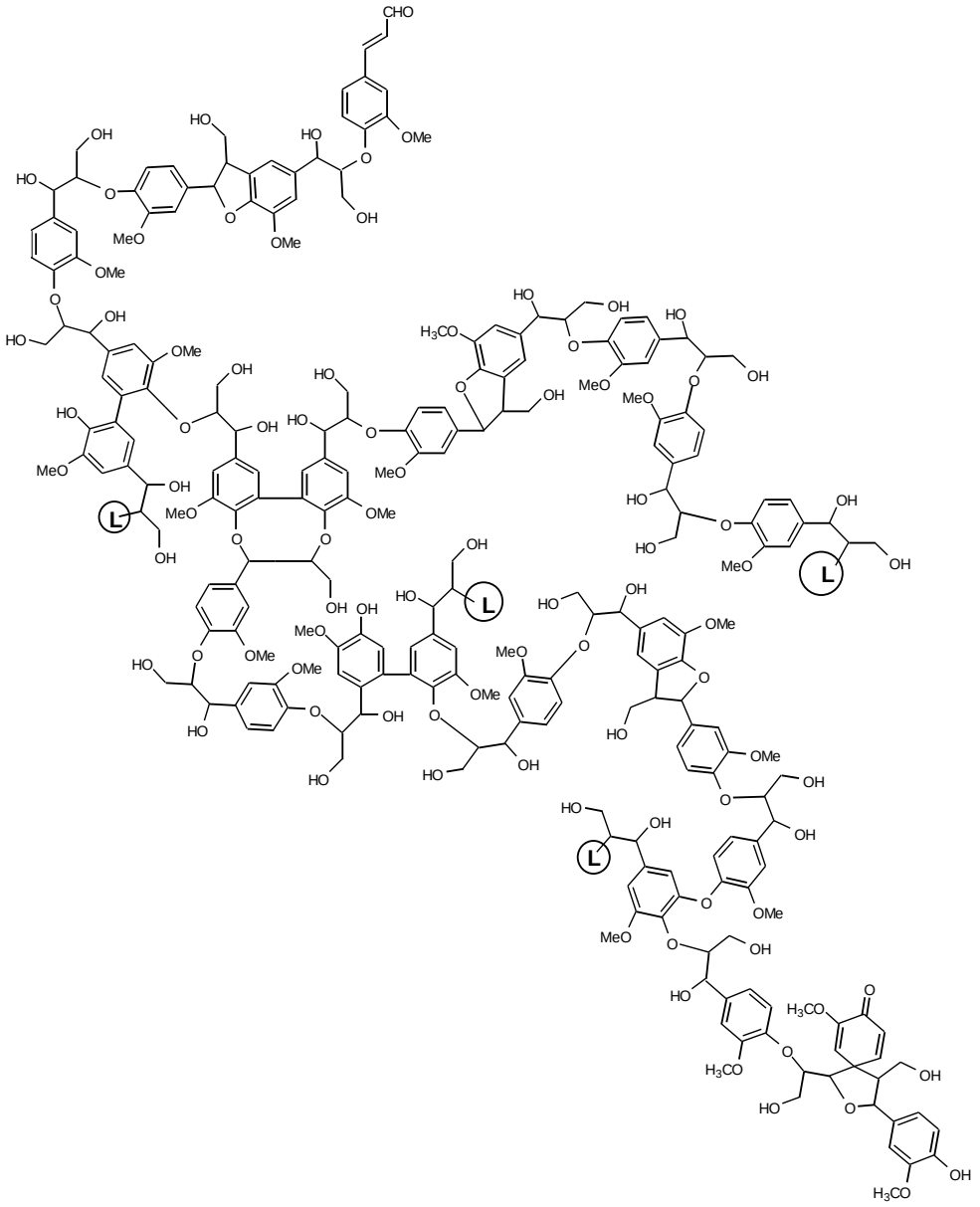


Figure 1. A suggested structure of softwood lignin, composed of coniferyl alcohol units (3).

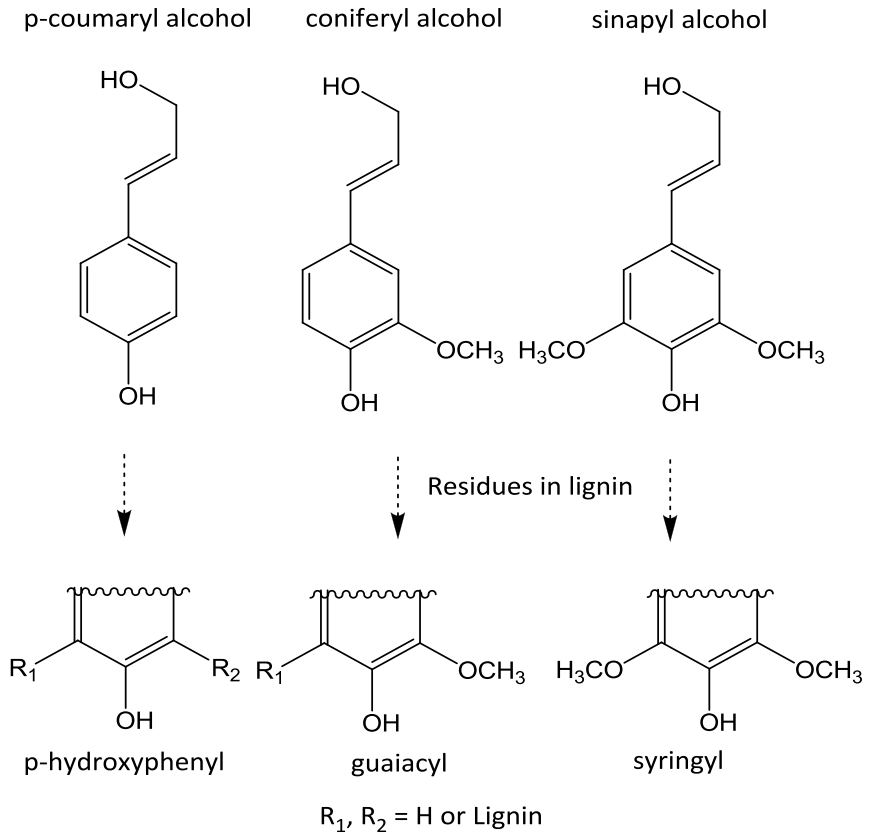


Figure 2. The three main precursors of lignin and their corresponding structures in lignin polymers.

The linkages in lignin appear to be randomly distributed (3). Approximately two-thirds of the linkages are ether linkages and approximately one-third are carbon-carbon linkages (4). The carbon-carbon bonds are generally more stable as compared with the ether bonds and are often resistant to processes such as chemical pulping. The most common linkage in lignin is the β-O-4' linkage, illustrated in Figure 3 together with the nomenclature. β-O-4' linkages constitute 35-70 % and 50-70 % of the linkages in softwood and hardwood, respectively (see Table 2) (3, 4). Of the β-O-4' linkages in hardwood, approximately 60 % are of the syringylic type while 40 % are of the guaiacylic type (4). Because of the differences in the chemical structure of softwoods and hardwoods, the hardwood structure is more linear and less branched. The higher proportion of β-O-4' and β-β' linkages in native hardwood lignin results from radicals being unable to attack the 5-position on the sinapyl alcohol unit and, hence, being limited to covalent bonds in the side-chain. The coniferyl alcohol monolignol mainly present in softwood opens possibilities of linkages such as β-5' and 5-5' created in the free 5-position, leading to a more branched and cross-linked structure as compared with that in hardwood lignins.

The phenolic hydroxyl groups and the methoxyl groups are functional groups in lignin, which are important for the reactivity of the lignin (4). The presence of sinapyl alcohol in hardwood leads to a higher content of methoxy groups as compared to softwood. Phenols are the most reactive site in lignin, and the amount of these sites is important during biodegradation and bleaching among others. Of the aromatic rings in lignin, only approximately 10-13 % of the oxygen atoms in the 4-carbon

position are free phenolic; the others form ether bonds (3). The lignin can also build complexes to hemicelluloses, or so-called LCC-bonds (lignin carbohydrate complex).

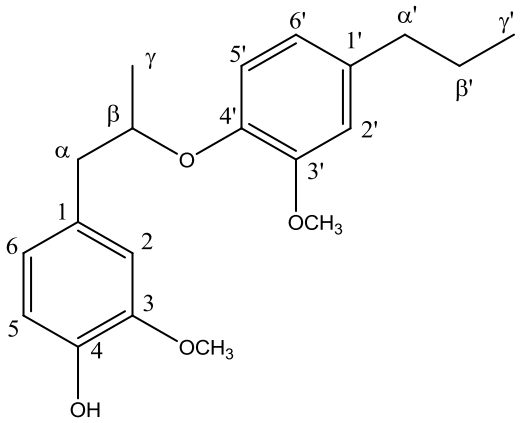


Figure 3. A fragment of guaiacyl units in lignin. The most important bond in lignin is the β-*O-4' linkage, which is susceptible to pulping, bleaching and biological degradation reactions (3). The carbon number nomenclature is also indicated.*

Table 2. Inter-monolignolic linkages of lignin in wood as percent of total linkages (3).

Name	Type of linkage	Softwood (%)	Hardwood (%)
β-aryl ether	β-O-4'	35-60	50-70
Diaryl ether	4-O-5'	<4	7
Phenyl coumarane	β-5'	11-12	4-9
Dihydroxy biphenol	5-5'	10	≈5
Diaryl propane 1,3-diol	β-1'	1-2	1
Pinoresinol	β- β'	2-3	3-4
Dibenzodioxocin	5-5'-O-4	4-5	trace
Spiro-dienone	β-1'α-O- α'	1-3	2-3

1.2.2 Kraft Pulping

To produce pulp and paper, wood can be treated in different ways using processes such as kraft, sulphite or mechanical pulping. Kraft pulping is the most common pulping process in the world. White liquor consisting of an aqueous solution of sodium hydroxide and sodium sulphide is added to the chipped wood at high temperature, and cellulose is produced from the wood by dissolving almost all lignin and a large part of the hemicelluloses into the spent liquor i.e. black liquor. The cooking procedure is regulated with respect to time, temperature and alkalinity, which are suited depending on the source of wood and the target of pulp types. For pulping at harsh conditions, more lignin is dissolved into the black liquor. The amount of lignin in the pulp depends on the grade of pulp, which can be either of bleached paper grade (low-yield) or liner grade (high-yield). After cooking, the pulp

is processed by washing, bleaching and drying and further converted into paper, board or tissue grades.

Black Liquor

In the alkaline black liquor, the lignin and carbohydrates (mainly hemicelluloses) are partially degraded and dissolved. After evaporation of the black liquor, the cooking liquors are regenerated, and the organic substances in the black liquor are combusted in the recovery boiler and high pressure steam is produced (5, 6).

The organic content in black liquors differs with processing. Black liquor from a cook of bleached paper grade contains approximately 29-45 % lignin (Table 3), which is more degraded as compared with black liquor from a liner grade cook, which contains 8-16 % lignin (6). After cooking, the pH is above 12, and the chemical composition of the black liquor is composed of approximately two-thirds organic material and one-third inorganic material (5-7). The weight percent of the components and the organic material of a typical black liquor are provided in Table 3. The hydroxy acids mainly originate from the peeling reaction that occurs for both cellulose and hemicelluloses during pulping (7).

Table 3. The organic composition of a typical black liquor (5). The elemental composition is provided on the left, and the composition of the organic material is provided on the right.

Element	Weight (%)	Organic material	Weight (%)
Carbon	34-39	Lignin	29-45
Hydrogen	3-5	Hydroxy acids	25-35
Oxygen	33-38	Extractives	3-5
Sodium	17-25	Formic acid	≈5
Sulphur	3-7	Acetic acid	≈3
Potassium	0.1-2	Methanol	≈1
Chlorine	0.2-2		
Nitrogen	0.05-0.2		

Kraft Pulping Chemistry

During kraft pulping, the lignin is degraded, with the cleavage of the β-O-4’ linkage that connects the different phenylpropane units being the most common reaction (see Figure 4) (8). A quinone methide is formed under alkaline conditions through equilibrium with phenolic benzyl alcohol. Equilibrium is achieved with the hydrosulphide ion present in the kraft cook connecting to the α-carbon on the side-chain of the lignin. Furthermore, the hydrosulphide ion acts as a nucleophile on the β-carbon and forms an episulphide structure together with a phenolic end group. Elemental sulphur is then formed from the unstable episulphide, and polysulphide is formed in the cooking liquor. The further the cooking process continues, the more degraded the lignin becomes, resulting in an increase in free-

phenolic groups and a decrease in β-O-4’ linkages. Other competing reactions also occur via the quinone methide intermediate during kraft pulping. For example, enol ethers can be formed through the elimination of the γ-hydroxymethyl group.

Cleavage of non-phenolic β-O-4’ structures is possible when the structures contain an α- or γ-hydroxyl group. The reaction mechanism is similar to that illustrated in Figure 4; a nucleophilic attack will result in cleavage of the β-O-4’ linkage.

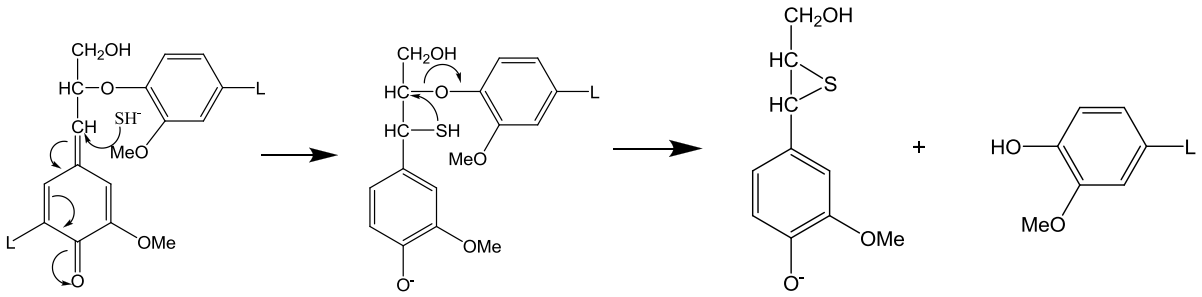


Figure 4. In kraft pulping, the HS^- is the active nucleophile during cleavage of the phenolic β-O-4’ linkage, and an equimolar amount of free-phenolic groups is formed.

1.2.3 The Biorefinery (Paper V)

There is an ongoing change in the pulp and paper industry today due to increasing competition and increasing prices of the wood raw material and oil. Usually, the mills produce only pulp and paper with chemical recycling and internal and sometimes external energy production. A biorefinery utilises the whole raw material by integrating the conversion of biomass with production of biofuel, energy, heat and biobased products. By utilising the side streams in the process, the mills have possibilities to be transformed into biorefineries. Both the lignin and the hemicelluloses have clear potential for application in more value-added products than as fuel for internal energy production (9). A partial withdrawal of lignin from the process for other uses would enable an increase in pulp production. The isolated lignin (Figure 5), could for example, be used as fuel in the lime kiln, which today uses oil combustion, or for more value-added products such as carbon fibres. One possible approach to isolate large quantities of kraft lignin is using the LignoBoost® process (10, 11). Figure 6 provides a schematic overview of the current process of kraft pulping, with the new possible lignin isolation step that can include a purification step, such as ultrafiltration.

Figure 5. Kraft lignin after isolation from the black liquor.

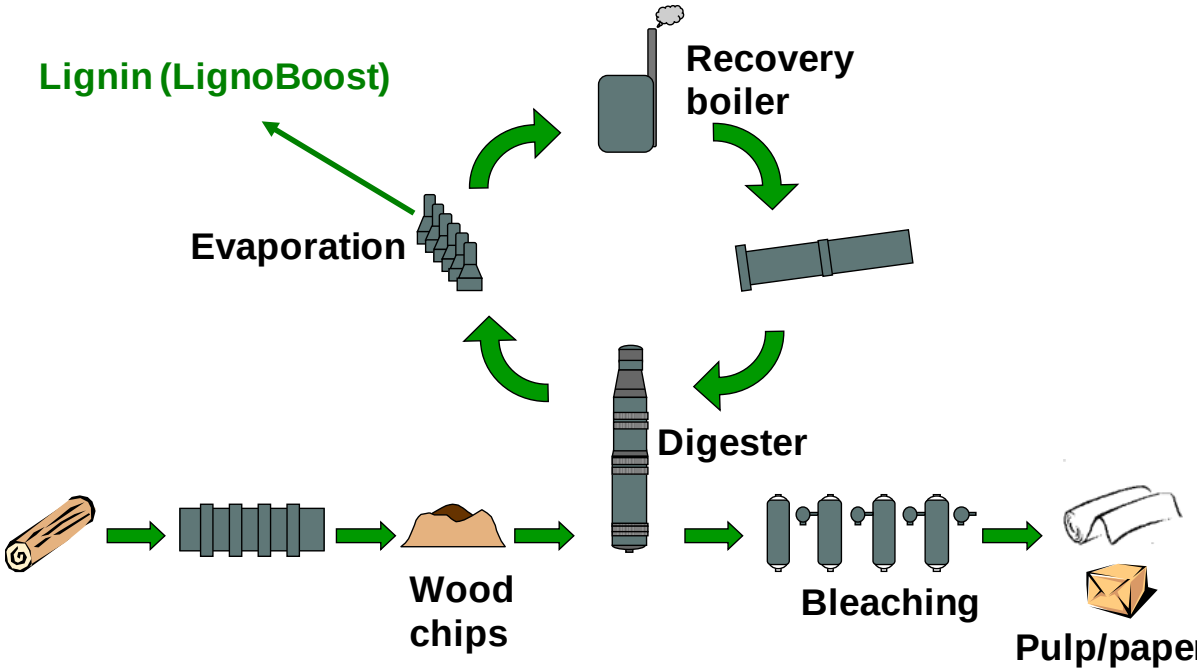
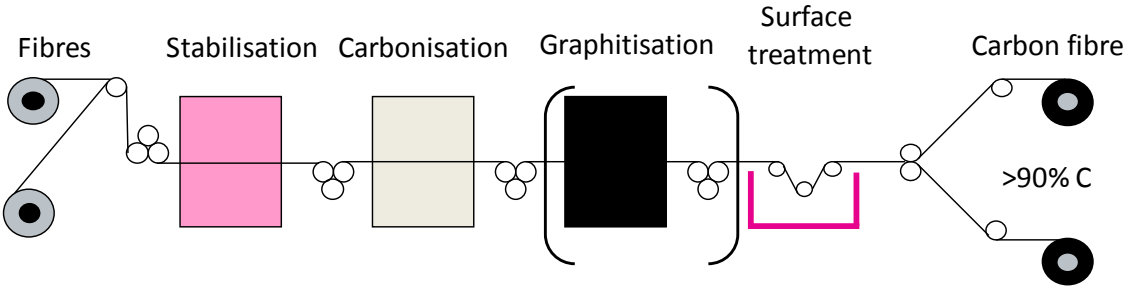


Figure 6. An overview of the process of kraft pulping with the potential point for withdrawal and isolation of lignin and further conversion to e.g. carbon fibre.

1.2.4 Carbon Fibre

Carbon fibre contains at least 90 % carbon by definition (12). This lightweight material has high strength and stiffness as well as high resistance against heat and corrosion. Many applications exist for carbon fibre today in aircrafts, space industry and sport applications, among others. The main drawback is the high production cost, which limits the supply, despite a growing demand. The principal processing steps for the production of carbon fibre are illustrated in Figure 7 and typically include spinning, stabilisation, carbonisation and sometimes graphitisation (12). Today, the polyacrylonitrile (PAN) precursor represents approximately half of the production costs (Figure 7), and the equipment is associated with approximately one third of the production costs (13). Many industries are interested in carbon fibres as a new and lightweight material with the potential to replace, for example, the steel in cars and the glass fibres in blades in wind power stations.

The main precursor for the manufacturing of carbon fibre today is PAN, which constitutes approximately 90 % of all commercial carbon fibre produced (1). The two other precursors are petroleum pitch and regenerated cellulose (rayon). Regarding the properties of precursors, lignin is most similar to petroleum pitch.



PAN, %	51	16	23		4	6
PAN, $/kg	11.1	3.4	5.1		0.8	1.3
Lignin, $/kg	1.1	1.7	1.4	1.5	0.2	0.3

Figure 7. The principal processing steps for the manufacture of carbon fibre together with the estimated relative cost calculations for polyacrylonitrile (PAN) and lignin as precursors (14, 15).The cost estimations correspond to each processing step, where the first step include both precursor and fibre spinning costs.

Fibre Spinning

Depending on the raw material properties, different methods of fibre spinning are used for producing the precursor fibre. The spinning methods typically used are wet, dry and melt spinning (12). Melt spinning can be used for most thermoplastic materials, as these materials are shear thinning and hence will soften when shear stresses are applied (16). The pitch-based process uses melt spinning, which is a relatively inexpensive method but not suitable to use for PAN (12). Instead, the PAN is dissolved into solution before wet or dry spinning.

Similarly to thermoplastic materials, lignin has commonly been spun using melt spinning. A lignin suitable for melt spinning, exhibits some thermoplastic properties, as it has a detectable T_g and softens upon heating. However, the processability of lignin has been observed to depend on its chemical structure, which is affected both by its origin and how the lignin is isolated from the source. Various methods of improving the processability have been suggested, such as chemical modification (17), pre-treatments (18-20) and the addition of softening agents (19, 20). Figure 8 shows a bobbin of a kraft lignin fibre after melt spinning.

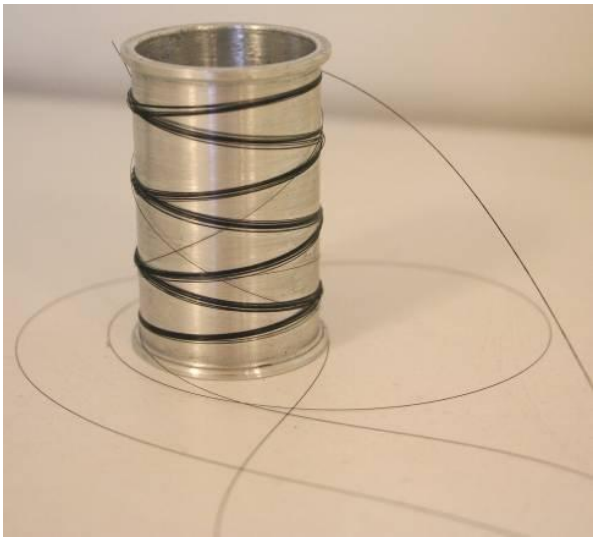


Figure 8. Kraft lignin fibre after melt spinning.

Stabilisation

During stabilisation, the thermoplastic behaviour of the precursor fibres is removed. Instead, the fibres obtain thermosetting properties that inhibit fusing of the fibres upon further heating (12). Oxidative stabilisation is most widely used and involves a slow temperature increase in an oxidising atmosphere (12). Oxidative stabilisation of a fibre is a function of the amount of oxidant, temperature and time (12). In pitch, the reactions during stabilisation include oxidation, dehydrogenation, cyclisation, elimination, condensation and cross-linking (21-23). A typical reaction during oxidative stabilisation for pitch-based fibres is depicted in Figure 9 and involves the addition of oxygen into the chemical structure and the release of water during cross-linking of the structure.

One of the greatest challenges during stabilisation is achieving homogenous stabilisation throughout the entire fibre. For pitch-based fibres, it has been observed that the formation of a so-called skin-core structure prevents oxygen from penetrating deeper into the structure (24). This phenomenon is caused by the competition of chemical reactions on the surface of the fibre and diffusion. To prevent the appearance of skin-core structures, a decrease in the reaction temperature and/or an increase in the oxygen partial pressure are the most important steps according to a model of the kinetics of oxidative stabilisation (24). Using a large diameter fibre has also been suggested to have a negative impact on the skin-core structure because of the relatively limited penetration of oxygen into the pitch fibre.

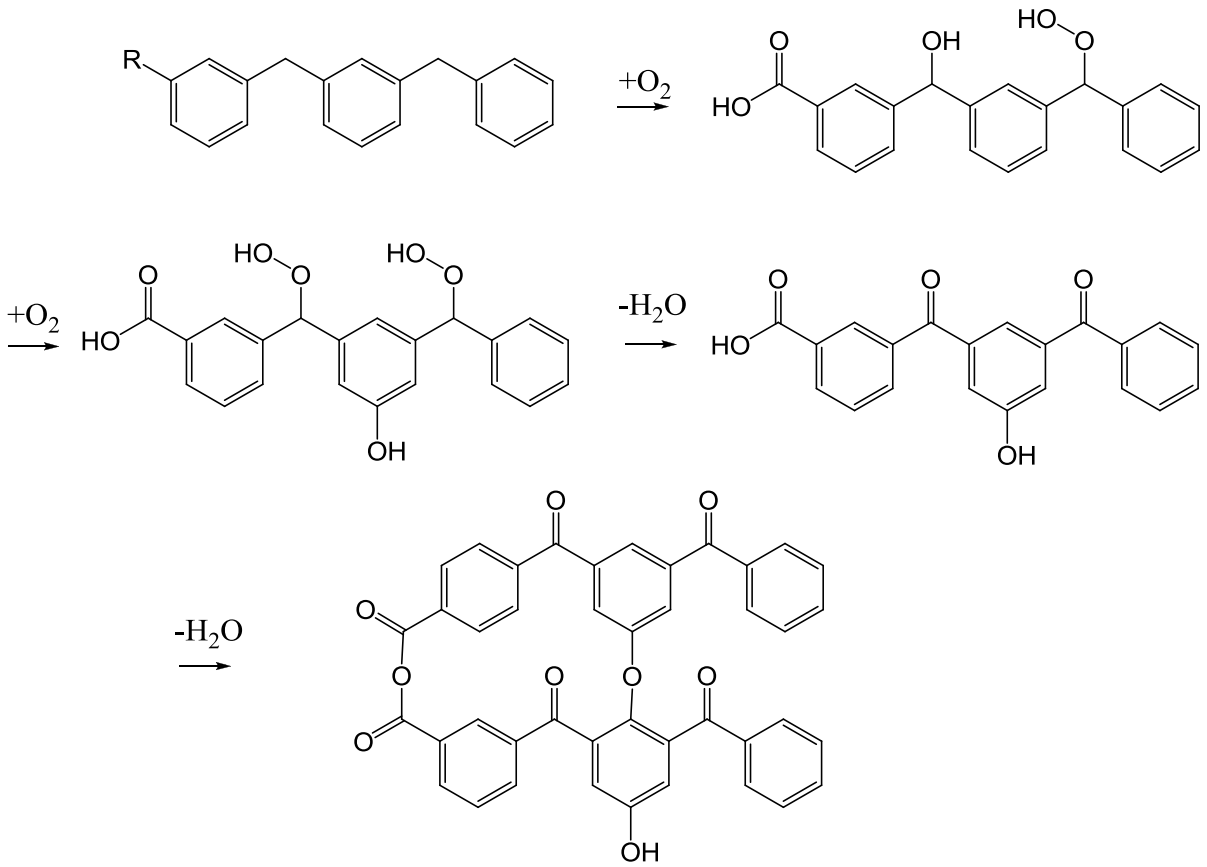


Figure 9. One possible reaction of pitch fibres during oxidative stabilisation, leading to the introduction of oxygen into the chemical structure and cross-linking (12).

Regarding lignins, stabilisation is only reported for hardwood kraft lignins in the literature because of the difficulties of spinning softwood kraft lignin (25). In the carbon fibre process, the stabilisation step is the most time-consuming step, and for hardwood lignins, the heating rate is 0.5°C/min or slower (18, 26), causing the total stabilisation time to often exceed 12 hours. The structural differences between softwood and hardwood kraft lignins not only affect the spinning properties but also the cross-linking ability of lignins.

In line with pitch fibres, the reactions in lignin during oxidative stabilisation include mainly oxidative, radical and rearrangement reactions (26). Radical reactions introduced by homolytic cleavage of the β-O-4’ bond during heat treatment (Figure 10) might be sufficient to stabilise the lignin and transform it into a thermoset.

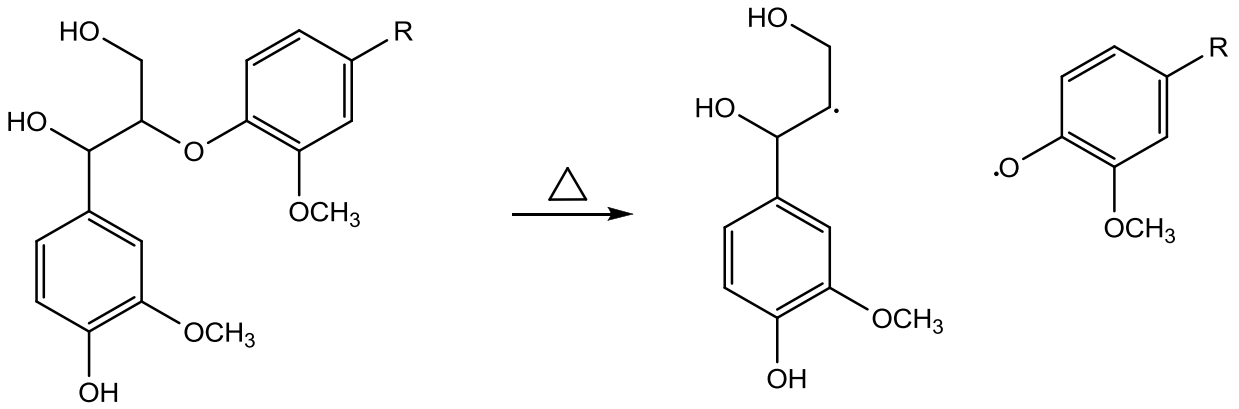


Figure 10. The homolysis reaction of the β-O-4' bond initiated by heat treatment is a common lignin reaction during stabilisation. The formed radicals react further with the lignin.

Carbonisation

During the carbonisation step, the stabilised fibre is converted into a carbon fibre. The carbonisation proceeds under pyrolytic conditions in an inert atmosphere at various temperatures between 1000°C to 2000°C, depending on the raw material used and the intended fibre quality. The purpose is to remove the heteroatoms and improve the mechanical, electrical and thermal properties of the carbon fibre by forming a graphitical-layered structure. For pitch-based carbon fibres, the aromatics are known to be condensed, cross-linked and cyclised, giving off water, carbon dioxide, carbon monoxide, hydrogen gas and tar (12). The reactions during a typical carbonisation of pitch are illustrated in Figure 11. The structure of the material becomes more graphitic the longer the carbonisation proceeds.

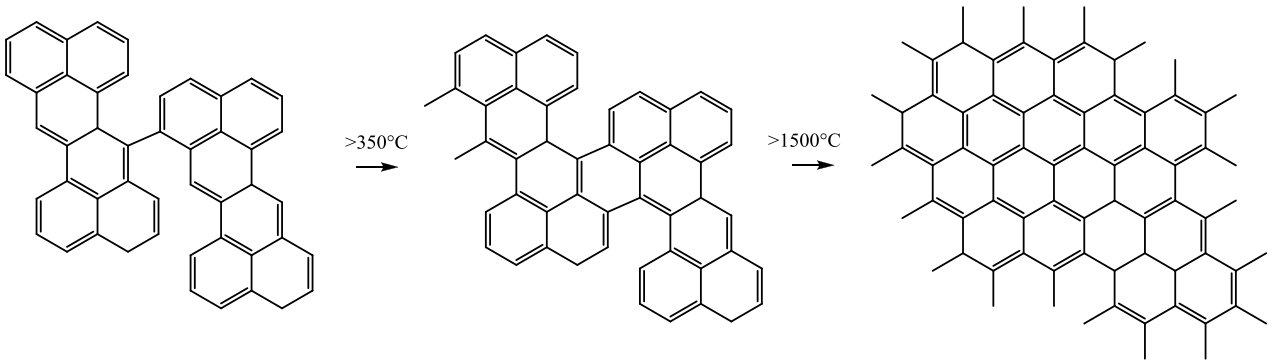


Figure 11. The change in the chemical structure for pitch during carbonisation. A graphitical structure is formed during elimination of heteroatoms that improves the mechanical, electrical and thermal properties of the carbon fibre (12).

Graphitisation

Sometimes after carbonisation, a graphitisation step is included, but it depends on the final usage of the produced carbon fibre. The properties of pitch based CFs changes rapidly after heat treatment at temperatures between 2000 to 3000°C. For the so-called mesophase pitch raw material, the tensile strength and modulus increase with increasing temperature; however, for the so-called isotropic pitch raw material the tensile strength decrease with increasing temperature, while the modulus increases. PAN-based CFs shows the same behaviour as isotropic pitch. For Rayon-based CFs, a graphitisation step is required to obtain satisfactory mechanical properties. Usually, the Rayon-based fibres are graphitized under tension at a temperature above 2800°C. The Modulus of elasticity of the fibres increases with increased temperature and effective stretch of the fibres (12).

Surface Treatment and Sizing

CFs are used as the strength bearing component in composites. To achieve a strong composite, it is important to have good interaction between the CFs and the resin matrix. To improve the fibre-matrix interface, the surface of the CFs is made more active by performing surface treatment. The surface treatment can be performed by the commonly used oxidative or a non-oxidative treatment. After the surface treatment, the fibres are covered with a thin resin layer, which is called sizing. The sizing facilitates handling of the fibres and improves the mechanical properties (27).

1.2.5 Lignin-based Carbon Fibre (Paper V)

In contrast to PAN and petroleum pitch, lignin is a renewable material. Lignin has a carbon content of more than 60 % (28). Furthermore, lignin is; available in large quantities; possible to isolate and eventually modify, and still obtainable as a relatively cost-competitive raw material, as compared with PAN. Cost estimations for lignin as precursor is presented in Figure 7 and shows potential of a remarkably cost reduction as compared to PAN based precursor (15).

Thus far, only one carbon fibre with lignin as a precursor has been commercialised, the so-called Kayocarbon fibre produced by Nippon Kayaku Co. during 1967-1973. The precursor used was lignosulphonate, which is a technical lignin originating from the sulphite process. Polyvinylalcohol was added as a softening agent (29). In addition, several studies concerning other lignin types as possible carbon fibre precursors have been conducted.

Organosolv and Steam-explosion Lignin

In addition to kraft lignin (discussed below), organosolv lignins and steam-explosion lignins are the two types of lignin most investigated for carbon fibre applications.

Organosolv lignins are lignins produced from different organic solvent-based systems, and the two most common organosolv processes are ethanol/water pulping (Alcell) and pulping with acetic acid containing a small amount of mineral acid such as hydrochloric acid or sulphuric acid (Acetosolv). In 1993, Uraki and co-workers demonstrated that fibres could be produced by melt spinning of hardwood acetic acid lignin isolated from spent liquor (30). The spinnability of Alcell lignin in various blends with polyethylene oxide (PEO) was studied by Kadla and co-workers. During the

stabilisation and carbonisation step, the lignin blends were very sensitive to the heating rate and thermally unstable, thus fusing (19).

One of the most active research groups studying carbon fibres from lignin is Oak Ridge National Laboratory, which has set a target to manufacture a lignin-based carbon fibre with a tensile strength of 1.72 GPa and a modulus of 170 GPa, which are mechanical properties that are sufficient for the automotive industry. The best reported carbon fibre thus far originates from hardwood Alcell lignin purified using an organic solvent and has a tensile strength of 1.1 GPa and a modulus of 69-83 GPa (Table 4).

Steam explosion refers to defibration of wood by treating the wood with steam at high temperature and pressure, followed by a rapid release of the pressure. After extraction, steam-explosion lignin is produced (4). The first carbon fibre that was based on steam-explosion lignin was reported by Sudo and Shimizu. The lignin used was extracted using methanol from steam-exploded birch wood. Further treatment on hydrogenated steam-explosion lignin using phenolysis that introduces phenolic groups in the lignin structure, increased the CF yield to 43.7 % as compared to non-phenolysed lignin (17).

Kraft Lignin

The first produced carbon fibre originating from neat hardwood kraft lignin was reported by Kadla and co-workers. The mechanical properties were poor but could be improved by adding PEO before spinning (19). Different proportions of PEO were tested, and the best CF was obtained using an addition of 5 % (Table 4). Amounts of softening agent greater than 5 % made the fibres thermally unstable, and they fused during carbonisation and thus did not have the desired thermosetting properties. Kadla and co-workers observed that an addition of 5 % polyethylene terephtalate (PET) to hardwood kraft lignin resulted in the best reported kraft lignin-based CF thus far (20). To date, no reported carbon fibres have been produced from softwood kraft lignin. Some reports indicate that softwood kraft lignin (Indulin AT) chars upon heating, implying that instead of softening, the lignin begins to degrade (31-33).

The mechanical properties of carbon fibres originating from different lignin types and commercial carbon fibres are provided in Table 4. Note that none of the carbon fibres from lignin have attained the mechanical properties of the general performance (GP) carbon fibre from pitch.

Table 4. Mechanical properties and yield of carbon fibres produced from different types of lignins compared with petroleum pitch- and polyacrylonitrile (PAN)-based carbon fibres. GP = general performance, HP = high performance, HKL = hardwood kraft lignin, PET = polyethylene terephtalate, SW =softwood, HW = hardwood.

Carbon fibre composition	Elongation (%)	Tensile strength (MPa)	MOE[1] (GPa)	Yield (%)	Reference
HKL	1.12	420	40.0	45.7	(32)
HKL/PET 95/5	1.06	670	84.0	-	(20)
HKL-organic purified	-	520	28.6	-	(18)
Alcell hardwood lignin	-	1100	69-83	-	(34)
Alcell lignin[2]	1.00	390	40.0	40.0	(32)
Steam explosion lignin[3]	1.63	660	40.7	15.8-17.4	(35)
Steam explosion lignin[4]	1.22	390	-	43.7	(17)
SW Acetic acid lignin	0.71	30	3.6	23.3	(25)
HW Acetic acid lignin	1.03	160	15.2	8.7	(36)
Kayocarbon	1.0	250	27.0	-	(37)
Pitch (GP)[5]	-	780-980	39-49	-	(12)
Pitch (HP)[6]	-	1300-2400	170-960	-	(12)
PAN[7]	-	2700-7100	290-590	-	(12)

[1]Modulus of elasticity, [2]Repap, [3]Methanol extraction and hydrogenation, [4]Phenolysis with phenol, [5]Nippon, [6]Amoco, [7]Torey Industries,

Kraft Lignin Chemical Properties and Thermal Behaviour

Several properties of lignin are important when using it as a carbon fibre precursor. To enable continuous melt spinning into a lignin fibre, the melt ability is important. However, the melt ability of a lignin is always affected by its chemical properties, such as the molecular mass and the purity of the lignin. The weight-average molecular mass (M_w), the number-average molecular mass (M_n) and the molecular mass distribution (MMD) are used to characterise the lignin. Carbohydrates, also present in the black liquor, are a common impurity in kraft lignin that has a negative influence on the melting ability of the lignin, and can be observed as an increased MMD, as it mainly is composed of large molecules. The width of the distribution, the polydispersity (M_w/M_n) is preferred to be low, and the removal of carbohydrates would gain a more homogenous kraft lignin.

Because softwood lignin only contains the guaiacylic type of phenylpropane unit, with a free 5-position on the aromatic ring, its structure is more branched as compared with hardwood lignin, thus resulting in a higher M_w and a broader MMD.

Every step in the manufacturing of carbon fibres involves some type of heat treatment. Therefore, the thermal properties of lignin are significant. Similar to others amorphous polymers, the different lignin macromolecules are randomly distributed without any internal order. The glass transition

temperature (T_g) is commonly defined as the inflection point of the glass transition and indicates at what temperature the material goes from a glassy to a rubbery state upon heating due to micro-Brownian motion (38). For amorphous polymers, the viscosity continues to decrease upon further heating as the molecules gain movement, until the material is completely melted. Therefore, a distinct melting temperature cannot be determined. The more branched and/or cross-linked structure present in softwood lignins leads to a slightly higher T_g as compared with hardwoods (39).

2 EXPERIMENTAL

This section provides an overview of the materials and methods used, the details of which are presented in the papers.

2.1 MATERIALS

Different kraft lignin samples have been used and are listed in Table 5. All lignins originate from industrial black liquors during chemical pulping to obtain kraft pulps for further conversion to fully bleached pulps. Hardwood and softwood kraft lignin are denoted as HKL and SKL, respectively. After ultrafiltration of the black liquor before isolation of the lignin, the permeates (P) are denoted as HKLP and SKLP and the retentates (R) are denoted as HKLR and SKLR, respectively. Depending on the cut-off of membrane used during fractionation, a (5) or (15) is added to the end of the sample name; for example, HKLP15 corresponds to a permeate hardwood kraft lignin fractionated through a 15 kDa membrane before isolation. After oxidative stabilisation using the programme 0.5°C/min to 250°C at 60 min, the samples are denoted "Ox" before the sample name.

Table 5. Four different industrial black liquors have been used in the thesis and two originating from hardwood and two from softwood, respectively. The different black liquors used in the different papers are shown.

Black liquor	Kraft lignin	Paper I	Paper II	Paper III	Paper IV
1,2	HKL	1	1	1,2	
3,4	SKL	3	3	3	4
1	HKLP5	1			
1,2	HKLP15	1	1	1	2
1	HKLR	1			
3	SKLP5	3			
3,4	SKLP15	3	3	3	4
3	SKLR	3			

2.1.1 Black Liquors (Papers I-IV)

Industrial black liquors from kraft pulping of softwood (pine/spruce wood mixture) and hardwood (birch/aspen) were used. Before isolation of the lignins, some of the black liquors were fractionated using ultrafiltration to remove carbohydrates and large particles to obtain a purified lignin (permeate). The black liquors were fractionated at the laboratory at a temperature of 120°C through a ceramic membrane with either a 5 kDa or 15 kDa cut-off (see Figure 12).

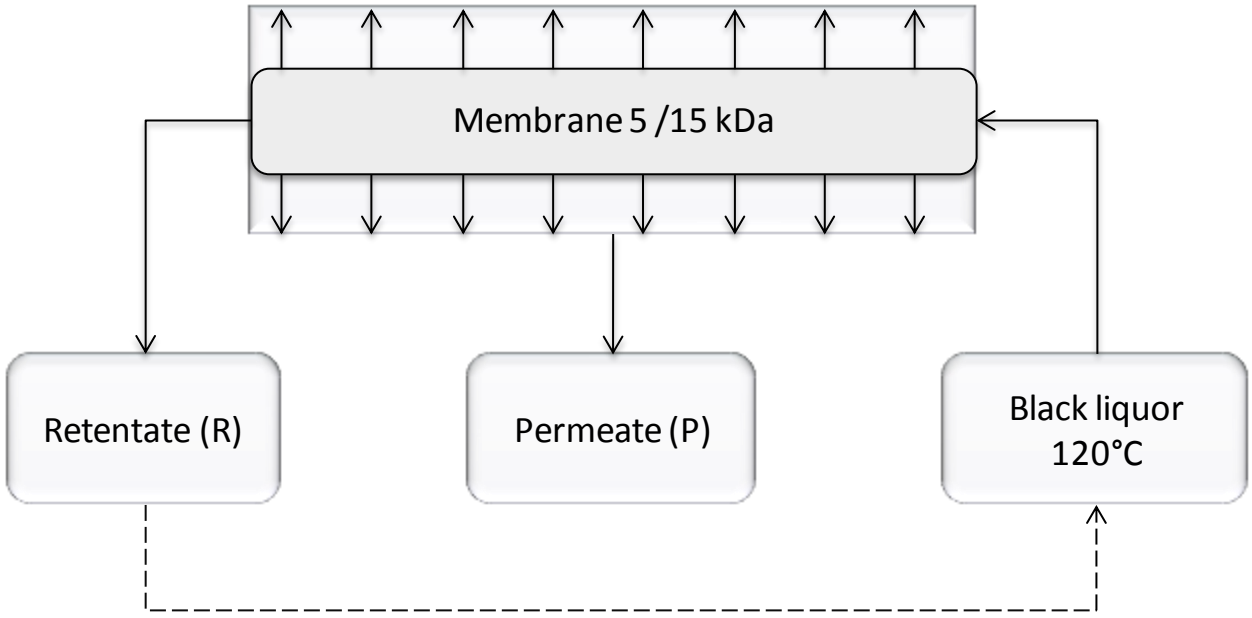


Figure 12. A schematic picture of the ultrafiltration procedure. The separation was continued by recirculation until 50 % of the starting volume of black liquor was in the permeate fraction.

2.1.2 Lignin Isolation (Paper I)

Precipitation of the kraft lignins from the black liquors was performed by acidification with gaseous carbon dioxide to pH ≈ 9 according to the LignoBoost approach. The temperature during acidification was selected such that no clogging occurred, which was 60°C and 70°C for hardwood and softwood-derived black liquor, respectively. The precipitation step was followed by filtration under nitrogen pressure of 1-2 bar followed by a re-slurrying step, where the lignin cake was suspended in water and acidified with sulphuric acid to pH ≈ 2, filtered, washed with deionised water and dried at room temperature.

2.1.3 Ion Exchange (Papers I-III)

Approximately 2 g of dried lignin was dissolved in approximately 15 ml of acetone-water 7:3. The solution was slowly passed through a strong cation exchange column, Amberlite IR-120(H^+). The eluate was evaporated, and the lignin was freeze-dried. The products were stored under phosphorus pentoxide until use.

2.2 Melt-spinning (Papers III+IV)

The temperature used during the melt extrusion depended on the T_g of the lignin and was usually set to approximately 40°C above the T_g (40). During the extrusion, approximately 7 g of the lignin or lignin blend was placed into the extruder (HAAKE Minilab II, Thermo Fischer, Germany) equipped with twin-screws and a die with a diameter of 0.5 mm together with a take-up system (TUS, Dynisco, United Kingdom). After recycling the lignin for 10 min, the lignin fibre was collected on a bobbin.

2.3 Stabilisation (Papers II-IV)

2.3.1 Oxidative Stabilisation

Powders: Approximately 500 mg of each permeate lignin powder was placed in ceramic ships and oxidised in air (no flow-through) in a tube furnace (VTF 50/15-L, Entech, Sweden).

Fibres: The lignin fibres were placed vertically in a hanging position and placed in a conventional GC-oven (HP 5890). Stabilisation was performed at different heating rates in an air atmosphere.

2.3.2 Thermal Stabilisation

Thermal stabilisation refers to stabilising a lignin fibre in the absence of oxygen, which implies that the presence of heat alone is sufficient to transform the lignin fibres into a thermoset. The fibres were placed in a closed vial that was filled with nitrogen (≥99.999 %) before stabilisation. The stabilisation proceeded in a conventional GC oven (HP 5890) at various heating rates, temperatures and holding times.

2.4 Carbonisation (Paper IV)

The stabilised lignin fibres were placed in a ceramic ship and placed into a tube furnace (VTF 50/15-L, Entech, Sweden). The carbonisation was performed in a nitrogen atmosphere (15-20 ml/min) at 20°C/min to 250°C, 1°C/min to 600°C and 3°C/min to 1000°C.

2.5 Chemical Analysis (Papers I, III-IV)

2.5.1 Characterisation of the Lignin Samples (Paper I)

Characterizing the lignin sample composition, or the content of carbohydrates and inorganics, is important because it is claimed to affect the carbon fibre processing steps. Both acid hydrolysis and the determination of ash content was performed using industry standard methods (41, 42). The carbohydrate composition after acid hydrolysis was analysed using ion chromatography (IC) using a DX500 system equipped with a gradient pump GP50 (Dionex) with a flow of 1 ml/min and an electrochemical detector ED40 (Dionex). The column was a PA1 (Dionex) together with an RP-1 Dionex post-column pump. The eluents was sodium hydroxide, sodium acetate and water at various compositions.

Determination of the elemental composition and the methoxyl groups of the lignin powders was performed by Analytische Laboratorien GmbH, Lindlar, Germany.

2.5.2 Size Exclusion Chromatography (SEC) (Paper I)

The samples were acetylated to facilitate dissolution in tetrahydrofuran (43). Size exclusion chromatography in a tetrahydrofuran system with a flow of 0.8 ml/min was used. The separation system used had three styragel columns (Styragel HR2 and HR1, Ultrastyragel 10^4 Å; Waters) in series, a Scantec 625 HPLC pump and a Waters 410 RI detector. Calibration of the columns was performed with a series of 5 polystyrene standards covering the molecular mass range of

1.38-115 kDa. Calculations were performed using PL Cirrus GPC software, version 3.1, Polymer Laboratories, Varian.

2.5.3 Functional Groups in the Lignin and Lignin Fibres (Papers I, III-IV)

For a more thorough analysis of the functional groups in the lignin powders after isolation, both thioacidolysis for the determination of the β-O-4 structures in the lignin (44) and ^{31}P-NMR to determine the phenolic and aliphatic hydroxyl groups were used (45).

Fourier Transformation Infrared spectroscopy (FTIR)

FTIR is a quick method to analyse both solutions and solid-state samples (46). This technique provides information on the functional groups in the sample and the principle is described by Harris (47). The FTIR analysis was performed on a tablet containing mortared lignin and KBr (ratio ≈ 1:100). A Varian 680-IR, FT-IR spectrometer was used for the analysis, and the measurements were performed in transmission mode with a MCT (mercury-cadmium-telluride) detector in air.

Cross polarized/magic angle spinning ^{13}C nuclear magnetic resonance (CP/MAS ^{13}C-NMR)

NMR is a technique suitable for solid samples, even though it is most widely used for solutions. The principle is described by Macomber (48). The CP/MAS ^{13}C-NMR analysis was performed according to the procedure used by Nilsson and co-workers; however, the lignin samples were dry and mortared before analysis (49).

Analysis of the functional groups in the lignin, lignin fibres and stabilised lignin fibres was performed using FTIR and CP/MAS ^{13}C-NMR.

Environmental Scanning Electron Microscopy (ESEM)

To examine the surface and the cross-section and to measure the elemental composition of a fibre, a quick method involves using ESEM together with energy dispersive spectroscopy (EDS). ESEM micrographs were taken using a Philips XL30 environmental scanning electron microscopy field emission gun equipped with a backscattered electron detector in low-vacuum mode. The working conditions used were as follows: the acceleration voltage was between 10 kV and 12 kV, the pressure in the sample chamber was approximately 0.8 mbar and the working distance was set between 8 mm and 10 mm. No conductive coating was used for the analysed samples. EDS with an Inca X-ray analysis system detects X-ray signals from all elements present in the analysed material simultaneously and provides semi-quantitative analysis results.

X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a chemical surface analysis technique. The chemical composition of a sample on the outermost surface, 2-10 nm deep, can be quantitatively determined. All elements except for

hydrogen and helium are detected together with the different oxidative stages of an element. This implies that the functional groups, the oxidation state and the chemical bonding of an element can be determined (see Table 6). The principle is based on radiation of well-defined X-ray energy on the surface of a sample placed under high vacuum, resulting in the emission of the outermost photoelectrons to the detector. Calculation of the binding energy of the photoelectrons by analysing the kinetic energy reveals their origin in relation to the element and the electron shell.

Table 6. The different carbons obtainable using XPS together with the possible functional groups.

Carbon	Number of bonds to oxygen	Functional groups
C1	No bond to oxygen	C-C, C=C-H
C2	One bond to oxygen	C-O, C-O-C
C3	Two bonds to oxygen	C=O, O-C-O
C4	Three bonds to oxygen	O-C=O, C(=O)-OH

The XPS measurements were performed using a Kratos AXIS Ultra^{DLD} XPS instrument (Kratos Analytical, Manchester, UK). The monochromatic Al K_α X-ray source was operated at 150 W (10 mA/15 kV). The analysis areas selected were either large areas, with most of the signal from an area of 700 x 300 µm (for lignin powders), or XPS small-spot analysis was performed with the 27 µm aperture detecting approximately 90 % of the signals from a circular area that was 27 µm in diameter (single fibre analysis). However, to determine the positions for the small-spot analysis, XPS parallel images (over a 400 x 400 µm area) were first taken to locate a single fibre; then, 27 µm small-spot analysis was performed on the outer surfaces and on freshly cleaved cross-sections. Because of this procedure, the stated points are correct within a few µm.

2.6 Pyrolysis- GC/MS (Paper II)

Analytical pyrolysis is a useful tool for qualitatively identifying the composition of an organic sample (50). The pyrolysis was performed using a filament pulse pyrolyser (PYROLA 2000, Pyrol AB, Lund, Sweden). Samples of weight 1-100 µg were pyrolysed for 3 sec. The GC/MS system consisted of a gas chromatograph from Fisons Instrumental (GC 8065) and a mass spectrometer from Fisons Instrumental (MD800 Quadropole). The capillary column used was a BPX5 low-bleed/MS, 30 m x 0.25 mm i.d.; film thickness 0.25 µm (SGE) (Chrompack). The following temperature programme was used: 60°C for 1 min, 19°C/min to the final temperature of 300°C, held for 10 min. The mass spectrometer was operated in the electron impact mode (EI, 70 eV). For specific analysis of very volatile compounds, the capillary column used was a CP-Sil 5 SCB WCOT, 60 m x 0.32 i.d.; film thickness 8.0 µm (Varian). All the lignin samples were evaluated with fractionated pyrolysis starting at 200°C and increases in the temperature in 100°C increments to 900°C. In addition to fractionated pyrolysis, regular pyrolysis was performed at 600°C for each sample. The low-molecular-mass compounds were analysed at pyrolysis temperatures of 350°C and 600°C.

2.7 Thermal Analysis (Papers I-IV)

2.7.1 Thermal Gravimetric Analysis (TGA)

A Perkin Elmer TGA7 instrument was used with a flow rate of the purge gas (He) of 20–35 ml/min, and a balance purge gas (N_2) at 40–60 ml/min was used. Approximately 4 mg of the sample was dried at 105°C for 20 min before being heated at a rate of 15°C/min to 300°C for determination of T_d or to 1000°C for determination of the total mass loss.

2.7.2 Differential Scanning Calorimetry (DSC)

2-5 mg of the sample was very accurately weighted in a pan used for DSC measurements. A Waters DSC Q1000 V9.4 Build 287 instrument was used. Each sample was dried by increasing the temperature to 150°C at a rate of 1°C/min and then cooled and equilibrated at 20°C before the measurements. The heating rate during the measurement was 3°C/min. All reported data are averages of duplicates.

3 RESULTS AND DISCUSSION

The results and discussion section has been divided into six subsections. Section 3.1 concerns the characterizations of the hardwood and softwood kraft lignins. The chemical characterisation and thermal behaviour of the lignin with respect to the raw material used for the carbon fibre production are also discussed. This section is followed by a discussion of the behaviour of lignins during thermal treatment in section 3.2. The effect on the yield of the lignins before and after oxidative and thermal stabilisation is discussed in section 3.3. Much focus has been placed on the stabilisation step to optimize the stabilisation step for both softwood- and hardwood-based kraft lignin fibres. In section 3.4, the structural changes in the lignin structure during oxidative stabilisation of hardwood kraft lignins are discussed, followed by a discussion of the stabilisation of softwood kraft lignin fibres in section 3.5. Finally, in section 3.6, the produced carbonised kraft lignin fibres are evaluated.

3.1 LIGNIN CHARACTERISATION (PAPER I)

The lignin raw materials must be well characterized to determine the differences between softwood and hardwood kraft lignin (SKL, HKL) with respect to the carbon fibre precursor. The effect of the fractionation of softwood and hardwood (SKLP, HKLP) with respect to homogeneity was also studied. The purity of the lignin is of importance because of its influence on the softening of the lignin. After fractionation, a remarkable decrease in the carbohydrate content was observed regardless of the cut-off of the membrane used (Table 7), indicating that 15 kDa is sufficient for purification of the black liquor before lignin isolation. Furthermore, the content of inorganics is of importance for a carbon fibre precursor, mainly because inorganics can cause voids in the structure by acting as a catalyst during the carbonisation step and, thus, lower the mechanical properties. An ash content lower than 0.1 % for lignins has been reported as suitable for a carbon fibre precursor (19). Because the ash content after isolation was 0.5-2.5 %, an ion-exchange process was performed to achieve a lignin with low ash content, which was successfully obtained for all the isolated lignins (Table 7). Acid wash is another possible purification method for reducing inorganics, which has been shown to be sufficient for kraft lignins produced with the LignoBoost technique as well as other kraft lignins (19, 51).

Table 7. Chemical composition of the different birch lignin fractions. Unfractionated birch lignin (HKL), the permeate lignins fractionated through either a 5 or 15 kDa membrane (HKLP5, HKLP15) and the corresponding retentate (HKLR5, HKLR15).

Composition, %	**Lignin Fraction**				
	HKL	**HKLP15**	**HKLR15**	**HKLP5**	**HKLR5**
Klason lignin	89.3	93.0	78.9	90.9	77.6
Acid soluble lignin	8.2	8.7	8.8	10.6	8.3
Carbohydrates[1)]	4.1	0.2	11.1	0.2	13.9
Inorganics (ash)	0.5	1.4	0.7	2.5	0.8
Total	102.1	103.2	99.5	104.2	100.6
Ash after ion exchange	0.09	0.08	0.06	0.09	0.11

[1)] Xylose as predominant component

In general, the large polydispersity of kraft lignins contributes to a non-meltable lignin or to softening over a broad temperature range. Because the carbohydrates and some high-molecular-mass lignins were removed to a large extent during fractionation, a more homogenous lignin with a lower polydispersity and a slightly lower weight average molecular mass is expected. The fractionated lignins exhibit a more narrow distribution as compared with the unfractionated lignins (Table 8), which would contribute to a more distinct softening and would facilitate melt spinning. As expected, the use of different membrane cut-off results in a lower M_w for the 5 kDa membrane compared to the 15 kDa membrane, but has hardly any effect on the polydispersity. Both the M_w and M_n values correspond well with earlier reported molecular mass values for hardwood and softwood kraft lignins (52). The larger M_w for the softwood kraft lignins results from the structural difference, leading to a more cross-linked structure as compared with the hardwood kraft lignins.

Table 8. Average molecular masses and polydispersity for the unfractionated softwood and hardwood kraft lignins (SKL, HKL) and the permeate lignins fractionated through either 5 or 15 kDa membranes (SKLP5, SKLP15, HKLP5, HKLP15).

Molecular mass Property	**Lignin Fraction**					
	SKL	**SKLP15**	**SKLP5**	**HKL**	**HKLP15**	**HKLP5**
Weight average, M_w	4500	2900	1700	1600	1100	980
Number average, M_n	1000	580	490	440	360	320
Polydispersity	4.5	3.9	3.5	3.6	3.1	3.1

The small amount of β -O-4’ linkages together with a relatively high content of phenolic hydroxyl end-groups shown in Table 9 clearly reflects the harsh cooking conditions (i.e., time, temperature and alkalinity) required for both softwood and hardwood kraft lignins. During kraft pulping, elimination and degradation reactions in side chains remove hydroxyl groups originally present in the lignin, and hence, less than 40 % of the originally present aliphatic groups remain (53). The syringylic units present in hardwood lignins produce a higher degree of phenolic hydroxyl groups as compared with softwood lignins.

Several factors contribute to the thermal behaviour of lignins: the wood type, pulping conditions, the purification method used and the conditions in the LignoBoost process among others. The higher presence of β-O-4’ structures in softwood kraft lignin may hinder thermal motion during heating and, thus, the softening of the lignin. T_g, measured as the inflection point of the glass-transition, decreased for all lignins after fractionation, which indicates an increase in homogeneity (Table 9). In general, the T_g is higher for softwood lignins because of the more branched and cross-linked structure as compared with that of the hardwood lignins.

Understanding the lignin behaviour during heating is important to know for all the steps in the carbon fibre process. The extrusion proceeds at a temperature between the softening and the degradation temperature of the used lignin. The decomposition temperature, T_d, was gravimetrically measured when 95 % of the starting material remained. For both the softwood and hardwood lignin,

the T_d decreased after fractionation, most likely due to the loss of large-molecular-mass structures during fractionation.

Table 9. Amounts of hydroxyl groups and β-O-4' linkages together with the glass transition temperature (T_g) and decomposition temperature (T_d) for unfractionated softwood and hardwood kraft lignins (SKL, HKL) and the corresponding lignins fractionated through a 15 kDa membrane (HKLP15, SKLP15).

Property	Lignin Fraction			
	SKL	SKLP15	HKL	HKLP15
Phenolic OH, mmol/g	4.0	4.5	4.3	5.0
Aliphatic OH, mmol/g	2.3	1.8	1.7	1.3
Carboxyl, mmol/g	0.5	0.4	0.5	0.3
β -O-4, (G) µmol/g	260	300	210	130
β -O-4, (S) µmol/g	-	-	370	270
T_g (°C)	148	132	119	102
T_d (°C)	267	250	254	246

Because both the chemical and thermal properties (not shown for cut-off 5 kDa) of the fractionated lignins were similar regardless of membrane cut-off used, only the permeate lignin fractionated through the 15 kDa membrane was used for subsequent experiments. The 15 kDa membrane produces a higher yield and a lower filtration pressure drop as compared with the 5 kDa membrane and is thus more technically relevant. The samples are hereinafter denoted as SKLP and HKLP, respectively.

3.2 Thermal Behaviour of Kraft Lignins (Paper II)

During extrusion, the temperature is often approximately 200°C, and in the following stabilisation step, the temperature reached between 200-300°C. Furthermore, carbonisation is performed at temperatures higher than 1000°C. The thermal treatment of the lignin fibres causes a release of organic compounds and results in a loss in yield. Pyrolysis-GC/MS, which is a well-suited analytical tool for lignins (50, 54), was used to identify the compounds released at certain temperatures (55).

3.2.1 Identification of Released Compounds by Isothermal Pyrolysis

To obtain an overview of the differences between the identified structures between hardwood and softwood before and after kraft pulping, native milled wood lignin (MWL) from birch and spruce were compared with HKLP and SKLP by the use of isothermal pyrolysis. All the peaks identified with the use of GC/MS were quantified by calculating the relative percentage of the sum of all the peak areas.

In MWL from spruce, the two largest peak areas corresponded to coniferyl alcohol + coniferaldehyde (non-separable peaks) and vanillin; after pulping, the dominating compounds were 4-methylguaiacol and 4-vinylguaiacol. The structures are shown in Figure 13.

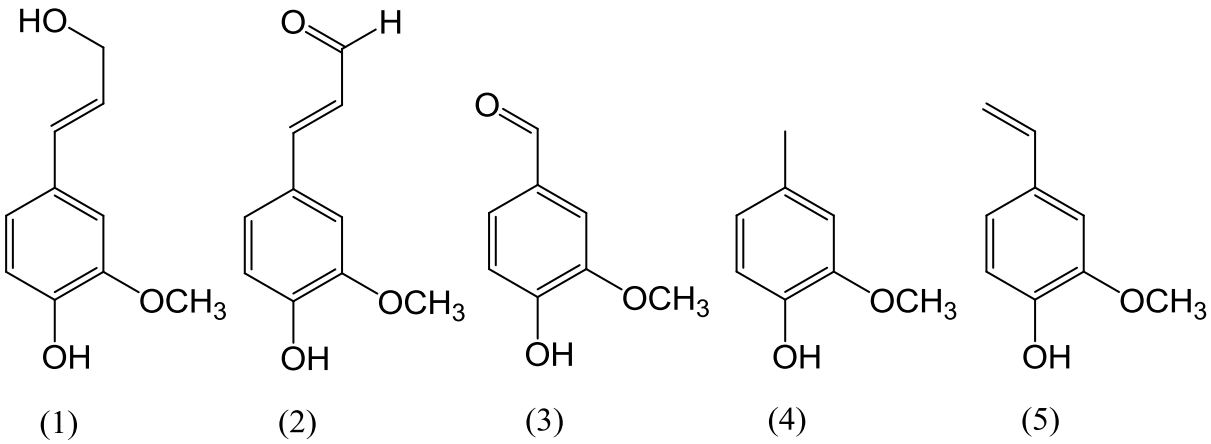


Figure 13. The largest peak areas of the relative distribution after pyrolysis at 600°C for milled wood lignin from spruce (1-3) and softwood kraft lignin (4-5). 1 = coniferyl alcohol, 2 = coniferaldehyde, 3 = vanillin, 4 = 4-methylguaiacol and 5 = 4-vinylguaiacol.

For MWL from birch (Figure 14), syringaldehyde and 4-propenylsyringol + homosyringaldehyde (non-separable peaks) were the dominating peaks, whereas after pulping, 45 % of the relative distribution consisted of syringol, 4-methylsyringol and 4-propenylsyringol + homosyringaldehyde (non-separable peaks).

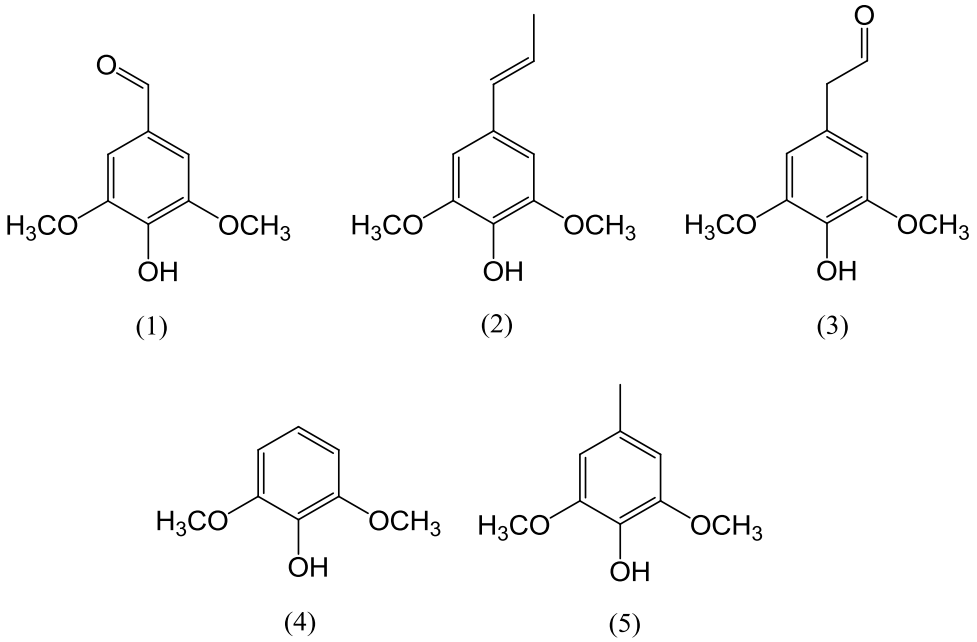


Figure 14. The largest peak areas of the relative distribution after pyrolysis at 600°C for milled wood lignin from birch (1-3) and hardwood kraft lignin (2-5). 1 = syringaldehyde, 2 = 4-propenylsyringol, 3 = homosyringaldehyde, 4 = syringol and 5 = 4-methylsyringol.

As previously demonstrated, both HKLP and SKLP lack lignin end-groups such as coniferyl (sinapyl) alcohol and conifer-(sinap-)aldehyde, which are degraded during pulping (8). The cleavage of β -O-4' linkages and the formation of phenolic end-groups during pulping could also be seen as an increase of guaiacol (softwood) and syringol (hardwood) units. In the lignin side-chain, the α-carbon atom containing oxygen (vanillin) content has decreased, and the 4-methylguaiacol and 4-methylsyringol contents have increased during pulping.

After all the pyrolysis measurements, a substantial amount of material was left on the sample holder, indicating thermally stable structures and/or charring of the lignin.

3.2.2 Step-wise Pyrolysis

To obtain more detailed information, the compounds released at a certain temperature were identified using step-wise pyrolysis on the fractionated hardwood and softwood lignins (HKLP, SKLP). These results were compared with those obtained from the step-wise pyrolysis of oxidative treated lignins. The lignin powders were oxidatively treated in an air atmosphere using a heating rate of 0.5°C/min to 250°C for 1 hour to simulate stabilisation (OxHKLP, OxSKLP). In Figure 15, the relative distribution of the products after pyrolysis is plotted for the hardwood and softwood kraft lignins before and after oxidative stabilisation. For each lignin sample, pyrolysis was performed between 200°C and 900°C at 100°C increments; however, no compounds were detected at temperatures above 700°C for any of the lignins.

Lignin Powders

The small fraction of the HKLP released at 200°C was analysed using a GC column suitable for the separation of low-molecular-mass compounds. After pyrolysis at 600°C, formation of carbon dioxide and the sulphur containing compounds methylthiol and sulphur dioxide was detected. It is well known that a small amount of sulphur is organically bonded in kraft lignins. The carbon dioxide can be assumed to be formed from carboxyl groups present in the lignin. At 350°C, no compounds were detected, and thus, the release during 200-300°C corresponds to low-molecular-mass phenols such as guaiacol. The release of bonded water by elimination of hydroxyl groups in the lignin side-chain, can also contribute to the loss in yield.

The main release of compounds occurred at 500-600°C for both HKLP and SKLP. In softwood lignin, more than half of the amount of released compounds at both 500°C and 600°C consisted of 4-methylguaiacyl and 4-ethylguaiacol (see Figure 16). Of the identified compounds, only a minor amount contains oxygen in the side-chain, which might result from the release of water during the condensation reactions. At 700°C, only a minor amount of lignin fragments (phenol and cresol) were detected for softwood lignin, indicating a more degraded lignin, and at higher temperatures, no compounds were detected.

The hardwood lignins seem to be less thermostable as compared with the softwood lignins because the release of degradation products is distributed at lower temperatures (Figure 15). One reason for this result might be that the more linear structure of hardwood lignin may be more sensitive to thermal motions. The majority of the compounds are released at 500-600°C, where syringol, 4-methylsyringyl and 4-vinylsyringol constitute approximately 60 % of the material. At 600°C, the

guaiacylic counterpart is also present to a large extent. For structural information, see Figure 16. The phenols contained the substantial amount of the compounds released at 400°C.

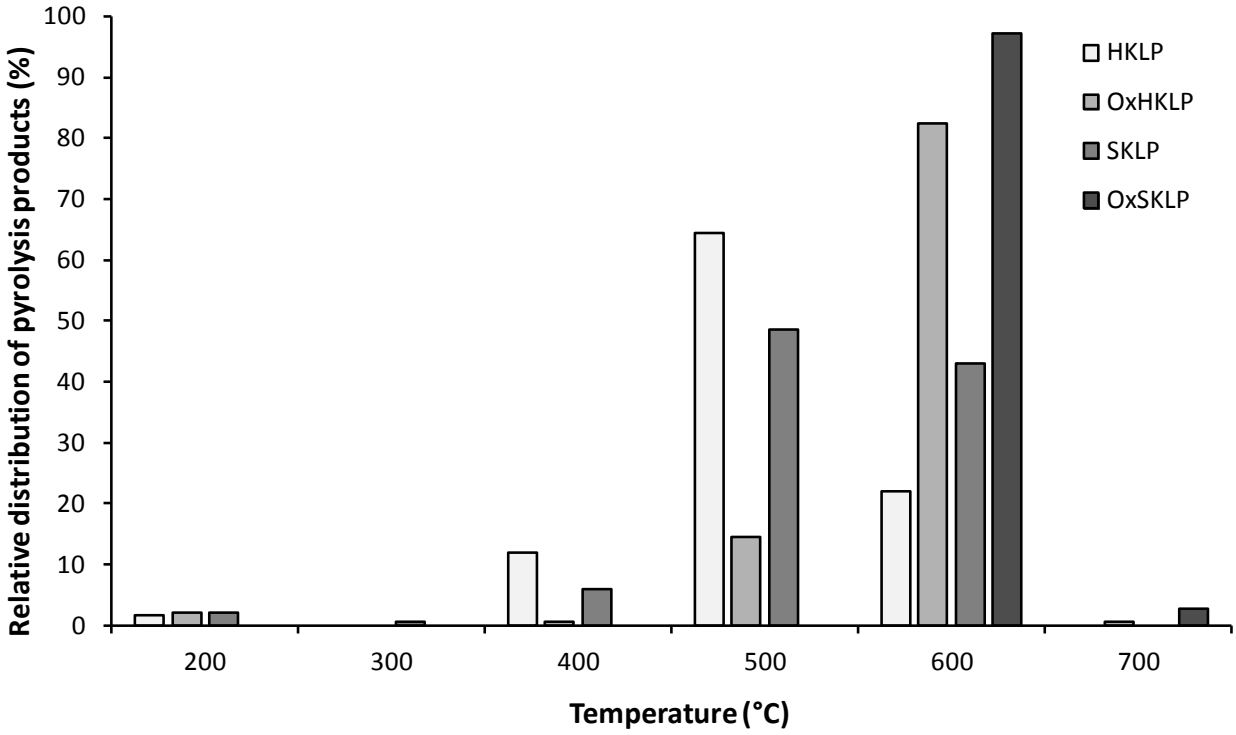


Figure 15. The relative distribution of pyrolysis products after step-wise pyrolysis of hardwood and softwood kraft lignin powders before (HKLP, SKLP) and after oxidative thermal treatment (OxHKLP, OxSKLP), respectively.

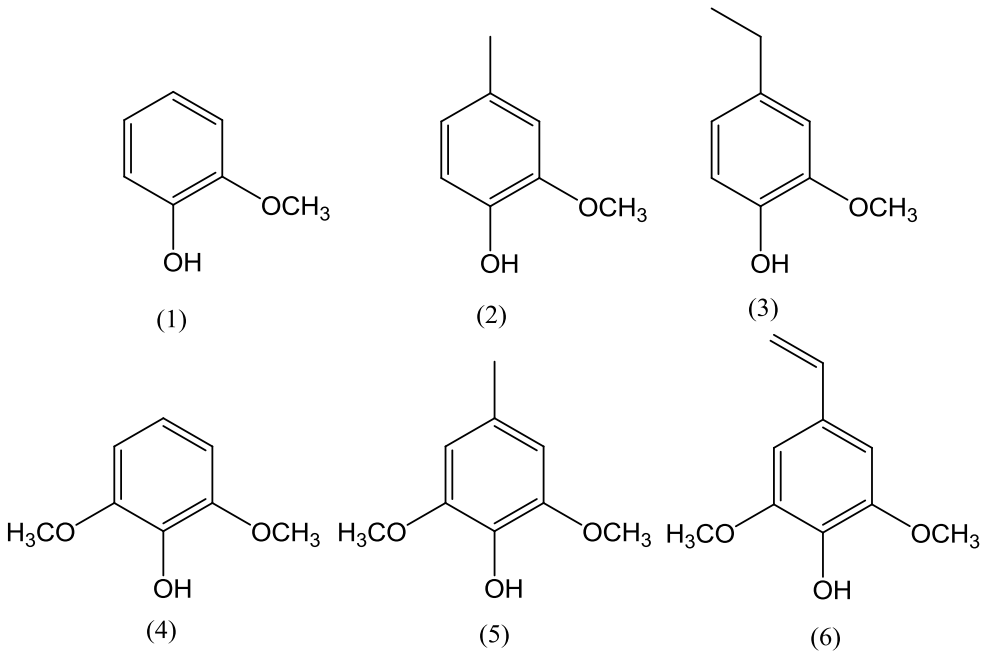


Figure 16. The dominating compounds released for softwood kraft lignins at 500-600°C (1-3) and for hardwood kraft lignins at 500°C (4-6). 1 = guaicacol, 2 = methylguaiacol, 3 = ethylguaiacol, 4 = syringol, 5 = methylsyringol and 6 = vinylsyringol.

Oxidative Thermal Treatment of Lignin Powders

The production of carbon fibre often requires an oxidative pre-treatment before the carbonisation step to hinder self-fusion of the fibre. After oxidative thermal treatment of softwood and hardwood kraft lignins, major differences were observed as compared with before oxidation. As illustrated in Figure 15, a shift towards higher temperatures of the released compounds was observed. No compounds were released below 600°C for oxidative-treated SKLP. The HKLP was less thermally stable as compared with SKLP, where a minor release of compounds was detected at 500°C (Figure 15). This result indicates an increase in thermal stability for both HKLP and SKLP after oxidative thermal treatment.

For the softwood lignin, the difference before and after oxidation is mainly the newly formed lignin fragment compounds methylphenol, phenol and toluene, together with several new oxygen-containing compounds detected after oxidation. However, the dominating compounds were still the same as those before oxidative thermal treatment: guaiacol, 4-methylguaiacol and 4-ethylguaiacol in softwood, followed by syringol and 4-methylsyringol in hardwood. At 600°C for the hardwood lignin, formation of new structures such as methylphenol and cathecol were detected, which indicate more severe degradation. 2-methylphenol and 4-methylphenol are common fragments produced upon pyrolysis of lignin (50) and have been observed in previous pyrolysis studies (56).

Before oxidation, the relative amount of lignin structures with oxygen in the side-chain were low, 3 and 8 % for softwood and hardwood, respectively. The introduction of oxygen during oxidation was mainly reflected by the compounds vanillin and acetoguaiacone in softwood and syringaldehyde and acetosyringone in hardwood (Figure 17). The relative oxygen content after oxidation was 14 and 13 % for softwood and hardwood, respectively.

In general, for both the softwood and hardwood lignins, a broader spectra of compounds was detected after oxidative thermal treatment of the lignin powders. Both the hardwood and softwood kraft lignins also became more thermally stable after oxidative thermal treatment as compared with their pre-oxidative behaviour.

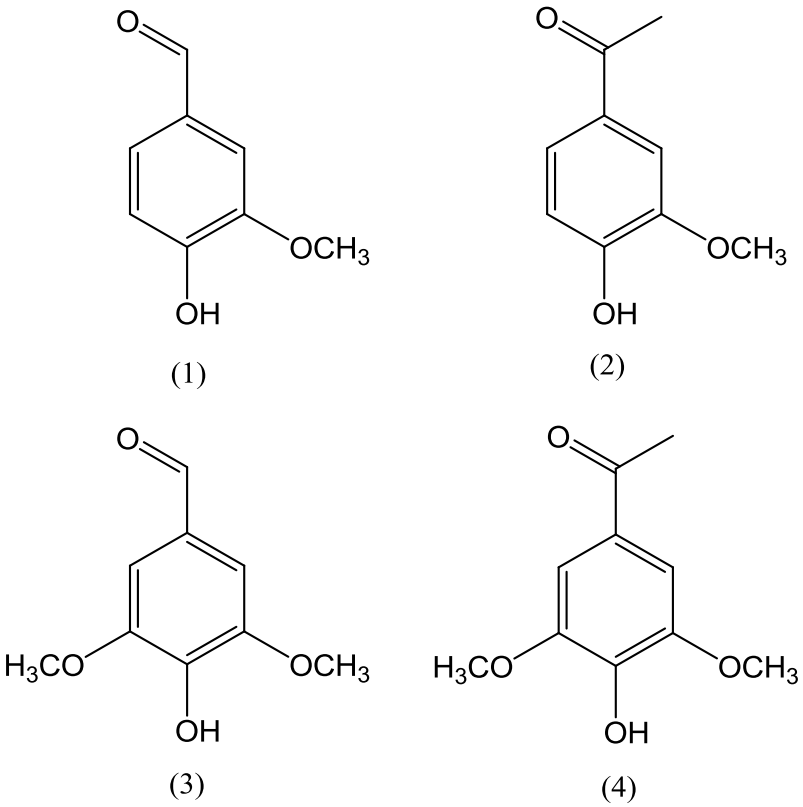


Figure 17.The oxygen containing compounds detected for softwood kraft lignin (1-2) and hardwood kraft lignin (3-4) after oxidative stabilisation to 250°C with a heating rate of 0.5°C/min and a holding time of 1 h. 1 = vanillin, 2 = acetoguaiacone, 3 = syringaldehyde and 4 = acetosyringone.

3.3 YIELD AFTER STABILISATION AND CARBONISATION (PAPERS II+III)

Stabilisation of the lignin fibre is one of the steps during production of carbon fibres that induces thermosetting properties, which prevent fusing of individual fibres in the later processing steps. Stabilisation is usually performed by slowly heating the sample to 200-350°C in an oxidising atmosphere (12, 26, 57). From an economical point of view, the yield is of importance to make the process of manufacturing carbon fibre from kraft lignin profitable.

A loss in yield does occur during the ultrafiltration step; however, this loss is not of any technical significance because the future industrial LignoBoost process with membrane separation will be completely integrated with the pulping process. However, the yield loss during the ultrafiltration step was constant because the procedure was the same for all filtrations. The dominant loss in yield during carbon fibre production occurs during the carbonisation step (58).

TGA is a useful tool for measurements of the yield and has been widely used for lignin characterisations (59, 60). The HKLP and SKLP lignins were oxidatively stabilised in an air atmosphere according to Table 10.

Table 10.The different conditions used during oxidative stabilisation of hardwood and softwood permeate kraft lignin powders (HKLP, SKLP) together with the glass-transition temperature (T_g). All lignins were oxidised in an air atmosphere except for the thermal treated lignin, which was stabilised in a nitrogen atmosphere.

Stabilisation Conditions	**Final temperature (°C)**	**Holding time (min)**	**Heating rate (°C/min)**	**T_g HKLP (°C)**	**T_g SKLP (°C)**
Untreated lignin	-	-	-	102	132
"Mild" oxidation	230	30	1.0	128	169
"Medium" oxidation	255	1	0.6	139	198
"Harsh" oxidation	280	2	0.2	n.d.	n.d.
Thermal treatment	280	2	0.2	-[1]	-[1]

n.d. = not detected, [1]not measured

In line with earlier studies on the change of T_g at different heating rates (26), the T_g increased at slower heating rates and "harsher" stabilisation conditions. At the harshest conditions, no T_g could be detected, which is an indication of complete stabilisation. The yield after the stabilisation step was gravimetrically measured ($Y_{treated}$) and compared with the yield after carbonisation to 1000°C with a heating rate of 15°C/min as determined with TGA ($Y_{1000°C}$) (see Figure 18). For all the lignin types, the $Y_{treated}$ decreased as the conditions during the stabilisation step became harsher, which was expected. The harshest condition resulted in a final temperature near the decomposition temperature of the lignin, and mass loss was already evident.

Of the parameters used during stabilisation (final temperature, heating rate and holding time), the most important parameter for increasing the yield was observed to be the holding time. This finding implies that a small change in the holding time might produce large effects on the yield. The $Y_{1000°C}$ has almost the opposite result on the yield (see Figure 18). For all the lignins used, a mild oxidative stabilisation produces hardly any improvement in the final yield.

For the hardwood lignins, the harshest oxidative stabilisation condition (250°C, 0.2°C/min, 2 h) produces the largest improvement in the yield after carbonisation. This result indicates that the introduction of oxygen in the lignin structure makes the lignin more thermally stable. However, achieving fully stabilised fibres is still more important than achieving the highest yield.

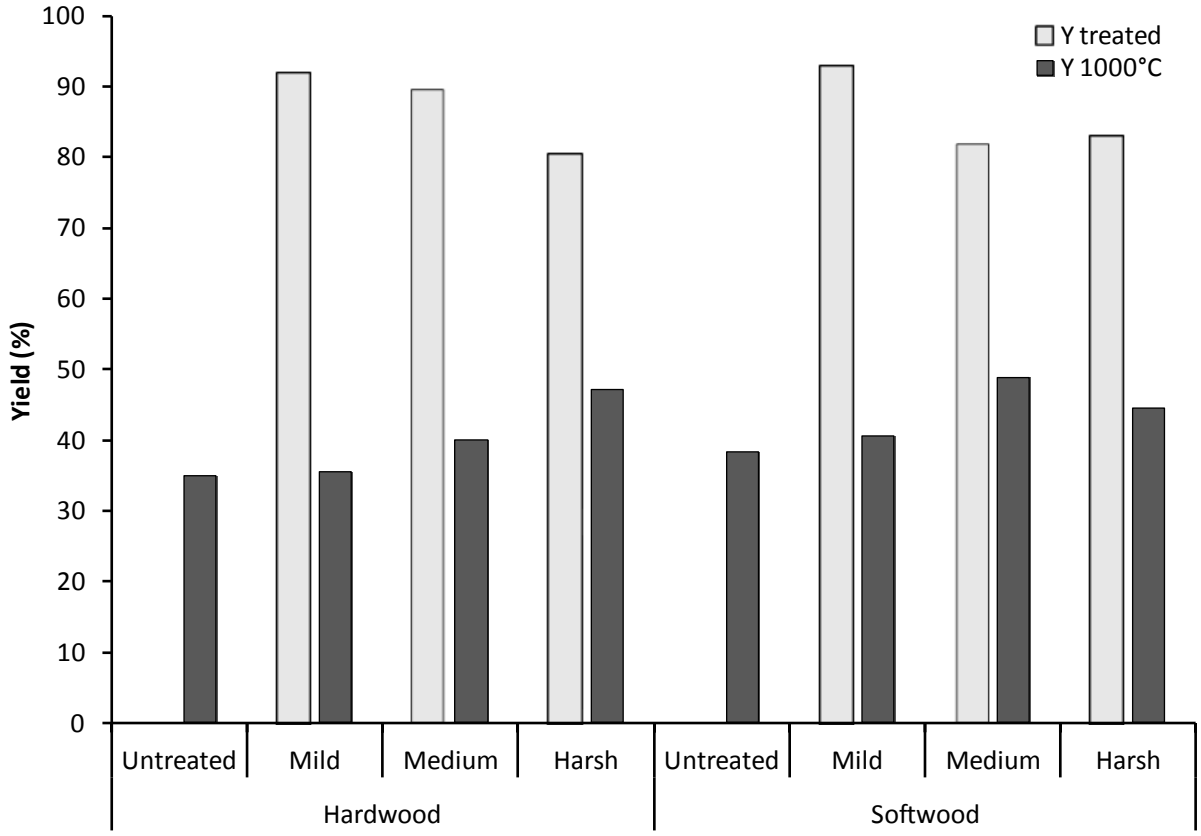


Figure 18. The yield after oxidative stabilisation at various conditions (Y treated) and after TGA measurement at 1000°C (Y 1000°C) for hardwood and softwood permeate kraft lignin powders. Both the untreated lignins and oxidative stabilised lignin powders at different conditions were analysed. For the oxidative stabilisation conditions, see Table 10.

For comparison with the oxidative stabilised lignins, the softwood lignin was also thermally stabilised in a nitrogen atmosphere at a heating rate of 0.5°C/min to 250°C for 60 minutes to examine the thermal influences. In Figure 19, the weight loss at temperatures between 100-800°C is plotted for SKLP. The mass loss during the stabilisation step is included in the graph as a lower starting yield. No loss of material was observed at temperatures below 300°C for the stabilised lignins, which indicates an increase in thermal stability after stabilisation.

The carbon content of the original kraft lignins was approximately 60 % as revealed using elemental analysis. The yield after heating SKLP to 800°C was approximately 40 %, which indicates that a certain loss of material occurs during heating. Thermal stabilisation in a nitrogen atmosphere demonstrated that the final mass loss after heating to 800°C is approximately the same as that for the untreated lignin. For the oxidative-stabilised lignin, however, the yield at 800°C increased by 10-20 % as compared with that of the untreated lignin (see Figure 19). The trend is the same for both HKLP and SKLP. The main weight loss occurs between 300°C and 600°C.

Thus, oxidative stabilisation appears to be a possible approach to increase the yield when manufacturing carbon fibre from kraft lignin.

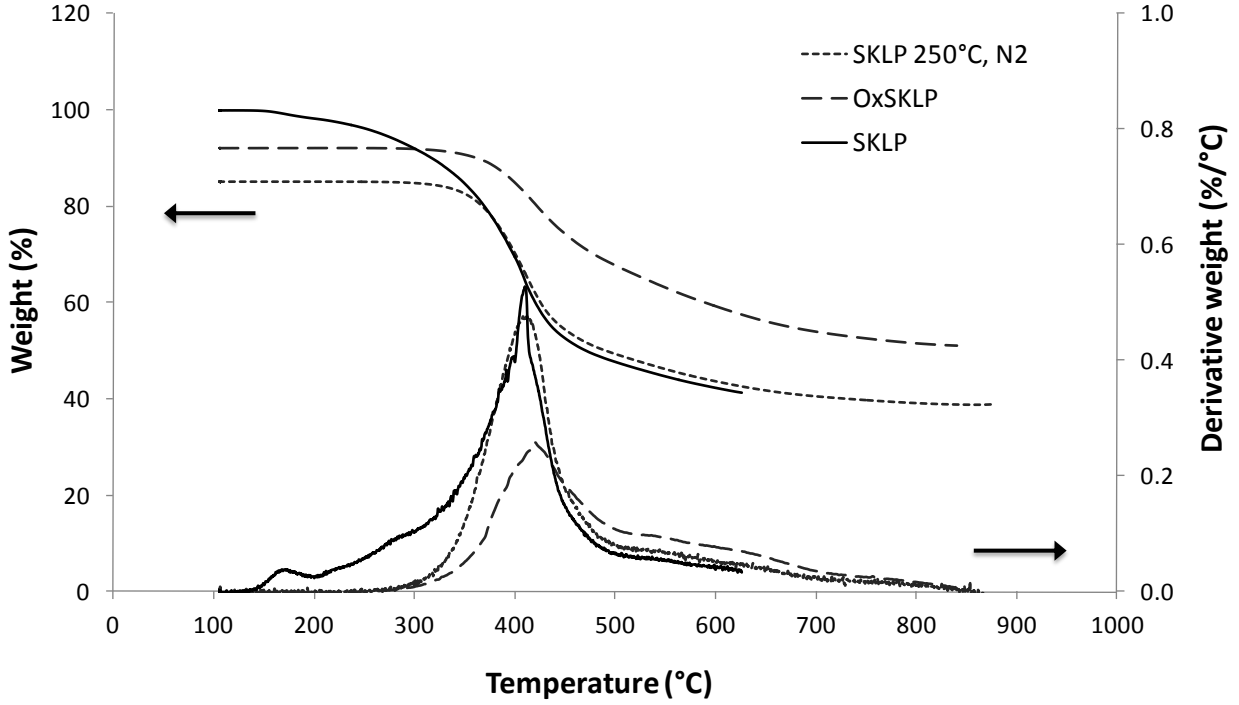


Figure 19. Mass losses for SKLP measured by TGA before and after stabilisation in an oxygen and nitrogen atmosphere. The conditions during the thermal treatment were 0.5°C/min to 250°C for 60 min, and the yield loss during this step is included in the figure.

3.4 Characterisation of Oxidatively Stabilised Hardwood Kraft Lignins (Paper III)

Both XPS analysis of PAN-based carbon fibres (61) and of lignins (26) has proved to be useful for surface analysis with respect to structural changes during material modifications. To observe structural changes between the HKLP powder, HKLP fibre and stabilised HKLP powder and fibre, the XPS analysis was used (62). The effect of the thermal treatment on the lignins was evaluated by estimating the C1 (carbon) and O1 (oxygen) spectral lines. High-resolution spectra of HKLP powder and HKLP powder thermal treated in the absence of oxygen and "harsh" oxidative thermally treated HKLP powder are presented in Figure 20. The different carbon peaks with no, one, two or three bonds to oxygen, C1-C4 (defined in Table 6) are defined according to Beamson and Briggs, and the peaks with binding energies higher than C4, 290.5-294 eV, are shake-up peaks that indicate the presence of aromatic groups (63). For all the elements detected, carbon and oxygen were the main components, at 72-81 % and 18-26 %, respectively, and as is typical in kraft lignins, approximately 1 % sulphur was detected.

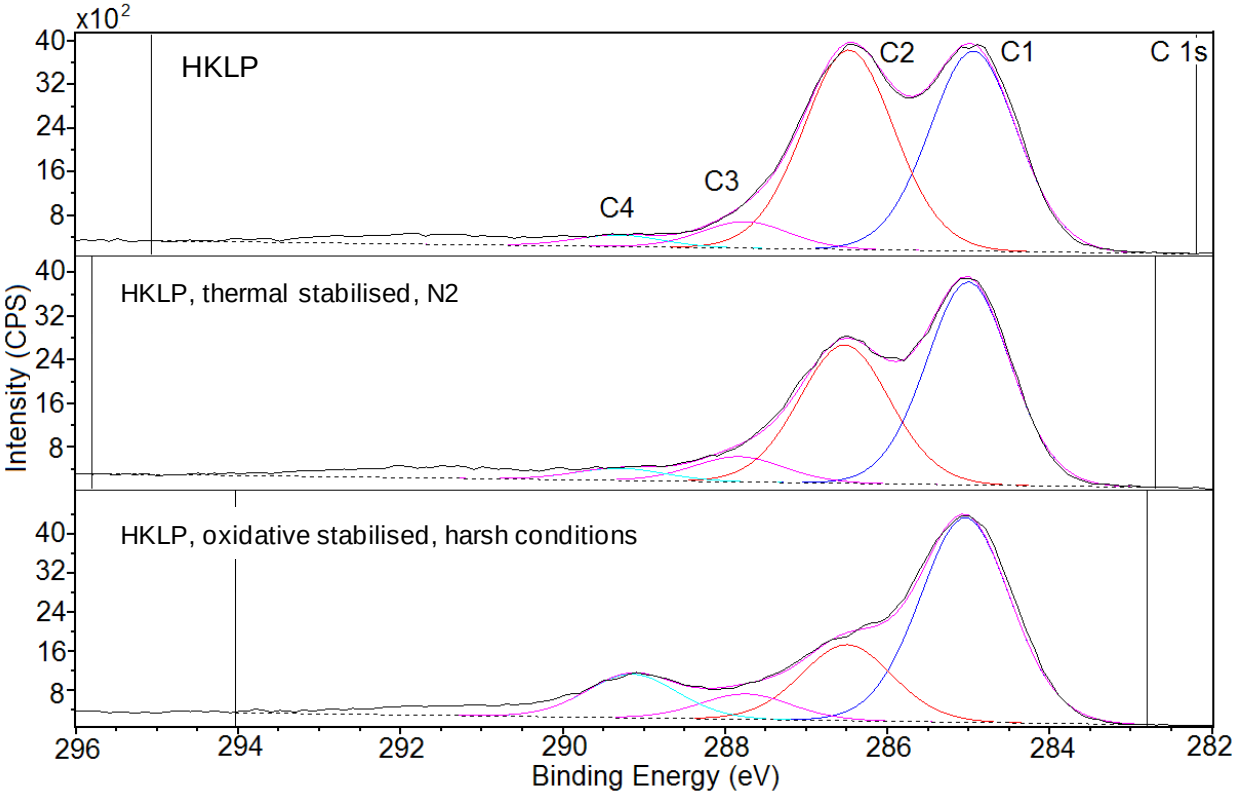


Figure 20. High-resolution spectra of hardwood kraft lignin permeate (HKLP), thermal-stabilised HKLP and harsh oxidised HKLP. For stabilisation conditions, see Table 10. C1 = no bond to oxygen, C2 = one bond to oxygen, C3 = two bonds to oxygen, C4 = three bonds to oxygen.

As discussed in section 1.2.4, the reactions during oxidative stabilisation of lignins have been demonstrated to include mainly oxidative, radical and rearrangement reactions (26). After thermal stabilisation in the absence of oxygen (see Figure 20), a slight decrease in the C2 carbon with one bond to oxygen can be observed. The same trend can be observed after mild oxidation (spectra not shown). The decrease in the C2 carbon can be explained by a rearrangement reaction on the β-carbon (64), illustrated in Figure 21, initiated by the well-known homolytic cleavage of the β-O-4' bond (Figure 10). However, mild oxidation and thermal stabilisation produces similar changes in the lignin structure. After harsh oxidation conditions, a larger decrease in the C2 carbons was observed at the same time as the C4 carbons with three bonds to oxygen increased. This result indicates that an introduction of esters and/or carboxylic bonds into the lignin structure occurs (see Figure 21). The C3 carbon (e.g., aldehyde) is similar during all the oxidation conditions, which can be explained by a rapid further oxidation to C4 carbon (e.g. carboxyl acid).

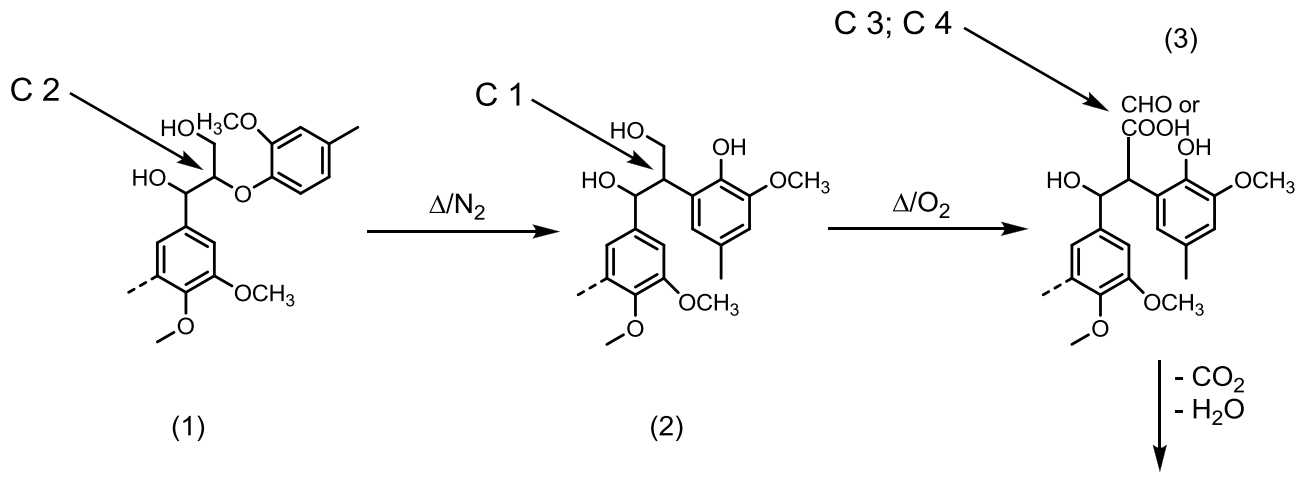


Figure 21. Possible reactions that occur in lignin during oxidative stabilisation.

Oxidative stabilisation using the harsh conditions with a heating rate of 0.2°C/min to 280°C for 2 h, as shown in Table 10, was also performed on a lignin fibres obtained from melt spinning of HKL with the addition of 5 % PEO. To verify the homogeneity of the oxidative stabilisation, a cross-section of a fibre stabilised using the harsh conditions was analysed using XPS. The diameter of the fibre used was approximately 100 µm, and the cross-section was measured at three different locations: on the surface (Pt1), near the surface (Pt2) and in the core of the fibre (Pt3) (see Figure 22).

The carbon content (relative %) for the fibre before and after harsh oxidation is also reported in Figure 22; the same trend on the surface as for the stabilised powders was observed (increase in C1 and C4 and decrease in C2). For the fibre cross-section, differences between the surface (Pt1) and the core of the fibre (Pt3) were observed, indicating an inhomogeneous stabilisation and formation of a so-called skin-core structure. The core (Pt3) was still quite similar as compared with before stabilisation, even though an increase in the C1 carbon content occurred.

Stabilisation of pitch fibres with the presence of oxygen has been demonstrated to involve competition between chemical reactions on the fibre surface and diffusion reactions penetrating into the core of the fibre, sometimes leading to the formation of a so-called skin-core structure (24). The surface chemical reactions are faster as compared with the diffusion, and the oxidation of the surface prevents the oxygen from further diffusion and thereby reaction in the interior of the fibre.

The largest change observed in the fibre after harsh oxidation was the decrease of C2 carbons on the surface (Pt1). This result clearly demonstrates that the diffusion distance (the diameter of the fibre) affects the chemical composition and thereby the homogeneity of the stabilisation of a hardwood kraft lignin fibre. The formation of a skin-core structure after oxidative stabilisation has also been observed for pitch-based fibres (24), which is caused by the chemical reactions on the surface of the fibre that prevent the diffusion reactions from further penetrating into the core of the fibre. The effect of the skin-core structure are not known; however, it may have a negative impact on the carbonisation and graphitisation steps in the carbon fibre process and thereby on the mechanical properties of the final carbon fibres.

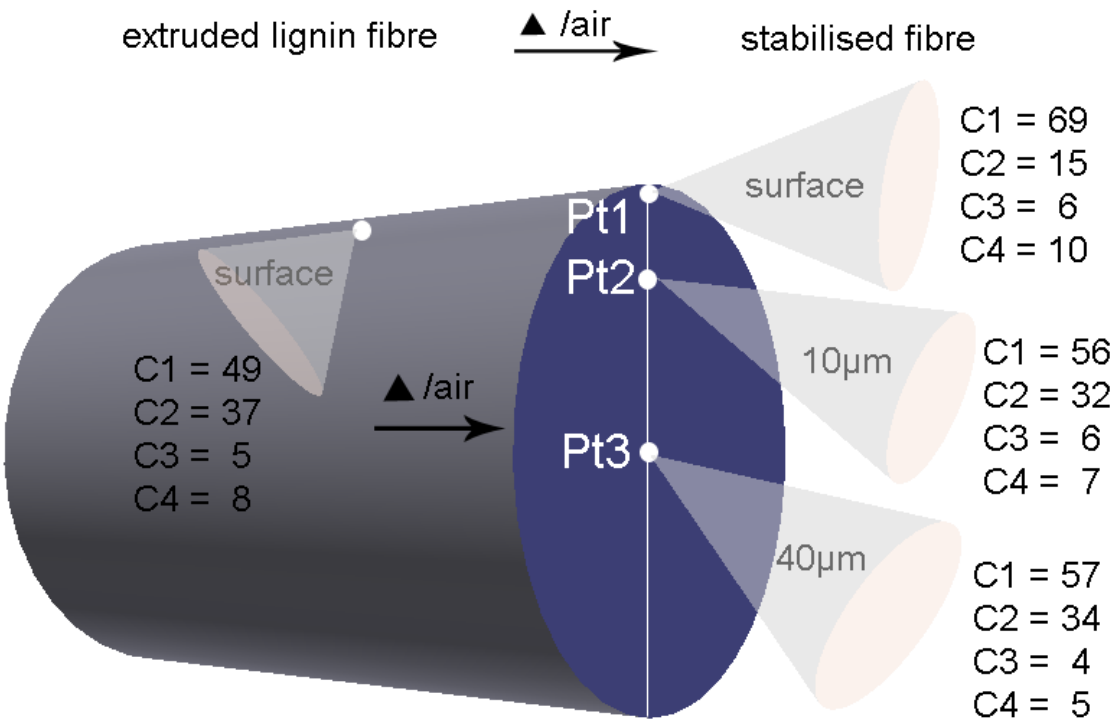


Figure 22. The XPS analysis of a hardwood kraft lignin fibre with the addition of 5 % PEO before and after harsh oxidative treatment (0.2°C/min, 280°C, 2 h). C1-C4 are explained in Table 6.

3.5 Stabilisation of Softwood Kraft Lignin Fibres (Paper IV)

The difference in structure between softwood and hardwood is assumed to cause different behaviour in the stabilisation step. SKL has a more branched and cross-linked structure as compared with HKL. In addition, the amount of guaiacyl units is higher than HKL, which may lead to a faster stabilisation procedure for SKL. Furthermore, the relatively high oxygen content in the SKL structure as compared with petroleum pitch and PAN might be sufficient for stabilisation using only heat. Spinning of softwood-based lignins has been demonstrated to be very difficult (25); however, SKLP or the addition of HKLP as a softening agent to the SKL has enabled continuous fibre spinning (65). In this section, the stabilisation behaviour of SKLP fibres and SKL+10 % HKLP fibres is investigated using thermal and oxygen conditions together with various heating rates and holding times.

3.5.1 Evaluation of Thermal Properties after Stabilisation

For the first time, stabilisation of softwood-based fibres could be achieved in the absence of oxygen. After stabilisation, the fibres were evaluated with respect to their inter-fibre separation, fusion tendency and T_g. Hereinafter, stabilisation in an air atmosphere and stabilisation in a nitrogen atmosphere are referred to as oxidative stabilisation and thermal stabilisation, respectively.

Table 11 lists the fastest performed thermal and oxidative stabilisation conditions. The fastest possible thermal stabilisation was performed using pure SKLP at a heating rate of 4°C/min. This rate

is faster than for the HKL-based lignin fibres, which have been reported to require a stabilisation of 0.2°C/min to maintain good fibre formation without the fibres sticking together (26). Thermal stabilisation was also possible at a heating rate of 1°C/min for fibres made using an addition of HKLP to SKL. This process is slower as compared with pure SKLP, which most likely is due to the presence of HKLP, which is less reactive. In general, an increasing amount of softening agent has been observed to decrease the T_g and, at a certain blending ratio, makes the blend unsuitable for stabilisation because of fibre fusing (19, 66).

The fastest successful stabilisation was performed using oxidative stabilisation of SKLP, and a good fibre form with intact, separable fibres was obtained. A heating rate of 15°C/min was used in combination with a holding time of 30 min at 250°C, resulting in a total stabilisation time of 45 min (Table 11). This rate is remarkably faster as compared with the standard method used for HKL-based lignins, 0.2°C/min.

T_g could not be detected for any of the oxidatively and thermally stabilised SKLP fibres, which indicates fully stabilised fibres. For the thermally stabilised SKL+10 % HKLP, a T_g was obtained. Even though it was higher as compared with that before stabilisation, it is an indication of incomplete stabilisation. However, in the evaluation after the stabilisation procedure, intact and separable fibres that were not fused together were observed.

Table 11. The conditions used during stabilisation of fractionated softwood kraft lignin (SKLP) fibres and softwood kraft lignin with addition of fractionated hardwood kraft lignin (SKL+HKLP) fibres. The glass-transition temperature (T_g) for each lignin fibre and stabilised fibre is also reported.

Type of fibre	Atmosphere	Heating rate (°C/min)	Holding time at 250°C (min)	Total time (min)	T_g (°C)
SKLP lignin fibre	-	-	-	-	140
SKL+10 %HKLP lignin fibre	-	-	-	-	138
SKLP	Air	0.2	60	1185	n.d.
SKLP	Air	15	30	45	n.d
SKLP	Nitrogen	4	30	86	n.d
SKL+5 %HKLP	Air	0.2	60	1185	n.d.
SKL+10 %HKLP	Air	0.2	60	1185	182
SKL+10 %HKLP	Air	3	30	105	n.d
SKL+10 %HKLP	Nitrogen	1	30	255	195

n.d. = not detected

3.5.2 Characterisation of Stabilised Softwood Kraft Lignins

In section 3.4, the structural changes for HKL during oxidative stabilisation were discussed. In this section, the chemical reactions and the structural changes of both oxidative and thermal stabilisation of SKLP are investigated using FTIR and CP/MAS ^{13}C-NMR as analytical tools. These techniques are commonly used for the analysis of lignins (26, 67-69). In this study, SKLP powder was compared with SKLP fibre using one thermally stabilised SKLP fibre (10°C/min, 250°C, 60 min) and one oxidatively stabilised SKLP fibre (0.2°C/min, 250°C, 60 min).

In Figure 23, CP/MAS ^{13}C-NMR spectra are presented for SKLP together with oxidatively stabilised and thermally stabilised SKLP fibres, respectively. The spectra are normalised at the methoxyl signal (55 ppm), which has been observed to be stable under thermal conditions at temperatures up to 250°C (68, 70). The elemental composition determined for the oxidative-treated kraft lignin powders (SP15) was also observed to contain approximately the same amount of methoxyl groups as for untreated lignin powders (see Table 12).

Table 12. The elemental composition of fractionated softwood kraft lignin (SKLP) powder after oxidative stabilisation in air and thermal stabilisation in nitrogen atmosphere. The stabilisation program was 0.5°C/min to 250°C and a holding time of 60 min.

Sample	**Elemental composition[a]**
SKLP	$C_{8.5}H_{7.4}O_{1.9}S_{0.09}(OCH_3)_{0.9}$
SKLP; under N_2	$C_{8.5}H_{6.3}O_{1.5}S_{0.05}(OCH_3)_{0.8}$
SKLP; under air (O_2)	$C_{8.5}H_{6.3}O_{1.8}S_{0.08}(OCH_3)_{0.8}$

[a] Based on the assumed number of 8.5 carbons in an average lignin monomer unit, cf. (53).

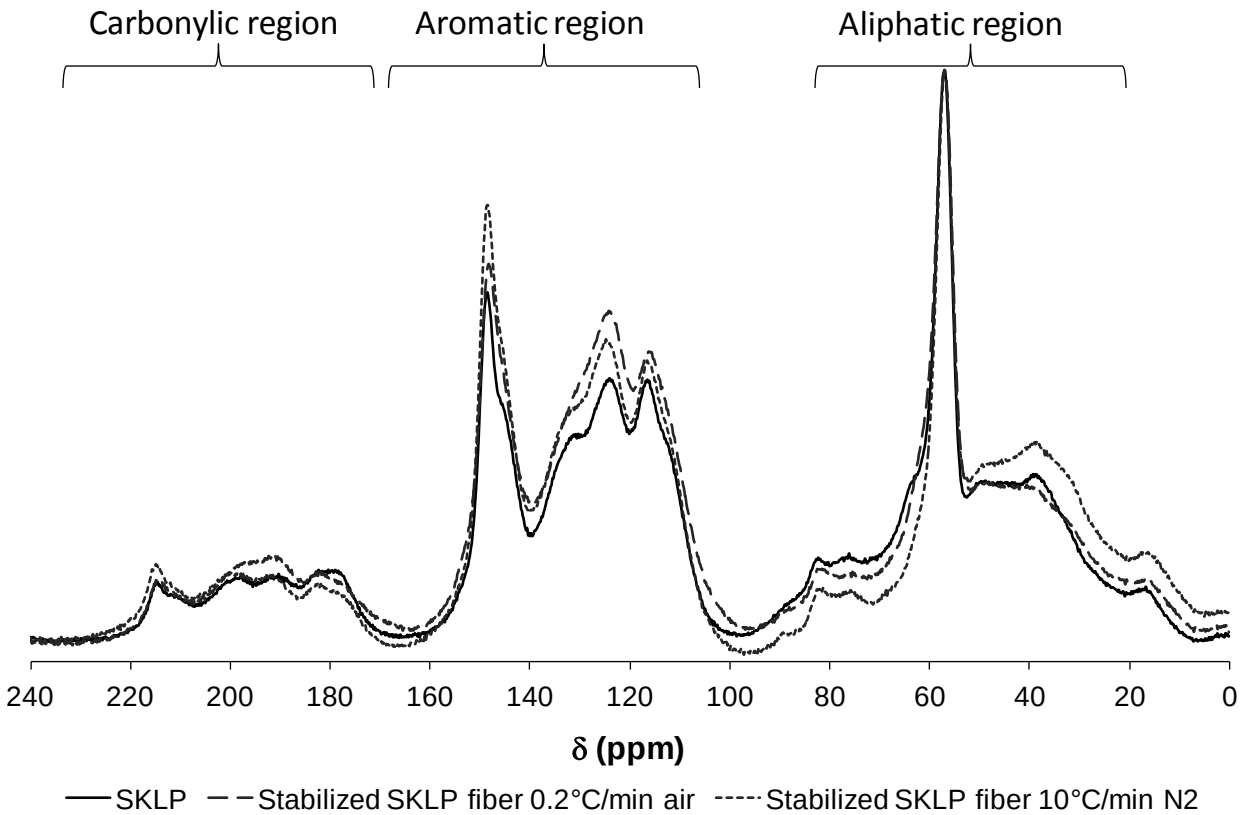


Figure 23. CP/MAS ^{13}C-NMR spectra for fractionated softwood kraft lignin (SKLP) and SKLP fibre after stabilisation in an air and nitrogen atmosphere, respectively.

However, the NMR spectra indicated that structural changes occurred during stabilisation. In the aliphatic region in Figure 23, the carbon linked to oxygen (65-90 ppm) decreased at the same time as the carbon linked to carbon (25-50 ppm) increased after stabilisation. This result indicates a possible cleavage of the β-O-4-linkages and a possible rearrangement reaction as illustrated in Figure 21, reaction (1-2). In the aromatic region, an increase is observed at approximately 110-130 ppm, which might result from an increase in olefinic carbons by formation of a stilbene structure and loss of water (Figure 24).

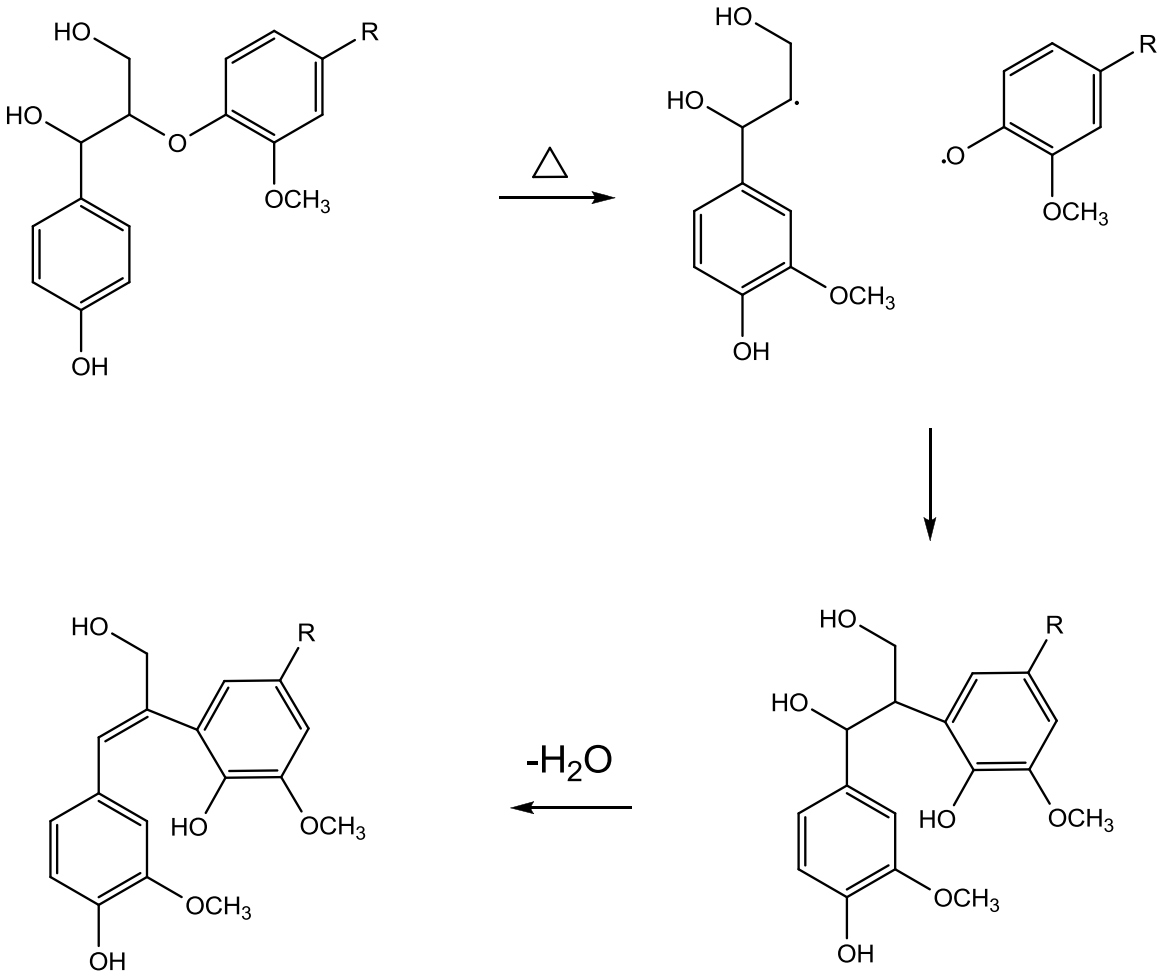


Figure 24. One possible reaction of softwood kraft lignins during heat treatment. The homolytic cleavage of the β–O-4' linkage is followed by a rearrangement reaction and formation of a stilbene structure by loss of water.

Earlier studies on the pyrolysis of technical lignins have demonstrated that the major changes in the structure occur at temperatures above 350°C, including mainly radical reactions in the side-chain and in the methoxy groups on the aromatic ring (68, 69). In Figure 25, FTIR spectra for SKLP are compared with those of SKLP fibres before and after oxidative and thermal stabilisation, respectively. After spinning, hardly any changes in the spectra are observed, which indicates small changes in the lignin structure during melt spinning at the used spinning conditions. The trend was the same for the NMR spectra (not shown) as well as for T_g, which was the same before and after spinning. After stabilisation, a new peak at 1384 cm^{-1} appeared, which might represent the formation of a new phenolic hydroxyl group during radical or rearrangement reactions (see Figure 21 reaction (1-2)). The aromatic C–H stretching (780-860 cm^{-1}) changed after stabilisation, which is an indication of cross-linking reactions at the C5 position on the aromatic ring during stabilisation. In all the spectra, a C=O stretch (1715 cm^{-1}) is observed, which might be explained by autoxidation reactions.

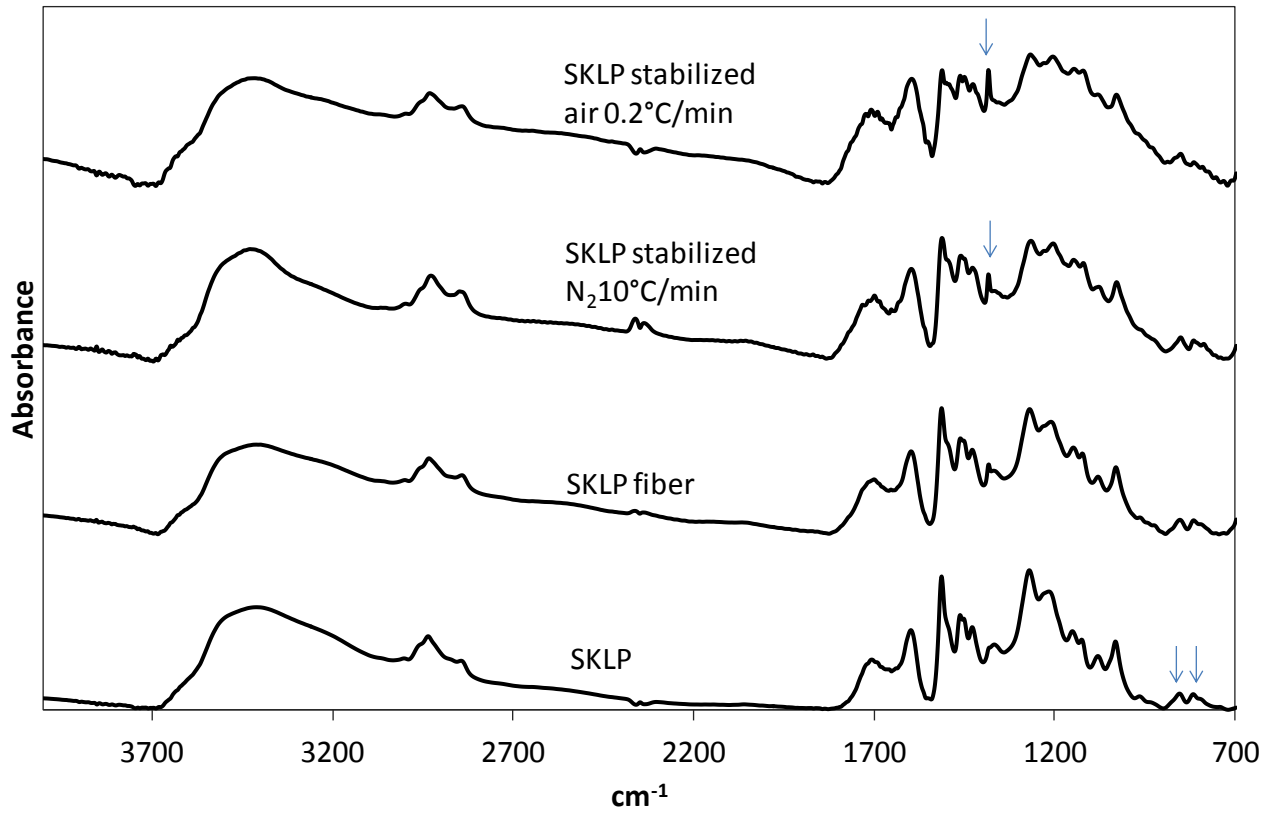


Figure 25. FTIR spectra for fractionated softwood kraft lignin (SKLP) and SKLP fibre and SKLP fibre after stabilisation in air and under a nitrogen atmosphere, respectively.

3.6 CARBONISATION (PAPER IV)

3.6.1 Carbonisation of stabilised softwood kraft lignin fibres

All the fibres described in Table 11 exhibited solid and homogenous cross-sections after carbonisation, regardless of the stabilisation conditions used. The definition for a carbon fibre requires a carbon content of >90 %, which was achieved for all the fibres described in Table 11. A carbon content of approximately 96 atomic % was detected in the cross-section for all fibres. The elements after carbonisation of the SKLP fibre are shown in Table 13. On the cross-section, only carbon, oxygen and sulphur was detected, which shows a pure carbon fibre. On the outer surface on the other hand, the carbon content was only 85.8 atomic %, which indicates an oxidation on the carbon fibre surface occurring during storage of the fibre after carbonisation. The small amount of inorganic elements is assumed to be ash or "particles" entering the fibre after carbonisation.

An ESEM picture of a SKLP-carbonised fibre that was oxidatively stabilised using the fastest possible conditions (15°C/min, 250°C, 30 min) is presented in Figure 26. The outer surface was smooth, except for some irregularities originating from the die in the fibre spinning process.

Table 13. The detected elements after carbonisation of softwood kraft lignin permeate (SKLP) fibre stabilised at a heating rate of 15°C/min to 250°C for 30 minutes in air.

Element	Surface (atomic %)	Cross-section (atomic %)
C	85.8	96.5
O	11.6	2.6
Na	0.4	-
Si	0.2	-
S	1.6	0.9
Cl	0.1	-
K	0.4	-

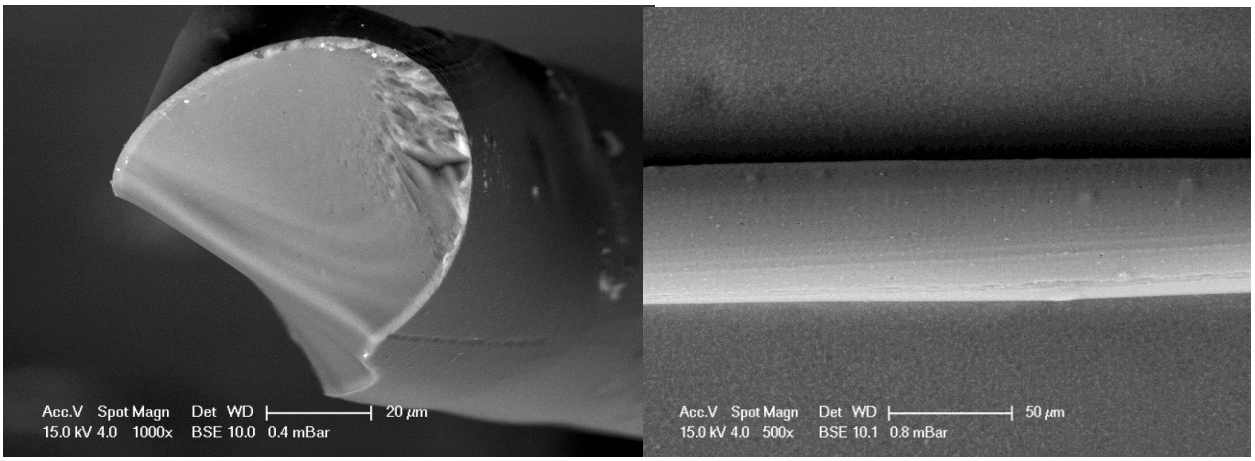


Figure 26. ESEM pictures of carbonised softwood kraft lignin permeate (SKLP) fibre stabilised at a heating rate of 15°C/min to 250°C for 30 minutes in air. The cross-section is shown to the left and the outer fibre surface to the right.

3.6.2 Stabilisation and Carbonisation in a One-step Operation

The carbon fibre process would be faster and more effective if the stabilisation step could be omitted. Successful thermal stabilisation of SKL-based fibres enabled the performance of an experiment where the stabilisation and carbonisation occurred in a one-step operation in a nitrogen atmosphere. After such experiments using both SKLP and SKL+10 %HKLP fibres, smooth and homogenous fibres that did not stick together were obtained. The carbon content was >90 %. These results indicate that it is possible to perform the stabilisation and carbonisation step in a one-step operation.

4 CONCLUSIONS

Carbon fibres have been produced from kraft lignins originating from both softwood (spruce/pine) and hardwood (birch/aspen). Fractionation with respect to molar mass of the kraft lignins was observed to produce more homogenous lignin. This finding enabled continuous melt spinning of the fractionated kraft lignin into fibres, either as such or as a softening agent for unfractionated lignin.

Oxidative stabilisation makes the fractionated kraft lignins more stable against thermal degradation and, hence, improves the yield of carbon fibres after carbonisation. After oxidative stabilisation, an increase of oxygen in the lignin structure was detected.

Softwood kraft lignin fibres can be oxidatively stabilised 26 times faster than hardwood kraft lignin fibres. A heating rate of 15°C/min and a holding time of 30 min at 250°C were used to achieve separable fibres with good fibre formation.

For the first time, thermal stabilisation in a nitrogen atmosphere was successfully performed on softwood kraft lignin fibres. Both pure fractionated softwood kraft lignin fibres and fibres of softwood kraft lignin with an addition of 10 % fractionated hardwood kraft lignin were stabilised and further processed into carbon fibres. Furthermore, stabilisation and carbonisation in nitrogen atmosphere in a one-step operation was successfully performed. This result opens the possibility of omitting the stabilisation step in the carbon fibre process through the use of softwood kraft lignin as a precursor.

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