PRECIPITATION AND VALORISATION OF LIGNIN OBTAINED FROM SOUTH AFRICAN KRAFT MILL BLACK LIQUOR

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Submitted in fulfilment of the academic requirements of Doctor of Philosophy in the
field of Chemical Engineering, School of Engineering,
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EXAMINERS COPY

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DECLARATION 2: PUBLICATIONS

List of Publications

Paper I: M. Namane, B.B. Sithole, D Ramjugernath, Centrifugal washing and recovery as an improved method for obtaining lignin precipitated from South African kraft mill black liquor, Journal of Scientific and Industrial Research, 74 (2015) 571-576.

Paper II: M. Namane, F. García-Mateos, B.B. Sithole, D. Ramjugernath, J. Rodríguez-Mirasol, T. Cordero, Characteristics of lignin precipitated with organic acids as a source for valorisation of carbon products, Cellulose Chemistry and Technology, 50 (3-4) (2016), In Press.

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Author's contributions:

Paper I: Designed and performed the experimental work, analysis, and writing of the manuscript. Suggestions were provided by B. Sithole and D. Ramjugernath.

Paper II: Designed and performed the experimental work, as well as analysis with assistance from F. García-Mateos and T. Cordero. I wrote the manuscript with suggestions and contributions from F. García-Mateos, T. Cordero, and B. Sithole.

Paper III: Designed and performed the experimental work and the analysis with assistance from F. García-Mateos and T. Cordero. I wrote the manuscript together with F. García-Mateos. Suggestions were provided by T. Cordero, B Sithole, and D. Ramjugernath

Other Related Publications

See Appendix C

Precipitation and valorisation of lignin in South African kraft mill black liquor – First stages
M. Namane, B.B. Sithole, D. Ramjugernath
Tappsa National Conference, October 22-23, Durban South Africa (2013). Poster presentation

Precipitation and characterisation of lignin obtained from South African kraft mill black liquor
M. Namane, B. Sithole, D. Ramjugernath
10th International Conference on Renewable Resources and Biorefineries, June 04-06, Valladolid Spain (2014). Poster presentation

Precipitation and characterisation of lignin obtained from South African kraft mill black liquor
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Characteristics of lignin precipitated with organic acids as a source for valorisation carbon products
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ABSTRACT

Lignin is a phenolic, carbon-rich, heterogeneous polymer that has, in recent years, become a focus of research in the biorefinery field, as a potential source of chemicals, energy and materials. Generally, research on lignin in the biorefinery field mainly focuses on three aspects: understanding lignin and its chemistry; the forms in which it can be extracted/obtained from biomass or processing liquids, and ultimately: its valorisation into valuable compounds or materials.

The pulp and paper industry kraft mill process produces a byproduct called black liquor, which contains lignin. In this form, lignin in the black liquor is processed in recovery operations where it is utilised as a source of energy for mill processes. However, it has become increasingly evident that this is an underutilisation of an important source of carbon. Additionally, kraft mills have limited capacity in their recovery operations and thus cannot process all the liquor. Hence there are opportunities to use the excess black liquor to collect lignin for use in biorefinery operations. Although biorefinery research is well-established, it has not received much attention in the South African context, which has prompted this research into valorisation of lignin in South Africa.

In this thesis, the isolation and recovery of lignin from kraft mill black liquor was examined, an in-depth characterisation of the polymer was undertaken, and finally, a method for the potential valorisation of the lignin from a South African kraft mill was established. Lignin was precipitated from kraft mill black liquor by utilising sulphuric acid and three organic acids (acetic, citric, and formic acids). During recovery of the lignin, it was noticed that recovery of the precipitated lignin was a long and tedious process, as has been reported in the literature. Consequently, a novel method for overcoming this limitation was developed. The recovery of the polymer was achieved by the newly developed stepwise centrifugal recovery and washing method. The method was optimised to achieve comparable yields to utilising filtration immediately after precipitation.

The precipitated lignin was characterised by a number of techniques, viz., Fourier transform Infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), size exclusion chromatography (SEC), and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). SEC data revealed a narrow molecular weight distribution with a small polydispersity index in the lignin sample – all desirable features for the further valorisation of

the lignin samples. Results from FTIR and NMR data showed the presence of both syringyl and guaiacyl functional groups thus confirming that the wood furnish used was a mixture of softwood (Pine) and hardwood (Eucalyptus). Py-GC/MS data was used to glean information on potential compounds that could be obtained via pyrolysis of the lignins: the major compounds that were identified were guaiacol compounds.

Further studies on lignin precipitation were conducted on black liquors obtained from separate softwood and hardwood pulping at the mill. The studies were to evaluate and compare precipitation of lignin by acidification with sulphuric acid, versus acidification with organic acids, viz, acetic, citric, and formic acids. Precipitation of lignin with organic acids can be considered as a novel ‘green’ alternative to utilising sulphuric acid as a precipitating agent.

The centrifugation recovery and washing method was optimised utilising all four acids and the results confirmed that the yields of the collected lignins were comparable with those obtained with vacuum filtration immediately after precipitation. The overall times for recovering the organic acid precipitated lignins varied between 2-4 hours depending on the acid. The lignin samples, together with commercial kraft lignin and Alcell® lignin used for comparison, were used for further investigation in valorisation studies of the lignin.

All lignin samples were analysed by elemental analysis, as well as thermogravimetry (TG), under air and nitrogen environments to investigate their thermal characteristics. The morphology of the chars obtained from the TG studies under nitrogen were also studied by scanning electron microscopy (SEM). Elemental analysis showed a carbon, hydrogen, and oxygen (CHO) profile that was typical of values reported in the literature for hardwoods and softwoods. The sulphur content was higher in hardwood lignin than in softwood lignin samples, but more importantly, organic acid precipitated lignin samples exhibited lower sulphur content than lignins obtained from precipitation with sulphuric acid. The fixed carbon and char yields observed from TG studies under nitrogen for all samples indicated that the black liquor, and hence the lignin raw material obtained in this work was ‘good biomass’ for further processing into valuable materials. The SEM morphology of the char samples produced under nitrogen displayed differences in their swelling characteristics with differently formed cracks and cavities in the char particles.

In this study, the pathway chosen for lignin valorisation was via production of chars and activated carbon. Lignin chars were prepared by carbonisation of the raw lignin samples

under a nitrogen environment. Lower carbonisation yields were observed for hardwood (34 – 43%) lignin samples than their softwood (39 – 47%) counterparts, due to the higher oxygen content in hardwood lignins. The chars obtained prior to activation showed spherical particles for softwood samples and a blend of particles for hardwood samples under SEM. Activated carbon were produced by means of physical activation through partial gasification of lignin chars with carbon dioxide.

Only softwood lignin samples were utilised for the activation reactions, due to their higher char yields. After activation, there was a significant increase in the porous structure of the activated carbon compared with the preceding chars, with specific surface areas of 1000–1300 m^2/g for all the softwood lignin samples studied. The micro-pores were also observed to show signs of broadening at the lower ends of the pores. Reactivity studies showed that the activation reactions were independent of temperature at higher temperatures. The gasification reactions had a high propensity toward mass-transfer limitation. The characteristics observed in the porous structure of the activated carbon obtained in this study displayed features suitable for applications such as adsorption, catalysis, energy storage, and molecular sieve uses.

In summary, lignin from South African black liquor can be collected and valorised after precipitation with acid. A faster method for isolation, recovery and washing of the precipitated lignin has been developed. Acidification with organic acids produces high-quality lignins that have less sulphur contamination – unlike lignins obtained by acidification of black liquor with sulphuric acid. The collected lignins can be valorised by conversion into activated carbon that have the potential for use in various industrial applications.

This work has resulted in 2 papers that have been published in peer-reviewed journals and one paper that has been submitted for publication in a peer-reviewed journal.

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LIST OF SYMBOLS OR ABBREVIATIONS (NOMENCLATURE)

HW	Hardwood	
SW	Softwood	
AA	Acetic acid	
CA	Citric acid	
FA	Formic acid	
SA	Sulphuric acid	
HWAA	Hardwood acetic acid	
HWCA	Hardwood citric acid	
HWFA	Hardwood formic acid	
HWSA	Hardwood sulphuric acid	
SWAA	Softwood acetic acid	
SWCA	Softwood citric acid	
SWFA	Softwood formic acid	
SWSA	Softwood sulphuric acid	
C-HWAA	Carbonised hardwood acetic acid	
C-HWCA	Carbonised hardwood citric acid	
C-HWFA	Carbonised hardwood formic acid	
C-HWSA	Carbonised hardwood sulphuric acid	
C-SWAA	Carbonised softwood acetic acid	
C-SWCA	Carbonised softwood citric acid	
C-SWFA	Carbonised softwood formic acid	
C-SWSA	Carbonised softwood sulphuric acid	
G-SWAA	Gasified softwood acetic acid	Activated
G-SWCA	Gasified softwood citric acid	
G-SWFA	Gasified softwood formic acid	
G-SWSA	Gasified softwood sulphuric acid	
CKL	Commercial kraft lignin	

Analytical procedures and symbols

FTIR	Fourier Transform Infrared spectroscopy
v	wavenumber
NMR	Nuclear magnetic resonance spectroscopy
δ	Chemical shift
Pyr-GC/MS	Pyrolysis gas chromatography mass spectrometry

rt	Retention time
SEC	Size exclusion chromatography
M_n	Number average molecular weight
M_w	Weight average molecular weight
M_z	Higher number average molecular weight
dn/dC	Refractive index increment
Đ	Polydispersity
EA	Elemental Analysis
CHNS-O	Carbon, hydrogen, nitrogen, sulphur and oxygen analysis
TG	Thermogravimetry
DTG	Differential Thermogravimetry
w	Weight
SEM	Scanning electron microscopy
A_{DR}	Apparent surface area
A_{tt}	External surface area
V_{DR}	Narrow micropore volume
V_{mes}	Mesopore volume
V_t	Micropore volume
E_a	Activation energy
X	Conversion
r	reactivity

1. INTRODUCTION

1.1 General Overview of Thesis

The South African pulp and paper industry is of a significant size and contributes approximately 0.6% to GDP. The major pulp and paper milling method used is the kraft mill. But while it is the most effective method, there are besetting problems related to a major by-product of the process called black liquor.

This study sets out to precipitate, wash and recover and valorise lignin from South African kraft mill black liquor within the parameters of a biorefinery concept. The biorefinery concept has not been realised within the South African context. This study seeks to advance biorefinery applications in the pulp and paper industry in the country.

The aim is to develop more effective methods for recovery of lignin from kraft mill black liquor, as well as valorisation of the obtained raw material into activated carbon. Certain problems encountered at the recovery and washing stages after lignin precipitation are addressed. Owing to environmental and process issues associated with sulphuric acid precipitation, alternative precipitating agents as potential replacements for sulphuric acids and carbon dioxide are studied. And finally, the lignin obtained from the alternative method of recovery is studied as a potential precursor for high-value products.

1.2 Context of the Research

In South Africa, 1.273 million hectares of land is used for plantations, with 40.6% and 51.1% of the plantation land occupied by eucalyptus and pine species respectively (Godsmark, 2013). The forest products industry on its own contributes about 1.2% to the gross domestic product (GDP) of South Africa (Department of Agriculture, Forestry and Fisheries, South Africa, 2012).

The major contributor to the forestry and forest products industry is the pulp, paper and board industry (0.6% GDP contribution), (Paper Manufacturing Association of South Africa (PAMSA), 2013), comprising approximately 18 mills situated around the country, which utilise 70% of round wood produced.

The kraft pulping process, which liberates fibrous material from wood by mechanical and chemical processes, has been identified as an effective means for processing of wood pulps due to its simplicity, rapidity, and the high quality of the resulting pulp (Gierer, 1980). The process involves removal of lignin and other organic materials to free cellulose fibres. A problem is that the pulp yield from a kraft mill is typically around 50%, with the rest of the biomass in the form of black liquor that contains lignin, hemicellulose, extractives and other minor materials.

This study has focussed specifically on the black liquor obtained during the kraft pulping process. The kraft pulping process, which dates back to the late 19th century, has not seen many alterations over the past century, except for the addition of the recovery unit operation in the 1930's (Kleppe, 1970). The recovery unit operation in a kraft pulp mill serves to recover cooking chemicals, as well as provide the mill with electricity by incineration of black liquor. There are nevertheless still problems that need to be solved in the recovery unit operation.

There is a bottleneck of black liquor encountered at the recovery unit, which means the unit does not have the capacity to process the amount of black liquor produced during the pulping process. Effectively, this limits the production capacity of kraft mills. The drawbacks in the kraft pulping process include high capital cost, low pulp yields, high temperatures, and odours produced by the degradation products (Ragauskas, 2008).

The major effluent liquor produced in a kraft mill, black liquor, is in certain cases, stored in 'black liquor' dams and/or tanks. Apart from the wasted opportunities due to loss of quality of the stored black liquor, these storage facilities for black liquors are a major environmental concern due to their alkalinity and corrosive nature. Part of the motivation for the study is to find a means to use the black liquor waste by-product from the process by adding value to it.

The methodology in this study is dictated by an overarching commitment to biorefinery. The biorefinery concept dictates that biomass should be utilised in its entirety from the plant material, all the way downstream to the waste generated from a certain process, to enhance productivity. Above all, the biorefinery concept seeks to utilise the waste generated to further extract more value, as it still contains biomass material.

The major constituent of black liquor is lignin. Lignin is an aromatic heterogeneous polymer, and the second most abundant carbon source preceded by cellulose. Due to its high heating value (26 MJ/kg) lignin forms the main organic source that is burnt to provide the mill with electricity. Being such a rich carbon source, exclusively burning lignin in the recovery unit operations is seen as underutilisation. As a result, lignin valorisation methods have been explored, whereby it has been found that even more value can be obtained from the polymer. However, it must first be extracted from the liquor.

Lignin has been obtained from black liquor by precipitation techniques that utilise mineral acids, and most recently, carbon dioxide, to acidify black liquor (Zhu and Theliander, 2011; Nagy *et al.*, 2010; Cardoso *et al.*, 2009; Ohman and Theliander, 2007). The precipitation process for lignin from black liquor is effortless, however, the recovery steps have been observed to be most challenging (Ohman and Theliander, 2007). Lignin precipitate forms a colloidal liquid that is difficult to separate by filtration.

Different research groups have sought to modify the precipitation processes, for example, by utilising a combination of sulphuric acid and carbon dioxide, as well as by designing specialised equipment to recover the final lignin product (Kim *et al*. 2007; Pu *et al*., 2007). There have been processes that have been commercialised for precipitation of lignin from black liquor, *viz* the LignoBoost® process from Sweden and LignoForce™ process from Canada (Zhu and Theliander, 2011; Kouisni *et al*., 2012; Tomani, 2010; Wallmo *et al*., 2009). In this thesis, an alternative method of recovery and washing, in the form of a centrifugal recovery, has therefore been investigated.

In accordance with biorefinery principles, a material like lignin can be valorised into novel high value products such as bio-oils, phenols, binders, surfactants, carbon black, as well as activated carbons (Chuck *et al*. 2013; Guo *et al.*, 2008; Wu *et al*., 2008; Ralph *et al*., 2007; Carrott *et al*, 2006a; Carrott *et al*, 2006b; Gonzalez-Serrano *et al*., 2004; Rodriguez-Mirasol *et al*., 1993; Ralph and Hatfield, 1991; Saiz-Jimenez and De Leeuw, 1986). The potential incomes accrued by valorised products are estimated to equal and even exceed those obtained from conventional methods.

Organic acids have not previously been studied as precipitating agents for lignin. In theory, similar to carbon dioxide, organic acid would not bring any chemical imbalance to the mill, and they would bring down the pH of black liquor during precipitation to lower values achieved by using carbon dioxide. Organic acids are also not costly, as some of them are by-products of other processes, and they are not toxic (Reddy and Yang, 2009). Organic acids have also been shown to increase the mechanical properties of polymers by crosslinking the hydroxyl groups (Wyrzykowski *et al*., 2011), thus it is expected that the use of organic acids for precipitation could have similar effects on the lignin polymer, which would be essential for valorisation.

1.3 Research Questions

The research contained in this thesis aims to address the following research questions

- Can lignin be isolated using an efficient method that resolves the difficulties experienced during the recovery and washing stages?

Precipitation of lignin from black liquor with acid is effortless, however, due to the formation of a colloidal suspension during the process, recovery of lignin is difficult. Different research groups have come up with different ways in which they recover lignin after precipitation. A stepwise centrifugal recovery and washing procedure was investigated as an improved method for the recovery of lignin precipitated from kraft mill black liquor.

- Can non-sulphur-containing precipitating agents serve as a better alternative for precipitation of lignin from black liquor?

Sulphuric acid is the most common precipitating agent for lignin from black liquor. In recent years, carbon dioxide has also been introduced as an alternative down to pH of approximately 9, followed by sulphuric acid down to target precipitation pH. Utilising sulphuric acid on a lab or pilot scale would not have any effect. However, it is envisaged that if the process of precipitation could be integrated into a kraft mill, utilisation of sulphuric acid could bring about sulphur imbalances within the mill. Furthermore, utilisation of sulphuric acid as a precipitating agent could also release foul gases such as H_2S or SO_2.

- Can valuable products be obtained from lignin precipitated from black liquor utilising alternative precipitating agents to sulphuric acid, as well as an alternative method of recovery and washing?

The biorefinery concept requires that high-value materials be obtained from biomass. Lignin is the second most abundant natural carbon source. It is agreed upon in the biorefinery space that, polymer rich in carbon like lignin has the potential to replace fossil fuel precursors as a source of valuable materials. Lignin can be a source of fuel, chemicals and materials. As seen in a kraft mill for an example, lignin is currently being used as fuel to generate electricity for the mill processes. Valorisation of lignin obtained with organic acid precipitation into activated carbon was investigated.

1.4 Aims and Objectives

The general aim of the following work is to promote the implementation of the biorefinery concept in South Africa. This aim would be realised through a number of steps by developing an alternative effective method for isolation, recovery and washing of lignin from kraft mill black liquor, and an in-depth characterisation of the obtained raw lignin product in preparation for valorisation into activated carbons. In order to realise the aim, the following objectives were developed:

An investigation of a centrifugal method of recovery as an alternative to the classical straightforward (vacuum) filtration process for the recovery and washing of the obtained precipitate.

An investigation of organic acids as alternative lignin precipitating agents compared with sulphuric acid.

An investigation of the quality of the lignin produced and its viability as a precursor for valuable products.

An investigation of the obtained raw lignins from the new method of recovery and organic acids as potential precursors from activated carbon by partial gasification and reactivity with carbon dioxide.

1.5 Outline of Layout of Thesis

Chapter 2 gives a brief general literature review of previous studies that have been performed that relate to this study.

Following the literature review, each chapter is mostly self-contained, containing a brief introduction for the motivation of the study through literature, materials and methods, results and discussion, and conclusions.

Chapter 3 focuses on research undertaken to develop an improved method of recovery of lignin precipitated from kraft mill black liquor. The obtained sample is characterised in an attempted to elucidate the wood species from which the back liquor was obtained.

Chapter 4 looks at organic acids as an alternative, and ‘greener’ precipitating agents, for lignin from hard- and softwood black liquor from a kraft mill in South Africa. In preparation for the valorisation studies, the thermochemical behaviour of the lignins is also studied in air and nitrogen with thermogravimetric analysis. Characterization of the raw lignin samples and the morphology of the sample studies under nitrogen is also provided in this chapter.

Chapter 5 investigates the valorisation of the lignin samples precipitated from South African kraft mill black liquor in multiple steps. Firstly, the carbonisation of the raw material for conversion into chars is undertaken. Thereafter, the chars are converted into activated carbon by physical activation utilising partial gasification with carbon dioxide. A reactivity study of the activation process is also covered.

Chapter 6, puts into context the main findings and gives further discussions on the work covered in the Chapters 3, 4, and 5.

Finally, Chapter 7 outlines the overall conclusions that were drawn from all the studies performed. Recommendations for future work are also provided in this chapter.

2. LITERATURE REVIEW

Chapter overview

This chapter attempts to provide information on the production context and science for the research chapters that follow. A background in the pulping industry is provided, followed by previous methods employed to obtain lignin as a raw material. Finally, the requirements and techniques for the valorisation of lignin are covered.

2.1. Chemical Composition of Wood

Wood is the most abundant biological resource found in nature and the most complex material found in the bio-based industry. Wood is composed of carbohydrates and lignin that are physically and chemically bound together. Its species can be classified into two groups, namely angiosperms and gymnosperms, or simply, hardwood and softwood respectively. Wood is essentially a matrix of tubular fibres strung together. These fibres are composed of three polymers; cellulose, hemicellulose and lignin. There are also low amounts of organic and inorganic extractives present in wood. These components of wood vary in their composition among different species of plants.

Cellulose is the most abundant polymer found in nature and due to its high degree of polymerization and linearization, it is adapted for strength functions in wood. Hemicelluloses are heteropolymers and act as a matrix for cellulose, but unlike cellulose, they are composed of shorter branched chains. They are also responsible for increasing the packing density of the cell wall fibre in association with lignin. Lignin, on the other hand, is a heteropolymer that acts as the ‘glue’ that holds wood fibres together, binding components within the cell wall of a wood fibre.

Table 2.1 shows the percentage distribution of wood components that are commonly found in industrially-utilised tree species. Generally, in wood fibres, the amounts of cellulose and hemicellulose are higher than that of lignin, with extractives commonly found in the lowest amounts. Lignin content is known to be higher in softwoods than in hardwoods. Hemicelluloses act as the linking material between cellulose and lignin. With regards to the strength of wood, it has recently been shown that earlier degradation of hemicelluloses results in the loss of strength in the wood at a later and mature stage (Winandy and Rowell, 2005; Jingjing, 2011). Wood strength is not known to be directly affected by lignin content.

Table 2.1. Percentage chemical compositions of various tree species (adapted from Winandy and Rowell, 2005)

	Softwood		Hardwood	
Constituent	Scots Pine (Pinus sylvestris)	Spruce (Picea glauca)	Silver Birch (Betula verrucosa)	Eucalyptus (Eucalyptus camaldulensis)
Cellulose	40.0	39.5	41.0	45.0
Hemicellulose				
-Glucomannan	16.0	17.2	2.30	3,10
-Glucuronoxylan	8.90	10.4	27.5	14.1
Other polysaccharides	3.60	3.00	2.60	2.00
Lignin	27.7	27.5	22.0	31.3
Total extractives	3.50	2.10	3.00	2.80

2.2. Lignin

2.2.1. Background

The composite nature of wood was first recognised by Anselme Payen in 1838 (Adler, 1977). In his work, he realised that treatment of wood with acid and alkaline solutions removed part of the wood, resulting in a major insoluble residue, cellulose. Analysis of the carbon content in wood compared to that of the isolated cellulose showed that there was more carbon in wood than that isolated. The additional carbon was classified as a carbon-rich encrusting material which embedded the cellulose in wood.

In 1865, F. Schulze coined the word lignin, which is derived from Latin lignum, meaning wood (Adler, 1977). Its 3-dimensional structure is a random heterogeneous polymer network that is made up of variously linked phenyl propane units (Sjöström, 1993). Being an aromatic compound, lignin is hydrophobic, which gives it a valuable function in water and nutrient transport. Lignin is also essential for the plant's own natural defence mechanism against foreign destructive substances (Ragauskas, 2007). The overall structure of lignin is derived from three phenyl propane monomers which differ in the level of their methoxylation. These monomers are hydroxycinnamyl alcohols of p-coumaryl, coniferyl and synapyl, which make up the backbone of lignin in a form of three phenylpropanoids -; p-hydroxyphenyl, guaiacyl and syringyl monomers, respectively (Figure 2.1) (Ralph *et al*., 2007).

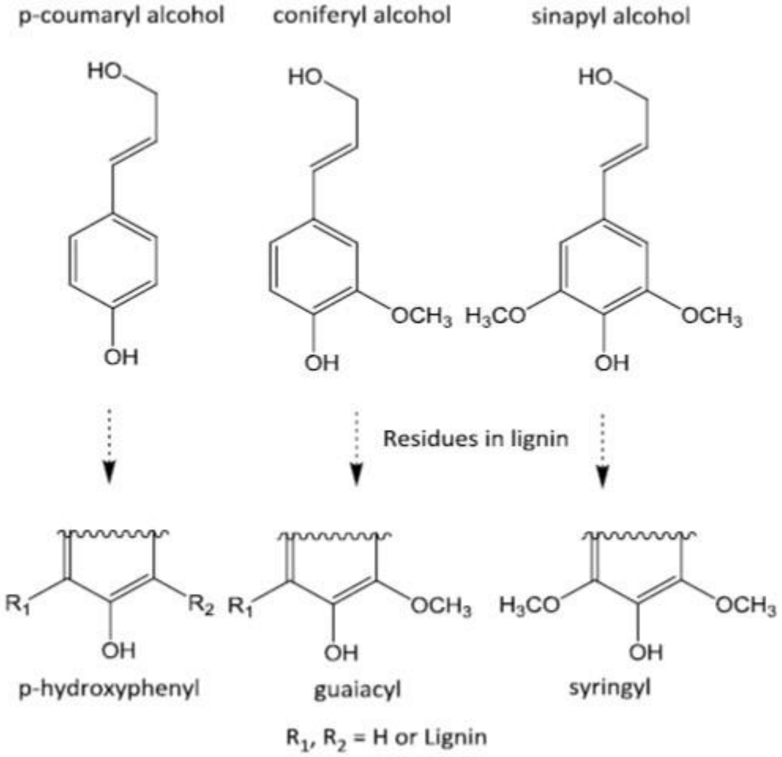


Figure 2.1. Hydroxycinnamyl precursor monomers of lignin, as well as the monolignol structures as found in lignin (adapted from Norberg, 2012)

Hardwood lignins consist principally of guaiacyl and syringyl monomer units, whereas softwood lignins are predominately composed of guaiacyl, with low levels of p-hydroxyphenyl units (Boerjan *et al.*, 2003). The biosynthetic pathway of lignin has been a subject of many discussions: it has been reported that lignification is a random process that is controlled by the cell and structural density with simple chemical coupling propensities (Boerjan *et al.*, 2003; Ralph *et al.*, 2001; Vanholme *et al.*, 2010). Unlike most polymers, lignin does not possess a native structure due to the random nature of the linkages in the polymeric structure. The diversity of functional groups that are found in lignin also has an impact on its synthesis and reactivity. The resulting structure of lignin is, therefore, a three-dimensional highly branched and interlocking structural network of essentially infinite molecular weight (Figure 2.2).

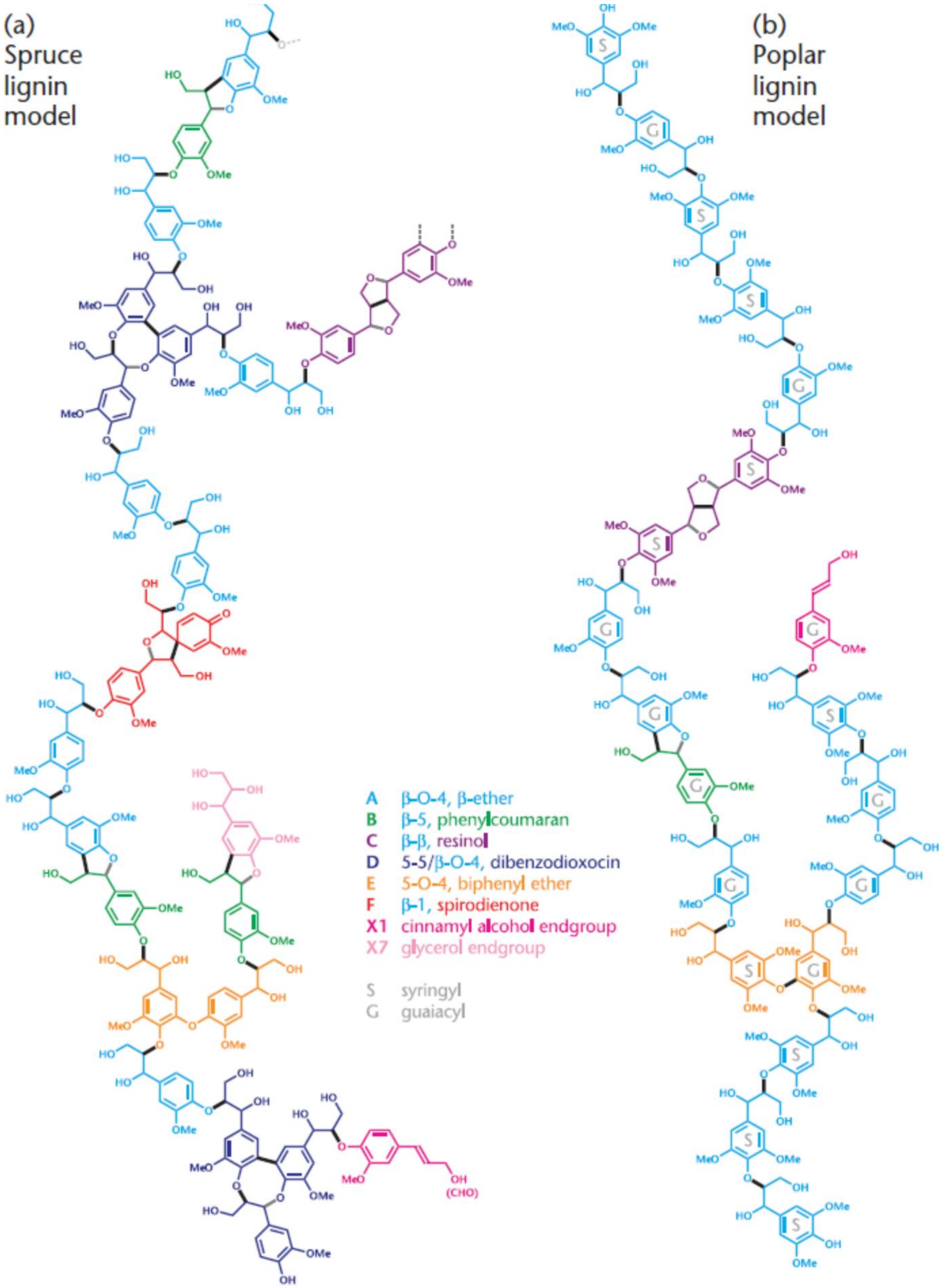


Figure 2.2. Suggested models of lignin polymer for Spruce and Poplar lignin (adapted from Ralph *et al.*, 2007)

Only β-β, β-O-4 and β-5 (Figure 2.3) linkages are prevalent during polymerization of lignin, in which two-thirds are composed of ether linkages and one-third of C-C bonds. The lignin chain grows one monolignol at a time by endwise coupling, whereby a dimer is first dehydrogenated into a radical preceding addition of another monomer (Adler, 1977; Vanholme *et al*., 2010). The frequency of linkages found in a lignin macromolecule is greatly influenced by monolignols. It has been found that the frequency of the β-O-4 coupling in softwoods is 45-50%, whereas in hardwood it is approximately 60-85% of the phenylpropane units (Chen, 1991). Further linkages such as 5-5 and 4-O-5 are essential as they may bring about branching in the growing chain (Adler, 1977). These multiple linkages in lignin bring about the difference in its chemical structure compared to other polymers. Hardwoods tend to form a linear structure with less branching than softwoods, because of the prevalent β-β and β-O-4 linkages, which mostly leave the 5-position on the sinapyl alcohol not attacked by free radicals to allow branching. The presence of only coniferyl alcohol in softwood gives way for a free 5-position, thus allowing for more branched and crosslinked tertiary structure.

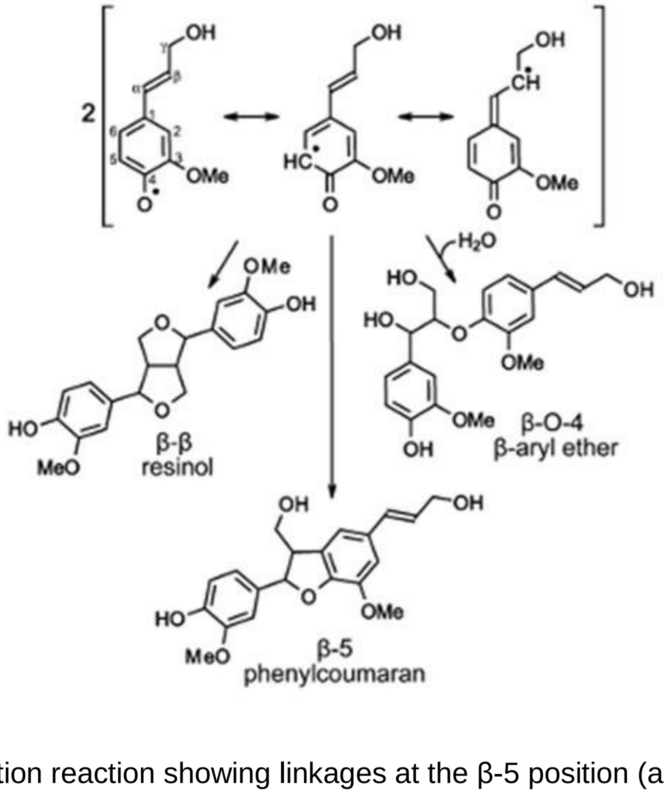


Figure 2.3. Condensation reaction showing linkages at the β-5 position (adapted from Vanholme *et al*. 2010)

2.2.2. Isolation of lignin

Background

Lignin in its native form exists in wood as a highly branched polymer that is associated with other polymers. In this form, lignin is known as protolignin. There are various established methods used to isolate lignin from wood, and the resulting lignin product is named according to the method of isolation. Broadly speaking, lignin isolation from wood can be achieved in two ways: by preferential dissolution of lignin; or by dissolution of the non-lignin components. The methods for lignin isolation will be briefly discussed in the following sections and benchmarked according to how much they are representative of protolignin (Table 2.2). In the later sections, there will be a strong focus on the chemical pulping process, as the lignin isolated in this work was obtained from a kraft pulping process spent liquor, called black liquor.

Table 2.2. Lignin isolation methods (Obst and Kirk, 1988)

Preparation	Methodology	Yield and protolignin representativeness
Milled wood lignin (MWL)	Aqueous dioxane extraction of finely milled wood	Obtained in about 20% yield considered to be representative of the original lignin
Milled wood enzyme lignin (MWEL)	Residue left after polysaccharidase hydrolysis of carbohydrate in finely milled wood	+95% yield, but contains 10-12% carbohydrate; not completely soluble in common lignin solvents
Cellulase enzyme lignin (CEL)	Solvent-soluble fraction of MWEL	Similar to MWL
Brauns' native lignin	Ethanol extract of ground wood (fine sawdust-size particles)	Lower yield and lower molecular weight than MWL
Brown rot lignin	Ethanol or aqueous dioxane extract of brown-rotted wood	Probably not severely altered, but some demethylation of methoxyl and oxidation of side chains have occurred
Chemical lignin (kraft and sulphite)	Dissolution of lignin at high temperature and pressure with chemicals	Not representative of the original lignin; major by-product in pulp production to make paper
Klason lignin	Insoluble, condensed residue left after	Not representative of the original lignin; often used

	hydrolysis of polysaccharides	as a measure of lignin content.

Lignin extraction from wood is important for further studying lignin, however, the drawback is that the lignin isolated by means of these different methods is not the same as the native lignin, protolignin. Milled wood lignin (MWL) has been observed as the most closely related to protolignin of all the isolated lignins (Björkman, 1956).

The length of time of isolation during this method is dependent on the type of milling that is used. For example, 1 hour for a very efficient vibratory ball mill, 12 hours for a large vibratory mill, and up to 3 weeks when utilising a rotating jar mill. The crude lignin yields observed for MWL are usually 20–30 %, containing approximately 10% residual carbohydrate. Higher yields of about 95% are observed for milled wood enzyme lignin (MWEL). The first step in this method is similar to that for MWL, followed by digestion of the carbohydrate component with cellulolytic (polysaccharidases) enzymes for about a week to 10 days. The lignin obtained has been observed to be the most representative of protolignin.

The disadvantage of lignins isolated by enzymatic action is that they contain high carbohydrate content which is caused by lignin-polysaccharide covalent linkages and has a high molecular weight distribution, thereby making the obtained lignin insoluble in common lignin solvents. Further fractionation of MWEL to remove some of the residual carbohydrate is a means to produce lignin that is solvent soluble, called cellulase enzyme lignin (CEL). Lower yields than MWEL are observed and lower residual carbohydrates (~ 4%) are observed for CEL. MWL is seen as adequate for studies on lignin isolated from wood, as the additional steps required to obtain CEL are unjustifiable (Obst and Kirk, 1988).

Another type of lignin can be isolated from ground wood, termed Brauns’ native lignin. The process to obtain this lignin first begins with a 2-day extraction of the ground wood to remove extraneous materials, followed by extraction by percolation for 8–10 days. Brauns’ native lignin is obtained after a number of further extraction and precipitation steps, resulting in a fine tan powder. Although similar to MWL, Brauns’ lignin is obtained in low yields (8%) and has a very low molecular weight distribution, which has resulted in this method of lignin isolation being disfavoured.

Enzymatically liberated or brown rot lignin is a lignin obtained by decaying wood with fungi to remove the carbohydrate component. The wood is decayed with brown rot fungi up to weight losses of about 60–70%, dried, then ground. Extraction and purification methods utilised for MWL and Brauns’ lignins are then utilised to isolate the lignin. Wood that is treated with brown rot fungi produces lignin that is substantially intact, resulting in about 20% yield of lignin. Brown rot fungi also result in the demethylation of the aromatic methoxy groups. However, the lignin is not severely damaged. One advantage of utilising brown rot lignin for further studies is that it allows for subsequent methylation with isotope labels for monitoring further lignin reactions (Obst and Kirk, 1988).

The Klasson method of lignin isolation produces the best intact lignin, however, the method is exclusively utilised to measure lignin content. The lignin constitutes the majority of the mass of lignin content that is found in most biomass material. It is a measure of the difference between acid soluble lignin and acid insoluble ash content. It is highly condensed, altered, and is obtained from hydrolysis of polysaccharides into water soluble sugars. Unlike MWL, MWEL, and native lignins, Klason lignin is unsuitable for characterisation and studies of depolymerisation of lignin, as it is not representative of the protolignin found in wood.

The final classification of lignins, which will be the main focus of this study, are chemical lignins. Chemical lignins are produced from chemical pulping processes, which utilise different chemical reactants to depolymerise and dissolve lignin from cellulose, the desired product. There are two types of chemical lignins, *viz*. kraft lignin, and lignosulphonates. These lignins are highly modified, and not representative of protolignin (Obst and Kirk, 1988). Kraft lignins have lower molecular weight compared to lignosulphonates. These types of lignins are industrial by-products.

Kraft lignin is the focus of the current study, and an extensive review of the kraft pulping process and methods for lignin isolation from kraft pulping effluent liquor will be covered in the following sections.

2.3. The Pulping process

2.3.1. Introduction

The pulping process is a process whereby fibrous material is liberated from wood by mechanical and/or chemical means. The pulp is primarily utilised to make paper, and paperboard products, or any other product derived from cellulose.

The mechanical pulping process involves the separation of fibres by utilising abrasive refining or grinding (Sixta, 2006). This method involves firstly pre-treating the wood with steam and/or a weak chemical solution. Several mechanical pulping methods are known; that is; thermo-mechanical pulping, chemi-mechanical, chemi-thermo-mechanical and a much older groundwood pulping. Mechanical pulping generally has the highest fibre yield (over 90%) compared to other pulping methods; however, the pulp produced usually has high lignin content with less intact fibres (Ince, 2004).

Chemical pulping, on the other hand, is the preferred method for production of pulp. The process utilises chemical reactants, as well as heat to treat the wood to remove lignin (delignify). Wood chips are cooked in a solution of chemicals in a heated pressure vessel/digester for a certain period of time. There are several known chemical pulping methods, e.g.; the kraft (alkaline sulphate) pulping, acid sulphite pulping, and semi-chemical pulping. Chemical pulping produces intact cellulose fibres that are of low lignin content and other wood constituents. During chemical pulping, approximately 85-93% of lignin and 56-71% of hemicelluloses contained in wood are removed in the cooking process (Gårdfeldt and Svane, 2011). The pulp produced is used for numerous functions, and is processed and modified according to the desired final product.

For the purposes of the current work, the kraft pulping process will be extensively discussed. This discussion will include the process in general, a discussion on the effluent liquor produced, and the use of the effluent liquor as a source for isolation of lignin.

2.3.2. Kraft pulping

The kraft pulping process dates back to the late 19th century through a discovery by Carl F. Dahl. This process was realised through the work of Eaton in 1870 for the delignification of wood by utilising a mixture of sodium hydroxide and sodium sulphide. In furthering this work, Dahl discovered that the addition of sodium sulphate could compensate for chemical losses resulting from the recovery of cooking chemicals during the soda pulping process (Kleppe, 1970). The addition of sulphate in the recovery cycle resulted in a better recovery of alkaline sulphide.

The kraft process has not seen many alterations over the last century, because of its simplicity, speed, and the high quality of the resulting pulp produced (Gierer, 1980). This process is insensitive to the presence of bark and extent of extractives. Both soft- and hardwoods can be utilised in the process. There is also an efficient recovery of cooking chemicals and electric power production during the kraft process, thereby making the process self-sustainable in terms of energy utilisation. The drawbacks to the process include high capital cost, low pulp yields, high temperatures, and odours produced by the degradation products (Ragauskas, 2008). During the kraft pulping process, wood chips of a certain particle size are treated at high temperature and pressure in a solution of sodium sulphide and sodium hydroxide, known as white liquor, to dissolve the lignin that binds the cellulose fibres and produce the pulp. Process temperatures can be as high as 170°C for a period of about 120 minutes depending on the amount of delignification that is required. The delignification process should result in minimal damage to the cellulosic portion of the fibre. During the pulping process lignin is broken down into smaller alkali-water soluble fragments by reacting with hydroxide and hydrosulphide anions (Smook, 1992). Compared to other pulping processes (e.g. soda process), the kraft pulping process has a much shorter woodchip cooking residence time at high alkaline and elevated temperatures, since the sulphide speeds up the pulping process (Ragauskas, 2008).

The chemistry of kraft pulping involves three main delignification steps: they are the initial, bulk and residual delignification phases (Figure 2.4) (Ragauskas, 2008; Sjöholm, 1999). Throughout the delignification process, there are two contrasting reactions that occur, that is, the degradation reactions which increase the dissolution of lignin from the wood fibre by cleaving lignin into smaller fragments, and the unfavourable condensation reactions, which oppose the degradation reactions.

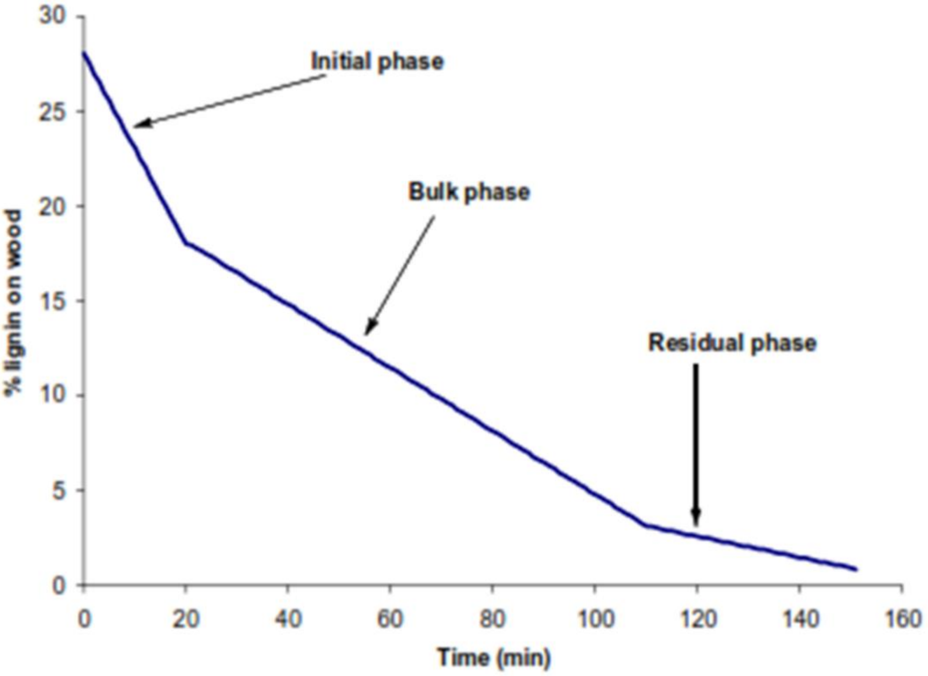


Figure 2.4. The kraft pulping process showing lignin content removal from wood over time and the concerned delignification phases (adapted from Ragauskas, 2008)

During the degradation process, the cleaved lignin fragments expose the phenylpropane hydroxyl groups, which in turn increase the solubility of lignin. The rates of the degradation reactions differ at the different phases of delignification. During the initial phase of delignification, diffusion controlled reactions occur, where cleavage of the α- and β-aryl ether bonds in the lignin molecule are achieved at temperatures lower than 150 °C (Figure 2.5) (Ragauskas, 2008). At this stage, approximately 15-20% of lignin is dissolved in solution. The main part of the process where approximately 60% of the lignin is removed is during the bulk delignification phase, where even the non-phenolic α- and β-aryl ether bonds are cleaved as well (Figure 2.6) (Sjöholm, 1999). These reactions occur at temperatures of 150 – 170 °C. The slowest rates occur at the final stages of cooking around a temperature of 170 °C, that is, the residual phase, resulting in approximately 10-15% dissolution of lignin. The slower rates observed during the residual phase are attributed to a possible cleavage of the C-C bonds (which will result in condensation reactions occurring) of lignin and also the increased selective degradation of carbohydrates, which is unfavourable (Gierer, 1980; Sjöholm, 1999).

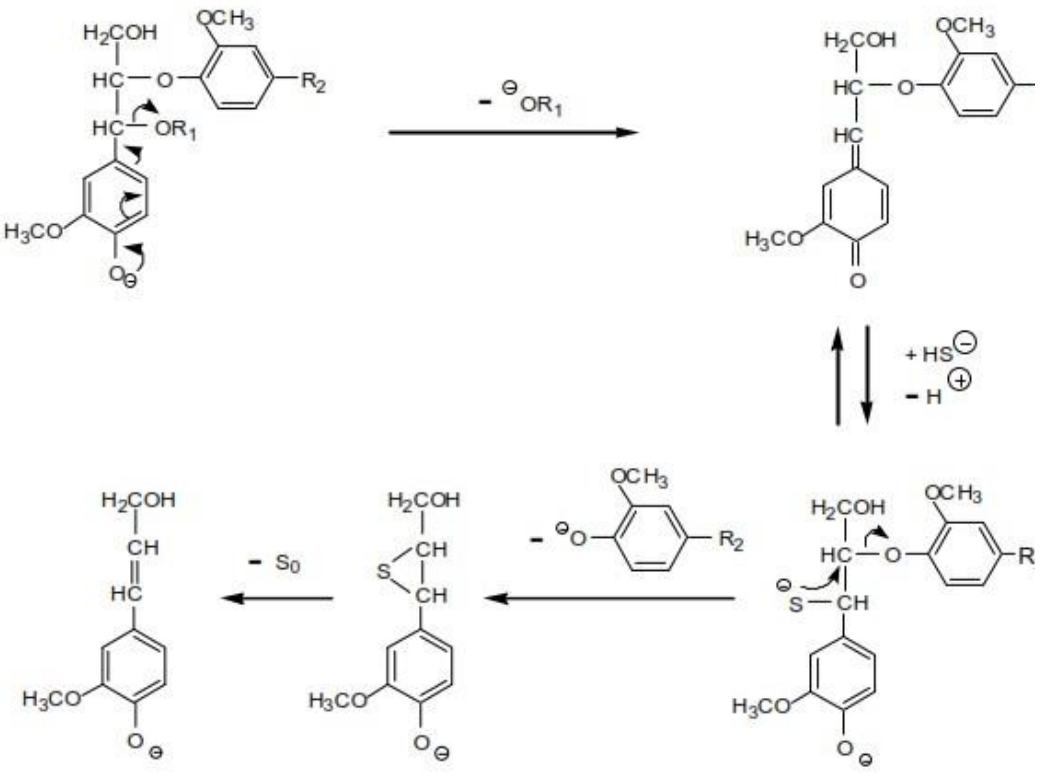


Figure 2.5. Cleavage of the aryl-ether bond during the delignification process (adapted from Sjöholm, 1999)

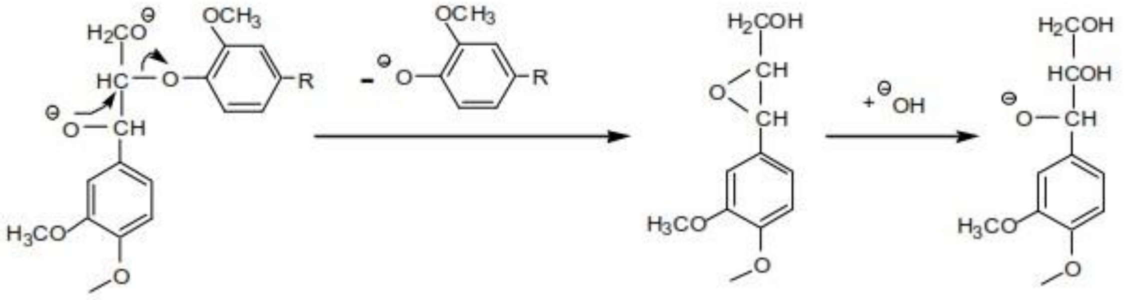


Figure 2.6. Cleavage of the non-aryl-ether bond during the delignification process (adapted from Sjöholm, 1999)

In distinction to the degradation reactions, condensation reactions may occur during the delignification process. These reactions occur between lignin-lignin and lignin-carbohydrate fragments during the cook by Michael addition reactions (Figure 2.7). These reactions may occur at any stage during the cooking process, but are most likely to occur towards the end of the cook. Precipitation of lignin inside the fibres may also occur during condensation reactions, and this is brought on by the lower alkalinity in the process at that stage (Gierer, 1980).

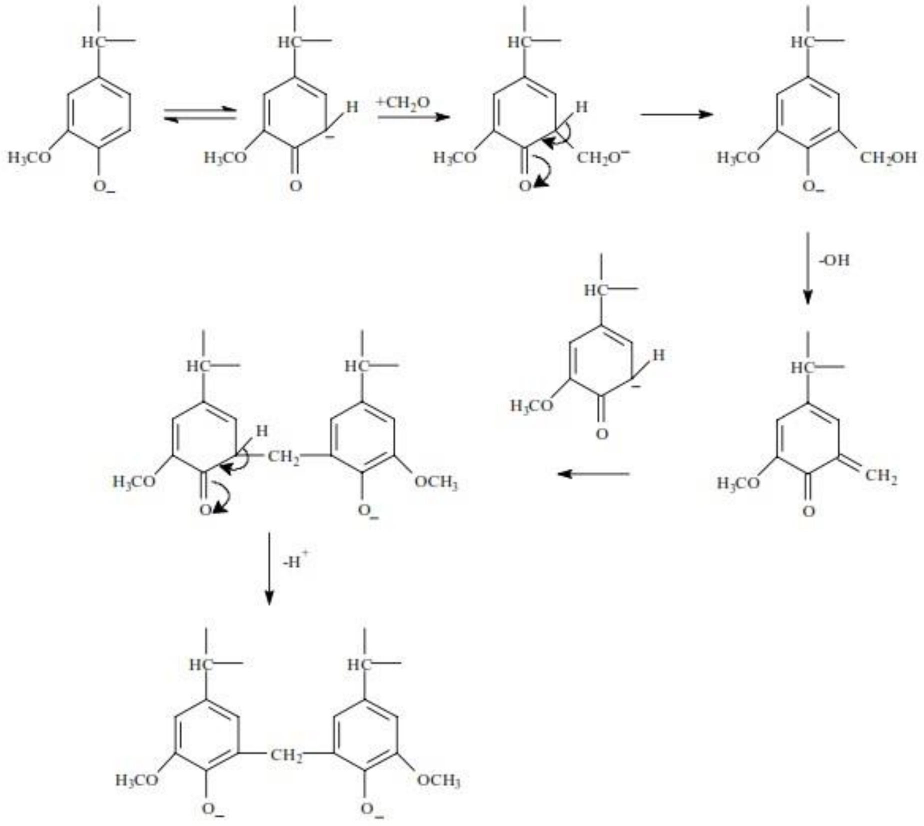


Figure 2.7. Michael addition reactions that may also occur during (or mainly at the final stages) of the kraft pulping process (adapted from Gierer, 1980)

During the kraft pulping process, lignin is dissolved and ends up in the by-product, black liquor. Black liquor contains all other dissolved substances from wood, as well as residual cooking chemicals. It is worth noting at this point that the pulp yield for a typical kraft process is approximately 50%.

2.3.3. Black Liquor

At the end of the cooking process in the kraft mill, the pulp is separated and further processed into a desired product. Black liquor is a by-product obtained after separation from the pulp. This by-product is a complex liquid, which is alkaline in nature with a pH value of 11.50-13.50. It contains some polysaccharide materials still bound to lignin, hemicelluloses, lignin and wood extractives, as well as white liquor chemicals (Cardoso *et al*., 2009).

Recovery of the spent cooking chemicals is essential in any kraft pulping process. Only around the 1930's were advances made to add a recovery unit operation within a kraft pulping mill, through the Tomlinson recovery furnace. This was an all-inclusive unit operation where evaporation, incineration of black liquor, heat and chemical recovery could be achieved (Kleppe, 1970).

The recovery unit processes start with weak black liquor (solid content usually 15-18%), which is concentrated in multiple effect evaporators resulting in concentrated black liquor with a solid content of 65-75 weight percentage (Cardoso *et al*., 2009; Andreuccetti *et al*., 2011). The concentrated black liquor is mixed with sodium sulphate before entering the recovery boiler.

As mentioned, through advances made by Eaton, the addition of sodium sulphate in the recovery unit promotes the recycling of the white liquor chemicals. White liquor chemicals precipitate and are recovered, whilst the rest of the organic material in the black liquor is burnt to produce steam for production of electricity for mill operation (Cardoso *et al*., 2009). The white liquor is recycled, after further processing, back into the digesters for the cooking process. This ideally renders the kraft mill a closed system. According to Gullichsen (1968), the recovery unit operation is responsible for;

- Evaporation of black liquor
- Combustion of black liquor in a recovery furnace to form sodium sulphide and sodium carbonate
- Causticizing sodium carbonate to sodium hydroxide
- Regeneration of lime mud in a lime kiln.

The properties of black liquor depend on the raw materials used for pulping (softwood, hardwood, fibrous), the pulping process conditions (temperature, duration, pressure, etc.), the type of digester utilised (batch, continuous), and the treatment of the liquor after processing of the pulp. The parameters that influence the nature of black liquor include the concentration of the different chemicals used in the cooking liquor, the chemical charge per weight of wood, and the cooking liquor-to-wood ratio. The resultant black liquor properties may also vary due to flow parameters of the liquor from the digesters, the washing of the pulp and storage of the black liquor, thereby affecting the viscosity, heating value and boiling point.

Black liquor is a mixture of different materials, and the typical average elemental analysis of dried black liquor showed that the largest fractions observed on average are carbon and oxygen, which can be attributed to the lignin content (Table 2.3). The sodium content has also been observed to constitute a significant component of black liquor. The dark colour of the black liquor is derived from chromophoric compounds such as quinones, as well as functional groups including carbonyl groups, carboxylic acid, hydroperoxy radicals and phenolic hydroxyl groups generated during lignin degradation (García *et al*. 2009; Mussatto *et al*., 2007).

Table 2.3. Typical elemental composition of black liquor (Marklund, 2009)

Element	w/w (%)
C	36.40
Na	18.60
S	4.80
H	3.50
K	2.02
Cl	0.24
N	0.14
O (by difference)	34.30
TOTAL	1000.00

The lignin present in black liquor is a macromolecular colloid that is stabilised by ionised phenolic carboxylic acid groups. The hemicelluloses are present as the sodium salts of various saccharinic acids and extractives are present as salts of resins and fatty acids (Grace, 1975). The presence of lignin, hemicellulose and extractives affect the behaviour of black liquor. Thermal degradation studies on black liquor have shown that the behaviour of dry solids in black liquor is strongly dominated by the behaviour of lignin and sodium salt fragments (Alén *et al*., 1995).

Weight loss during thermogravimetric analysis of black liquor was observed to occur at temperatures of 150 – 700 °C for a range of softwood species, resulting in weight losses of 30 – 35%, with maximum losses observed to occur at 250 – 500 °C (Alén *et al*., 1995). The components found in black liquor also affect its rheological behaviour, whereby high lignin and polysaccharide concentrations render it to be highly viscous, due to clustering and voluminous high molecular weight residues (Cardoso *et al*., 2009). Conversely, low viscosity in black liquor is attributed to agglomeration of lignin and polysaccharide residues in a more compact and spherical fashion (Figure 2.8) (Cardoso *et al*., 2009; Cardoso *et al*., 2006).

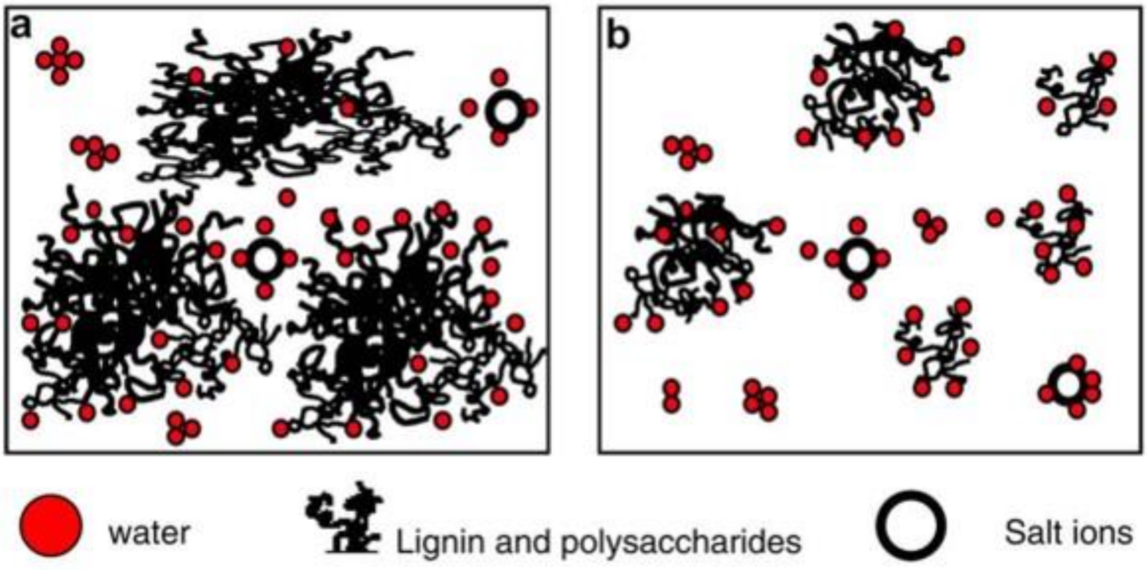


Figure 2.8. High (a) and low (b) viscous representations of black liquor showing the clustering differences between the two forms (adapted from Cardoso *et al*., 2009)

2.4. Lignin Recovery

2.4.1. Lignin recovery from black liquor

Integration of the biorefinery concept in the pulp and paper mill is a viable way for the mill to increase its production stream. Classical kraft mills are prone to have challenges at the recovery unit. An excess of black liquor causes a bottleneck at the recovery boiler, and the boiler's transfer capacity has been shown to limit pulp production (Nagy *et al.*, 2010). This has resulted in mills having to store their black liquor in tanks or dams, which in the long run decreases the quality of the black liquor, diminishing its heating value, and hence, its utility, and creating a cause of environmental concerns. In association with the biorefinery concept, a viable way to keep the mill constantly running would be to divert some of the black liquor from the process.

Integration of a unit operation within the mill that would immediately process the black liquor into other valuable products has been envisaged as a viable option to keep the mill running at maximum capacity. One way to achieve this could be by precipitation of the lignin (described below), which could increase the throughput of the recovery boiler. The precipitated lignin from black liquor could then either be sold or further processed in-house.
Merely burning the lignin for functions of energy production for the mill has in recent years been considered as a waste of a resource that is a potential raw material for a range of high-value useful products (Gargulak *et al.*, 2000). Lignin fractions recovered from black liquor

have a huge potential for bio-power, biochemical and biomaterial products (Nagy *et al.*, 2010). Current and potential uses of lignin are vast and the LigninMatch project has identified the following as possible lignin-based products: activated carbon, binders, carbon fibres, motor fuel, phenols, plastic materials, and sorbents (Gårdfeldt and Svane, 2011).

2.4.2. Precipitation of lignin from black liquor

Lignin can be recovered from black liquor by ultrafiltration or acid precipitation. The ultrafiltration method of lignin isolation from black liquor is essential when specific molecular weight cut-off sizes are required for an end-use product (Kekana, 2015). This process also plays an important role in the physical removal of hemicellulose in black liquor (Helander *et al*., 2013; Elegir *et al*., 2007). On the other hand, the acid precipitation of lignin has been found to be an economically viable method for isolation of lignin (Zhu and Theliander, 2011; Nagy *et al.*, 2010; Cardoso *et al*., 2009; Ohman and Theliander, 2007).

The mechanism for precipitation of lignin has been considered as coagulation of a colloid (Sundin, 2000). The solubility of lignin is controlled by pH, temperature and ionic strength of the black liquor. Lowering the pH of black liquor below a certain critical value (pH ~ 9) results in the precipitation of lignin. Precipitation with sulphuric acid and/or carbon dioxide is the most commonly used method for precipitation of lignin from black liquor (Ohman and Theliander, 2007). Other acids, such as hydrochloric and nitric acid are not used as they would result in corrosion and introduction of undesirable chemical species to the process.

Sulphuric acid has been the acid of choice for lignin precipitation due to its low cost and non-introduction of any foreign elements into the mill since it is compatible with the pulping chemicals (Gilarranz *et al*., 1998). However, a two-stage process has shown better yields of lignin after the precipitation process (Alén *et al.*, 1979). This process involved precipitation by both carbon dioxide and sulphuric acid, whereby black liquor was first treated with carbon dioxide to lower the pH to ~9, and finally with sulphuric acid to pH ~4–2. The method was found to be more economically viable when compared with utilising only sulphuric acid.

Even though sulphuric acid contains elements that might be comparable with pulping chemicals, it can be argued that its use in an integrated biorefinery might disturb the sulphur balance in the mill. Moreover, the introduction of more sulphur could also be a cause for environmental concern, due to the release of foul gases such as SO_2 and/or H_2S during the precipitation experiment (Helander *et al*. 2013; Uloth and Wearing, 1989). Therefore, it is worth exploring other acids that could have a similar precipitating effect, without any adverse effects to the pulping process. For example, CO_2 has already been found to be a good precipitating agent up to certain pH limits (Ohman and Theliander, 2007). Organic acids could also play a similar role, and at the same time manage to overcome the limitations experienced by utilising CO_2 only.

There are few studies in the literature, where researchers explored the use of organic acids for lignin extraction (Kamble and Bhattacharyulu, 2015; Watkins *et al*., 2015; Liu *et al*., 2009), both from wood and black liquor. In their study, Watkins *et al*. (2015) explored lignin extraction from different non-wood cellulosic sources such as wheat straw, pine straw, alfalfa, and flax fibre with formic acid after utilising the organosolv process. This study did not focus much attention on the organic acid used for extraction, but mostly on the characteristics of the lignin obtained from different non-wood sources.

Acetic acid was found to be a good precipitating agent for lignin obtained from hardwood/bamboo mixture black liquor (Kamble and Bhattacharyulu, 2015). From that study, acetic acid precipitated lignin showed higher lignin yields and better thermal stability for precipitation up to pH 9 when compared with H_3PO_4, H_2SO_4 and HCl. The authors also argued that an increase in the number of hydrogen atoms in the acid resulted in increased lignin yields.

Liu *et al*. (2009) utilised oxalic, citric and acetic acids for lignin precipitation from bamboo soda black liquor, utilising sulphuric acid as a control. All organic acids utilised showed lower yields compared with sulphuric acid, with citric acid being the better suited precipitating agent between the three organic acids. The authors deduced that the increased number of carboxylic groups in citric acid brought about a complete electrophilic substitution reaction.

There are two types of lignins that can be obtained from the pulping process, namely, residual lignin and acid precipitated lignin.

Residual lignin

In keeping with the biorefinery concept, residual lignin that is still contained in the pulp after the cooking process should also be recovered. Removal of residual lignin is essential for further processing of pulp into final products. The brown colour observed in the primary pulp has been attributed to the refractory nature of lignin to chemical reactions, as well as its oxidative alterations during the cooking process (Ibarra *et al*., 2004).

Several chemicals are utilised to treat residual lignin. Previously chlorinated reagents were used; however, these have fallen out of favour in recent years due to environmental concerns (Ibarra *et al*., 2005; Ibarra *et al*., 2004). Chlorine-free reagents such as peroxide, ozone and lignocellulosic enzymes have been shown to be more effective and preferred for removing residual lignin in the pulp (Ibarra *et al*., 2004; Bajpai, 1999).

In essence, it is difficult to isolate residual lignin because it is chemically linked to the carbohydrate component of the pulp. However, there have been proposed methods that are utilised to achieve isolation. One method that was used is acidolysis, which has fallen out of favour due to the nature of lignin that is obtained: structural modifications and low yields of the isolated lignin (Argyropoulos *et al*., 2002). Enzymatic isolation of residual lignin is a more attractive method, because the fractions obtained are rich in lignin and moreover they are representative of native lignin (Ibarra *et al*. 2005; Bajpai 1999), however it has been observed that the lignin obtained may be contaminated with protein and some polysaccharides (Ibarra *et al*. 2004).

Acid and carbon dioxide precipitated lignin

Precipitation of lignin from black liquor utilising acids and/or carbon dioxide is the main way kraft lignin can be obtained in high yields. Factors that mainly affect the precipitation process are pH, and to a lesser extent temperature and ionic strength. Poor filterability of the final solution has been shown to be a major hurdle to obtaining the final lignin product.

The pH where precipitation of lignin from black liquor occurs is an essential parameter during the process. García *et al*. (2009) studied selective precipitation of lignin from soda pulping black liquor of the *Miscanthus sinensis* plant species. Two distinct regions of precipitation were observed in the pH range, 12.64–0.72, that was studied in their experiments. Precipitation was observed to commence at pH 11–10, which was mainly attributed to the silicates in the raw material, followed by the region of pH 7–4, which was the main range where complete lignin precipitation was observed. Generally, lowering the pH resulted in increased lignin precipitation, as well as the observation of black liquor changing colour from black to lighter brown (Mussatto *et al*., 2007).

Temperature also affects lignin precipitation from black liquor. Zhu and Theliander (2011) studied the effects of temperature (45 – 75 ˚C) for the lignin precipitation process and observed that a decrease in temperature resulted in increased lignin yield after precipitation.

Black liquor with increased ionic strength also increases the yield of lignin during the precipitation step. For example, the addition of sodium to the black liquor was shown to increase the yield of lignin in the final step (Zhu and Theliander, 2011). Roberts *et al*. (1996) also showed that reduction of black liquor viscosity by salting-in with the addition of thiocyanate salts resulted in higher lignin yields.

Filtration of lignin precipitated from black liquor is a cumbersome process and studies have been performed for understanding and enhancement of the filterability of the lignin precipitate. The concentration of hydroxyl ions (OH^-) was found to strongly influence the filtration resistance (Ohman and Theliander, 2007). At around 0.60 mmol/L OH^- concentration (pH = 10.8), filtration resistance was found to be high for lignin samples precipitated with sulphuric acid. A similar trend was observed for carbon dioxide precipitated lignin, although it was at a lower end of the OH^- ion concentration range (pH ~ 10.5). The lower pH value observed for carbon dioxide precipitated lignin was attributed to the prolonged mixing times (Ohman and Theliander, 2007). Filtration resistance was also observed to be affected by temperature. Ohman and Theliander (2007) observed that lignin suspensions were difficult to filter at temperatures less than 70 °C. Different studies also showed that temperatures above 85 °C were unsuitable, due to coagulation, plugging and formation of larger lignin clumps (Uloth and Wearing, 1989; Merewether, 1962). Filtration resistance decreased with an increase in temperature only between 70 and 85 °C (Howell and Thring, 2000).

To improve the filterability of lignin, Kim *et al*. (2007) studied sulphuric acid precipitation of lignin by utilising a magnetic field in the presence of magnetite. Lignin suspensions were agglomerated on magnetite followed by removal with magnetic separation. The Higher charge brought by magnetite (1% w/w) and lower pH (1.2), resulted in ~68% removal of lignin. Dissolution of magnetite in organic solvents or ionic liquids gave a simple and direct method of lignin recovery (Kim *et al*., 2007; Pu *et al*., 2007).

Precipitation of lignin with organic acids has also been found to improve filterability of lignin after precipitation, due to the mild conditions they provide, which result in lesser lignin degradation (Liu *et al*., 2009). Citric acid was found to significantly improve the filterability of the lignin precipitate, compared with sulphuric acid.

Filterability of lignin after precipitation is also an avenue that needs to be fully explored. Even though different parameters have been used to improve filterability, as discussed above, there has been one group from Sweden that has fully shown specially designed equipment to achieve improved lignin filterability (Zhu and Theliander, 2011; Wallmo and Theliander, 2009; Ohman and Theliander, 2007) (see The LignoBoost®, Figure 2.9).

When it comes to the filterability of the precipitated kraft lignin, it has been observed during the literature survey that research is concentrated on achieving the precipitate, its characterisation, and utilisation. This is because precipitation of lignin and its recovery has become a standard process and most researchers follow already established methods and focus their studies more towards adding value to the lignin.

However, bench scale lignin recovery could prove to be different from pilot and industrial scale. Thus, careful consideration of the filterability of lignin should be applied. Centrifugation has also been explored by a few researchers, however, only as a faster recovery process for bench scale experiments (Gilarranz *et al*., 1998; Mussatto *et al*., 2007). For example, Mussatto *et al*. (2007) utilised only 20 mL of brewer's spent grain black liquor from soda pulping to recover lignin with a centrifuge. However, the authors did not provide much information regarding the efficiency of the centrifugal recovery. Gilarranz *et al*. (1998) also utilised a centrifuge for recovery of lignin from wheat straw black liquor in a three stage process, whereby black liquor is first processed in a biological treatment plant, followed by lignin precipitation up to the medium pH range, and finally further precipitation to lower pH range. In their process, a centrifuge was utilised as an intermediate recovery, before further resuspension and agitation (the focus of the study) of the recovered precipitate.

On an industrial scale, centrifugal recovery has been utilised in many manufacturing industrial processes, including food and agricultural business, pharmaceutical and biotechnology, environmental studies, and chemical industries (Beveridge, 2000). There are different classes of centrifuges that are utilised industrially, *viz*., sedimentation centrifuges and filter centrifuges.

Sedimentation centrifuges include continuous feed and batch feed types of centrifuges. These centrifuges suspend the solid to be separated on the walls of the rotating unit, while the liquid phase is being removed from the system. In filter centrifuges, the solids component is trapped on a filter element and the liquid drains and exits through the filter element.

Application of centrifugal technology has not been applied for lignin recovery, and it is envisaged that its integration into the pulp and paper mill could enhance lignin recovery. The current work suggests a novel centrifugal lignin recovery process that utilised a centrifuge for isolation and washing of lignin. Furthermore, Chapter 6 will discuss the types of centrifuges that could be applied on an industrial scale for lignin recovery.

Utilising recycled acid for precipitation of lignin would be the best way for a low-cost integrated biorefinery to function in a pulp mill. Howell and Thring (2000) utilised a generated waste acid from a Mathieson chloride dioxide generator, in a pulp mill, on black liquor from a blend of hardwood species. This work also aimed to estimate costs associated with the optimum precipitation pH when using generator acids to precipitate lignin. The lignin yield that was achieved was close to 80% with an optimum precipitation end pH of 8, providing the lowest cost. It was also concluded from the study that the stirring rate (agitation to allow better mixing of acid and black liquor) and the addition of acid should be kept to a minimum.

Recent advancements in the precipitation of lignin from black liquor have been shown by commercialisation of the LignoBoost® and LignoForce™ processes, which have been found to effectively recover lignin (Zhu and Theliander, 2011; Kouisni *et al*., 2012; Wallmo *et al*., 2009). The LignoBoost® process begins with acidification of black liquor recovered from the evaporation process at 40% solids content by using carbon dioxide (Figure 2.9). Treatment of black liquor with carbon dioxide decreases the pH to 9.5–9. The lignin in the black liquor becomes increasingly insoluble and at this stage begins to precipitate. The important optimised parameters for this process were temperature, end pH, mixing condition, the bubble size and concentration of gas (Wallmo *et al*, 2009). The LignoBoost® process also resolved the filterability challenges of lignin precipitated from black liquor by re-dispersing and acidifying the precipitate (step know as cake re-slurry) with sulphuric acid, followed by filtration and washing by means of displacement washing (Tomani, 2010). The filtrate from this step is then recycled into the black liquor evaporation chamber. The LignoBoost® process has been found to have the following advantages when compared to previous technologies:

- Lower investment cost; this is due to keeping the filter area and acid volume at lower values.
- Low operational costs; due to lower levels of sulphuric acid used
- Higher lignin yield
- Low ash and carbohydrate content in the lignin
- Higher dry content of lignin

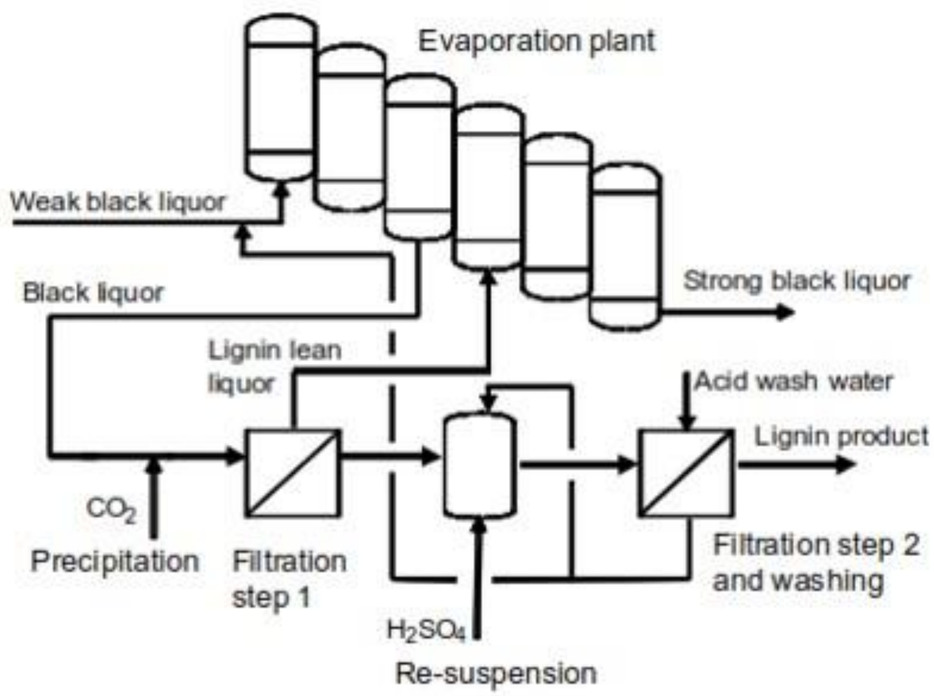


Figure 2.9. A representation of the LignoBoost® process (adapted from Tomani, 2010)

2.5. Biorefinery

The biorefinery concept has different schools of thought, and the versatility of the concept has brought many definitions which essentially converge towards employing the ‘nothing should be left behind’ thought process, as defined in the Council for Scientific and Industrial Research (CSIR) Forestry and Forest Products (FFP) Biorefinery group.

The biorefinery concept dictates that biomass should be utilised in its entirety from the plant material, all the way downstream to the waste generated from a certain process to enhance the productivity of the processes. This implies that the plant material, the leaves, stalks, bark, etc. should also be integrated into the process to extract as much value as possible, rather than the conventional way of discarding or burning all matter that is not used in the processes.

Above all, the biorefinery concept seeks to utilise the waste generated to further extract more value, as the waste also contains valuable biomass material. Valorisation of waste streams from industries would assist in the mitigation of the environment concerns because sustainability is an important aspect of the biorefinery concept. Additionally, such valorisation will result in increased revenues for the industry. For example, materials such as lignin, have much more value than what and how the industries are currently putting them to use.

2.5.1. Valorisation of lignin

Lignin as a source of materials

The earlier development of lignin as valuable material saw lignin being used as a reinforcement for rubber materials, because of its low density and lighter colour, which brings about lighter coloured rubber materials (Setua *et al*., 2000; Kumaran and De, 1978; Griffith and MacGregor, 1953).

There are two methods for preparing lignin-rubber composites, i.e. dry-milling or co-precipitation. In the dry milling method, lignin is ground in its powder form directly into the rubber matrix, whereas in co-precipitation, lignin is mixed with the rubber to form a homogeneous mixture (Sirianni and Puddington, 1976; Keilen and Pollak, 1947).

In one of the more interesting studies, lignin was modified into nano-lignin, and co-precipitation of the colloidal lignin cationic polyelectrolyte complexes and rubber latex resulted in a successful preparation of lignin/rubber nanocomposites (Jiang *et al*., 2013). Lignin was also found to be a good additive for phenol formaldehyde resins (PFs), and was shown to increase the molecular weight of the final resin products (Turunen *et al*., 2003).

Kosbar *et al*. (2000) introduced a novel approach for use of lignin-epoxy-based printed wiring boards for IBM in the microelectronics industry. Incorporation of lignin into polyolefins has also been shown to provide these polymers with enhanced performance (Cazacu *et al*., 2004; Gosselink *et al*., 2004). Lignin has been prepared for conversion into carbon fibres with thermal spinning by hydrocracking, phenolation, or hydrogenolysis. Kadla *et al*. (2002) reported that they were the first to produce lignin-based carbon fibres from commercial hardwood kraft lignin utilising the thermal extrusion process. The carbon fibres produced were found to have suitable properties for general performance grading.

Lignin as a source of fuel

Due to its complexity, lignin needs to be depolymerised to unlock its full chemical potential. Several methods of depolymerisation have been studied, and these include enzymatic, thermal or catalytic degradation, microwave irradiation, as well as ozonolysis (Chuck *et al*. 2013).

Depolymerised lignin would allow for its use in different valorisation products, such as fuel or as fuel additives and chemical precursors. Currently, the pulp and paper industry already utilises lignin as a fuel through combustion of the process liquor in the recovery unit operations to produce electricity for the mill. However, this method of lignin utilisation has fallen out of favour due to the foreseen under-exploitation of such a rich carbon source, as previously mentioned. Therefore, it is important to find alternative methods of modifying lignin into fuel. For example, a well-established method such as gasification could be a way for lignin to be converted into syngas.

Lignin-derived syngas has the potential to produce green fuel by the Sasol process which has and still is advancing technologies in this field. Syngas also has a potential to produce mixed alcohols and high-value chemicals. Pyrolysis is also another method that has been extensively researched to produce lignin bio-oils (Ralph *et al*., 2007; Ralph and Hatfield, 1991; Saiz-Jimenez and De Leeuw, 1986). Bio-oil from lignin pyrolysis are unstable for potential use as biofuels, however, these can be incorporated as additives or stabilisers of other forms of fuel.

Lignin as a source of chemicals

Pollutants removal has in recent years been in the forefront of many discussions for moderation of effects to the environment. Raw lignin has been successfully utilised as heavy metal adsorbent, where it was found to have high affinity for heavy metals in the following order Pb(II)>Cu(II)>Cd(II)>Zn(II)>Ni(II) with considerably higher adsorption capacities (Guo *et al.*, 2008). It was also observed that lignin contains two sites of adsorption, i.e. carboxylic- and phenolic-type surface group, where the latter was observed to have a higher affinity for metal ions. Cr(III) was also shown to be effectively removed in lab scale experiments from water by raw lignin, where the reaction occurs through an ion exchange mechanism, with affinity of lignin to the metal ions increasing with increasing pH (Wu *et al*., 2008). The authors suggested that Cr(III) forms inner-sphere complexes with lignin. Lignin-epoxy blends may also be applied in the adsorption of metals as shown by Gabaldón *et al*. (2000), where amination of these blends significantly enhanced adsorption of heavy metals.

Lignin as a source of activated carbon (main focus)

In general, activated carbon are known as the oldest adsorbents, due to their very porous structure possessing high internal surface area. As adsorbents, activated carbon have been used mainly in the removal of a variety of contaminants, both organic and inorganic (Carrott *et al*, 2006a; Carrott *et al*, 2006b; Malhas *et al*, 2002; McKay *et al*, 1985).

There are two types of activated carbon: granular activated carbon and powdered activated carbon, differentiated by their particle size. Powdered activated carbon are commonly used, and possess high adsorption capacities, because of large external surface areas provided by the particle size. Granulated activated carbon, on the other hand, possess a smaller external surface area, due to their larger carbon particle size. Coal was previously the main precursor for activated carbon (Ahmadpour and Do, 1996), however, there has been a growing attraction to utilising biomass as a source of activated carbon (Aygün *et al*, 2003; Márquez-Montesinos *et al*., 2001; Juang *et al*, 2000; Ahmadpour and Do, 1996).

Activated carbon are produced by two methods; physical and chemical activation. Physical activation utilises gases in a two-step process to obtain the desired activated carbon. In the first step of the process, a char material is produced by carbonisation/pyrolysis of the raw material under inert environments, usually nitrogen, followed by the activation stage where an oxidising gas such as carbon dioxide or steam is used to develop a micropore structure. In chemical activation, the raw material is first impregnated in substances such as H_3PO_4, KOH, NaOH, etc., followed by a carbonisation/activation step, where carbonisation and activation occur at the same time. The temperatures of activation vary between 200–800 °C for physical activation and 450–900 °C for chemical activation.

Studies on lignocellulosic materials have shown that the lignin component is the main source of char formation during the process of producing activated carbon (Razvigorova *et al*., 1998; Gergova *et al*, 1994; González *et al*. 2003). The hemicelluloses and cellulose components have been shown to be the volatile fractions (Gergova *et al*, 1994). Thus, lignin is a good precursor for activated carbon.

Activated carbon produced from lignin as a raw material have been extensively studied (Montané et al., 2005; Rodriguez-Mirasol et al., 1993; Rodríguez-Mirasol et al., 1993a; Rodríguez-Mirasol et al., 1993b). Physical activation of pre-carbonised Eucalyptus lignin by partial gasification with CO_2 at 850 °C for 20 hours produced activated carbon with a significantly high surface area (1853 $m^2.g^{-1}$) and micropore volume (0.57 $cm^3.g^{-1}$) (Rodríguez-Mirasol *et al*, 1993). It was also reported by the authors that there was an increased development of microporosity, as well as micropore widening in the activated carbons. In addition to the widening of the micropores, CO_2 was also responsible for the opening of the blocked micropores as well as the creation of new ones (Rodriguez-Mirasol *et al*, 1993a).

Reactivity studies of the gasification reaction showed that the reaction proceeds as a combination of catalysed and uncatalysed reactions (Rodríguez-Mirasol *et al*, 1993b). The catalysed reactions were reported at higher conversions, where it was proposed that the distribution of sodium on the lignin matrix caused this effect, while at lower conversions during the gasification reaction the uncatalysed reactions occur.

Chemical activation has been shown to have higher surface area activated carbon compared with those from physical activation (Gonzalez-Serrano *et al*., 2004; Gonzalez-Serrano *et al*., 1997; Rodriguez-Mirasol, *et al*, 1993). Activation with H_2PO_4 or alkali metals hydroxides is preferable to $ZnCl_2$, as the latter was found to be toxic (Gonzalez-Serrano et al., 2004). The surface areas of chemically activated carbon were found to be affected by an increase in temperature (350–500 °C), as well as the impregnation ratio. Recommended impregnation ratios for chemical/lignin were 1:2.3 for $ZnCl_2$ and 2 for H_3P0_4.

References

(including for Chapter 1)

Adler E. 1977. Lignin chemistry - Past, present and future. Wood Science and Technology 11: 169-218.

Ahmadpour A, Do DD. 1996. The preparation of active carbons from coal by chemical and physical activation. Carbon **34**(4): 471-479.

Alén R, Patja P, Sjöström E. 1979. Carbon dioxide precipitation of lignin from pine kraft black liquor. Tappi Journal **62**(11): 108-110.

Alén R, Rytkönen S, McKeough P. 1995. Thermogravimetric behaviour of black liquors and their organic constituents. Journal of Analytical and Applied Pyrolysis **31**: 1-13.

Andreuccetti MT, Leite BS, d´Angelo JVH. 2011. Eucalyptus black liquor – Density, viscosity, solids and sodium sulfate contents revisited. O PAPEL **72**: 52-57.

Argyropoulos DS, Sun Y, Palus E. 2002. Isolation of residual kraft lignin in high yield and purity. Journal of Pulp and Paper Science **28**(2): 50-54.

Aygün A, Yenisoy-Karakaş S, Duman I. 2003. Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties. Microporous and Mesoporous Materials **66**(2–3): 189-195.

Bajpai P. 1999. Application of enzymes in the pulp and paper industry. Biotechnology Progress **15**: 147-157.

Beveridge T. 2000. Large-Scale Centrifugation. In: ID Wilson, ER Adlard, M Cook, CF Poole (eds), Encyclopedia of Separation Science, London: Academic Press. pp 320-329

Björkman A. 1956. Studies on finely divided wood. Part 1. Extraction of lignin with neutral solvents. Svensk **59**: 477-485.

Boerjan W, Ralph J, Baucher M. 2003. Lignin biosynthesis. Annual Reviews in Plant Biology **54**: 519-546.

Cardoso M, Oliveira ED, Passos ML. 2006. Kraft black liquor of eucalyptus from Brazilian mills: Chemical and physical characteristics and its processing in the recovery unit. Papel **67**: 71-83.

Cardoso M, de Oliveira ED, Passos ML. 2009. Chemical composition and physical properties of black liquors on liquor recovery operation in Brazilian pulp mills. Fuel **88**: 756-763.

Carrott PJM, Mourão PAM, Ribeiro-Carrott MML. 2006a. Controlling the micropore size of activated carbons for the treatment of fuels and combustion gases. Applied Surface Science **252**(17): 5953-5956.

Carrott PJM, Ribeiro-Carrott MML, Mourão PAM. 2006b. Pore size control in activated carbons obtained by pyrolysis under different conditions of chemically impregnated cork. Journal of Analytical and Applied Pyrolysis **75**(2): 120-127.

Cazacu G, Mihaies M, Pascu MC, Profire L, Kowarskik AL, Vasile C. 2004. Polyolefin/lignosulfonate blends, 9. Macromolecular Materials and Engineering **289**(10): 880-889.

Chen CL. 1991. Lignins: Occurrence in woody tissues, isolation, reactions, and structure. In: M Lewin, IS Goldstein (eds), Wood Structure and Composition, New York: Marcel Dekker Inc. pp 183-261.

Chuck CJ, Parker HJ, Jenkins RW, Donnelly J. 2013. Renewable biofuel additives from the ozonolysis of lignin. Bioresource Technology **143**: 549-554.

Department of Agriculture, Forestry and Fisheries, South Africa. 2012. Integrated growth and development plan 2012. Department of Agriculture, Forestry and Fisheries. Pretoria, South Africa.

Elegir G, Bussini D, Antonsson S, Lindström ME, Zoia L. 2007. Laccase initiated cross-linking of lignocellulose fibres using a ultra-filtered lignin isolated from kraft black liquor. Applied Microbiology and Biotechnology **77(**4): 809–817.

Gabaldón, C, Marzal P, Seco A, Gonzalez JA. 2000. Cadmium and copper removal by a granular activated carbon in laboratory column systems. Separation Science and Technology **7**(35): 1039-1053.

García A, Toledano A, Serrano L, Egüés I, González M, Marín F, Labidi J. 2009. Characterization of lignins obtained by selective precipitation. Separation and Purification Technology **68**: 193-198.

Gårdfeldt K, Svane M. 2011. Future use of lignin in value added products – A possible roadmap for Nordic/Baltic innovation. Helsinki: ScanBalt Campus Knowledge Network Environmental Biotechnology. 1-13

Gargulak JD, Lebo SE, Glasser WG, Northey RA, Schultz TP. 2000. Lignin: Historical, Biological, and Materials Perspectives. Washington: American Chemical Society.

Gergova K, Petrov N, Eser S. 1994. Adsorption properties and microstructure of activated carbons produced from agricultural by-products by steam pyrolysis. Carbon **32**(4): 693-702.

Gierer J. 1980. Chemical aspects of kraft pulping. Wood Science and Technology **14**: 241-266.

Gilarranz MA, Rodriguez F, Oliet M, Revenga JA. 1998. Acid precipitation and purification of wheat straw lignin. Separation Science and Technology **33**(9): 1259-1377.

Godsmark, R. 2013. South African forestry and forest products industry facts – 2011. Forestry South Africa, South Africa, http://www.forestry.co.za/statistical-data/

González JF, Encinar JM, Canito JL, Sabio E, Chacón M. 2003. Pyrolysis of cherry stones: Energy uses of the different fractions and kinetic study. Journal of Analytical and Applied Pyrolysis **67**(1): 165-190.

Gonzalez-Serrano E, Cordero T, Rodriguez-Mirasol J, Rodriguez JJ 1997. Development of porosity upon Chemical Activation of kraft lignin with $ZnCl_2$. Industrial & Engineering Chemistry Research **36**(11): 4832-4838.

Gonzalez-Serrano E, Cordero T, Rodriguez-Mirasol J, Cotoruelo L, Rodriguez JJ. 2004. Removal of water pollutants with activated carbons prepared from H_3PO_4 activation of lignin from kraft black liquors. Water Research **38**(13): 3043-3050.

Gosselink RJA., Snijder MHB., Kranenbarg A, Keijsers ERP, de Jong E, Stigsson LL. 2004. Characterisation and application of NovaFiber lignin. Industrial Crops and Products **20**(2): 191-203.

Grace, MT. 1975. Solubility limits in black liquor. IPC Technical Paper Series Number 6. Appleton, Wisconsin: Institute of Paper Chemistry.

Griffith TR, MacGregor DW. 1953. Aids in vulcanization of lignin-natural rubber coprecipitates: Lead, copper, and bismuth oxides. Rubber Chemistry and Technology **26**(3): 716-730.

Gullichsen J. 1968. Heat values of pulping spent liquors. In: Proceedings of the Symposium on Recovery of Pulping Chemicals, 13-17 May, Helsinki, Finland. pp 85-100.

Guo X, Zhang S, Shan X. 2008. Adsorption of metal ions on lignin. Journal of Hazardous Materials **151**(1): 134-142

Helander M, Theliander H, Lawoko M, Henriksson G, Zhang L, Lindström ME. 2013. Fractionation of technical lignins: Molecular mass and pH effects. Bioresources **8**(2): 2270-2282.

Howell JF, Thring RW. 2000. Hardwood lignin recovery using generator waste acid statistical analysis and simulation. Industrial & Engineering Chemistry Research **39**: 2534-2540.

Ibarra D, del Río JC, Gutiérrez A, Rodríguez IM, Romero J, Martínez MJ, Martínez AT. 2004. Isolation of high-purity residual lignins from eucalypt paper pulps by cellulase and proteinase treatments followed by solvent extraction. Enzyme and Microbial Technology **35**: 173-181.

Ibarra D, del Río JC, Gutiérrez A, Rodríguez IM, Romero J, Martínez MJ, Martínez AT. 2005. Chemical characterization of residual lignins from eucalypt paper pulps. Journal of Analytical and Applied Pyrolysis **74**: 116-122.

Ince PJ. 2004. Pulping. In: J Burley, J Evans, JA Youngquist (eds). Encyclopaedia of Forest Sciences Vol. 2, Oxford: Elsevier Academic Press. pp 877-833.

Jiang C, He H, Jiang H, Ma L, Jia DM. 2013. Nano-lignin filled natural rubber composites: preparation and characterization. Express Polymer Letters. **7**(5): 480-493.

Jingjing L. 2011. Isolation of lignin from wood. Bachelor's in Paper Technology, SAIMAA University of Applied Sciences. South Karelia, Finland

Juang R, Wu F, Tseng R. 2000. Mechanism of adsorption of dyes and phenols from water using activated carbons prepared from plum kernels. Journal of Colloid and Interface Science **227**(2): 437-444.

Kamble SV, Bhattacharyulu YC. 2015. Selective Separation of Biomass from Black Liquor Waste by Inorganic and Organic Acids. International Journal **3** (1): 684-692.

Kadla JF, Kubo S, Venditti RA, Gilbert RD, Compere AL, Griffith W. 2002. Lignin-based carbon fibers for composite fiber applications. Carbon **40**(15): 2913-2920.

Keilen JJ, Pollak A. 1947. Lignin for reinforcing rubber. Rubber Chemistry and Technology **20**(4): 1099-1108.

Kekana PT. 2015, Ultrafiltration of lignin from black liquor obtained from South African kraft mill. MSc. Dissertation, University of Kwazulu-Natal, South Africa

Kim HD, Pu Y, Chandra RP, Dyer TJ, Ragauskas AJ, Singh PM. 2007. A novel method for enhanced recovery of lignin from aqueous process streams. Journal of Wood Chemistry and Technology **27**: 219-224.

Kleppe PJ. 1970. Kraft pulping. Tappi **53**(1): 35-47.

Kosbar LL, Gelorme JD, Japp RM, Fotorny WT. 2000. Introducing biobased materials into the electronics industry. Journal of Industrial Ecology **4**(3): 93-105.

Kouisni L, Holt-Hindle P, Maki K, Paleologou M. 2012. LignoForce system™: A new process for the production of high-quality lignin from black liquor. The Journal of Science & Technology for Forest Products and Processes **2**(4): 6-10.

Kumaran MG, De SK. 1978. Utilization of lignins in rubber compounding. Journal of Applied Polymer Science **22**(7): 1885-1893.

Liu Z, Luo XG, Li Y, Li L, Huang Y. 2009. Extraction of Lignin from Pulping Black Liquor by Organic Acid. Material Science Forum **620-622**: 571-575

Malhas AN, Abuknesha RA, Price RG. 2002. Removal of detergents from protein extracts using activated charcoal prior to immunological analysis. Journal of Immunological Methods **264**(1-2): 37-43.

Marklund M. 2009. Black liquor recovery: How does it work? The Black Liquor Gasification Research Program Communication, Energy Technology Centre, Piteå, Sweden.

Márquez-Montesinos F, Cordero T, Rodríguez-Mirasol J, Rodríguez JJ. 2001. Powdered activated carbons from *Pinus Caribaea* sawdust. Separation Science and Technology **36**(14): 3191-3206.

McKay G, Bino MJ, Altamemi AR. 1985. The adsorption of various pollutants from aqueous solutions onto activated carbon. Water Research **19**(4): 491-495.

Merewether JWT. 1962. The precipitation of lignin from eucalyptus kraft black liquors. Tappi Journal **45**(2): 159.

Montané D, Torné-Fernández V, Fierro V. 2005. Activated carbons from lignin: Kinetic modelling of the pyrolysis of kraft lignin activated with phosphoric acid. Chemical Engineering Journal, **106**(1), 1-12

Mussatto SI, Fernande M, Roberto IC. 2007. Lignin recovery from brewer's spent grain black liquor. Carbohydrate Polymers **70**: 218-223.

Nagy M, Kosa M, Theliander H, Ragauskas AJ. 2010. Characterization of carbon dioxide precipitated kraft lignin to promote its utilization. Green Chemistry **12**: 31-34.

Norberg I. 2012. Carbon fibres from kraft lignin. PhD. Dissertation, KTH Royal Institute of Technology, Sweden.

Obst JR., Kirk TK. 1988. Isolation of lignin. In: A Willis, ST Kellogg. Methods in Enzymology - Biomass, Part B, Lignin, Pectin, and Chitin Vol. 161. San Diego, CA: Academic Press, Inc. pp 3-12.

Ohman F, Theliander H. 2007. Filtration properties of lignin precipitated from black liquor. Tappi Journal **6**(7): 3-9.

Paper Manufacturing Association of South Africa (PAMSA). 2013. South African pulp and paper industry: Summary findings from 2012 production, import and export statistics. Woodmead, Sandton, South Africa

Pu Y, Jiang N, Ragauskas AJ. 2007. Ionic liquid as a green solvent for lignin. Journal of Wood Chemistry and Technology **27**(1): 23-33.

Ragauskas AJ. 2007. Lignin overview. Technical Report, Georgia Institute of Technology, Institute of Paper Science and Technology, Georgia, USA.

Ragauskas AJ. 2008. Basics of kraft pulping. Technical review, Georgia Institute of Technology, Institute of Paper Science and Technology, Georgia, USA.

Ralph J, Brunow G, Boerjan W. 2007. Lignins. Encyclopedia of Life Sciences, New Jersey: Wiley-Blackwell. pp. 1-10.

Ralph J, Lapierre C, Marita JM, Kim H, Lu F. 2001. Elucidation of new structures in lignins of CAD- and COMT-deficient plants by NMR. Phytochemistry **57**: 993-1003.

Ralph J, Hatfield RD. 1991. Pyrolysis-GC-MS characterization of forage material. Journal of Agricultural and Food Chemistry 39: 1426-1437.

Razvigorova M, Budinova T, Petrov N, Minkova V. 1998. Purification of water by activated carbons from apricot stones, lignites and anthracite. Water Research **32**(7): 2135-2139.

Reddy N, Yang Y. 2009. Citric acid cross-linking of starch films. Food Chemistry **118**(3): 702-711.

Roberts JE, Khan SA, Spontak RJ. 1996. Controlled black liquor viscosity reduction through salting-in. AIChE Journal **42**(8): 2319-2326.

Rodriguez-Mirasol J, Cordero T, Rodriguez JJ. 1993. Preparation and characterization of activated carbons from Eucalyptus kraft lignin. Carbon **31**(1): 87-95.

Rodríguez-Mirasol J, Cordero T, Rodríguez JJ. 1993a. Activated carbons from carbon dioxide partial gasification of eucalyptus kraft lignin. Energy Fuels **7**(1): 133-138.

Rodríguez-Mirasol J, Cordero T, Rodríguez JJ. 1993b. CO_2-reactivity of Eucalyptus kraft lignin chars. Carbon **31**(1): 53-61.

Saiz-Jimenez C, De Leeuw JW. 1986. Lignin pyrolysis products: Their structures and their significance as biomarkers. Organic Geochemistry **10**(4–6): 869-876.

Setua DK, Shukla MK, Nigam V, Singh H, Mathur GN. 2000. Lignin reinforced rubber composites. Polymer Composites **21**(6): 988-995.

Sirianni AF, Puddington IE. 1976. Reinforcing polymers with laundered amorphous lignin. U.S. Patent 3817974, USA. US3984362A

Sixta H. 2006. Chemical pulping. In: H. Sixta (ed) Handbook of Pulp, Weinheim: WILEY-VCH Verlag GmbH & Co. pp. 1-20.

Sjöström E. 1993. Wood Chemistry: Fundamentals and Application. Orlando: Academic Press.

Sjöholm E. 1999. Characterisation of kraft pulps by size-exclusion chromatography and kraft lignin samples by capillary zone electrophoresis. PhD dissertation, Royal Institute of Technology Department of Pulp and Paper Chemistry and Technology, Sweden.

Smook GA. 1992. Handbook for Pulp and Paper Technologists. 2nd ed. Vancouver: Angus Wilde Publishers.

Sundin J. 2000. Precipitation of Kraft Lignin Under Alkaline Condition. PhD dissertation, Stockholm: Royal institute of Technology, Sweden.

Tomani P. 2010. The lignoboost process. Cellulose Chemistry and Technology **44**(1-3): 53-58.

Turunen M, Alvila L, Pakkanen TT, Rainio J. 2003. Modification of phenol-formaldehyde resol resins by lignin, starch, and urea. Journal of Applied Polymer Science **88**(2): 582-588.

Uloth VC, Wearing JT. 1989. Kraft lignin recovery: acid precipitation versus ultrafiltration Part I. Laboratory test results. Pulp and Paper-Canada **90**(9): T310-T314.

Vanholme R, Demedts B, Morreel K, Ralph J, Boerjan W. 2010. Lignin biosynthesis and structure. Plant Physiology **153**: 895-905.

Wallmo H, Theliander H. 2009. The influence of hemicelluloses during the precipitation of lignin in kraft black liquor. Nordic Pulp and Paper Research Journal **24**(2): 165-171.

Wallmo H, Wimby M, Larsson A. 2009. Increase Production in Your Recovery Boiler with Lignoboost - Extract Valuable Lignin for Biorefinery Production and Replacement of Fossil Fuels. Tappi Engineering, Pulping and Environmental Conference Memphis, 11-14 October, Tennessee, USA. pp. 1-5

Watkins D., Nuruddin Md, Hosur M, Tcherbi-Narteh A, Jeelani S. 2015. Extraction and Characterization of Lignin from Different Biomass Resources. Journal of Materials Research and Technology **4** (1): 26-32.

Winandy JE, Rowell RM. 2005. Chemistry of wood strength. In: RM Rowel (ed). Handbook of Wood Chemistry and Wood Composites I. New York: CRC Press. pp. 303-347

Wu Y, Zhang S, Guo X, Huang H. 2008. Adsorption of Chromium(III) on lignin. Bioresource Technology **99**(16): 7709-7715.

Wyrzykowski D, Hebanowska E, Nowak-Wiczk G, Makowski M, Chmurzynski L. 2011. Thermal behaviour of citric acid and isomeric aconitic acids. Journal of Thermal Analysis and Calorimetry **104**: 731-735.

Zhu W, Theliander H. 2011. Equilibrium of lignin precipitation. Proceedings of the 16th ISWFPC, 8-10 June, Tianjin, China

3. CENTRIFUGAL WASHING AND RECOVERY AS AN IMPROVED METHOD FOR OBTAINING LIGNIN PRECIPITATED FROM SOUTH AFRICAN KRAFT MILL BLACK LIQUOR

(BASED ON PAPER I)

Abstract

Filterability of the colloidal suspension that forms during lignin precipitation from kraft black liquor is a cause of concern during the recovery and washing stages. This study investigates the use of a stepwise centrifugal recovery and washing method to improve the filterability of lignin isolated from black liquor obtained from a South African kraft mill. The initial precipitation of lignin was achieved by utilising 6 M sulphuric acid. The rate of attainment of the recovery of lignin was evaluated by comparing filtration after the centrifugal recovery method with filtration immediately after precipitation. At first, filtration immediately after precipitation showed higher lignin yields, however upon optimisation of the centrifugal recovery process, the yields between the two methods were comparable. The total washing and recovery time was reduced to 2 h or less utilising the centrifugal process compared with over 7 h observed for filtration immediately after precipitation. The centrifugal washing method also significantly improved the filterability of the sample at the final filtration step. To obtain more information regarding the source of wood for the black liquor utilised in this study, the molecular distribution of the lignin, as well as typical valorisation compounds; the obtained lignin precipitates were characterised by different analytical procedures. The lignin was characterised by FTIR, ^{1}H- and ^{13}C-NMR spectroscopies to elucidate the heterogeneity of the sample, as well as to provide information on the syringyl and guaiacyl content of the lignin. Size Exclusion Chromatography revealed that the dispersity of the polymer was uniform and pyrolysis-GC/MS analysis provided insights and identification of typical degradation compounds that could be obtained from the lignin sample.

3.1. Introduction

In recent years, there has been a global depletion of fossil fuel reserves. This has resulted in attention being given to utilising renewable resources in an attempt to replenish the energy resource gap that will emerge as fossil resources run out. South Africa is a developing economy, and its government, in keeping with the rest of the world, is focusing attention on green production (green chemistry and engineering), including the introduction of the biorefinery concept with a focus on the forestry, pulp and paper industry (de Vaal *et al.*, 2013).

The Biorefinery concept seeks to maximise the value derived from biomass feedstock. In the case of the pulp mill, the biorefinery concept dictates that, in addition to producing pulp, the mill can also draw value (and increase profits) from the rest of the biomass that is lost in the production. Lignin has been identified as a major product that can be obtained from black liquor (Wallmo *et al.*, 2009; Ibarra *et al.*, 2004).

As we have already seen, Lignin is the second most abundant biological material in the biosphere. Lignin extraction from black liquor has been at the centre of significant research in recent times (Zhu and Theliander, 2011; Nagy *et al.*, 2010; Ohman and Theliander, 2007; Ibarra *et al.*, 2005; Ibarra *et al.*, 2004; Argyropoulos *et al.*, 2002; Gilarranz *et al.*, 1998). Lignin precipitation from black liquor by acidification has been the most utilised method for isolation of the polymer. Sulphuric acid and carbon dioxide have been used successfully for precipitation of lignin from black liquor (Zhu and Theliander, 2011; García *et al*., 2009; Mussatto *et al.*, 2007; Ohman and Theliander, 2007; Alén *et al.*, 1979). The use of enzymatic action to assist in the precipitation of lignin has also been explored and has shown promise in the field (Ibarra *et al*., 2005; Argyropoulos *et al*., 2002).

Concerns with the precipitation of lignin have been raised at the recovery stage, where filtration of the polymer is a challenge due to the colloidal nature of the formed precipitate. Extensive studies on the filtration properties of lignin have been performed and it was shown that specially designed filtration equipment was required to improve the filterability of lignin precipitates (Zhu and Theliander, 2011; Wallmo and Theliander, 2009; Ohman and Theliander, 2007). In cases where such special equipment cannot be achieved, alternative methods of separating lignin precipitates from solution need to be explored.

A number of chemical characterisation techniques have been used in determining lignin structural features. Fourier transform infrared (FTIR) spectroscopy has been used to assist in resolving lignin heterogeneity features, where the guaiacyl and syringyl structural units of lignins can be predicted. More structural characteristics of lignin structures can be obtained from nuclear magnetic resonance (NMR) spectroscopic data (Kanitskaya *et al*., 1998; Pinto *et al*, 2002). Proton NMR assignments of the spectra offer quantitative estimates of the frequency of some structural elements of lignin (Lundquist, 1991). Size exclusion chromatography (SEC) offers important information on the isolated lignin, *viz* the molecular weight distribution. The information drawn from SEC sheds light on the kind of lignin obtained and determines whether this lignin can be processed further into fuel, chemicals, or materials (Tejado *et al.* 2007; Glasser *et al.*, 1993). Pyrolysis gas chromatography-mass spectrometry (Py-GC/MS) of lignins offers a wealth of information on the potential degradation products that can be obtained, specific to the lignin isolated (Ralph *et al*., 2007; Ralph and Hatfield, 1991; Saiz-Jimenez and De Leeuw, 1986).

This contribution represents a preliminary study that was performed to improve the recovery of lignin precipitated from kraft black liquor by using centrifugal washing and recovery. The objective of this work was to assess the centrifugal method as a potentially improved recovery method to that of filtration straight after precipitation. The lignin that was obtained was then characterised by elemental analysis (EA), FTIR, NMR, Py-GC/MS, and SEC to gain structural insight on the lignin typically obtained from South African mills, and attempt to identify the heterogeneity in cases where the wood source is unknown for the black liquor sample being investigated.

3.2. Materials and methods

3.2.1. Black Liquor Characterization

Black liquor was obtained from a kraft mill whose furnish was a mixture of softwood and hardwood. Its pH was measured to be 12.90 – 13.00 and the solid content was determined based on the TAPPI 650 om-05 method, with the following modifications; *ca* 10 g of black liquor was added to pre-weighed sawdust in Petri dishes, followed by evaporation in an oven set at 105 °C overnight. The final mass of the dried samples was then obtained following the TAPPI method mentioned. The inorganic matter was determined based on TAPPI T 211 om-93 method to determine the ash content. Total lignin in the black liquor was determined by UV-Vis spectrophotometry, whereby black liquor was diluted with NaOH and its absorbance measured at 280 nm. The absorptivity coefficient used to calculate the total lignin content in black liquor was 24.60 $L.g^{-1}.cm^{-1}$. Elemental analysis of the black liquor was also determined by CHNS/O analysis.

3.2.2. Lignin Precipitation from Black Liquor

Lignin was isolated by precipitation with H_2SO_4, according to the procedure described below. The bulk black liquor sample obtained from the mill was stirred for 3 hours to allow homogeneity. 100 mL of black liquor was sampled from the bulk sample, and 6M H_2SO_4 was added to the black liquor drop-wise while stirring until pH = 9 was reached (where most lignin is supposed to be precipitated according to Ohman and Theliander (2007)). The solution was left stirring for 1 hour to allow completion of the reaction. After this period, the sample did not show distinct signs of precipitation, and the solution appeared to still be black, although slightly viscous. The pH of the solution was thus further decreased by the addition of more H_2SO_4 until a visible sign of precipitation was observed (pH ~ 6), and some gas evolution. The final pH of the solution was established at 4. The solution was left stirring for a further 1 hour at the final pH.

Lignin was recovered from the solution by centrifugation at 3600 rpm for 20 minutes. The mother liquor was recovered and the dissolved lignin content was determined by UV-Vis spectrophotometry. The recovered lignin was subsequently washed with acid-water a number of times (4-5 times) (or until the supernatant was clearer), each time utilising a centrifuge to recover the washed precipitate. The concentration of the acid-water utilised during the washing process decreased with the number of washes (up to neutrality). For 15 mL centrifuge tubes used in this study, 8 – 10 mL was added to the tube for each wash. Finally, lignin was recovered by filtration with a Buchner funnel under vacuum suction.
Two methods for collection of the precipitated lignin were evaluated, viz.

i) **Filtration of the precipitated lignin.**

ii) **Centrifugation of the precipitated lignin prior to filtration**

The obtained lignin product was air-dried overnight and further dried in a vacuum oven at 40 °C.

3.2.3. Analytical Procedures

UV-Vis and Elemental analysis

The mother liquor supernatant obtained from the initial recovery step following the precipitation was analysed for dissolved lignin by UV-Vis spectrophotometry at 280 nm with a quartz cuvette with a path length of 1 cm, on a Varian 50 CONC spectrophotometer. Elemental analysis (CHNS/O) of the lignin precipitate (and black liquor) was performed on a Thermo Scientific Flash 2000 instrument.

FTIR

The lignin precipitate obtained was characterised by Fourier transform infrared (FTIR) spectroscopy equipped with attenuated total reflectance (ATR) sampling accessory on a Perking Elmer Spectrum 100 Series instrument. The data capturing settings for each spectrum were 10 scans, range: 4000 – 300 cm^{-1} and resolution: 4 cm^{-1}.

NMR

The structural features of the acetylated lignin (acetylation method found in the section for SEC analysis) samples were studied by NMR spectrometry using a Bruker Avance III spectrometer at 30 °C, where for ^1H spectra the following parameters were used: frequency of 600 MHz with 16384 data points, 13.36 μs pulse and pulse delay of 1.328 s. DMSO-d6 was used as a solvent. ^{13}C NMR spectra were obtained using a frequency of 150 MHz, 32768 data points, 13.35 μs and 1.328 s pulse delay. Chloform-d4 was also used as a solvent for another ^{13}C spectrum.

Py-GC/MS

Pyrolysis of approximately 200 μg of finely ground lignin sample was carried out for 10 s at 610 °C on a Frontier Lab EGA/PY-3030D multi-shot pyrolyzer, followed by gas chromatography-mass spectroscopy (GC/MS) performed on a Shimadzu Gas Chromatography GC-2010 plus linked to a GCMS-Q2010 mass spectrometer. The injector temperature of the GC/MS was kept at 280 °C and the MS transfer interface temperature was at 300 °C. The oven temperature was programmed from 40 °C to 300 °C at a heating rate of 6 °C/min, with the final temperature held for 15 min. The eluted compounds were identified by mass spectra comparison with NIST libraries.

SEC

Size Exclusion Chromatography was used to determine the molecular weight distribution of the lignin samples. The lignin samples were subjected to acetylation in order to enhance their solubility in the mobile phase solvent.(Tejado *et al*., 2007; Glasser *et al*., 1993). The acetylation reaction, which causes the substitution of the lignin hydroxyl functional groups by acetyl groups, was carried out by placing the lignin precipitate in a mixture of acetic anhydride and pyridine (1:1 v/v), with a final reaction mixture concentration of 0.033 g/mL. The reaction mixture was stirred at room temperature for 72 h (or longer to allow complete acetylation). Ethanol, equivalent to the solvent mixture, was added to stop the reaction, followed by evaporation under pressure at 60 °C. Continuous addition and evaporation of ethanol allowed for complete removal of the solvent mixture. The concentrate was dissolved in 20 mL chloroform and washed with water. The chloroform phase was dried over $MgSO_4$ and finally concentrated under reduced pressure at 50 °C. The resulting acetylated lignin was dried in a vacuum oven at 40 °C to constant weight and then dissolved in tetrahydrofuran (THF), to a concentration of 7 mg/L. The solution was filtered with a PTFE syringe filter prior to injection of 200 µL of the samples. SEC was performed on an HPLC pump (Rheos 2000) with THF at a flow rate of 1 mL/min. The eluted material was detected using a multi-angle laser light scattering (MALLS) detector (Wyatt Dawn EOS) in tandem with a UV detector (Perkin Elmer) and refractive index (Wyatt Optilab-T-rex) detector. The chromatography media consisted of SEC-columns (PSS – SDV, 10^4 and 10^6 Å connected in series, both 300 x 8 mm) in an oven (KNAUER Jetstream) at 35 °C. The system was also equipped with a guard column (PPS – SDV, 20 microns, 50 x 8 mm). The universal calibration curve for the instrument was based on polystyrene standards in the range 580 to 350 Daltons (Polymer Laboratories).

3.3. Results and discussions

3.3.1. Black liquor analysis

After repeatability and reproducibility studies on the sample, the moisture content of the black liquor was around 85%. This is typical of black liquors obtained prior to evaporation steps, *i.e.* weak black liquor. The inorganic material in black liquor was calculated to be 9%, and the total lignin content to be around 50%. The results obtained from the elemental analysis (C – 15.97, H – 7.97, O -46.45, S - 0.55) showed deviation from typical data obtained from the literature (Cardoso *et al*., 2009; Marklund, 2009). The major difference is observed on the carbon and oxygen content, whereby these two elements are usually found in more or less equal quantities. The black liquor sample in this experiment showed oxygen content that is approximately three times that of carbon.

3.3.2. Lignin characterisation

Lignin yield

The lignin yield obtained from precipitation experiments was approximately 83% on a dry-weight basis. The yield obtained was based on the lignin concentration in the black liquor. The method used to determine the amount of lignin in black liquor gives a reasonable estimate of the concentration, as other organics found in black liquor could also be absorbing at 280 nm, but it is known that lignin is the predominant material absorbing at that wavelength (Ohman and Theliander, 2007). The amount of lignin in the first supernatant was further analysed to obtain a better material balance of the precipitation procedure.

It was found that approximately 6% of the lignin was dissolved in the initial mother liquor during precipitation. Close to 10% of the lignin presumed to be contained in the original black liquor sample was unaccounted for, and this source of error could be attributed to the organic matter that absorbs with lignin at the same wavelength, as well as losses incurred in transferring the sample to and from the centrifuge tubes. Sample transfer between washes during centrifugation could also contribute to the estimated product losses.

Even though great care was taken during the experiments, some sample losses could not be avoided due to the small volumes that were used in the centrifuge utilised for these experiments. The absence of a large centrifuge necessitated the use of numerous sample transfers to process the samples. As mentioned, centrifugation was selected for this study due to its efficiency, as filtration was onerous.

Samples that were filtered straight after precipitation showed a higher lignin yield (93%), however, filtration of the sample took as long as an entire day to accomplish for only 100 mL of black liquor utilised for precipitation. Stepwise centrifugal washing of the precipitate, prior to filtration in the final step, on the other hand, was achieved in less than 2 hours.

Centrifugation of the sample allows for a better separation of the colloidal suspension formed as a result of lignin precipitation from black liquor. Furthermore, the centrifuge also assists in quick removal of the mother liquor during the stepwise washing, as compared with having to add more wash water to the filtration vessel, which will result in even much longer filtration time. It is also envisaged that centrifugation circles would also significantly decrease with more centrifugal force applied (i.e. increase in speed).

Improved lignin yields from centrifugal recovery comparable with straightforward filtration were obtained from optimisation studies carried out on a larger centrifuge after it was acquired (see Chapter 6 for a discussion).

Elemental analysis of the precipitated lignin sample showed the following data; C - 66.80%, H - 6.27%, N - 0.20%, S - 4.82%, O - 18.84%. The CHO ratio of the precipitated lignin was compared with the data reported in the literature for different wood species (Evtuguin *et al.*, 2001; Scholze *et al.*; 2001), and it was observed that the obtained lignin was closely related to that of Eucalyptus species. The information about the wood source utilised in the mill was not provided.

FTIR

The structure of lignin obtained was characterised by FTIR, ^{1}H-NMR, and ^{13}C-NMR spectroscopies. An FTIR spectrum of the lignin was measured in the range v/cm^{-1} 4000 – 400 as shown in Figure 3.1. In general, the spectra observed for this study were of low resolution, that is, the peaks observed had low transmittance. Scans were repeated a number of times to improve resolution; however, the spectrum shown in Figure 3.1 was the best observed for this work.

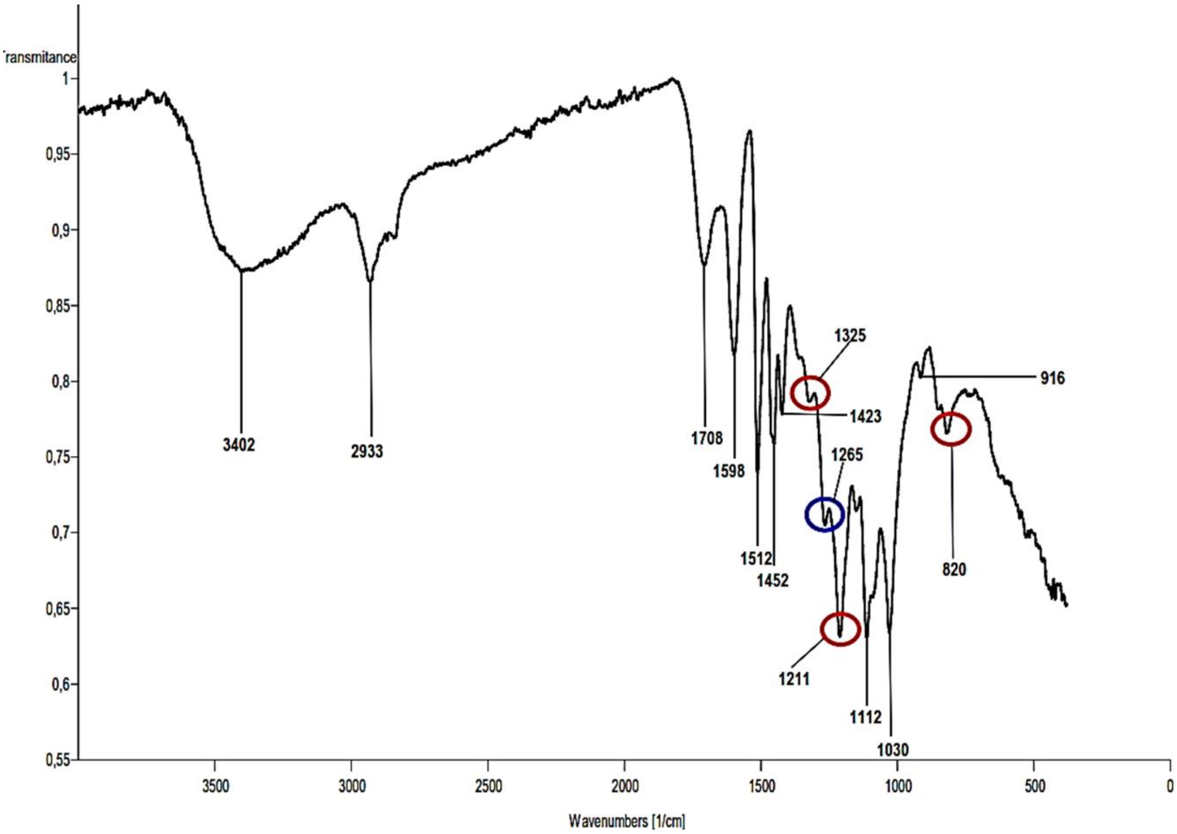


Figure 3.1. FTIR spectrum of lignin with assignment**s** for the main absorption peaks. The S-ring and G-ring moieties in the spectrum are also identified

Resolution of the spectrum and assignment of lignin absorption bands on the FTIR spectrum is possible only by approximation of the predominant contribution of certain atomic groups, due the complexity of its structural units and nature (Fitigău *et al*., 2013). The key peaks representing the structure of lignin are found in the range v_{max}/cm^{-1} 1708 – 820. The aromatic ring of lignin is represented by the following main absorption bands; v_{max}/cm^{-1} 1598, 1512, 1423, 915. The band at v_{max}/cm^{-1} 1423 represents aromatic ring stretching with in-plane C-H deformation. Ether and methoxy groups of lignin in the spectra are represented by the following absorption bands in the IR spectrum; v_{max}/cm^{-1} 1708, 1325, 1265 cm^{-1}. Hydroxyl groups in the spectrum are assigned to; v_{max}/cm^{-1} 3437, 1086, 1030 cm^{-1}. Vibration bands in infrared spectroscopy may also assist in recognising the syringyl (S-ring, circled red on the spectrum) and guaiacyl (G-ring, circled blue on the spectrum) units for a given lignin.

Table 3.1 assigns absorption bands that are commonly observed to represent the S- and G-ring in lignin IR. It is observed from this table that the lignin obtained in the current study was represented more by the syringyl type features than guaiacyl. With the knowledge that hardwoods contain more S-units than G-units, it can be stated that the 'FTIR data obtained showed more absorption bands in favour of S-units, thus the mixture of wood species might have been utilised, and the black liquor contained more hardwood than softwood species'.

Table 3.1. FTIR absorption assignments for syringyl and guaiacyl type rings

v (cm^{-1})	Band assignment	Ring type
1325	C-O stretch	S-ring
1265	C-O stretch	G-ring
1112	Aromatic C-H deformation	S-ring
820	C-H stretching	S-ring

NMR

Further structural characteristics of lignin were determined by ^{1}H and ^{13}C NMR spectra. The lignin sample was first acetylated to enhance its solvation in most organic solvents, as well as improvement of the resolution of NMR spectra. The proton NMR spectrum is shown in Figure 3.2a. The spectrum observed is typical of lignin, whereby chemical shifts of δ_H/ppm 8.58 belong to the syringyl unit directly attached to phenolic protons; δ_H/ppm 7.79 – 6.73 represent syringyl and guaiacyl units aromatic protons; the broad peak at δ_H/ppm 3.94 – 3.64 represents methoxy groups of lignin; δ_H/ppm 2.30 – 2.00 represents the benzyl protons; and aliphatic protons are represented by chemical shifts at δ_H/ppm 1.24 – 0.8 (Lundquist, 1991; Lundquist, 1992; Yuan *et al*., 2009).

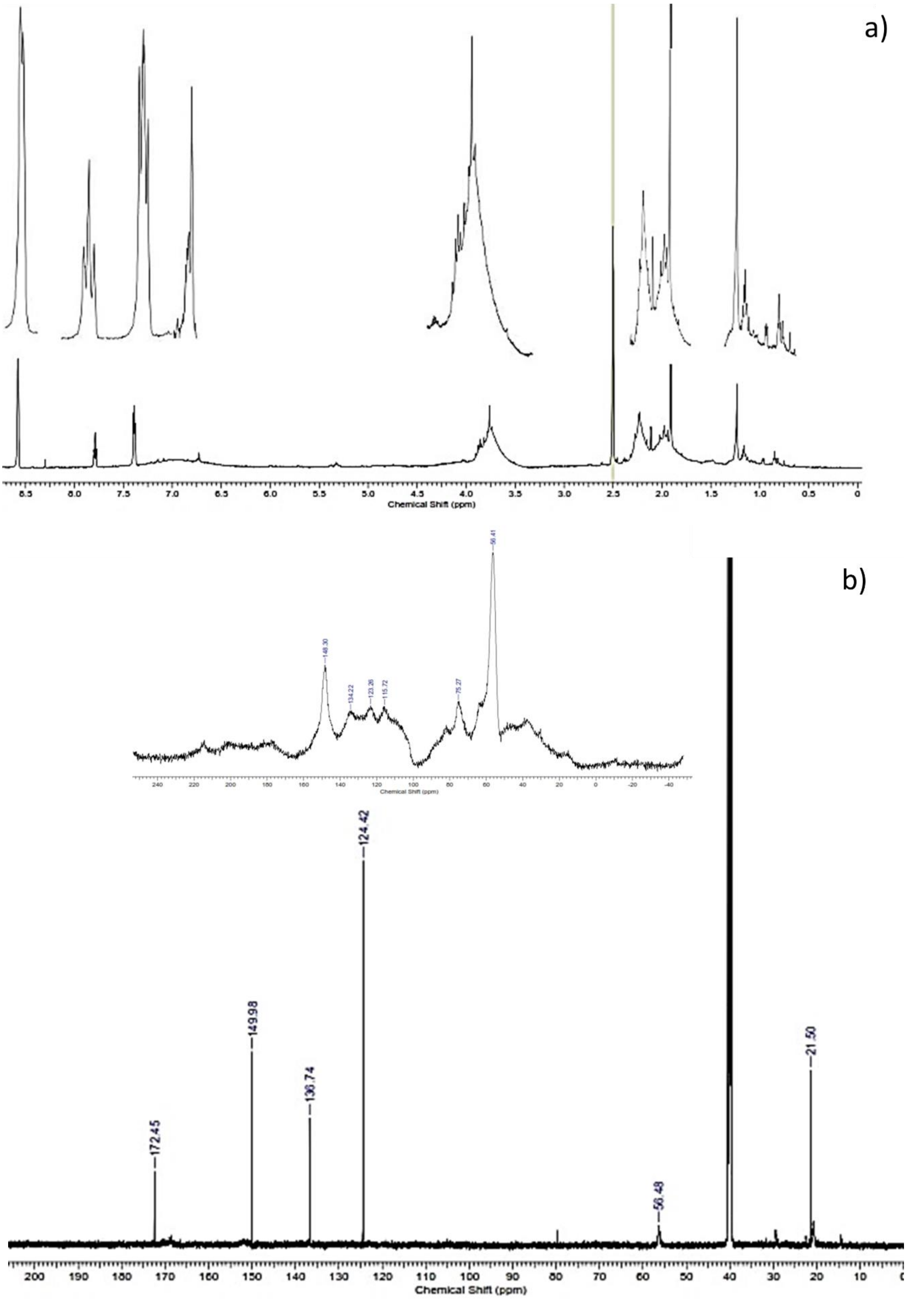


Figure 3.2. a) ^{1}H NMR spectrum of acetylated lignin sample. Peaks are also zoomed in to show the splits. b) ^{13}C NMR Spectrum of acetylated lignin sample. The ^{13}C spectrum shown

in the insert above is one obtained with $CDCl_3$ and present general features for commonly observed lignin ^{13}C NMR spectrum

The peak observed at δ_H/ppm 8.58 is specific for syringyl C-5 phenolic hydroxyl group protons, showing that the lignin sample obtained has a high content of syringyl units. This observation can further be validated with the reasoning that almost all phenolic hydroxyl groups in the molecule were expected to be acetylated (as the acetylation reaction was performed for 72 hours or more). However, the hydroxyl group signal was nonetheless detected with a very well defined peak with a double-doublet displaying three protons. Furthermore, the signal detected at δ_H/ppm 6.73 usually assigned to syringyl unit aromatic protons, also confirmed the assumption that the obtained lignin had higher syringyl content than guaiacyl (Yuan *et al*., 2009). The multiplet signal at δ_H/ppm 3.9 – 3.64 showed that there is a significant number of methoxy protons, representing ~ 33% of the total number of protons in the whole spectrum. These methoxy protons represent the syringyl and guaiacyl units of lignin.

The acetylated lignin sample was also analysed by ^{13}C NMR to further elucidate any additional structural features (Figure 3.2b). DMSO is known to be the best solvent for acetylated (as well as non-acetylated) lignin samples for obtaining NMR spectra. Prior to obtaining DMSO-d_6, ^{13}C NMR spectrum of the acetylated lignin sample was obtained by dissolving in chloroform ($CDCl_3$) (Figure 3.2b, top insert).

The spectrum obtained with chloroform was found to have a closely related general appearance to most lignin spectra found in literature, although missing a few peaks (Pinto *et al*., 2002; Lundquist, 1992; Lundquist, 1991). The signal detected (in the DMSO spectrum) at δ_C/ppm 172.45 represent aliphatic carbonyl carboxyl carbons. The aromatic region of the spectrum is indicated by peaks at δ_C/ppm 149.98, 136.74, 124.42 that represent etherified and non-etherified carbons of the syringyl and guaiacyl units in the lignin samples. The signal at δ_C/ppm 56.48.is representative of the methoxy groups in syringyl and guaiacyl units. The signal at δ_C/ppm 21.50 represents saturated hydrocarbons that are found in the side chains of the lignin molecules (Yuan *et al*., 2009; Sun and Tomkinson, 2001). These hydrocarbon side chains are understood to arise from kraft mills utilising a mixture of softwood and hardwoods during delignification cooking process (see Py-GC/MS data). The large broad peak at δ_C/ppm 40 is the solvent peak, DMSO.

Py-GC/MS

Py-GC/MS was used to evaluate the degradation products that could be obtained from the precipitated lignin. A typical chromatogram is shown in Figure 3.3. The structures of the pyrolysis products were determined using gas chromatographic retention times, mass spectrometry data, and identified using NIST libraries. The retention times and resulting products are shown in Table 3.2.

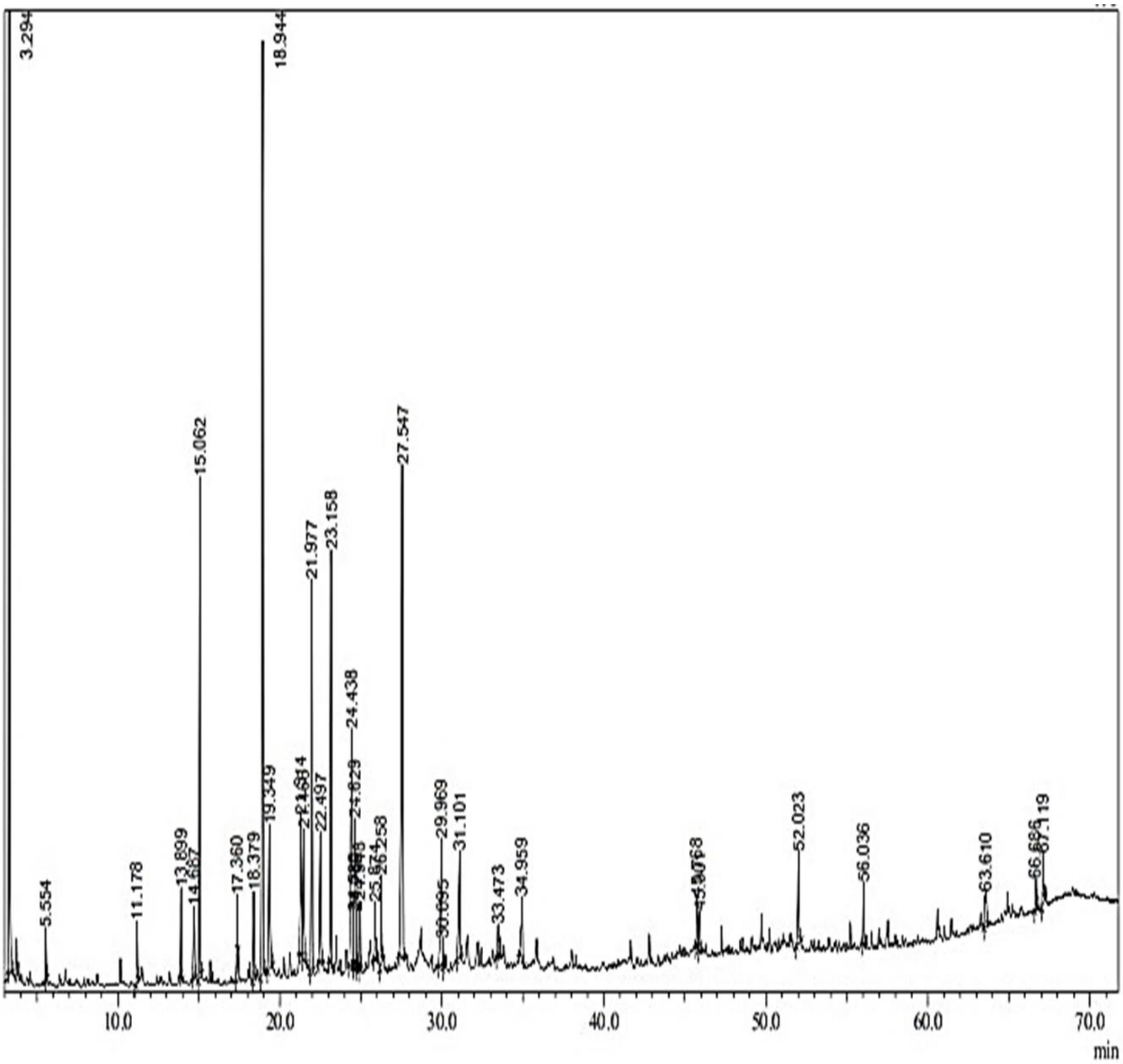
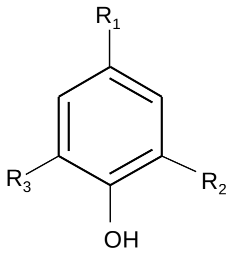


Figure 3.3. Py-GC/MS gas chromatogram of lignin showing peaks labelled according to their retention time for easy reference with Table 3.2

Table 3.2. Products generated from lignin pyrolysis.



Peak no.	Ret. Time	Base m/z	R1	R2	R3	Name
1	3.75	91.05				Toluene [#]
2	5.55	96.05				3-Furaldehyde, Furfural [#]
3	11.18	94.05				Phenol
4	13.90	108.1			CH3	2-methyl-phenol
5	14.69	107.1	CH3			p-Cresol
6	15.06	109.1		OCH3		2-methoxy-phenol
7	17.36	122.1	CH3	CH3		2,4-dimethyl-phenol
8	18.38	123.1			OCH3	2-Methoxy-5-methyl-phenol *****
9	18.94	138.1	CH3		OCH3	Creosol
10	19.35	110.1		OH		Catechol
11	21.31	140.1	OH		OCH3	1,4-Benzenediol, 2-methoxy
12	21.47	124.1	CH3		OH	1,2-Benzenediol, 4-methyl
13	21.98	137.1	CH2CH3	OCH3		Phenol, 4-ethyl-2-methoxy
14	22.50	124.1	CH3	OH		1,2-Benzenediol, 4-methyl
15	23,16	150.1	O=CCH3	CH3		4-Hydroxy-3-Methoxyacetophenone
16	23.49	138.1			OCH3	2-methoxy-3methyl-phenol *****
17	24.44	154.1		OCH3	OCH3	Phenol, 2,6-dimethoxy
18	24,63	164.1	CH2CH=CH2	OCH3		Eugenol
19	24.77	151.1	O=CCH3	OCH3		Apocynin
20	24.95	137.1	CH2CH2(CH3 or OH)	OCH3		Phenol, 2-methoxy-4-propyl or Homovanillyl alcohol
21	25.58	164.1	CH=CHCH3	OCH3		Phenol, 2-methoxy-4-(1-propenyl)-, (Z)
22	25.88	164.1	CH=CHCH3	OCH3		trans-Isoeugenol
23	27.55	168.1	O=COH		OCH3	3-Hydroxy-4-methoxybenzoic acid
24	29.97	167.1	CH3	OCH3	OCH3	Benzene, 1,2,3-trimethoxy-5-methyl [+]
25	31.10	180.1	O=CCH3	OCH3	OCH3	3',5'-Dimethoxyacetophenone [+]
26	33.60	194	CH2CH=CH2	OCH3	OCH3	4-allyl-2,6-dimethoxy phenol[+]
27	45.77	55.1				cis-Vaccenic acid [#]
28	52.02	239.2				Dehydroabietic acid [#]

Smaller aromatic hydrocarbons, and furan compounds, and other compounds that can be obtained from lignin.

* R1 group represents hydrogen.

\+ The OH group is not present in these compounds.

The other products that were obtained from lignin pyrolysis, such as furans, aromatic hydrocarbons, and long chain acids are also shown in Table 3.2 (peak no. 1, 2, 3, 27 and 28). Major lignin phenolic compounds are obtained between ca 15 – 30 mins in the chromatogram (peak no. 5 - 26). The monolignols released belong to the guaiacol and syringol families. The chromatogram shows 7 major peaks belonging to guaiacol (6), 2-methyl-5-methoxyphenol (8), 4-ethylquaiacol (13), acetovanillone (15), 4-methylguaiacol (17), syringol (17), trans-isoeugenol (23) moieties. Guaiacol compounds are released first during pyrolysis (rt 6 – 23 mins), followed by syringol compounds (rt 24 – 30 mins).

From Table 3.2, it can be seen that most of the lignin compounds obtained display a guaiacol characteristic and are intact (6, 8, 9, 13, 16, 18, 20), whereas only two syringol type compounds can be obtained (17 and 26). Since syringol compounds are larger than their guaiacol counterparts, the data showed that there is a possibility that the syringol compounds were broken down (resulting in the loss of the other methoxy group) and detected as guaiacol compounds. The long chain hydrocarbon, peak 27, coincides with the information reported earlier that the lignin obtained in this study could originally be from a mixture of hardwood and softwood cook.

SEC

The molecular weight distribution of the acetylated lignin sample was determined by SEC. The resulting chromatograms (Figure 3.4) were acquired by three different methods, that is, assuming 100% mass recovery in the SEC columns, utilising refractive index increment (dn/dC) of 1.65 cm^{-3}.g^{-1}, and dn/dC of 1.80 cm^{-}3.g^{-1}. The dn/dC of 1.80 cm^{-}3.g^{-1} belongs to polystyrene standards, and it has been shown that lignin and polystyrene standards display similar patterns throughout a wide range of molecular weights (Botaro and da Silva Curvelo, 2009; Ferhan, *et al*., 2013). In their study on the accurate measurement of the dn/dC of lignin, Contreras *et al*. (2008), found the dn/dC of *Eucalyptus globulus* lignin to be 1.65 cm^{-3}.g^{-1}.

The molecular weights and distribution calculated from the three methods were then compared (Table 3.3). The larger peaks in the profile in Figure 3.4 represent higher molecular weight lignins, and the smaller peaks that elute at a later stage represent lower molecular weight lignin fractions. Lower molecular weight fractions depicted by these smaller peaks in the elution profile can also be predicted to be closely related to monomers of lignin. The number average molecular weight (M_n), and the weight average molecular weight (M_w) calculated from both the above mentioned dn/dC values showed a close relation with each other, with a difference of 16500 and 17200 g.mol^{-1}, respectively.

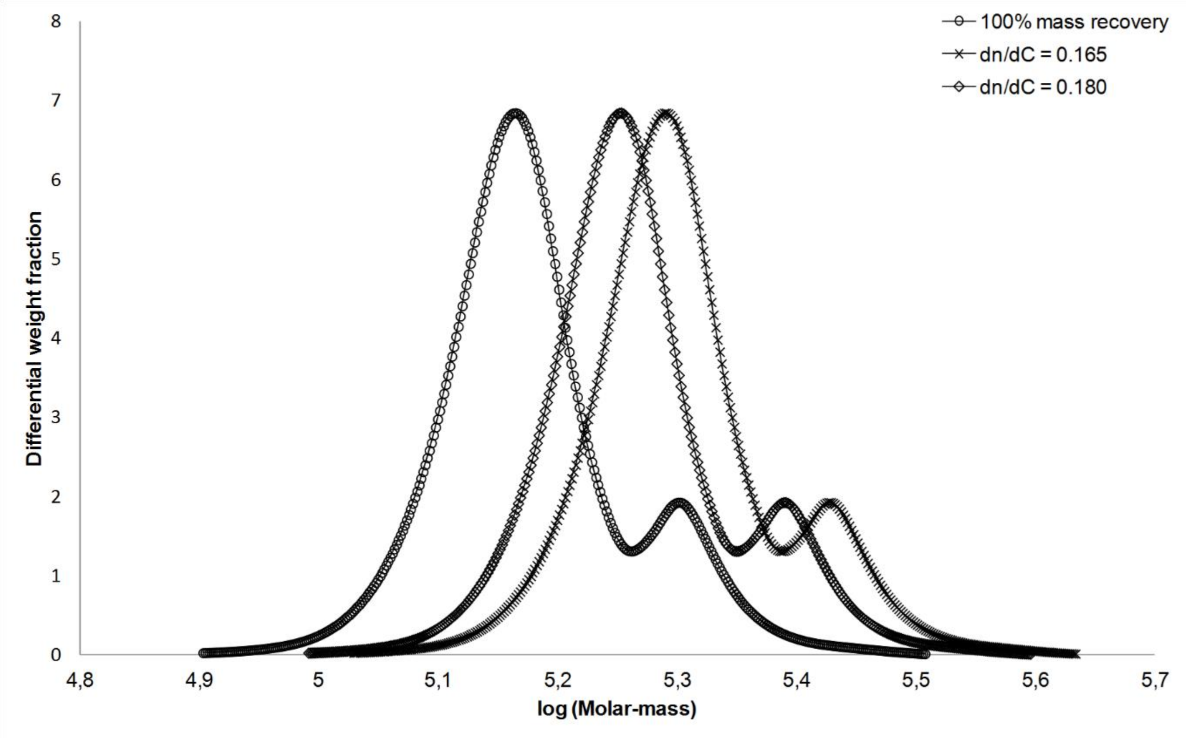


Figure 3.4. SEC curves showing three different methods to determine the molecular weight distribution of the lignin sample.

Table 3.3. Size exclusion chromatography results for acetylated lignin sample

Method	Mn (g.mol^{-1})	Mw (g.mol^{-1})	Mz (g.mol^{-1})	Polydispersity (cm^{-3}.g^{-1})	
				Mw/Mn	Mz/Mn
100% mass recovery	1.48E+05	1.54E+05	1.60E+05	1.03 (± 0.058)	1.07 (± 0.106)
dn/dC 0.165	1.98E+05	2.06E+05	2.14E+05	1.03 (± 0.058)	1.07 (± 0.106)
dn/dC 0.180	1.82E+05	1.89E+05	1.96E+05	1.03 (± 0.58)	1.07 (± 0.106)

A large difference in the averages is observed with the calculation where 100% mass recovery in the columns was assumed, with a close to 50000 g.mol^{-1} difference across the three methods. These lower values for M_n and M_w displayed by this method can only mean that less than 100% of the mass injected was recovered in the columns. The dn/dC for polystyrene standards would be a much better reference for comparing, for the reason that the ‘true’ origin of the species of lignin sample in this study was not provided, as well as different species would differ from country to country even though they might be from the same *genus*. Thus, utilising polystyrene as a reference, it can be proposed that *ca* 82% of the mass was recovered in the columns from our SEC system. The dispersity (replacing polydispersity index) for the lignin sample was observed to be Đ = 1.036 cm^{-3} g^{-1}. The current definition for dispersity is that it is a ratio of M_n and M_w to measure the spread of the molar mass in a polymer (Stepto et al., 2009). The Đ value obtained for the sample studied is observed to show that the lignin polymer displayed a close to uniform structure, and falls in the narrow polymer range. Lignins with a narrow molecular weight distribution are preferred for valorising.

3.4. Conclusions

This study demonstrated that centrifugal washing and recovery of lignin is much better than filtration straight after precipitation. The centrifugal method improved washing and recovery time for the samples significantly. Since the wood species from which the black liquor sample was obtained was not provided, characterisation of the lignin samples showed a predominance of syringyl moieties, indicating that more hardwood than softwood was utilised during the pulping process. SEC data revealed high molecular weight averages in the lignin sample; whereby Đ = 1.036 $cm^{-3}.g^{-1}$ of the lignin sample fell in the narrow molecular weight region, revealing uniformity in the polymer. Thus, the centrifugal method of recovery of the precipitated lignin also provides a sample that has good prospects for further modification. Py-GC/MS analysis provided identification of potential compounds that could be obtained through pyrolysis of the sample. Such products provide a scope for the valorisation of lignin in future studies.

References

Alén R, Patja P, Sjöström E. 1979. Carbon dioxide precipitation of lignin from pine kraft black liquor. Tappi Journal **62**(11): 108-110.

Argyropoulos DS, Sun Y, Palus E. 2002. Isolation of residual kraft lignin in high yield and purity. Journal of Pulp and Paper Science **28**(2): 50-54.

Botaro VR, da Silva Curvelo AA. 2009. Monodisperse lignin fractions as standards in size-exclusion analysis: Comparison with polystyrene standards. Journal of Chromatography A **1216**(18): 3802-3806.

Cardoso M, de Oliveira ED, Passos ML. 2009. Chemical composition and physical properties of black liquors on liquor recovery operation in Brazilian pulp mills. Fuel **88**: 756-763.

Contreras S., Gaspar A.R., Guerra, A., Lucia, L.A., Argyropoulos, D.S. 2008. Propensity of lignin to associate: Light scattering photometry study with native lignins. Biomacromolecules **9**(12): 3362-3369.

Evtuguin DV, Pascoal NC, Silva AMS, Domingues PM, Amado FML, Robert D, Faix O. 2001 Comprehensive study on the chemical structure of dioxane lignin from plantation Eucalyptus globulus wood. Journal of Agricultural and Food Chemistry **49**(9): 4252-4261.

de Vaal PL, Barker LF, du Plessis EC 2013. Chapter 20 Biorefining: A green tribological perspective. In M Nosonovsky, B Bhushan (eds.), Green tribology: Biomimetics, Energy Conservation and Sustainability. Berlin, Heidelberg: Springer. pp. 565-605

Ferhan M, Yan N, Sai M. 2013. A new method for demethylation of lignin from woody biomass using biophysical methods. Journal of Chemical Engineering & Process Technology **4**(5): 160.

Fitigău IF, Peter F, Boeriu CG 2013. Structural analysis of lignins from different sources. World Academy of Science, Engineering and Technology **76**: 107-112.

García A, Toledano A, Serrano L, Egüés I, González M, Marín F, Labidi J. 2009. Characterization of lignins obtained by selective precipitation. Separation and Purification Technology **68**: 193-198.

Gilarranz MA, Rodriguez F, Oliet M, Revenga JA. 1998. Acid precipitation and purification of wheat straw lignin. Separation Science and Technology **33**(9): 1259-1377.

Glasser WG, Dave V, Frazier CE 1993. Molecular weight distribution of (semi-) commercial lignin derivatives. Journal of Wood Chemistry and Technology **13**(4): 545-559.

Ibarra D, del Río JC, Gutiérrez A, Rodríguez IM., Romero J, Martínez M.J, Martínez, ÁT. 2004. Isolation of high-purity residual lignins from eucalypt paper pulps by cellulase and proteinase treatments followed by solvent extraction. Enzyme and Microbial Technology **35**: 173-181.

Ibarra D, del Río JC, Gutiérrez A, Rodríguez IM., Romero J, Martínez MJ, Martínez ÁT. 2005. Chemical characterization of residual lignins from eucalypt paper pulps. Journal of Analytical and Applied Pyrolysis **74**: 116-122.

Kanitskaya LV, Kozlov IA, Babkin VA, & Deryagina EN. 1998. Quantitative ^{1}H and ^{13}C NMR spectroscopy of lignin. Chemistry of Plant Raw Materials **2**(N3): 35-40.

Lundquist K. 1991. ^{1}H NMR spectral studies of lignins: Quantitative estimates of some types of structural elements. Nordic Pulp and Paper Research Journal **3**: 140-146.

Lundquist K. 1992. Proton (^{1}H) NMR spectroscopy. In SY Lin, CW Dence (eds.), Methods in lignin chemistry. Berlin, Heidelberg: Springer-Verlag. pp. 242-249

Marklund M 2009. Black liquor recovery: How does it work? The Black Liquor Gasification Research Program Communication, Energy Technology Centre, Piteå Sweden.

Mussatto SI, Fernande M, Roberto IC. 2007. Lignin recovery from brewer's spent grain black liquor. Carbohydrate Polymers **70**: 218-223.

Nagy M, Kosa M, Theliander H, Ragauskas AJ. 2010. Characterization of carbon dioxide precipitated kraft lignin to promote its utilization. Green Chemistry **12**: 31-34.

Ohman F, Theliander H. 2007. Filtration properties of lignin precipitated from black liquor. Tappi Journal 6(7): 3-9.

Pinto PC, Evtuguin DV, Neto CP, Silvestre AJD, Amad FML. 2002. Behaviour of eucalyptus globulus lignin during kraft pulping II: Analysis by NMR, ESI/MS, and GPC. Journal of Wood Chemistry and Technology **22**(2-3): 109-125.

Ralph J, Brunow G, Boerjan W. 2007. Lignins. Encyclopaedia of Life Sciences, John Wiley & Sons, Ltd. pp. 1-10.

Ralph J, Hatfield RD. 1991. Pyrolysis-GC-MS characterization of forage material. Journal of Agricultural and Food Chemistry 39: 1426-1437.

Saiz-Jimenez C, De Leeuw JW. 1986. Lignin pyrolysis products: Their structures and their significance as biomarkers. Organic Geochemistry **10**(4–6): 869-876.

Scholze B, Hanser C, Meier D. 2001. Characterization of the water-insoluble fraction from fast pyrolysis liquids (pyrolytic lignin). Part II. GPC, carbonyl groups, and carbon13 NMR. Journal of Analytical and Applied Pyrolysis **58-59**: 387-400.

Stepto RFT, Gilbert, RG, Hess, M, Jenkins, AD, Jones, RG, Kratochvíl P. 2009. Dispersity in polymer science. IUPAC, Pure and Applied Chemistry **81**(2): 351-353.

Sun R, Tomkinson J. 2001. Fractional separation and physico-chemical analysis of lignins from the black liquor of oil palm trunk fibre pulping. Separation and Purification Technology: **24**(3): 529-539.

Tejado A, Pena C, Labidi J, Echeverria JM, Mondragon I. 2007. Physico-chemical characterization of lignins from different sources for use in phenol–formaldehyde resin synthesis. Bioresource Technology **98**: 1655-1663.

Wallmo H, Theliander H. 2009. The influence of hemicelluloses during the precipitation of lignin in kraft black liquor. Nordic Pulp and Paper Research Journal **24**(2): 165-171.

Wallmo H, Wimby M, Larsson A. 2009. Increase production in your recovery boiler with LignoBoost - extract valuable lignin for biorefinery production and replacement of fossil fuels. Tappi Engineering, Pulping and Environmental Conference, Memphis, Tennessee. pp 1-5.

Yuan T, He J, Xu F, Sun R. 2009. Fractionation and physico-chemical analysis of degraded lignins from the black liquor of *Eucalyptus Pellita* KP-AQ pulping. Polymer Degradation and Stability **94**(7): 1142-1150.

Zhu W, Theliander H. 2011. Equilibrium of lignin precipitation. 16th International Symposium on Wood, Fiber and Pulping Chemistry, Tianjin, China. pp. 195-199.

4. CHARACTERISTICS OF LIGNIN PRECIPITATED WITH ORGANIC ACIDS AS A SOURCE FOR VALORISATION INTO CARBON PRODUCTS

(BASED ON PAPER II)

Abstract

Lignin is a by-product of multiple lignocellulosic biomass-derived industries. Hardwood (HW) and softwood (SW) lignin were obtained by precipitation from black liquor. Elemental analysis of the samples indicated that the sulphur content varied between the wood species, with SW organic acid precipitated samples showing the lowest sulphur content. Fourier transform infrared spectroscopy (FTIR) showed differences in the intensities of the absorption peaks for each sample. Thermogravimetric (TG) analysis of the lignin samples in the presence of air revealed differences in the main degradation region of the TG/DTG curves. The type of organic acid used for precipitation appeared to influence the thermal degradation of the lignin samples. TG analysis under nitrogen resulted in carbon yields that were acceptable for the lignin samples to be considered as raw materials for carbon preparation. Scanning electron microscopy (SEM) images of the samples showed swelling in the lignin chars and revealed differences in morphology of their structure, showing that different precipitation media would produce different carbon structures.

4.1. Introduction

The biorefinery concept dictates that maximum value be drawn from biomass, rather than producing only a single product and discarding the rest of the biomass as waste (Clark *et al*., 2009; Demirbas, 2009; Antizar-Ladislao and Turrion-Gomez, 2008). Integrating biorefinery systems into current technologies, for example, in the kraft pulping process, would see mills achieving maximal usage of the biomass, as well as add to the product stream of the mill, thereby increasing profits. For example, instead of burning the whole biomass material for fuel purposes, the biomass can be pre-processed to isolate the hemicellulose component for use in ethanol production, and thereafter the rest of the biomass could be utilized as solid fuel (Sassner and Zacchi, 2008; Wooley *et al*., 1999).

The kraft pulping process produces black liquor as a by-product. This by-product contains lignin, sugars, cooking chemicals, and extractives. In current kraft mills, the black liquor is processed in a recovery boiler to recover cooking chemicals, as well as to provide energy by combustion of the lignin component. Ideally, this would render a kraft mill a closed system. However, in older mills the capacity of the recovery boiler is limited, consequently resulting in a bottleneck of black liquor processing, which in turn causes complications in the mill.

Several methods have been proposed in recent years to replace recovery boilers with methods such as black liquor gasification, which could add more value to the mills to produce energy, as well as chemicals (Bludowsky and Agar, 2009; Naqvi *et al*., 2010a; Naqvi *et al*., 2010b). Gasification of black liquor has a potential to produce electricity, chemicals, as well as fuels such as dimethyl ether, synthetic gas (syngas), methanol, hydrogen, etc. (Naqvi *et al*., 2010a; Naqvi *et al*., 2012; Neimark *et al*., 2008). Another way to offload the excess black liquor would be to extract lignin. Due to its abundance, aromaticity, and carbon content, lignin has been identified as a resource that could have a high potential in the chemical industry, so much that it has been envisaged to be adequate enough to replace fossil fuel resources (Ibarra *et al*., 2004; Ragauskas *et al*., 2006; Wallmo et al., 2009).

Traditionally lignin is obtained from black liquor by precipitation methods involving the use of acids, mostly with sulphuric acid, and more recently with a combination of carbon dioxide and sulphuric acid (Zhu and Theliander, 2011; Tomani, 2010; García *et al*., 2009; Alén *et al*., 1979). At pH ~4, complete lignin precipitation has been observed by most researchers. Utilization of H_2SO_4 has also been shown to release foul gases such as SO_2 and/or H_2S during the precipitation experiments (Helander *et al*., 2013; Uloth and Wearing, 1989). The release of these environmentally unfriendly gases when utilizing H_2SO_4 for lignin precipitation could prove to be an inefficient acidification technology on an industrial scale. Therefore, it is worth exploring other acids for lignin precipitation that would have much greener consequences to the environment, more especially when envisaging integrated biorefineries. Organic acids can be effective alternatives for lignin precipitation. Carbon based acids can serve as good precipitating agents because they would not introduce any objectionable elements during the precipitation process, thereby producing a ‘more green’ lignin product.

Organic acids are also not costly, as some of them are by-products of other processes, and they are nontoxic (Reddy and Yang, 2009). Polycarboxylic acids such as citric acid, have been shown to increase the mechanical properties of polymers such as cellulose and regenerated protein fibres by crosslinking the hydroxyl groups, as well as utilized as non-polymeric fillers for size modification and porosity control of nano-powders (Wyrzykowski *et al*., 2011; Reddy and Yang, 2009). These characteristics could also be beneficial for lignin valorisation into carbon fibres and activated carbon because polymer stability is essential for pre-treatment steps (Rosas *et al*., 2014; Ruiz-Rosas *et al*., 2010).

The objective of the contribution was to investigate the thermal behaviour of lignin samples precipitated from kraft black liquor with three organic acids (formic, acetic, and citric acid). The purpose of utilizing organic acids was to avoid the negative effects of using sulphuric acid. To gain insight of the hard- and softwood lignin samples, their characteristics were examined by elemental analysis (EA) and Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TG), as well as scanning electron microscopy (SEM) after carbonisation.

4.2. Materials and Methods

4.2.1. Lignin Isolation

A new batch of hardwood (HW) and softwood (SW) black liquor samples were obtained from a kraft mill in South Africa for the studies in this chapter. The mill used mostly eucalyptus (80%) and some pine wood (20%) furnishes. The black liquor samples were stirred for 3 hours at room temperature to assure homogeneity in the bulk samples. Lignin was then isolated by precipitation with sulphuric acid (SA), as well as three organic acids, viz., formic (FA), citric (CA), and acetic (AA). An efficient procedure for precipitation, isolation, and recovery of the lignin has been described in Chapter 3 and in a published paper (Namane *et al*., 2015), was utilised.

4.2.2. Characterization

The lignin samples were dried in an oven at 70 °C overnight. Elemental analysis for carbon, hydrogen, nitrogen and sulphur (CHNS) was performed on a Perkin-Elmer 2400-C instrument (Malaga, Spain), and O content was evaluated by difference. TG experiments were performed using a model CI Electronics Ltd. Thermobalance (Malaga, Spain). The initial sample weight was constantly adjusted to approx. 10-12 mg and a continuous gas (air or nitrogen) flow rate of 150 mL/min (STP), with a linear heating rate of 10 °C/min until a temperature of 900 °C was reached to obtain the TG and differential TG curves. The temperature signal for the controller was measured by means of a chromelalumel thermocouple placed inside the reaction tube. The sample weight loss was continuously recorded in a microcomputer data acquisition system.

The dried lignin samples were characterized by Fourier transform infrared (FTIR) spectroscopy on a Bruker Optics Tensor 27 FT-IT spectrometer (Malaga, Spain): 50 scans, scanning range 4000-400 cm^{-1} and a resolution of 4 cm^{-1}. The ratio between sample and KBr, as well as the weight of the disk, was kept constant for the samples for FTIR.

Scanning electron microscopy (SEM) micrographs were obtained by utilizing JEOL JSM-6490LV instrument (Malaga, Spain).

4.3. RESULTS AND DISCUSSION

4.3.1. Elemental Analysis

A representative elemental composition of the lignin samples precipitated from different acids is shown in Table 4.1. Elemental analysis showed a distribution of CHO that is commonly observed for lignin (Montané *et al*., 2005; Rodriguez-Mirasol *et al*., 1993; Rodríguez-Maroto *et al*., 1993). Analyses of Alcell® lignin and a commercial kraft lignin (CKL) are also included for comparison. The CHO profile of the SW samples was closely related to that of Alcell® lignin, whereas that of HW was close to CKL, except for the oxygen content of the latter.

Sulphur content in the samples is an important parameter to consider because this could be a major concern for the environment when upscaling the precipitation reactions. The different acids for lignin samples precipitated from HW black liquor showed higher sulphur content than their SW counterparts. As expected, Alcell® lignin showed no sulphur content, while CKL showed higher sulphur content than SW and HW samples. Organic acids for this work were utilized with expectations that they would result in less sulphur content in the lignin samples. However, it appeared that acid strength, as well as wood type, played a role.

Compared with SA samples, the organic acid samples showed lower sulphur content, except for the HWFA sample. The higher sulphur content may be due to differences in wood chemistry between HW and SW, where HW contains the syringyl groups which are not present in SW. Thus, the sulphur (sulphites and sulphates) retained during the cooking process could react with the –OH groups of the syringyl to produce $–SO_2H$ groups in the lignin samples. As observed in the previous chapter, there is gas evolution (probably H_2S and CO_2) during the H_2SO_4 precipitation process, and CO_2 could be the main gas released for organic acids reactions.

The release of CO_2 during organic acid precipitation could be observed as an added advantage as the gas can be captured and utilized as a precipitating agent as well.

Table 4.1. Elemental and immediate analyses of commercial kraft lignin, Alcell® lignin, and kraft lignin samples precipitated with H_2SO_4, and organic acids

Lignin Sample	% C	% H	% O	% N	% S	% Ash (db)	% Volatile matter (db)	% Fixed Carbon (db)	% Char Yield
HWSA	58.44	5.12	31.77	0.22	4.43	1.58	69.82	28.59	30.17
HWFA	57.52	5.44	30.97	0.21	5.84	2.81	63.26	33.92	36.73
HWAA	52.49	5.34	38.62	0.17	3.37	3.74	64.36	31.89	35.64
HWCA	52.37	5.19	40.54	0.19	1.71	2.81	61.27	35.92	38.73
SWSA	62.52	6.00	28.32	0.24	2.92	0	66.86	33.14	33.13
SWFA	63.38	6.06	29.04	0.21	1.29	2.49	73.83	23.68	26.17
SWAA	61.78	6.00	30.85	0.20	1.16	2.05	67.24	30.70	32.75
SWCA	63.57	6.05	28.43	0.25	1.70	1.37	59.43	39.20	40.57
CKL	52.08	4.85	40.13	0.15	2.80	12.60	75.03	12.37	24.97
Alcell®	65.91	6.28	27.57	0.24	0	0	66.44	33.56	33.56

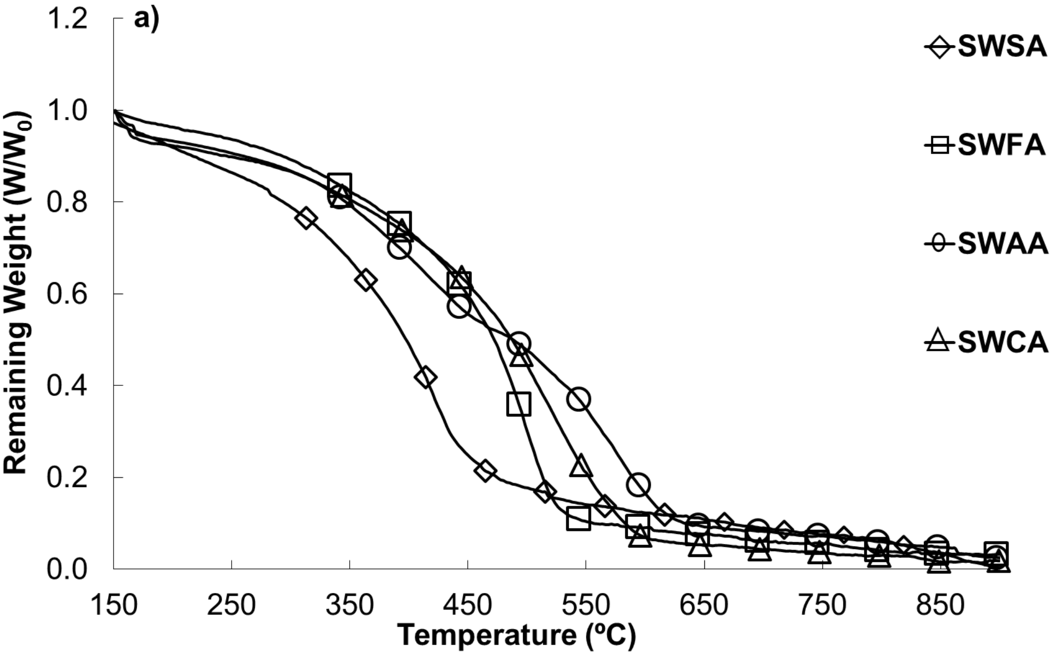
db - dry basis, HW - hardwood, SW - softwood, SA - sulphuric acid, FA - formic acid, AA - acetic acid, CA - citric acid, CKL - commercial kraft lignin

4.3.2. Thermogravimetric Analysis

Representative TG curves, under air atmosphere, obtained for SW lignin precipitated organic acids and sulphuric acid are shown in Figure 4.1; a) TGs and b) DTGs. Hardwood samples followed a similar trend and the TG and DTG curves are shown in Appendix A1.

All four lignins from each wood species showed behaviour typical for a general TG profiles for lignins, although some differences were observed for each lignin. The DTG profiles make it possible to better observe the different temperatures where weight loss occurs. For the SW samples, it can be observed that the DTG curves show clear weight loss regions for all samples; SWSA displayed main loss of weight between 260–490 °C; for SWFA, that shifted to 310–550 °C. For the SWAA sample, double peaks were observed between 290–460 °C, as well as between 480–640 °C. Finally, for the SWCA samples, weight loss occurred between 290–610 °C.

The differences in the DTG curves for the weight loss of the samples observed provide a clear indication that precipitation with different organic acids have different effects on kraft lignin, and provides a larger range of weight loss regions. HWSA and HWFA samples displayed a more or less similar weight loss trend with the main peak occurring at around 450–550 °C. HWAA and HWCA displayed the main weight loss regions at lower temperatures, 250–450 °C and 250–380 °C respectively. There was a further weight loss in both HW-AA/CA sample observed at a higher temperature close to the final temperature, around 790–850 °C. It is suggested that weight loss observed in these regions could be due to the inorganic matter that could be present in the samples (see Chapter 6 for a discussion).



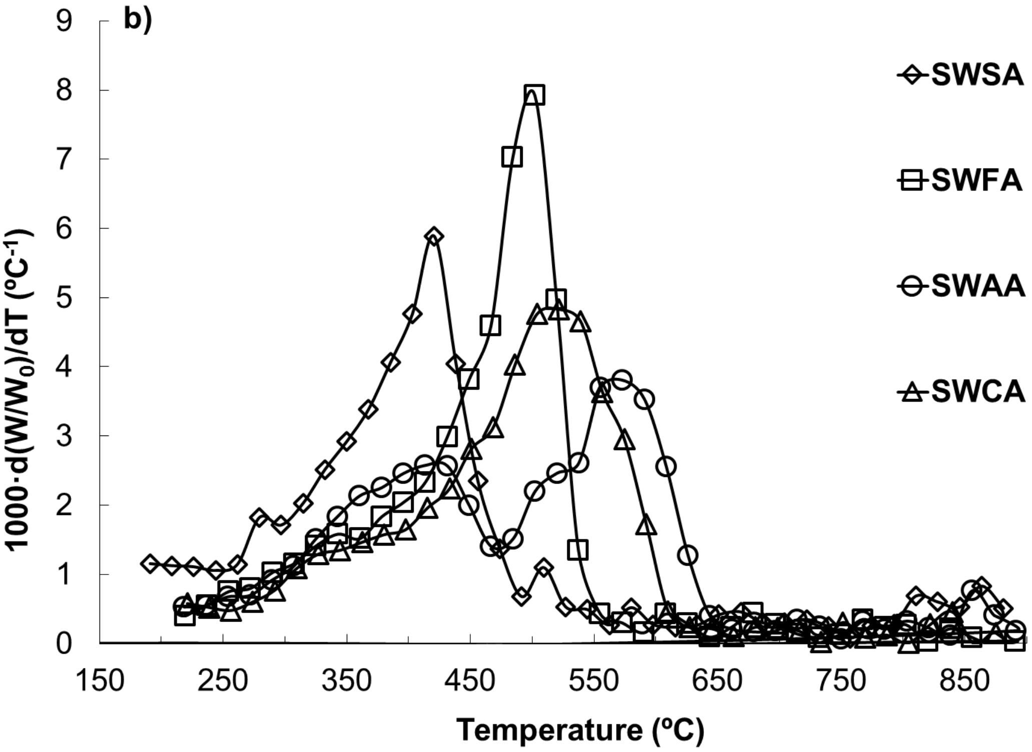


Figure 4.1. a) TG and b) DTG profiles obtained in atmospheric air for softwood kraft lignin precipitated with SA, FA, AA, and CA

To assess the suitability of the obtained lignin samples as potential precursors for carbon materials, similar TG analyses were performed for all samples, however in this case under a nitrogen environment, to measure the volatile matter, the fixed carbon content, and the char yield of each sample (shown in Table 4.1).

The results for fixed carbon content and char yields were sufficient to consider the lignins as good prospects for future processing into valuable carbon products (Kifani-Sahban *et al*., 1997; Rodriguez-Mirasol *et al*., 1993). The lignin samples also exhibited expansion and/or swelling at the end of each experiment as illustrated in the SEM micrographs (Figure 4.2). The micrographs of the raw lignin samples prior to thermal treatment under nitrogen displayed similar granular structures as the particle size remained constant for all HW and SW samples. However, after carbonization the samples displayed different morphologies. Differences in the swelling of the samples were observed, and this is a commonly observed behaviour for lignin samples, typically showing cracks and cavities, where the volume of particles increases, indicating plastic deformation by cavitation.

Due to their high ash content, HWAA and CKL samples showed no signs of swelling, which agrees with the work reported by Rodriguez-Mirasol *et al*. (1993), who observed that above 2.5% ash content, lignin tends to not swell when carbonized. However, as can be observed with HWSA, HWFA, and HWCA samples, there are structural modifications that are different from cavitation and are closely related to the Alcell lignin carbonized sample. This observation could further support the deduction that organic acids modify kraft lignin during precipitation.

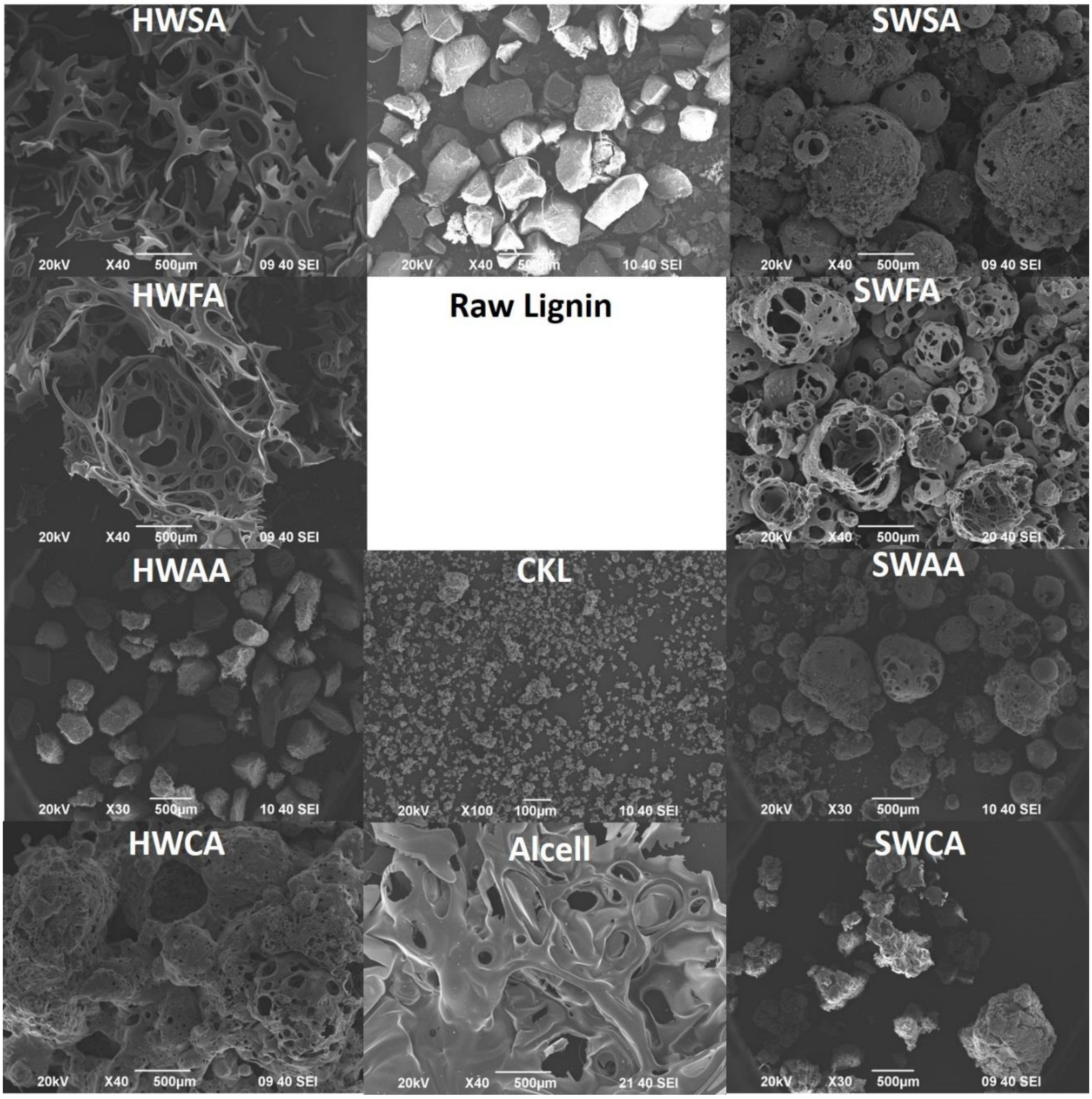


Figure 4.2. SEM micrographs of carbonized lignin samples

4.3.3. FTIR

FTIR was performed to analyse for differences in the functional groups of the different lignin samples obtained (Figure 4.3). The FTIR spectrum of commercial kraft lignin (CKL) was utilized as a reference, since the hardwood and softwood black liquor samples in this work were obtained from a kraft mill. The fingerprint region where lignin functional groups are commonly observed is around v/cm^{-1} 1800 – 900.

There were subtle differences, mainly in the intensity of the absorption peaks, observed in the spectra in Figure 4.3 for each lignin sample when compared to each other individually, as well as with the CKL. For this reason, the peak intensities observed for the lignin samples were sufficient to enable differentiation among the samples.

The HW and SW samples also had common peaks between them (*approx.* v_{max}/cm^{-1} 1600. 1525, 1440, 1217, 1034 and 910), which represented the common features of the backbone monomers (guaiacyl and syringyl) of a lignin molecule. Assigning of the main IR peaks observed in the lignin samples are shown in Table 4.2.

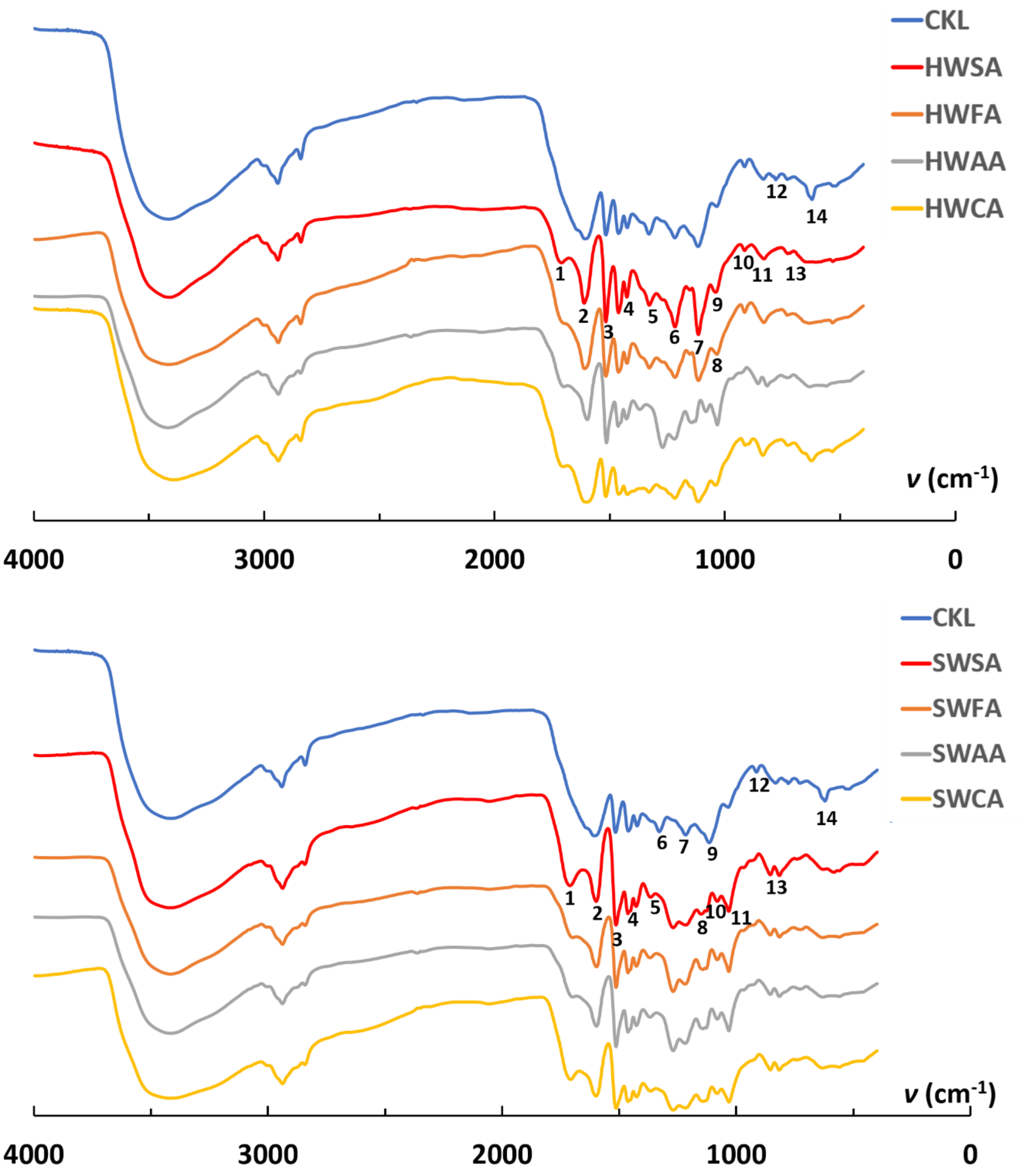


Figure 4.3. FTIR spectra of the HW (top) and SW (bottom) acid precipitated lignin samples with CKL as reference spectrum, with assignments of IR peaks

Table 4.2. Assignments of the IR peaks for the spectra in Figure 4.3

Peak #	v (cm^{-1})	Assignments
1	1710	ethers, methoxy
2	1606	aromatic skeletal
3, 4	1514 , 1458	methyl and methylene deformation
5	1421	C-H aromatic stretching with
6	1330	ethers, methoxy
7	1215	carbonyl deformation
8	1114	deformation C-H or S-O (sulphate)
9	1033	C-H deformation in G-unit
10	914	aromatic skeletal
11, 12, 13	829, 721, 612	typical for S-O bonds stretching
14	621	sulphate O-S-O deformation

For HW samples (Figure 4.3, top), there was shoulder peak observed at v_{max}/cm^{-1} 1710 (1, ether and methoxy groups) for the three acid lignin samples (SA, FA, and CA) and not observed for AA and CKL. This peak is more defined for FA compared with the other two organic acids. In contrast to SW samples (Figure 4.3, bottom), this small peak is visible for all the samples. It can be suggested that this peak represents the guaiacyl methoxy/ether groups of the monomer since it is observed in all the SW samples as well. The peaks for the HW samples at v_{max}/cm^{-1} 1606 (2, aromatic skeletal); v_{max}/cm^{-1} 1215 (7, carbonyl deformation) and v_{max}/cm^{-1} 1114 (8, C—H deformation or sulfate S—O deformation) showed broadening and shortening as the acid strength decreased for all acids. The peaks at v_{max}/cm^{-1} 1514 (3, methyl and methylene deformation), v_{max}/cm^{-1} 1458 cm^{-1} (4, methyl and methylene deformation), and v_{max}/cm^{-1} 1421 cm^{-1} (5, aromatic stretching with C—H) showed higher intensities compared to CKL, as well as their intensities decreasing with the decrease in acid strength for the samples.

All spectra also showed a lot of activity below the v_{max}/cm^{-1} 914 peak (v_{max}/cm^{-1} 829, 721, 612) and this region of the spectra is typical for S—O bonds stretching. The peak at v_{max}/cm^{-1} 621 (14, sulfate O—S—O deformation) which is sharp for CKL, is absent for HWSA and HWFA, however, broader for HWAA and HWCA. The absence of this peak for HWFA, which has the highest sulfur content according to elemental analysis, might signify that the sulphur contained in this sample is not in the form of a sulphate.

4.4. CONCLUSIONS

Precipitation of lignin from kraft lignin using organic acid instead of sulphuric acid or carbon dioxide results in lignin samples that have different physical and chemical characteristics from those produced using inorganic acids. The lignin samples had lower sulphur content, more especially so for lignin from softwood kraft black liquor. Sulphuric and formic acid precipitated lignin samples displayed major weight loss during thermal decomposition, while acetic and citric acid precipitated samples showed least weight losses. Samples with ash content higher than 2.5% showed no modifications after carbonization.

FTIR spectra showed that the lignins had similar functional groups. However, there were differences in absorption peak intensities, peak sharpening, and broadening in each of the samples.

The fixed carbon content and char yields from the carbonized lignins showed that the precipitated lignin samples in this work are good biomass for further processing into valuable compounds.

References

Alén R, Patja P, Sjöström E. 1979. Carbon dioxide precipitation of lignin from pine kraft black liquor. Tappi Journal **62**(11): 108-110.

Antizar-Ladislao B, Turrion-Gomez JL. 2008. Second-generation biofuels and local bioenergy systems. Biofuels, Bioproducts and Biorefining **2**(5): 455-469.

Bludowsky T, Agar DW. 2009. Thermally integrated bio-syngas-production for biorefineries. Chemical Engineering Research and Design **87**(9): 1328-1339.

Clark JH, Deswarte FEI, Farmer TJ. 2009. The integration of green chemistry into future biorefineries. Biofuels, Bioproducts and Biorefining **3**: 72-90.

Demirbas MF. 2009. Biorefineries for biofuel upgrading: A critical review. Applied Energy **86**: S151-S161.

García A, Toledano A, Serrano L, Egüés I, González M, Marín F, Labidi J. 2009. Characterization of lignins obtained by selective precipitation. Separation and Purification Technology **68**: 193-198.

Helander M, Theliander H, Lawoko M, Henriksson, G, Zhang L, Lindström ME 2013. Fractionation of technical lignins: Molecular mass and pH effects. Bioresources **8**(2): 2270-2282.

Ibarra D, del Río JC., Gutiérrez A, Rodríguez IM, Romero J, Martínez MJ, Martínez ÁT. 2004. Isolation of high-purity residual lignins from eucalypt paper pulps by cellulase and proteinase treatments followed by solvent extraction. Enzyme and Microbial Technology **35**: 173-181.

Kifani-Sahban F, Kifani A, Belkbir L, Zoulalian A, Arauzo J, Cordero T. 1997. A physical approach in the understanding of the phenomena accompanying the thermal treatment of lignin. Thermochimica Acta **298**: 199-204.

Montané D, Torné-Fernández V, Fierro V. 2005. Activated carbons from lignin: Kinetic modelling of the pyrolysis of kraft lignin activated with phosphoric acid. Chemical Engineering Journal **106**(1): 1-12.

Namane M, Sithole BB, Ramjugernath D. 2015. Centrifugal washing and recovery as an improved method for obtaining lignin precipitated from South African kraft mill black liquor. Journal of Scientific and Industrial Research **74**: 571-576.

Naqvi M, Yan J, Fröling M. 2010a. Bio-refinery system of DME or CH4 production from black liquor gasification in pulp mills. Bioresource Technology **101**(3): 937-944.

Naqvi M, Yan J, Dahlquist E. 2010b. Black liquor gasification integrated in pulp and paper mills: A critical review. Bioresource Technology **101**(21): 8001-8015.

Naqvi M, Yan J, Dahlquist E. 2012. Bio-refinery system in a pulp mill for methanol production with comparison of pressurized black liquor gasification and dry gasification using direct causticization. Applied Energy **90**(1): 24-31.

Neimark AV, Sing KSW, Thommes M. 2008. Surface area and porosity. In G Ertl, H Knözinger, F Schuth, J Weitkamp (eds.), Handbook of heterogeneous catalysis (2nd ed.), Wiley Online Library. pp. 721-738.

Ragauskas AJ, Nagy MK, DH, Eckert CA, Hallett JP., Liotta CL 2006. From wood to fuels: Integrating biofuels and pulp production. Industrial Biotechnology, **2**(1): 55-65.

Reddy N, Yang Y. 2009. Citric acid cross-linking of starch films. Food Chemistry **118**(3): 702-711.

Rodríguez-Maroto JM, García F, Rodríguez-Mirosol J, Cordero T, Suau R, Rodríguez JJ. 1993. Characterization of liquid wastes from eucalyptus wood and kraft lignin charring. Journal of Environmental Science and Health Part A **A28**(3): 651-662.

Rodriguez-Mirasol J, Cordero T, Rodriguez JJ. 1993. Preparation and characterization of activated carbons from eucalyptus kraft lignin. Carbon **31**(1): 87-95.

Rosas JM, Berenguer R, Valero-Romero MJ, Rodríguez-Mirasol J, Cordero T. 2014. Preparation of different carbon materials by thermochemical conversion of lignin. Frontiers in Materials **1**(Article 29): 1-17.

Ruiz-Rosas R, Bedia J, Lallave M, Loscertales IG, Barrero A, Rodrıíguez-Mirasol J, Cordero T. 2010. The production of submicron diameter carbon fibers by the electrospinning of lignin. Carbon **48**: 696-705.

Sassner P, Zacchi G. 2008. Integration options for high energy efficiency and improved economics in a wood-to-ethanol process. Biotechnology for Biofuels **1**(4): 1-11.

Tomani P. 2010. The LignoBoost process. Cellulose Chemistry and Technology **44**(1-3): 53-58.

Uloth VC, Wearing JT. 1989. Kraft lignin recovery: Acid precipitation versus ultrafiltration part I. laboratory test results. Pulp and Paper-Canada **90**(9): T310-T314.

Wallmo H, Wimby M, Larsson A. 2009. Increase production in your recovery boiler with LignoBoost - extract valuable lignin for biorefinery production and replacement of fossil fuels. Tappi Engineering, Pulping and Environmental Conference, Memphis, Tennessee. pp. 1-5.

Wooley R, Ruth M, Glassner D, Sheehan J. 1999. Process design and costing of bioethanol technology: A tool for determining the status and direction of research and development. Biotechnology Progress **15**(5): 794-803.

Wyrzykowski D, Hebanowska E, Nowak-Wiczk G, Makowski M, Chmurzynski L. 2011. Thermal behaviour of citric acid and isomeric aconitic acids. Journal of Thermal Analysis and Calorimetry **104**: 731-735.

Zhu W, Theliander H. 2011. Equilibrium of lignin precipitation. 16th International Symposium on Wood, Fiber and Pulping Chemistry, Tianjin. pp 195-199.

5. PREPARATION OF ACTIVATED CARBON BY PARTIAL GASIFICATION OF KRAFT LIGNINS OBTAINED BY PRECIPITATION WITH ORGANIC ACIDS: CO_2 REACTIVITY STUDIES

(BASED ON PAPER III)

Abstract

Lignin has been envisaged as a potential source of future chemicals, materials, and energy. Its high carbon content makes it a very good candidate as a replacement for fossil fuel product precursors. The following study investigates the behaviour of lignins obtained by precipitation with organic acids and H_2SO_4, as a potential precursor for activated carbon. Char samples were prepared by carbonisation from softwood (SW) and hardwood (HW) raw lignin samples precipitated from black liquor. SW char samples showed higher carbonisation yields (39 - 47%) than HW chars (34 - 43%), as well as possible retention of the acid during the precipitation step, which resulted in partial chemical activation during carbonisation. After carbonization, HW chars were observed to swell more than the SW chars, with the latter showing distinct spherical particles under scanning electron microscopy (SEM). Preparation of activated carbon was achieved by partial gasification of the lignin chars with CO_2. Due to their higher char yields, only SW samples were utilised for the activation experiments. Reactivity studies showed that gasification was temperature-independent at higher temperatures (>850 °C), resulting in the gasification reactions being mass-transfer limited. SW chars were found to be reactive with CO_2 at temperatures above 700 °C, and consequently, 800 °C was chosen to be the gasification (activation) temperature. There was a significant formation of the porous structure in the lignin activated carbon samples studied. The narrow micropore was observed to have increased in the activated carbon, and the bottom end of the micropore was observed to also have widened. The specific surface area observed for the SW activated carbon was 1000-1300 m^2/g. Activated carbon obtained in this study showed a high propensity for samples that could be used in applications such as liquid phase adsorption, catalysis, energy storage, as well as molecular sieves.

5.1. Introduction

Recently, lignin has become the subject of many research studies due to it being the frontrunner as an alternate carbon source. It is abundantly available, easily isolated and modified, as well as the having the potential to be a feedstock for chemical production (Fitigăue *et al*., 2013; Kouisni *et al*., 2012; Norberg, 2012; Gårdfeldt and Svane, 2011). It is the major constituent of the waste product, black liquor, which is produced in the kraft pulping process.

Lignin has found multiple uses in many branches of industry. At first, lignin was used as a dispersant, emulsifier, and binder (Adler, 1977). In recent years the polymer has found many other uses. Due to its low cost and limited solubility in water, raw lignin has also been studied as an adsorbent for heavy metals in water purification (Šćiban *et al*., 2011; Guo *et al*., 2008). Klapiszewski *et al*. (2013) have shown that lignin can be incorporated into inorganic substrates, such as silica, to produce biocomposites that could behave as polymer fillers or absorbents of harmful chemicals, as well as have good electrokinetic ability. Lignin has also been used as an additive to synthetic polymers to alter their distinctive features, such as tensile strength, thermal decomposition temperatures, oxidation induction time, etc (Kunanoppara *et al*., 2012; Morandim-Giannetti *et al*., 2012).

Conversion of biomass into activated carbon has been researched extensively, and there have been a number of studies that have shown different procedures and applications that have utilised biomass residues for production of activated carbon for functions such as adsorption (García-Mateos *et al*., 2015; Cotoruelo *et al*., 2012), catalysis (Bedia *et al*., 2009) and electrochemical processes (Berenguer *et al*., 2015). In an attempt to further increase valorisation of lignin, production of activated carbon from this polymer has also gained great momentum. Rosas *et al*. (2014) and Suhas *et al*. (2007) have written extensive reviews on this subject with large bibliographies.

Activated carbon from lignin can be prepared by chemical or physical activation (Montané *et al*., 2005; Rodriguez-Mirasol *et al*., 1993; Rodríguez-Mirasol *et al*., 1993a; Rodríguez-Mirasol *et al*., 1993b). Different activation methods result in different porosities, as well as specific surface areas of the lignin-based activated carbon.

Chemical activation is achieved by using chemical agents, such as alkali metal compounds, $ZnCl_2$, NaOH, or phosphoric acid, that are used as impregnating agents for raw lignin prior to the carbonisation step, resulting in activated carbon of significantly improved porosities and surface area (Carrott *et al*., 2008).

Physical activation, on the other hand, is a two-step process achieved by firstly carbonising the raw lignin to obtain chars, followed by partial gasification of chars with carbon dioxide, steam, air, or flue gases (Fu *et al*., 2013; Carrott *et al*., 2008). The optimum temperature for carbonisation has been found to be in the range of 700 – 800 °C, and this results in char products with a minimum average size of micropores. It is also important to understand the rates of activation reactions, such as for gasification, for the purposes of reactor and process design. Factors that affect gasification rates are char porosity, particle size, the inorganic material content, temperature, and partial pressure of the gasifying agent (Mani *et al*., 2011).

In this chapter, lignin chars were activated by partial gasification with CO_2. Studies on CO_2 gasification have been performed and reported on different biomass materials, including lignin (Mani *et al*., 2011; Khalil *et al*., 2009; Baumlin *et al*., 2006; Tancredi *et al*., 1996; Rodríguez-Mirasol *et al*., 1993b). However, no such studies have been performed on lignin obtained from black liquor sourced from a South African kraft mill.

Since methods for the valorisation of lignin are constantly changing and improving, this contribution investigated physical activation by partial gasification with CO_2, of lignin samples precipitated from kraft black liquor with organic acids and sulphuric acid to produce activated carbon. Reactivity studies of the activation process were performed to obtain ideal gasification temperatures and activation energies of the activation process.

5.2. Material and Methods

5.2.1. Precipitation of lignin from kraft black liquor

Hard- and softwood (HW and SW) black liquor samples were obtained from a kraft mill in South Africa, and the lignin precipitated with sulphuric (SA), formic (FA), acetic (AA), and citric (CA) acids was recovered by centrifugation using a previously described process (Namane *et al*., 2015).

5.2.2. Carbonisation process for preparation of chars

All lignin samples precipitated from different acids, as well as commercial kraft (CKL) and Alcell® lignin, were carbonized at a temperature ramp of 10 °C/min, and thereafter held for 2 hours at 800 °C in a 99.999% N_2 atmospheres (150 mL/min flow rate). The carbonisation process for all lignin samples was carried out in a conventional horizontal furnace (Carbolite CTF 12/65) consisting of a 120 cm length and 7 cm i.d steel tube heated by electrical resistance at a controlled temperature. The samples were then allowed to cool down to room temperature while maintaining the N_2 flow. The carbonized samples were washed with 2% aqueous HCl solution at 60 °C to remove as much of the inorganic matter as possible, and thereafter also washed with deionised water at a similar temperature. The char samples were then dried in an oven at 80 °C overnight and collected to calculate the carbonization yields. The samples were ground and sieved to a particle size between 300-400 μm.

5.2.3. Reactivity Studies

CO_2 reactivity studies were carried out in a model CI Electronics thermobalance consisting of a 200 mm length and 20 mm i.d. silica-glass tube fitted with an electrobalance and heated by a cylindrical electric resistance furnace with a temperature controller and heating rate programmer. The temperature signal for the controller was measured by means of a chromelalumel thermocouple placed inside the reaction tube. Approximately 10 mg of each carbonized sample with particle sizes of 300-400 μm were utilized for all reactivity studies, as well as gasification experiments. For reactivity studies for each sample, the reaction vessel was first kept in an N_2 (99.999% purity) atmosphere, followed by heating the sample at 10 °C/min heating rate up to the reaction temperatures (775, 800, 815, 825 °C). The gas feed was then switched to oxygen-free CO_2 (99.999% purity) at 100 cm^3/min (STP), and the reactivity experiment carried out isothermally. The reactivity values, r, were obtained from the following equation:

$$r = -\left(\frac{1}{w}\right)\frac{dw}{dt}$$

where, *w* (g) represents the solid weight of the sample remaining at a specific time, *t* (h). Conversion, *X*, was obtained as a function of sample weight loss when the reaction temperature was reached and the carrier gas switched to CO_2, by use of the following equation:

$$X = \frac{w_0 - w}{w_0 - w_f}$$

with w_0 (g), w_f (g) and w (g) representing the initial weight, final weight and weight at time t (h), respectively.

5.2.4. Preparation of activated carbon

Physical activation experiments were performed by gasification of the chars with CO_2 in the same furnace used for the carbonization experiments. Each carbonised lignin sample was heated under N_2 flow (150 cm^3/min), using a heating rate of 10 °C/min to the final temperature of 800 °C. When the temperature was constant, the gas was switched to CO_2 (200 cm^3/min) and the gasification reaction performed isothermally at 800 °C for a period of 2h. After the gasification reaction, the samples were left to cool down inside the furnace under an N_2 atmosphere. The activated carbon samples were collected and measured to calculate the burn-off, and thereafter characterised.

5.2.5. Characterization of lignin, chars and activated carbon

Lignin samples precipitated with different acids were characterised for carbon, hydrogen, nitrogen and sulphur (CHNS) composition by elemental analysis, with the oxygen content calculated by difference, by using high temperatures and excess of oxygen in a LECO® CHNS-932 instrument (Malaga, Spain). The porous structure of carbonized and gasified samples was characterised by N_2 adsorption at -196.15 °C (77 K) and by CO_2 adsorption at 0 °C (273 K) in an ASAP 2020 equipment (Micromeritics) (Malaga, Spain). Samples were outgassed at 150 °C and 10^{-5} torr for 8h. The specific surface areas (A_{BET}) were calculated using the BET equation (Brunauer *et al.*, 1938) from the N_2 isotherms. The t-method (Kaneko, 1994; Kaneko and Ishii, 1992; Kaneko *et al.*, 1992) was used to calculate the microporous volumes (V_t) and external surfaces (A_t), utilising non-porous carbon black as a standard. The mesopore volumes (V_{mes}) were calculated by the difference between the adsorbed volume of N_2, at a relative pressure of 0.995, and the microporous volume (V_t). Pore size distribution was calculated from the N_2 adsorption isotherms using the 2D-NLDFT heterogeneous surface model (Jagiello and Olivier, 2013), and by applying the solution from the adsorption integral equation using Splines software. The narrow micropore volumes (V_{DR}) and apparent surfaces areas (A_{DR}) were obtained applying the Dubinin-Raduschevich equation using data from CO_2 adsorption (Dubinin *et al.*, 1947). Morphologies of the char samples were analysed by scanning electron microscopy (SEM) in a JEOL JSMV 6940 instrument (Malaga, Spain).

5.3. Results and Discussion

5.3.1. Preparation and characterization of chars

Different chars were prepared by carbonization at 800 °C from various kraft lignins samples precipitated with organic acids. Table 5.1 shows the char yields (weight char/weight of raw lignin) obtained in this process.

Table 5.1. Chars yields of carbonised (C-) samples studied

Sample	C-HWSA	C-HWFA	C-HWAA	C-HWCA	C-SWSA	C-SWFA	C-SWAA	C-SWCA
Char yields (%)	34.0	37.9	42.5	40.6	38.8	45.0	46.2	45.6

The char yields for all samples studied were fairly high, ranging between 34 – 46 % and the values obtained were found to be similar to those reported in the literature` (Rosas *et al.*, 2014; Montané *et al.*, 2005; Rodriguez-Mirasol *et al.*, 1993). The SW organic acid precipitated samples generally showed the highest chars yields (Table 5.1).

In general, the organic acid precipitated sample showed higher carbonisation yields when compared with SA precipitated sample. As observed in the thermogravimetric analysis of the same lignin samples in a previous study (Namane *et al.*, 2016), organic acid lignin samples display a somewhat different behaviour compared with other lignins, thereby giving an indication that there are certain modifications or enhancements on the lignin structure that are brought by precipitation utilising organic acids.

The oxygen content of raw lignin also affected the carbonisation process, as shown by Ruiz-Rosas *et al*. (2010) in their studies for carbonization of lignin fibres, in that higher oxygen content could act as an activating agent, thereby decreasing the char yields for the carbonisation process. Thus, the higher the oxygen content in a sample that is being carbonised, the lower the char yield. As can be seen in Table 5.2 from previous studies (Namane *et al*., 2016), the elemental analysis (dry basis, ash free) of the raw lignin samples showed a higher O-content (calculated by difference) for the HW samples. It is known that

HW lignin comprises of more monolignols (guaiacyl and syringyl) than SW lignin, thus increased oxygen content compared with SW.

Table 5.2. Composition of raw lignin material by elemental analysis (Namane *et al.*, 2016)

Lignins Samples	% C	% H	% N	% S	% O
HWSA	59.38	5.20	0.22	4.50	30.69
HWFA	59.18	5.60	0.22	6.01	28.99
HWAA	54.53	5.55	0.18	3.50	36.25
HWCA	53.88	5.34	0.20	1.76	38.82
SWSA	62.52	6.00	0.24	2.92	28.32
SWFA	65.00	6.21	0.22	1.32	27.25
SWAA	63.07	6.13	0.20	1.18	29.41
SWCA	64.45	6.13	0.25	1.72	27.44

The porous structure of the carbonised lignin samples was studied by N_2 (-196.15 °C) and CO_2 (0 °C) adsorption (Table 5.3). All the observed N_2 isotherms (Figure 5.1) of char samples obtained were of type I adsorption isotherms, corresponding to microporous solids. Overall, HW samples displayed a higher adsorption volume of N_2 than the SW samples, which is in accordance with the lower char yields and higher oxygen content observed. The char samples from lignin precipitated with weaker acids (AA and CA) showed lower adsorption volumes, with C-SWCA displaying the lowest adsorption volume from all the chars studied. FA precipitated samples displayed the highest adsorption volume in lignins from both wood species, followed by SA precipitated samples. This observation could be due to the acids used in the precipitation step, whereby it is probable that some of the acids could have been retained in the internal structure of the resultant lignin raw materials. This results in a slight chemical activation during the carbonisation process.

Activation of lignin samples by impregnation with chemical agents, e.g., phosphoric acid, has been shown to improve the porosity as well as the surface areas of lignin (Rosas *et al.*, 2014; Gonzalez-Serrano *et al.*, 2004) - thus FA may also play a similar role during the precipitation process. The structural parameters of all carbonised samples are shown in Table 5.3. The micropore volumes for all samples display a higher CO_2 than the N_2 volume of adsorption, which has been explained by the reaction occurring during carbonisation being chemically controlled (Rodríguez-Mirasol *et al.*, 1993b). The relationship between $V_{DR\text{-}N2}/V_{DR\text{-}CO2}$ for C-SW samples varied between 0.20–0.67, indicating the porosity of the chars to be mainly of narrow microporosity, whereas their C-HW counterparts showed a range of 0.64–1.06, indicating that the samples had wider microporosity. This observation could also be explained by the higher oxygen content in the HW raw material, which could have resulted in activation during the carbonization step. The A_{BET} values obtained were 297 to 814 m^2/g for C-HW and 121 to 462 m^2/g for C-SW samples. All C-HW and C-SW (except for C-SWCA) samples were observed to possess higher specific surface areas than chars obtained for Alcell® and commercial kraft lignin, viz. 164 and 308 m^2/g respectively.

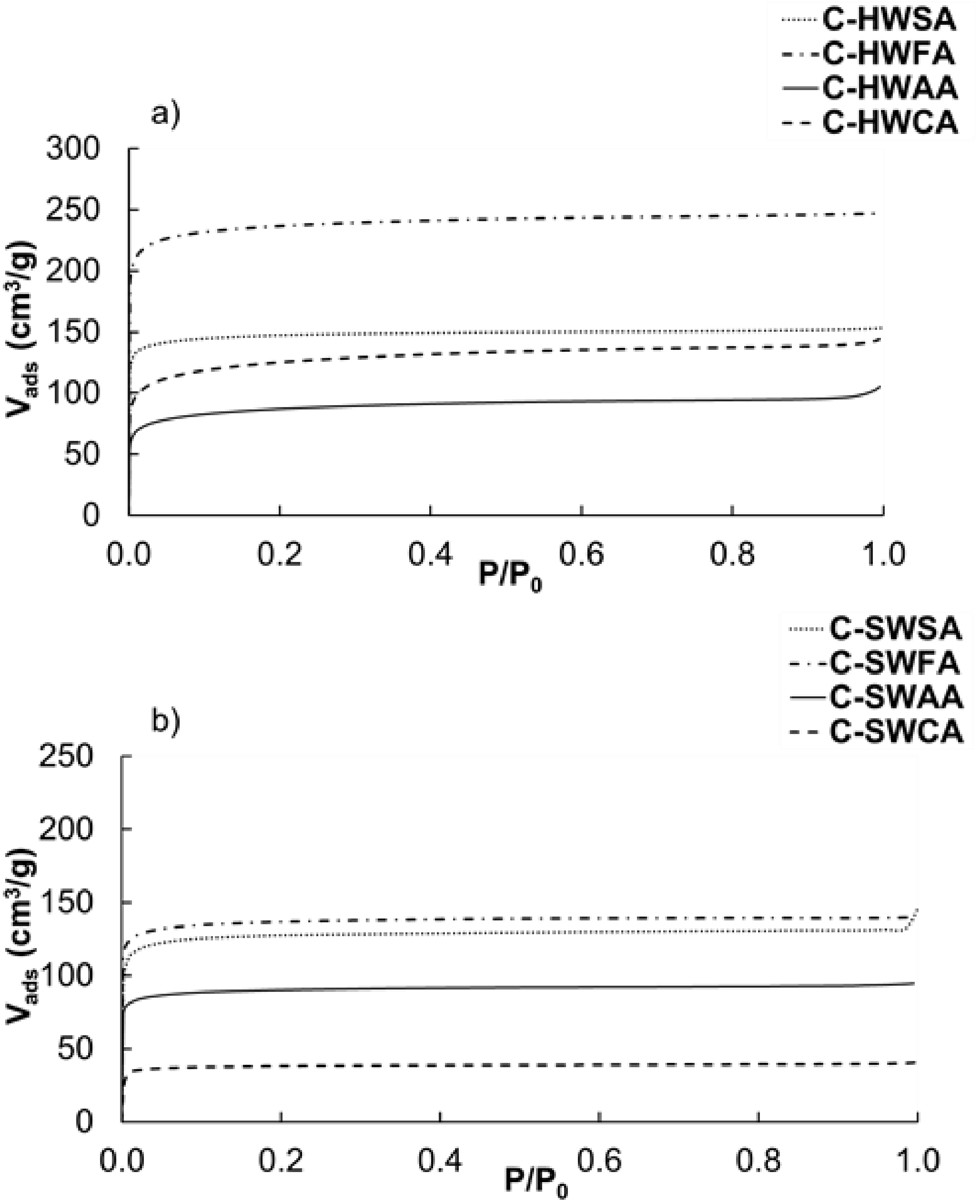


Figure 5.1. N_2 adsorption-desorption isotherms at -196.15 °C (77 K) for C-HW (a) and C-SW (b) lignin chars.

Table 5.3. Structural parameters of the carbonised samples measured by N_2 and CO_2 adsorption

	N_2 Adsorption						**CO_2 Adsorption**	
SAMPLE	**A_{BET} (m^2/g)**	**A_t (m^2/g)**	**V_t (cm^3/g)**	**$V_{0.995}$ (cc/g)**	**V_{meso} (cc/g)**	**V_{DR} (cm^3/g)**	**A_{DR} (m^2/g)**	**V_{DR} (cm^3/g)**
C-HWSA	494	7	0.226	0.237	0.010	0.229	683	0.273
C-HWFA	814	9	0.370	0.381	0.011	0.369	929	0.372
C-HWAA	296	19	0.130	0.162	0.032	0.135	528	0.211
C-HWCA	438	32	0.185	0.222	0.036	0.194	455	0.182
C-SWSA	393	9	0.194	0.223	0.029	0.200	745	0.298
C-SWFA	461	7	0.210	0.220	0.009	0.214	801	0.321
C-SWAA	292	7	0.137	0.148	0.010	0.141	612	0.245
C-SWCA	121	2	0.057	0.067	0.009	0.059	703	0.281

The contrast in the physical appearance of the chars for all samples (C-HW and C-SW) in this study was interesting. After carbonisation, the HW samples exhibited a clear swollen appearance whereas the SW samples did not display this type of swelling. This observation does not mean that the SW samples did not swell at all, as can be observed from SEM micrographs in Figure 5.2. However, compared with the HW samples' swelling and brittle nature of the final char, the C-SW samples displayed less expansion, as well as exhibiting more hardness than the C-HW chars. The micrographs of C-SW samples' swelling during carbonization showed spherically shaped particles, whereas a blend of the lignin particles was observed in the C-HW samples (however, in lesser amounts than in C-HWAA).

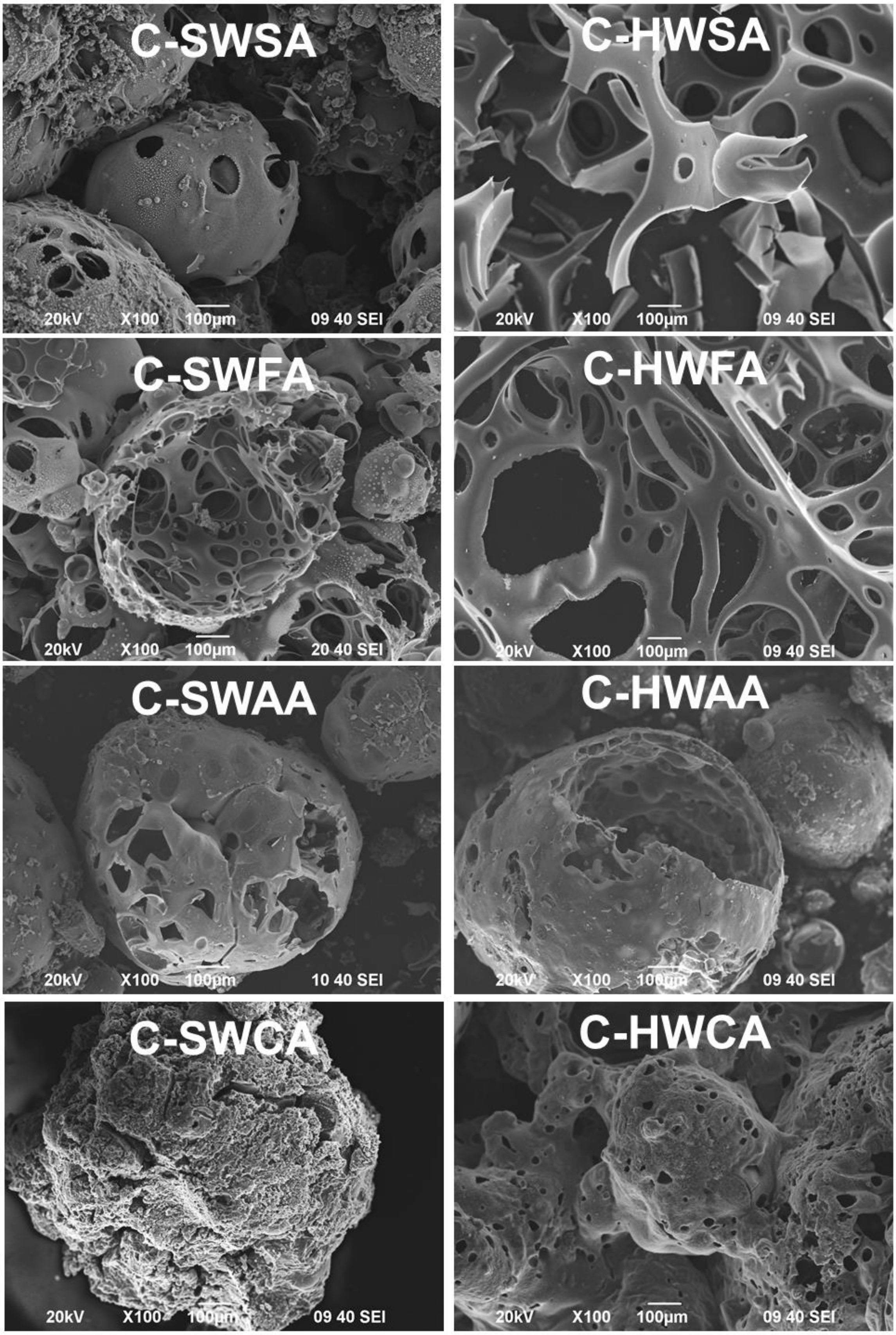


Figure 5.2. SEM micrographs of SW and HW char samples.

5.3.2. Reactivity Studies

Prior to carrying out the gasification of different chars, CO_2 reactivity experiments were performed at temperatures of 775, 800, 815, and 825 °C for all the C-SW lignin samples. Figure 5.3a shows the reactivity curves, r, versus conversion, X, for isothermal gasification of all C-SW samples at 815 °C and Figure 5.3b shows similar curves for the sample C-SWAA at different temperatures (from 775 to 825 °C) (See Appendix B1 for all the reactivity curves). At low to intermediate conversion, the curves for all samples show a more or less slow increase until higher conversion, where a steeper rise is observed. As also observed by Tancredi *et al*. (1997), the slight increases observed at low to intermediate conversions can be attributed to the increase in the A_{BET} during the gasification process. The steep increase observed at higher conversion values was unlikely due to the development of the surface area in any way. Instead, it was found to be due to the catalytic effects that may be occasioned by inorganic materials, such as alkali metals that might still be present in the chars. Thus, the shapes of the reactivity curves can be explained by both the catalytic effects at higher burn-off, as well as non-catalytic effects at lower to intermediate burn-off. At higher temperatures (815 and 825 °C), the reactivity of all G-SW samples (only G-SWAA shown in Figure 5.3b) were almost indistinguishable, and gasification reactions that do not show any significant change in reactivity at different temperatures are usually under mass transfer control in that range.

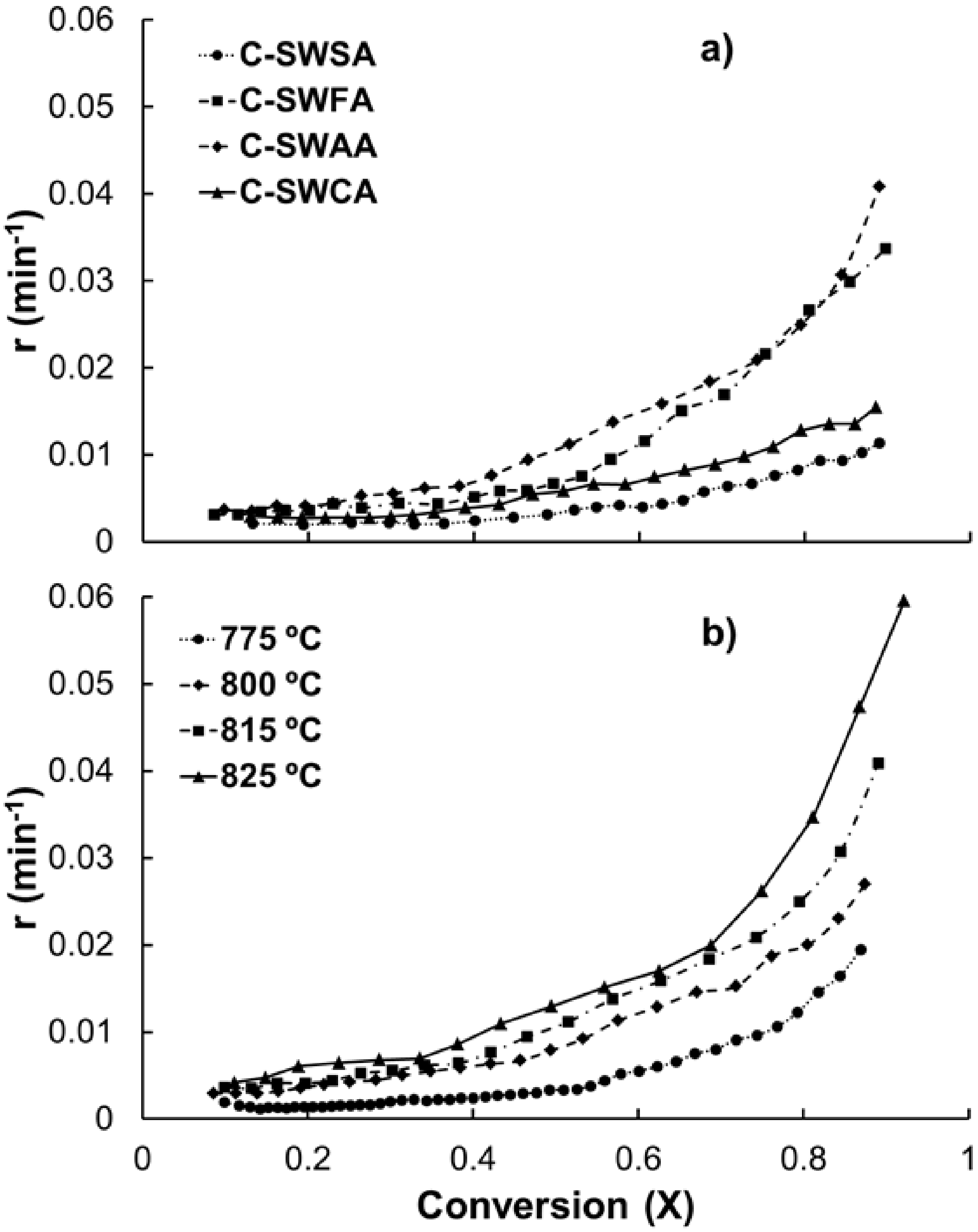


Figure 5.3. a) Reactivity curves for partial gasification at 815 °C of C-SW lignin chars and b) reactivity curves for partial gasification at different temperatures of C-SWAA.

From the reactivity curves, Arrhenius plots could be obtained for all samples. A typical plot is shown in Figure 5.4, as an example, for C-SWAA sample, obtained for the conversion range (X = 0.1 – 0.8) at the temperatures of gasification studied (See Appendix B2 for all Arrhenius plots). The Arrhenius plots obtained for all our samples essentially showed parallel lines for each conversion studied - however, not as many similar slopes per line as the plots obtained for partial gasification of kraft lignins by other researchers (Rodríguez-Mirasol *et* al., 1993a; Rodríguez-Mirasol et al., 1993b; Saiz-Jimenez and De Leeuw, 1986).

It is known in reaction kinetics that, even if the data does not follow common Arrhenius behaviour, the E_a values can still be attained by utilizing the slope of the $\ln r$ vs $\frac{1}{T}$ plot (Atkins and de Paula, 2002). Ideally, during the gasification process, parallel lines observed in the Arrhenius plots inform that the reactions did not have any mass-transfer limitations. The activation energies (E_a) obtained from these curves also varied for each sample. The observed E_a values fall within the commonly observed range for CO_2 partially gasified activated biomass, 200 – 300 kJ.mol^{-1} (Baumlin *et al*., 2006; Rodríguez-Mirasol *et al*., 1993a; Rodríguez-Mirasol *et al*., 1993b). Lower activation energy values of less than 200 kJ.mol^{-1} were observed for the SWFA for most of the conversion range. Of all three organic acid precipitated samples, SWFA showed the highest A_{BET} in the char before activation, thus CO_2 activation for this sample required the least amount of E_a.

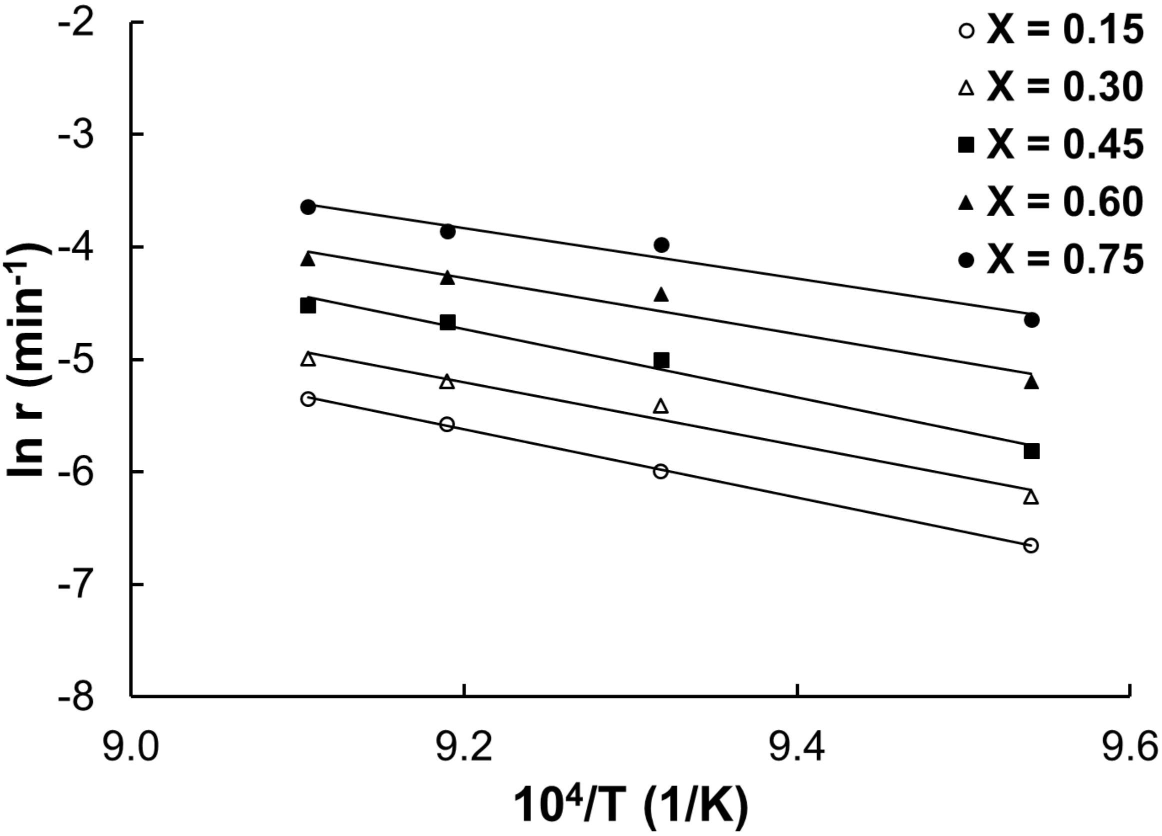


Figure 5.4. Arrhenius plots for gasification of C-SWAA with CO_2 at different conversion values.

5.3.3. Preparation and characterization of activated carbon

The higher carbonisation yields observed for SW samples prompted for use of these samples in the reactivity study. Therefore, the activation of the chars by partial gasification with CO_2 was conducted on only SW samples. From the reactivity study, the gasification temperature was chosen to be 800 °C for preparation of a series of activated carbon from C-SW samples. Gasification time also plays an important role during preparation of activated carbon by partial gasification. For the time required for activation time, isothermal TG analysis experiments were carried out at 800 °C under pure CO_2 atmosphere. Figure 5.5 shows the isothermal gasification profiles produced for the C-SW samples. From these experiments, 2 h was selected as activation time for the preparation of different activated carbon with burn offs from around 20 % for C-SWSA to 60 % for C-SWAA, as can be seen in Figure 5.5.

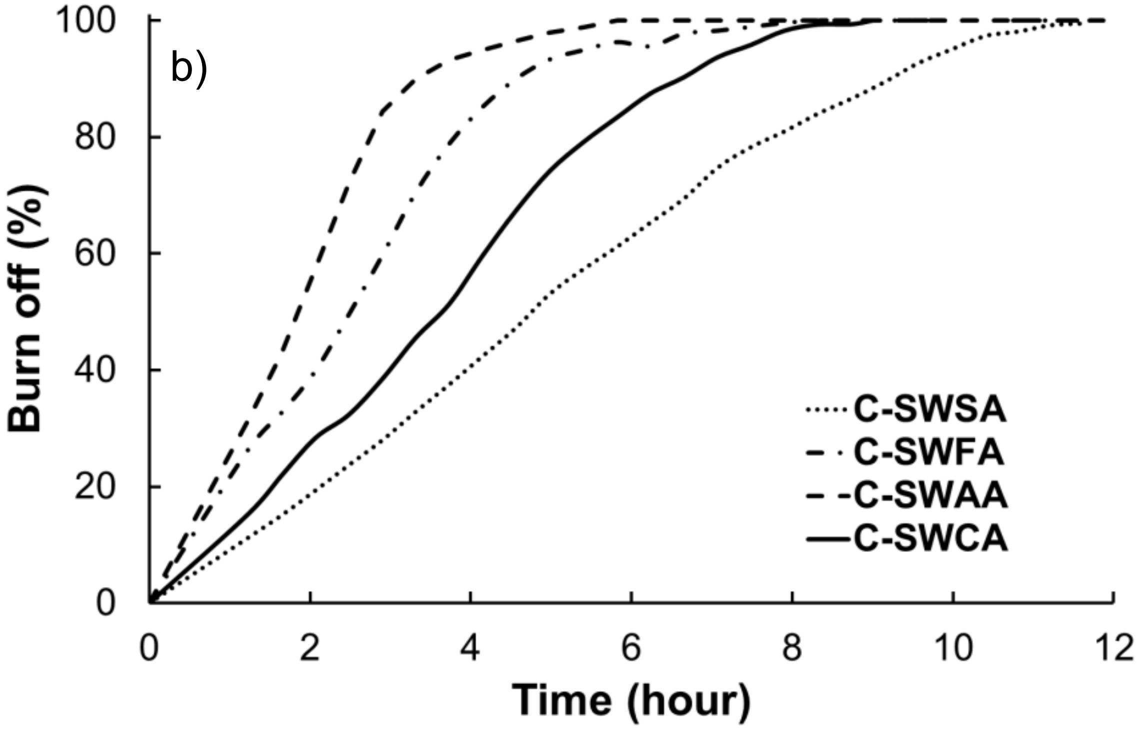


Figure 5.5. Isothermal (800 °C) CO2-gasification experiment for C-SW samples.

G-SW activated carbon were obtained by partial gasification of C-SW samples with CO_2. Table 5.4 shows the different burn-off percentage values of the activated carbon produced.

Burn-off refers to the initial char weights and it is indicative of the weight loss during gasification. Figure 5.6 shows the N_2 adsorption isotherms, wherein the isotherms obtained for chars (Figure 5.6a) and activated carbon obtained by gasification (Figure 5.6b) were compared.

Activated carbon isotherms clearly show that the partial gasification with CO_2 brought about a significant increase in the volume of N_2 adsorbed, due to the development of the porous structure. The surface area and pore volume measured with N_2 and CO_2 are shown in Table 5.5. The isotherms observed for the activated carbon (Figure 5.6b) resembled type I adsorption isotherm behaviour, although it can also be argued that there is a slight deviation of G-SWFA and G-SWAA towards type II/IV adsorption isotherms, with an increasing slope observed after the knee.

Partial gasification with CO_2 also resulted in increases of the A_{BET}, the specific surface area, for each sample ranging between 900-1250 m^2/g. There was also an increase in the external surface area (A_t) and the mesoporous volume (V_{mes}) observed for all samples (in comparison with the carbonized samples). This indicated that gasification of the samples resulted in widening of the bottom ends of the micropores. In essence, the overall porous structure of the activated carbon had been enlarged, as shown by the relationship between $V_{DR\text{-}N2}/V_{DR\text{-}CO2}$, where all the values of the ratio are greater than 1, with a maximum value of 1.52 for G-SWFA. Furthermore, as much as the widening of the base of the micropores is observed after gasification, the increases observed for the surface areas and pore volumes measured with CO_2 (A_{DR} and $V_{DR\text{-}CO2}$) further indicated increases in the narrow micropore region.

Table 5.4. Burn off (%) obtained in the gasification of SW samples

Sample	G-SWSA	G-SWFA	G-SWAA	G-SWCA
Burn off (%)	21.9	42.1	59.6	26.0

Table 5.5. Structural parameters of the activated carbon samples measured by N_2 and CO_2 adsorption

	N_2 Isotherm						**CO_2 Isotherm**	
SAMPLE	**A_{BET} (m^2/g)**	**A_t (m^2/g)**	**V_t (cm^3/g)**	**$V_{0.995}$ (cc/g)**	**V_{meso} (cc/g)**	**V_{DR} (cm^3/g)**	**A_{DR} (m^2/g)**	**V_{DR} (cm^3/g)**
G-SWAA	1214	199	0.455	0.676	0.220	0.531	904	0.362
G-SWCA	919	45	0.390	0.432	0.042	0.405	931	0.373
G-SWSA	1014	36	0.434	0.480	0.046	0.448	950	0.380
G-SWFA	1226	144	0.516	0.656	0.139	0.550	890	0.356

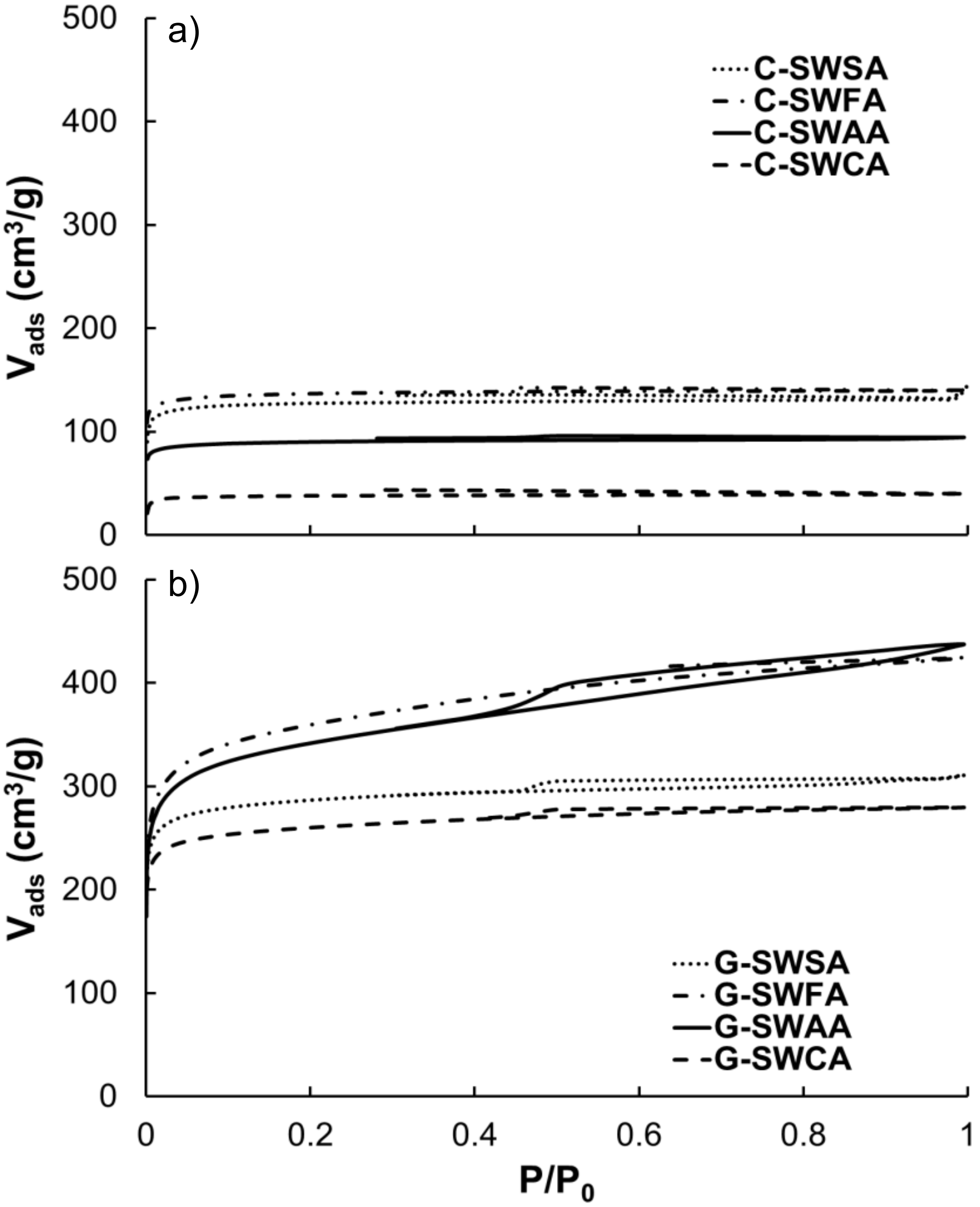


Figure 5.6. The 77 K N_2 adsorption isotherms for a) SW lignin chars (carbonised - C), and b) activated SW samples with partial gasification (G) with CO_2.

The pore size distribution of the chars (a) and the activated carbon (b) are compared in Figure 5.7. The char samples showed pore size mean diameter of between 6 and 10 Ǻ (Figure 5.7a), whereas for the activated carbon pore size mean diameter of between 10 to 50 Ǻ were observed for all samples (Figure 5.7b). Increases observed for the pore size diameter from chars to activated carbon further revealed the higher development of the porous structure with increased pore width after gasification. Thus partial gasification with CO_2 has been shown to be a viable process for activation of chars obtained from precipitation of lignin with organic acids.

The data obtained from the porous structure analysis of the activated carbon could allow for the SW samples to be used in multiple applications, for example, in liquid phase adsorption, catalysis, as well as energy storage. The higher A_{BET} observed for the samples plays an important role in these applications. In addition, the wider pore feature that is observed for the samples also favours the molecule diffusion toward narrow micropores. The differences between A_{BET} and A_{DR} in the carbonised samples also offers an interesting observation, whereby such differences in these parameters make the samples attractive for use as molecular sieves (Li *et al*., 2009; Siriwardane *et al*., 2001).

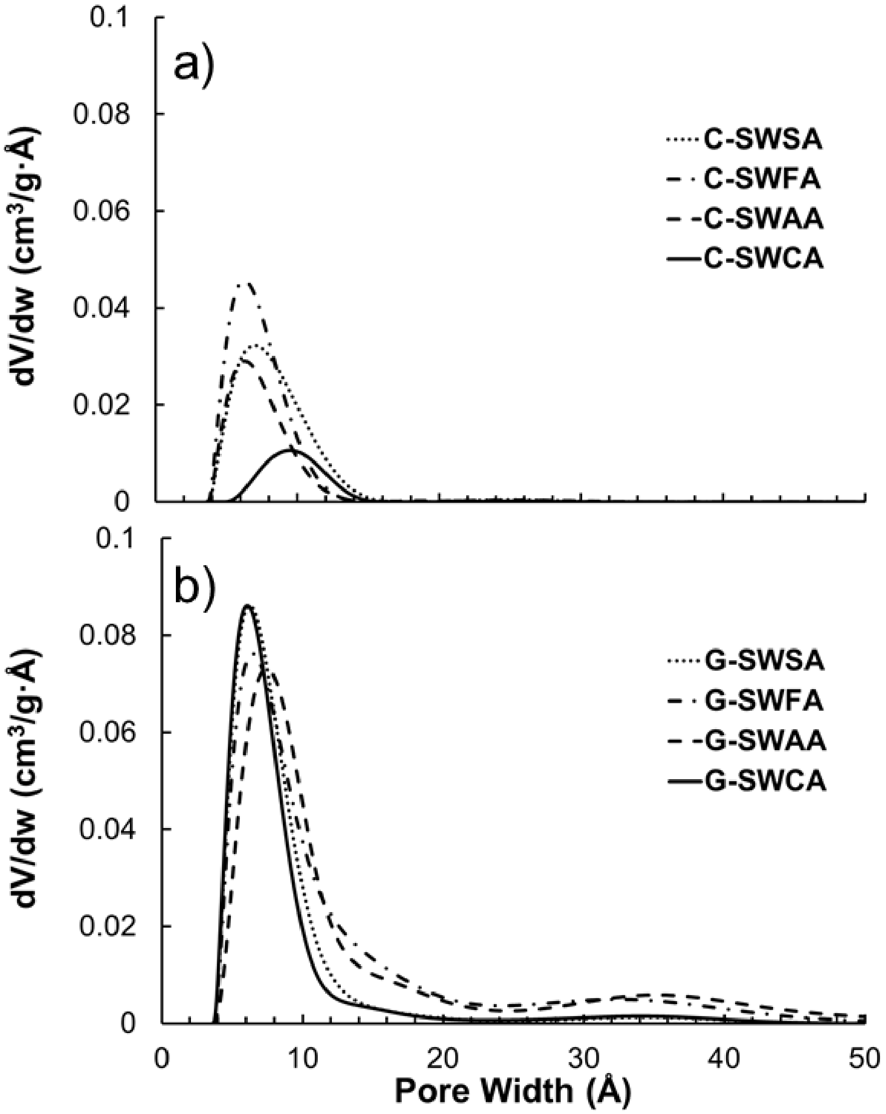


Figure 5.7. Pore size distribution of SW chars (a) and activated carbon samples (b).

5.4. Conclusions

Lignin from SW black liquor showed higher carbonisation yields than that obtained from HW black liquor samples. This also applied to lignins obtained by organic acid precipitation versus those obtained by acidification with H_2SO_4. Oxygen content in the raw lignin material affected the carbonisation yields; the higher the oxygen content, the lower the carbonisation yields. Carbonisation yields were also affected by possible semi-impregnation of the lignin samples during precipitation with stronger acids (SA and FA), where there is a probability that the acids were retained within the internal structure of lignin, and resulted in slightly higher chemical activation during the carbonisation process.

SW chars displayed narrow microporous volumes, compared to HW chars. The physical and morphological appearances of the SW and HW chars were also important, as the former showed high physical structural integrity in the chars after carbonisation, as well as a consistent morphological appearance of spherical particles, whereas the latter had a blend of particles and a softer and weaker physical appearance.

C-SW lignin chars were observed to be reactive with CO_2 above temperatures of 700 °C. A difference in the SW lignin samples precipitated with organic acids was observed with the burn-off during activation with partial gasification with CO_2, whereby there was no specific trend followed for the acids. There was a significant development of the porous structure resulting from the activation method chosen as observed from the positive increases in the structural parameters from chars to activated carbon.

Gasification resulted in the widening of the bottom ends of the micropores, as well as the overall increase in the narrow micropore region. Reactivity studies of the lignin chars showed that activation by partial gasification with CO_2 was based on non-catalytic and catalytic reactions at lower and higher conversions, respectively. Higher temperatures (815 and 825 °C) had an insignificant impact on the reactivity of the chars with CO_2, thus these reactions are under slight mass transfer limitations.

Organic acid precipitated lignin activated carbon in this study were found to be good candidates for applications in liquid phase adsorption, catalysis, energy storage, as well as molecular sieve applications.

References

Adler, E. 1977. Lignin chemistry-past, present and future. Wood Science and Technology, **11**: 169-218.

Atkins P, de Paula J. 2002. Atkins' physical chemistry (7th ed). New York, USA: Oxford University Press Inc. pp. 879-881

Baumlin S, Broust F, Bazer-Bachi F, Bourdeaux T, Herbinet O, Ndiaye FT, Lédé J. 2006. Production of hydrogen by lignins fast pyrolysis. International Journal of Hydrogen Energy. **31**: 2179-2192.

Bedia J, Rosas JM, Márquez J, Rodríguez-Mirasol J, Cordero T. 2009. Preparation and characterization of carbon based acid catalysts for the dehydration of 2-propanol. Carbon, **47**(1): 286-294. doi:http://dx.doi.org/10.1016/j.carbon.2008.10.008

Berenguer R, García-Mateos F, Ruiz-Rosas R, Cazorla-Amorós D, Morallón E, Rodríguez-Mirasol J, Cordero T. 2015. Biomass-derived binderless fibrous carbon electrodes for ultrafast energy storage. Green Chemistry, Advance Article.

Brunauer S, Emmett PH, Teller E. 1938. Adsorption of gases in multimolecular layers. Journal of the American Chemical Society, **60**(2): 309-319.

Carrott PJM, Suhas, Ribeiro-Carrott MML, Guerrero CR, Delgado LA. 2008. Reactivity and porosity development during pyrolysis and physical activation in CO_2 or steam of kraft and hydrolytic lignins. Journal of Analytical and Applied Pyrolysis, **82**: 264-271.

Cotoruelo LM, Marqués MD, Díaz FJ, Rodríguez-Mirasol J, Rodríguez JJ, Cordero T. 2012. Adsorbent ability of lignin-based activated carbons for the removal of p-nitrophenol from aqueous solutions. Chemical Engineering Journal, **184**: 176-183.

Dubinin MM, Zaverina ED, Radushkevich LV. 1947. Sorption and structure of active carbons. Adsorption of organic vapors. Journal of Physical Chemistry (USSR), **21**:1351-1362.

Fitigău, I. F., Peter, F., & Boeriu, C. G. 2013. Structural analysis of lignins from different sources. World Academy of Science, Engineering and Technology, **76**:107-112.

Fu K, Yue Q, Gao B, Sun Y, Zhu L. 2013. Preparation, characterization and application of lignin-based activated carbon from black liquor lignin by steam activation. Chemical Engineering Journal, **228**: 1074-1082. doi:http://dx.doi.org/10.1016/j.cej.2013.05.028

García-Mateos FJ, Ruiz-Rosas R, Marqués MD., Cotoruelo L.M., Rodríguez-Mirasol J, Cordero T. 2015. Removal of paracetamol on biomass-derived activated carbon: Modeling the fixed bed breakthrough curves using batch adsorption experiments. Chemical Engineering Journal, **279**: 18-30. doi:10.1016/j.cej.2015.04.144

Gårdfeldt, K., & Svane, M. 2011. Future use of lignin in value added products – A possible roadmap for Nordic/Baltic innovation. Helsinki: ScanBalt Campus Knowledge Network Environmental Biotechnology.

Gonzalez-Serrano E, Cordero T, Rodriguez-Mirasol J, Cotoruelo L, Rodriguez JJ. 2004. Removal of water pollutants with activated carbons prepared from H_3PO_4 activation of lignin from kraft black liquors. Water Research **38**(13): 3043-3050.

Guo X, Zhang S, Shan X. 2008. Adsorption of metal ions on lignin. Journal of Hazardous Materials, **151**(1): 134-142. doi:http://dx.doi.org/10.1016/j.jhazmat.2007.05.065

Jagiello J, Olivier JP. 2013. 2D-NLDFT adsorption models for carbon slit-shaped pores with surface energetical heterogeneity and geometrical corrugation. Carbon, **55**: 70-80.

Kaneko K, Ishii C. 1992. Superhigh surface area determination of microporous solids. Colloids and Surfaces, **67**: 203-212.

Kaneko, K. 1994. Determination of pore size and pore size distribution: 1. Adsorbents and catalysts. Journal of Membrane Science, **96**(1–2): 59-89. doi:http://dx.doi.org/10.1016/0376-7388(94)00126-X

Kaneko K, Ishii C, Ruike M. 1992. Origin of superhigh surface area and microcrystalline graphitic structures of activated carbons. Carbon, **30**(7): 1075-1088.

Khalil R, Várhegyi G, Jäschke S, Grønli MG, Hustad J. 2009. CO_2 gasification of biomass chars: A kinetic study. Energy and Fuels, **23**: 94-100.

Klapiszewski Ł, Nowacka M, Szwarc-Rzepka K, Jesionowski T. 2013. Advanced biocomposites based on silica and lignin precursors. Physicochemical Problems of Mineral Processing, **49**(2): 497-509.

Kouisni L, Holt-Hindle P, Maki K, Paleologou M. 2012. LignoForce system™: A new process for the production of high-quality lignin from black liquor. The Journal of Science & Technology for Forest Products and Processes **2**(4): 6-10.

Kunanopparat T, Menut P, Morel M, Guilbert S. 2012. Improving wheat gluten materials properties by kraft lignin addition. Journal of Applied Polymer Science, **125**(2): 1391-1399. doi:10.1002/app.35345

Li J, Kuppler RJ, Zhou H. 2009. Selective gas adsorption and separation in metal–organic frameworks. Chemical Society Reviews, **38**(5): 1477-1504.

Mani T, Mahinpey N, Murugan P. 2011. Reaction kinetics and mass transfer studies of biomass char gasification with CO_2. Chemical Engineering Science, **6**: 36-41.

Montané D, Torné-Fernández V, Fierro V. 2005. Activated carbons from lignin: Kinetic modeling of the pyrolysis of kraft lignin activated with phosphoric acid. Chemical Engineering Journal, **106**(1): 1-12.

Morandim-Giannetti AA, Agnelli JAM, Lanças BZ, Magnabosco R, Casarin SA, Bettini SHP. 2012. Lignin as additive in polypropylene/coir composites: Thermal, mechanical and morphological properties. Carbohydrate Polymers, **87**(4): 2563-2568.

Namane M, Sithole B.B, Ramjugernath D. 2015. Centrifugal washing and recovery as an improved method for obtaining lignin precipitated from South African kraft mill black liquor. Journal of Scientific and Industrial Research, **74**: 571-576.

Namane M, García-Mateos FJ, Sithole B, Ramjugernath D, Rodríguez-Mirasol, Cordero T. 2016. Characteristics of lignin precipitated with organic acids as a source for valorisation of carbon products. Cellulose Chemistry and Technology, **50** (3-4): 355-360.

Norberg I. 2012. Carbon fibres from kraft lignin. PhD. Dissertation, KTH Royal Institute of Technology, Sweden.

Rodriguez-Mirasol J, Cordero T, Rodriguez JJ. 1993. Preparation and characterization of activated carbons from eucalyptus kraft lignin. Carbon, **31**(1): 87-95.

Rodríguez-Mirasol J, Cordero T, Rodríguez JJ. 1993a. Activated carbons from carbon dioxide partial gasification of eucalyptus kraft lignin. Energy Fuels, **7**(1)

Rodríguez-Mirasol J, Cordero T, Rodríguez JJ. 1993b. CO_2-reactivity of eucalyptus kraft lignin chars. Carbon, **31**(1): 53-61. doi:http://dx.doi.org/10.1016/0008-6223(93)90155-4

Rosas JM, Berenguer R, Valero-Romero MJ, Rodríguez-Mirasol J, Cordero T. 2014. Preparation of different carbon materials by thermochemical conversion of lignin. Frontiers in Materials, **1**(Article 29): 1-17. doi:10.3389/fmats.2014.00029

Ruiz-Rosas R, Bedia J, Lallave M, Loscertales IG, Barrero A, Rodrıíguez-Mirasol J, Cordero T. 2010. The production of submicron diameter carbon fibers by the electrospinning of lignin. Carbon, **48**: 696-705.

Saiz-Jimenez C, De Leeuw JW. 1986. Lignin pyrolysis products: Their structures and their significance as biomarkers. Organic Geochemistry, **10**(4–6): 869-876. doi:http://dx.doi.org/10.1016/S0146-6380(86)80024-9

Šćiban MB, Klašnja MT, Antov MG. 2011. Study of the biosorption of different heavy metal ions onto kraft lignin. Ecological Engineering, **37**(12): 2092-2095. doi:http://dx.doi.org/10.1016/j.ecoleng.2011.08.006

Siriwardane RV, Shen M, Fisher E.P, Poston J.A. 2001. Adsorption of CO_2 on molecular sieves and activated carbon. Energy & Fuels, **15**(2): 279-284.

Suhas, Carrott PJM, Ribeiro-Carrott MML. 2007. Lignin – from natural adsorbent to activated carbon: A review. Bioresource Technology, **98**(12): 2301-2312. doi:http://dx.doi.org/10.1016/j.biortech.2006.08.008

Tancredi N, Cordero T, Rodríguez-Mirasol J, Rodríguez JJ. 1996. CO_2 gasification of eucalyptus wood chars. Fuel, **75**(13): 1505-1508.

Tancredi N, Cordero T, Rodríguez-Mirasol J, Rodríguez JJ. 1997. Activated carbons from eucalyptus wood. Influence of the carbonization temperature. Separation Science and Technology, **32**(6): 1115-1126.

6. SUMMARY AND DISCUSSIONS

This chapter gives a summary of the findings of this thesis. The overall objective of the work covered in the thesis was to expand on the introduction of the biorefinery concept in South Africa. The overall theme of the biorefinery concept through turning waste materials into a value added products was followed in three separate, but interconnected studies.

Black liquor, a chemical pulp waste by-product, was utilised to extract a valuable raw material precursor, lignin. The recovery of lignin was obtained by an efficient centrifugal method that reduced recovery times compared with vacuum filtration. In addition, organic acids were introduced as alternative and 'greener' precipitating agents for lignin from kraft black liquor. A comprehensive study was performed on the viability of the obtained lignin samples, by means of different organic acids and sulfuric acid, as precursors for valuable products. Finally, conversion of the lignins into activated carbon by partial gasification with carbon dioxide was investigated.

Below is a summary of the papers (PI, PII, PIII) that comprise the thesis, as well as further discussions of results that were not included in the journal papers as per publication requirements. Additionally, further discussion of the work discussed below gives an overall outlook of the work that was performed for the thesis, but could not be included in the papers.

6.1. Further discussions on the findings

6.1.1. Discussions based on PI

Chapter 3 (based on Paper I) examined the development of an alternative method that improved the recovery of lignin after precipitation from black liquor with H_2SO_4. This method was developed in-house and utilised centrifugation in a multistep procedure for washing and recovery of the lignin (Figure 6.1). There were significant improvements in the total recovery time of the lignin samples by utilising this method when compared with immediate vacuum filtration after precipitation. The average total time of recovery of the lignin sample observed for the centrifugal process was *approx*. 2 hours, compared with filtration straight after precipitation, which took over 8 hours for recovery of the lignin sample (Table 6.1).

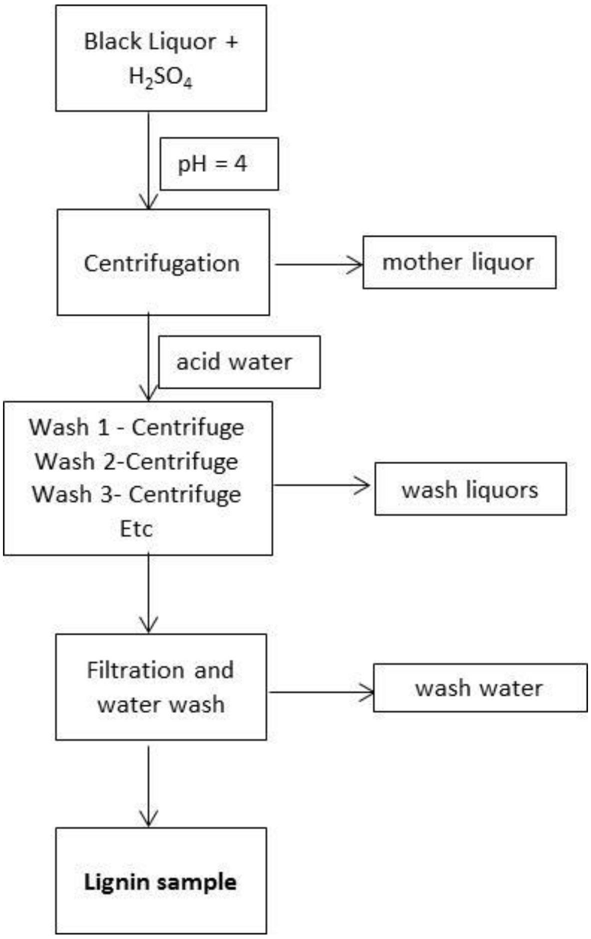


Figure 6.1. Lignin precipitation and centrifugal washing and recovery method.

Table 6.1. Comparison between the centrifugal washing and recovery method with filtration straight after precipitation.

Recovery Method	Lignin Conc. in BL (g/L)	Recovered Lignin Conc. (g/L)	% Yield	Filtration time (h)
Centrifuge	49.90	41.40	82.97	0.5 – 2
Filtration		46.90	93.99	> 7

At first, the centrifugal process seemed not viable due to the lignin yield obtained being lower than that obtained from the straightforward filtration: 83% and 93%, respectively. Two sources of error were identified during the centrifugal process investigation, *viz*.

- Sample losses during transfer between centrifuge tubes during the washing process.
- Organic matter that absorbs at the same wavelength as lignin when measuring the yield in UV-Vis.

For this investigation, it must be noted that the centrifuge that was utilised had a maximum speed of 4500 rpm, and only accommodated 4x15 mL centrifuge tubes, which then made the recovery process a bit tedious. Even though great care was taken, the major source of error for this investigation was due to sample losses during transfer at the washing stages. However, the shorter recovery times achieved from the centrifugal method still compensated for the lower yield in terms of the power input into both processes.

Furthermore, there was an improvement in the physical quality of the lignin sample that was observed at the final filtration stage after the centrifugal washing. Comparing the lignin obtained by immediate filtration after precipitation, the centrifugal method lignin was easily filterable. This was due to a decrease of the colloidal nature of the lignin suspension during the washing stages.

The centrifugal process was optimised and up-scaled upon acquiring a bigger centrifuge, where the yields between the two processes were observed to be equivalent. At this stage, new batches of black liquor were obtained from the mill, *viz*. hardwood (HW) and softwood (SW) black liquor.

The optimisation studies included investigation of precipitation of lignin from both wood species separately, with sulphuric acid and three organic acids. Organic acids in this study and the studies reported in Papers II and III were introduced on the basis that they could serve as 'greener' alternatives to H_2SO_4, as well as be more effective than utilising CO_2.

Precipitation of the lignin with organic acids (also sulphuric acid) first commenced with the optimisation and upscaling of the centrifugal method of recovery to increase the lignin yield observed in the work performed in Paper I. A similar precipitation, washing, and recovery method was followed in this study. Instead of the 100 mL of black liquor utilised above, 500 mL was utilised for precipitation. As reported in Paper I, there was a significant amount of sample that was lost and unaccounted for during the recovery process (~10%).

Therefore, careful measures were taken during the recovery process to ensure maximum sample transfer. From these studies, the lignin yield increased to values ranging from 90 to 96%, which was comparable with utilising filtration straight after precipitation (Table 6.2). This further confirmed that the centrifugal method of recovery was effective.

Table 6.2. Comparison between sulphuric and organic acid data obtained for precipitation of lignin from hardwood (HW) and softwood (SW) kraft mill black liquor

Precipitating Agent	Amount of acid utilised (mL)		Lignin conc in BL (g/L)		Total recovery time (h)	% Lignin yield		Cost of acid per 500 mL (ZAR)
	HW	SW	HW	SW	HW/SW	HW	SW	
SA	48.50	30.00	78.4	57.8	~ > 7	91.14	96.08	200
FA	114.00	62.00			~2 – 2.5	96.67	86.47	277
CA	130.00	64.00			~2.5 – 3.5	93.83	93.33	323 /500g
AA	70.00	45.50			~2.5 – 3	91.14	97.16	264

It is important to consider whether the centrifugal process could be viable on pilot and industrial scales as the centrifugal process has not been previously used for lignin recovery. However, there are a number of other known industrial processes that utilise centrifugal recovery (discussed in section 2.5.1), and it is envisaged that similar methods can be applied to lignin recovery.

The colloidal suspension nature of the lignin solution that forms during precipitation also makes it a good candidate for centrifugal recovery. Centrifugation would ensure faster separation of the solid component (lignin) from the spent liquors, as shown in the process of this work. Three typical industrial centrifuges are predicted to have good applications during lignin recovery, *viz*. decanter centrifuges, filter centrifuges, as well as hydro-cyclones.

For example, industrial decanter centrifuges have process capabilities that can allow 3–50% (w/w) feed slurry, with a 40–99% (w/w) solid recovery. The maximum rotational speed that can be achieved is 3500 rpm, with power consumptions ranging from 25–450 KW. More importantly, the temperature range of operation is 69–180 °C, which will suit higher temperatures experienced in the mill. Generally, in a typical kraft pulping process, 2 t of biomass input results in 10 t of black liquor as well as 1 t of pulp. However, in a 1000 t per day pulp producing kraft mill, the recovery boiler can handle 1500–1700 t of black liquor to produce 25–35 MW of energy. Total energy production in a pulp mill is known to exceed the mill needs, whereby this excess is sold or utilised in other processes. Thus, the inclusion of the centrifuge such as a decanter centrifuge in the process would not have any additional energy expenses. As mentioned, since the recovery boiler has limited capacity for black liquor, directing the black liquor towards precipitation of lignin would be viable in this case. The cost that would be incurred by integration of a centrifugal process into mill processes would be the capital for setting up the process. An all-encompassing precipitation, washing and recovery unit is suggested below.

Further research from this study will look into modifications of a filter centrifuge for an all-encompassing reactor that could have the precipitation reactions, washing, and recovery all occurring in the same system. If incorporated in the pulp mill, this process would involve continuous pumping of the excess black liquor from the pulping unit into a reactor that would feed the precipitating agent for precipitation to commence. Stirring of the solution could occur either by stirrers and/or slow rotation of the centrifugal unit.

Upon completion of the precipitation reaction, a filter would be introduced and the system would be spun down to separate the mother liquor from the solids. Washing of the lignin could also occur in the same system, where spray nozzles could be fitted in the centrifuge. On completion of washing, compressed air could be introduced to partially dry the lignin, or alternatively, the lignin can be removed. In-depth studies of such a system would look into whether the process could be made a batch or continuous. Moreover, if not used as a recovery unit, hydro-cyclones can also be used to concentrate the lignin colloidal suspension which can then be fed into a filter centrifuge for easy separation.

The mother liquor produced from the centrifugation unit would still contain dissolved inorganic material, as well as dissolved sugars (organics). This liquor can be redirected towards the evaporators followed by the recovery boiler to add to the organic material that is burnt, and recovery of the inorganic matter as cooking chemicals. The wash water in the centrifugal unit could be treated in the kraft mill’s waste water treatment plants, which are already in place.

In Chapter 3 FTIR and NMR spectroscopies were used to characterise the lignin sample, obtained by precipitation with sulphuric acid and recovered with the centrifugal method, in an attempt to identify the wood species that constituted the black liquor sample from the mill. A molecular weight distribution of the lignin sample was obtained with SEC. And finally, bearing in mind the ultimate objective of the overall study, that is, valorisation of the lignin, Py-GC/MS was utilised to identify typical compounds of value that can be obtained by pyrolysis of lignin.

FTIR analysis of the sample showed more syringyl type vibrational absorption bands than guaiacyl, indicating that the wood species from which the black liquor sample originated contained hardwood – as softwoods do not contain any syringyl groups. NMR showed the general lignin backbone mostly observed in the literature. However, there were chemical shifts in the ^{1}H spectrum that represented syringyl unit protons by comparison with spectra observed in the literature. The syringyl protons observed further corroborated the information provided by FTIR that there were more syringyl moieties in the lignin sample. From these observations, it was concluded that the unidentified black liquor sample that was obtained from the mill for this work, was a mixture of hardwood and softwood species.

SEC showed two peaks representing higher and lower molecular weight lignins. Dispersity of the sample was calculated to be $Đ = 1.036\ cm^{-3}\ g^{-1}$, which signified uniformity in the polymer, as well as the polymer falling in the narrow molecular weight distribution. Uniformity in the polymer and a narrow molecular weight distribution rendered the lignin in this study a good candidate for valorisation.

Py-GC/MS was utilised to predict the kind of products that could be obtained from lignin, with the main phenolic products obtained after 15-30 minutes. There were more guaiacol type compounds than syringol observed, with the former getting released before the latter. The observation of more guaiacol compounds was attributed to the probability that the syringol compounds were further broken down, resulting in the loss of the methoxy group. Identification of the pyrolysis products provided a scope for the valorisation of lignin into chemicals.

6.1.2. Discussions based on PII

Chapter 4 (based on Paper II) studied organic acids for precipitation of lignin from hard- and softwood black liquors. Characteristics of the lignins obtained were studied, as well as their conversion into chars by carbonisation. Alcell and commercial kraft lignins were also studied for comparison.

A comparison among the lignins obtained from precipitation with organic acids was not extensively covered in Paper II, and will be discussed in this section. The concentration of all precipitating agents was kept constant at 6 M, as this was the concentration of sulphuric acid mostly utilised in literature. Sulphuric acid, as the strongest acid, compared to organic acids required less volume for 500 mL of black liquor (Table 6.2). Moreover, hardwood black liquor samples required more lignin precipitating agents compared with softwood black liquor samples. This can be attributed to hardwoods containing additional syringyl moieties while

softwoods do not. These syringyl moieties present more –OH groups that require protonation during the precipitation procedure.
The yields for lignin precipitated with organic acids were more or less comparable. On an industrial scale, considering the scenario where 2 t of biomass is utilised in a kraft pulping mill, as mentioned above, 10 t of black liquor would be produced. Approximately 15–17 % percent of this black liquor can be accommodated for processing in the recovery boiler. If the hardwood lignin concentration in black liquor is considered from Table 6.2, the total lignin concentration in weak black liquor produced would be 0.663 t (w/w). Taking the average yield of all the organic acids to be 94%, this would result in the lignin yield of 0.623 t per tonne of black liquor. Constant removal of excess black liquor directed towards lignin precipitation could result in the mill performing at higher efficiency with regards to pulp production. In addition, high fresh quality black liquor would be used for lignin recovery, because over time, black liquor loses its chemical integrity.

The costs of each acid utilised in this study did not show significant variation (Table 6.2). Therefore, the amount of acid utilised for precipitation was the more important parameter. To account for the higher amount of organic acids utilised, a higher concentration of acid could be used.

There were additional advantages in using organic acids versus using sulphuric acid in lignin precipitation. The mother liquor resulting from sulphuric acid precipitation had a strong odour compared with those obtained from organic acid precipitation. It was also observed to be much darker compared to those precipitated with organic acids. From these observations, it could be suggested that the waste generated from sulphuric acid lignin precipitation would require more treatment compared to the odourless and less dark mother liquor obtained from organic acid precipitated samples.

Furthermore, the use of sulphuric acid on a larger scale, for example in an integrated lignin-based biorefinery, would result in sulphur imbalances in the mill. To further lessen the costs of organic acid precipitating agents in an integrated mill, CO_2 can be recovered from the flue gases of the recovery boiler and lime kiln, as well as the spent acid from the chlorine dioxide generator (Périn-Levasseur *et al*., 2011). The captured CO_2 could then be used as the initial precipitating agent up to pH ~ 9, followed by the use of organic acid to complete the reaction.

The following summary presents added advantages as a function of the characteristics of the lignin obtained from organic acid precipitation as discussed in PII.

Elemental analysis showed low sulphur content for the organic acid precipitated samples compared with the H_2SO_4 precipitated and commercial kraft lignin. The lowest sulphur content was observed for softwood samples, as well as showing CHO content that was closely related to that of Alcell lignin. As there was an evolution of gas observed during the precipitation processes, it was proposed that H_2S/SO_2 were released during sulphuric acid precipitation and that for organic acid precipitation, CO_2 could be the gas released. As CO_2 gas is also a known lignin precipitating agent from kraft black liquor up to pH ~ 9, its evolution in the organic acid precipitation process could result in the gas being recycled back into the system and used for the first stages of precipitation. This will result in the reduction of the use of organic acid in the process.

Thermogravimetric analysis, under air environment, of the lignin samples, indicated differences in the thermal behaviour for each acid utilised for precipitation. This observation indicated that, on a micro scale, the chemical behaviour of the samples was different for all samples studied, although technically similar. The DTG curves for all samples showed different temperature ranges for the main weight loss region across all wood species, as well as each acid of precipitation. The range of weight loss temperature was extended for organic acids, whereby some samples showed two distinct regions of weight loss in the DTG. Further weight loss was observed for HWAA and HWCA, and this was attributed to two probabilities: (i) weight loss due to inorganic material, or (ii) weight loss due to condensation of stable degradation products.

Carbonisation of the lignin samples resulted in chars with reasonably good yields. The fixed carbon yields obtained indicated that raw lignin obtained from kraft black liquor was good biomass for valorisation into different materials, as well as activated carbon. SEM morphology studies of the chars displayed different swelling patterns. The difference in cavities formed on the samples during carbonisation showed that the acids utilised for precipitation have different micro-effects in the lignin structure.

Characterisation with FTIR, as in Paper I, did not reveal much information as the spectra for all samples were more or less similar. However, there were slight differences observed in the absorption peaks for each sample, where there were slight peak shifts and broadenings. The differences observed in the FTIR absorption peaks showed that the different organic acid lignins were slightly different, signifying differences in the functionalisation of the lignin.

Additional experiments were performed to give a possible description for the phenomenon observed for the HWAA and HWCA weight loss that occurred at higher temperatures, 790 – 850 °C. This result was not included in Paper II, due to that, it was a not appropriately understood and that there was a need to perform more investigations on it. However, a plausible discussion is proposed below in an attempt to shed some light on this phenomenon. Appendix A2 also gives further studies that could be performed to understand this occurrence better. The TG and DTG curves for HWAA and HWCA are shown in Figure A1 in Appendix A1.

The additional weight loss observed for HWAA and HWCA did not occur in all other (both HW and SW) lignin samples, and this was observed over a number of repetitions of the same experiments. Furthermore, to ascertain this further weight loss, a separate experiment was performed. A TG analysis was performed as before, but in two tandem steps, both under (i) nitrogen-air (-NA), and under (ii) air-air (-AA) environments. In the first step of the experiment, the temperature was increased only up to a 500 °C in nitrogen (and in air for (ii)), followed by cooling down to temperatures below than 100 °C, and finally heated again to the final temperature of 900 °C in air for both experiments (i) and (ii). The resulting second part of the TG profile and the original TG for HWAA are shown in Figure A2 in Appendix A2. The final mass loss, as observed in the original TG profile is also observed in the new profiles. This suggests that HWAA and HWCA lignin samples may have contained additional materials that decomposed at higher temperatures compared to all other samples. This suggested that there may be strongly bonded modified broken down lignin compounds that form products of increased stability during earlier stages of heating (Afifi *et al*., 1989). This phenomenon is also observed during the delignification process, whereby condensation reactions can occur instead of degradation (Section 2.3.2).

Moreover, on top of the stronger bonded monomers that decompose at higher temperatures, there is a possibility of S-O bonds that may have formed, as shown by the FTIR data. AA and CA as precipitating agents may not have dissolved all the sulphate (-ide) ions that are found in the original black liquor. The higher sulphur content observed in the elemental analysis for AA and CA also sheds light on the existence of sulphur in the final lignin sample. Comparing these samples with the SWAA and SWCA counterparts, sulphur ions would be more susceptible to bond with HW lignin since there are also syringyl groups (with more O-groups). Although these compounds may contain sulphur, it is clear from the TG data that this stability may also provide resistance to oxidation of the lignin samples, which may be good for further processing of the samples into valuable materials.

6.1.3 Discussions based on PIII

Chapter 5 (based on Paper III) carried on from the TG experiments performed under N_2 in Chapter 4 to obtain bulk lignin char samples, with an objective to utilise these for the production of activated carbon. The char yields obtained for all samples were considerably high, and SW lignin chars showed higher yields than HW lignin samples. Higher oxygen content in the HW samples (due to the monolignol-oxygen distribution) was shown to play a role as an activating agent, thereby decreasing the char yields. The porous structure of all the char samples showed microporosity of type I in the N_2 absorption isotherms. HW samples showed higher absorption volumes of N_2 compared with SW samples, and this was also attributed to the higher oxygen content in the HW char samples.

Chars that were obtained from stronger acid (SA and FA) precipitated lignins displayed higher N_2 absorption volumes. For this observation, it was proposed that there could have been retention of the acid during the precipitation procedure, which resulted in partial chemical activation during the carbonisation process. As with SEM micrographs in Paper II, SW char samples possessed more distinct spherically shaped particles, whereas the HW char samples displayed more blended particles. The physical appearance of the char samples also showed distinct differences between the wood species, whereby SW samples were harder and more compact than the HW samples, which were brittle and soft.

CO_2 reactivity studies revealed that gasification experiments were both catalytically and non-catalytically controlled, at higher and lower conversions, respectively. The development of the porous structure was attributed to non-catalytic reactions. Arrhenius plots obtained for the reactivity studies showed that the gasification reactions were under slight mass transfer limitations under experimental conditions in this work. Comparing all the three organic acids initially utilised to precipitate the lignin from kraft black liquor, SWFA char required the least amount of activation energy to obtain the activated carbon.

Preparation of activated carbon was achieved by partial gasification of the lignin chars with CO_2 for the SW samples, due to their higher yields and stability of chars. Non-isothermal and isothermal experiments of the char samples showed low to no CO_2 reactivity at temperatures lower than 600 °C, as well as for gasification temperatures performed for 2 hours, respectively. There was a significant enhancement of the porous structure of the obtained activated carbon, as observed by the increased specific surface area, 1000 – 1300 m^2/g.

The increase in the external surface area, as well as mesoporous volume, supported the observation postulated in Chapter 4, that there was a widening of the bottom end of the micropores, which increased the surface area. Higher development of the porous structure was also observed from the significant increases in the pore diameter from char to activated carbon, thereby showing that activation by partial gasification with CO_2 was a viable process for the production of lignin activated carbon. The activated carbon obtained in this study had characteristics for applications in catalysis, liquid phase adsorption, energy storage, and molecular sieves.

References

Afifi AI, Hindermann JP, Chornet E, Overendt RP. 1989. The cleavage of the aryl-O-CH3 bond using anisole as a model compound. Fuel 68: 498-504.

Périn-Levasseur, Z., L. Savulescu, and M. Benali. 2011. Lignin Production Path Assessment: Energy, Water, and Chemical Integration Perspective. Journal of Science and Technology for Forest Products and Processes 1 (3): 25

7. CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH

From this study it can be concluded that:

- Centrifugal washing and recovery method studied for precipitation of lignin from kraft mill black liquor was an efficient process. This is a novel process that has not previously been reported.
- It is possible to deduce the origin of the wood species from which the black liquor was obtained by analysis of the precipitated lignin sample.
- Precipitation of SW lignin with organic acids yielded lignins with the lowest sulphur content – thus, this can be a way to produce "green" lignins.
- The type of acid utilised for precipitation directly influences the microstructure and behaviour of the obtained lignin
- Both hard- and softwood lignins obtained in this study provided good biomass for valorisation, according to the fixed carbon yield that was observed from the carbonisation of the sample.
- SW lignin chars showed higher carbonisation yields than HW lignin chars
- The chars showed very good reactivity with CO_2, thereby enabling the use of partial gasification with CO_2 as a viable method for the valorisation of lignin into activated carbon.
- Conversion of chars into activated carbon results in the development of high porosity in the carbons.
- Kraft lignin activated carbon produced in this study have the potential for use in different applications.

7.1. OUTLOOK AND FUTURE WORK

The preceding section draws general conclusions from the work performed in this thesis, based on Papers I, II, and III. The results from each study yielded further potential avenues for investigation, and these will be discussed below. Lignin has been shown both in literature and the current work, to be a valuable product that could have multitudes of functions in the biorefinery space. Thus, this valuable polymer needs to be explored further to understand its chemistry and functionality.

Future avenues that can be explored, as drawn from Paper I, and in the South African context, would be to perform a complete study that investigates the overall production capacity of kraft black liquor in the country, how much of it can be processed in recovery boilers, and how much excess can be used for precipitated lignin.

As has been shown, organic acids would be good candidates for production of a more ‘green’ precipitated lignin. The strength of the acid seemed to play a role in the quality of lignin, and more importantly, the chars that are produced. Therefore, a more detailed study that investigates the characteristics of the lignin produced by precipitation with organic acids could be beneficial to understand the behaviour of different organic acids as precipitating agents.

The gases evolved during the precipitation process are also an avenue to be explored. As stated, if CO_2 is the gas evolved in the organic acid precipitation process, it would be of value to capture the gas and utilise it for the first stage of the precipitation up to pH ~ 9, and thereafter utilise the organic acids. This would reduce the cost of organic acid utilisation for precipitation.

From Paper II, a further investigation into the thermal behaviour of the lignins obtained from different acids would be useful. It would be worthwhile to attempt to understand the different temperatures at which the weight loss is observed, as well as to understand why some samples show two weight loss temperatures. The high-temperature weight loss for HWCA and HWAA lignins also needs to be fully understood.

Lignin can be valorised into different materials, chemicals, and fuel, and an investigation of the best products that could be obtained from our lignins is also an avenue to be explored in the future. The current work had already begun investigating the possibility of obtaining carbon fibres from the raw lignin samples by electrospinning. We have already been exploring the possibility of producing carbon fibres from the kraft lignin with and without the addition of a binder, however, the results so far have not been promising.

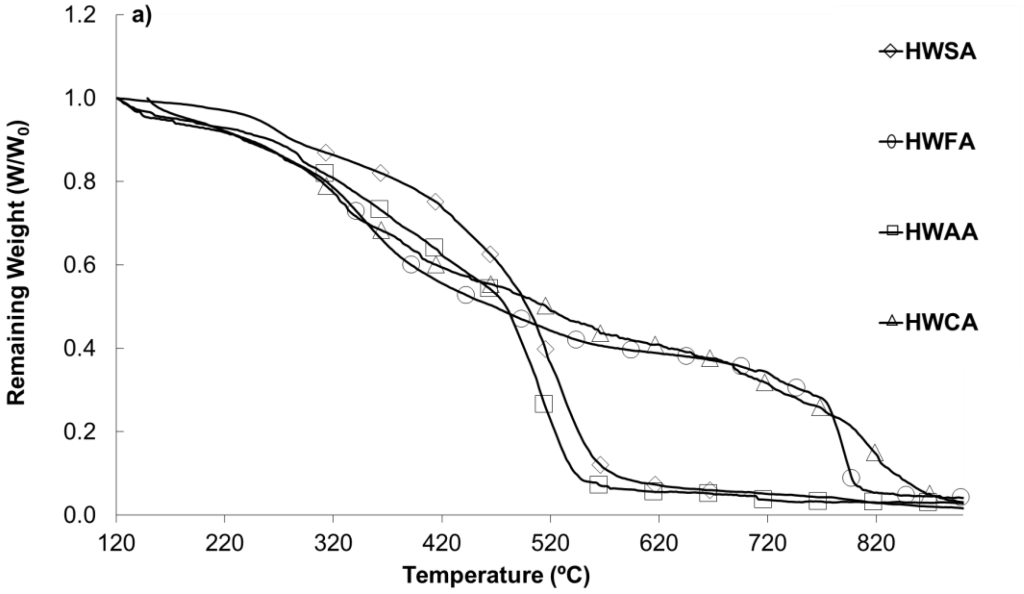
As a potential use of the activated carbon obtained, there is already a study planned to investigate these samples as potential adsorbents for metal ions in wastewaters.

Therefore, having established a method that improves the recovery of lignin from kraft black liquor, the possible applications for the lignin obtained can be pursued in future studies, both to investigate the physical and chemical properties of the lignins, as well as different pathways that can be followed for the valorisation of the polymer.

APPENDIX

Appendix A

A1 Hardwood TG and DTG curves



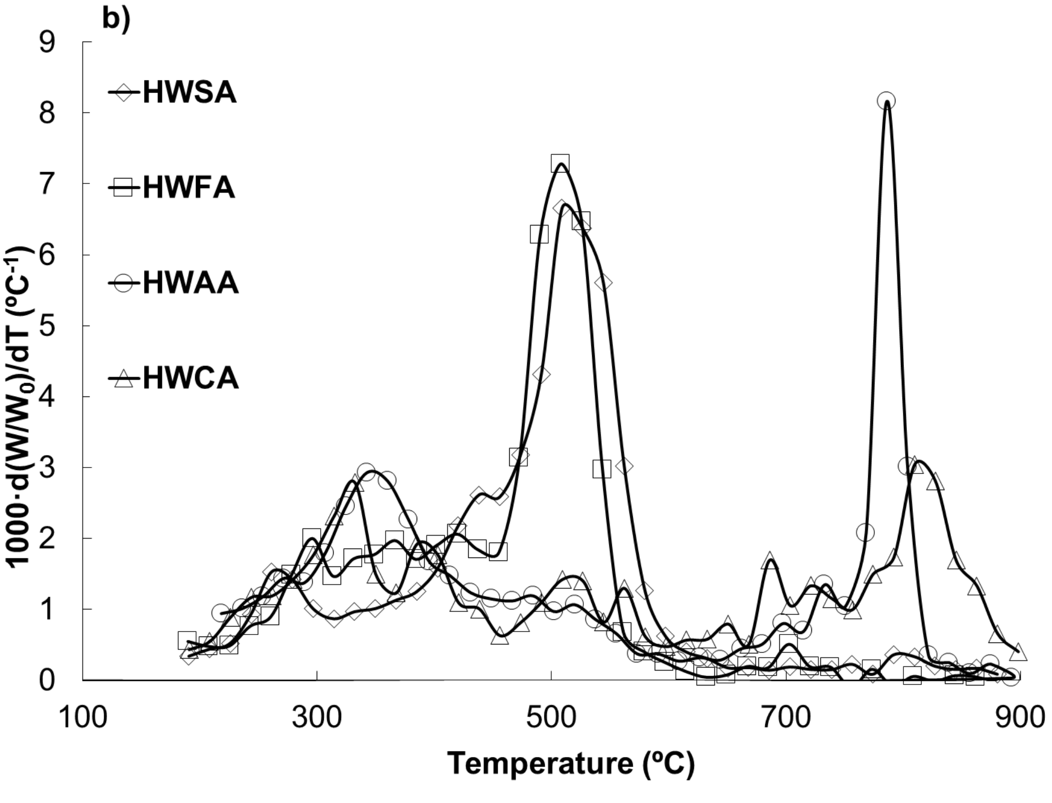


Figure A1. (a) TG and (b) DTG profiles obtained in air atmosphere for hardwood kraft lignin precipitated with SA, FA, AA, and CA

A2. Weight loss of HWAA and HWCA at higher temperatures

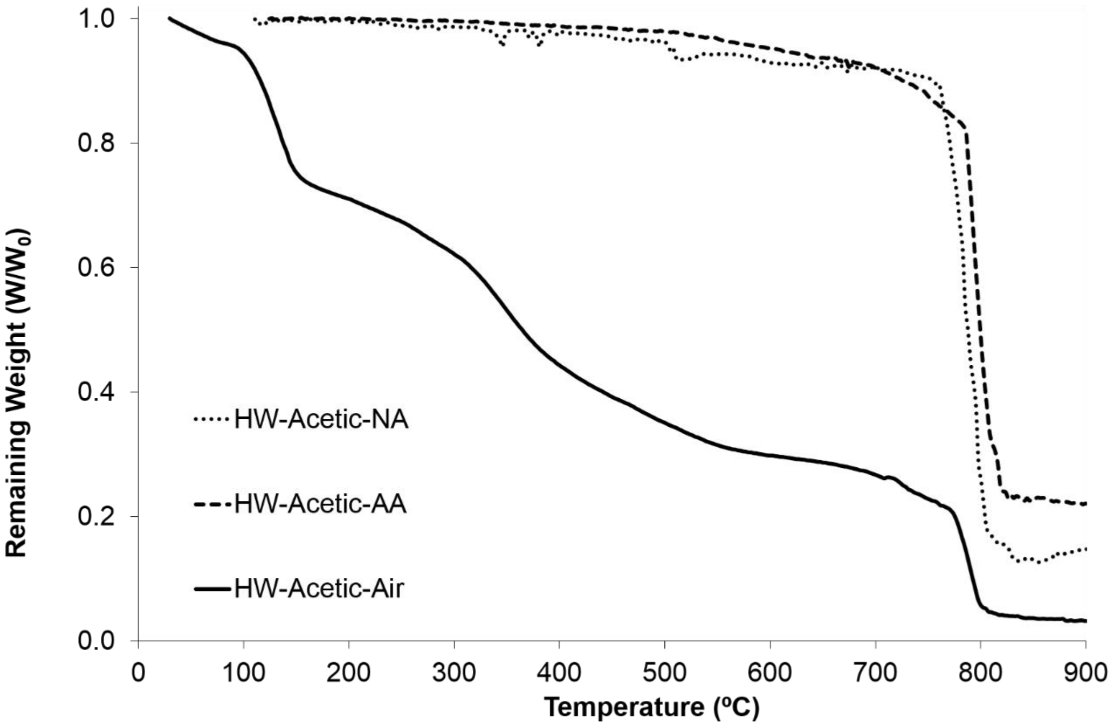


Figure A2. HWAA TG curve showing the consistent weight loss that occurs at higher temperatures performed in (i) N_2-air (HW-Acetic-NA), and (ii) air-air (HW-Acetic-AA), as well as the original HWAA TG profile (HW-Acetic-Air).

Further studies

The observed late weight loss of the HWAA and HWCA needs to be fully studied to understand the phenomenon occurring. Further studies need to be performed to evaluate the importance (or non-importance thereof) of this observation, as it could share more light in the alterations of the lignin samples during precipitation, more especially with weaker organic acids. Future studies in this work could include attempting to remove as much of the inorganic material as possible from the acetic/citric acid precipitated lignin samples, to observe if the effect is brought by the acid during precipitation. In cases where the effect is not brought by any inorganic material, this could mean that there are stable derivatives of lignin that may be caused by precipitation with weaker organic acids. Such materials could be valuable, since they are resistant to oxidation, and if isolated could add even more value in the lignin valorisation scale. If it is true that the material that has such higher temperatures of degradation and may contain sulphur, very stable heat resistant plastics could be obtained from such materials.

Appendix B

The following figures represent reactivity curves (B1) and Arrhenius plots (B2) of the rest of the samples that were not discussed in Chapter 5. It is worth noting that only one sample was discussed in Chapter 5 because all SW samples showed a similar trend for the samples. Representation of these samples here is the completeness of the results, as all samples were always mentioned throughout the thesis.

B1 Reactivity Curves

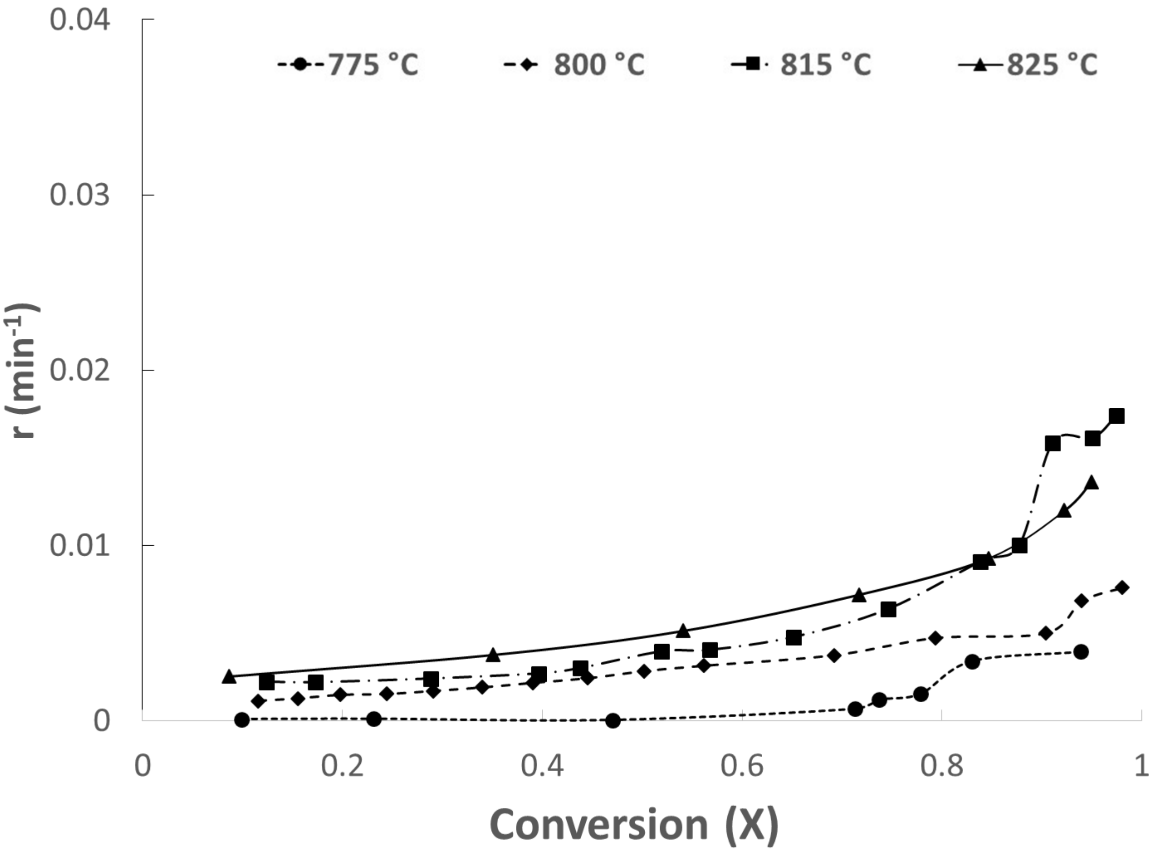


Figure C1. Reactivity curves for partial gasification of SWSA at different temperatures.

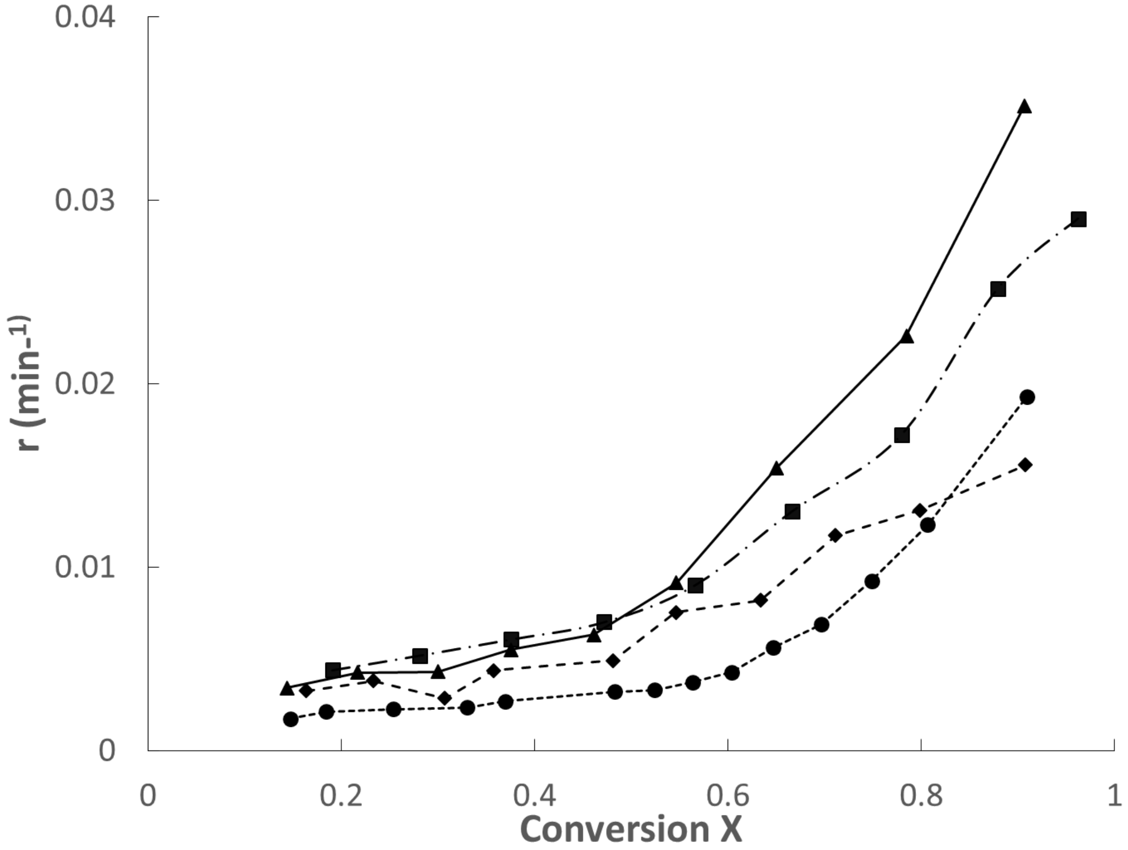


Figure C2. Reactivity curves for partial gasification of SWFA at different temperatures.

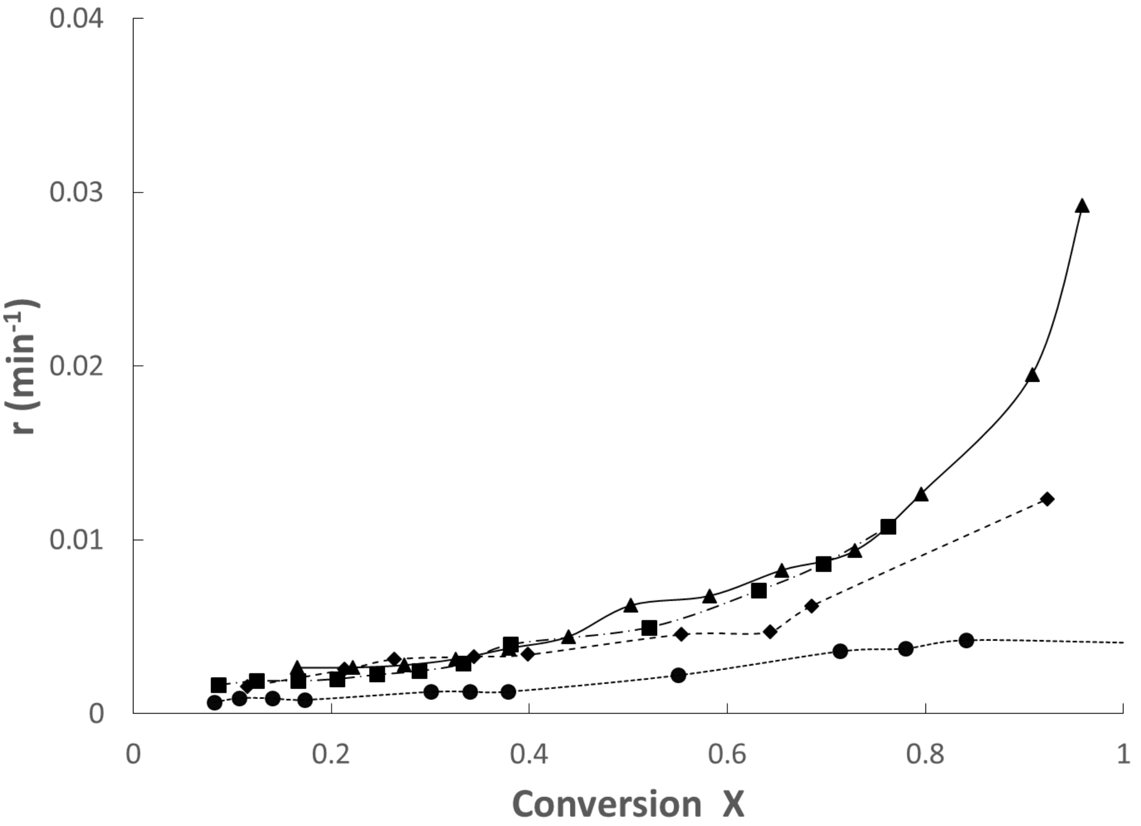


Figure C3. Reactivity curves for partial gasification of SWCA at different temperatures.

B2 Arrhenius Plots

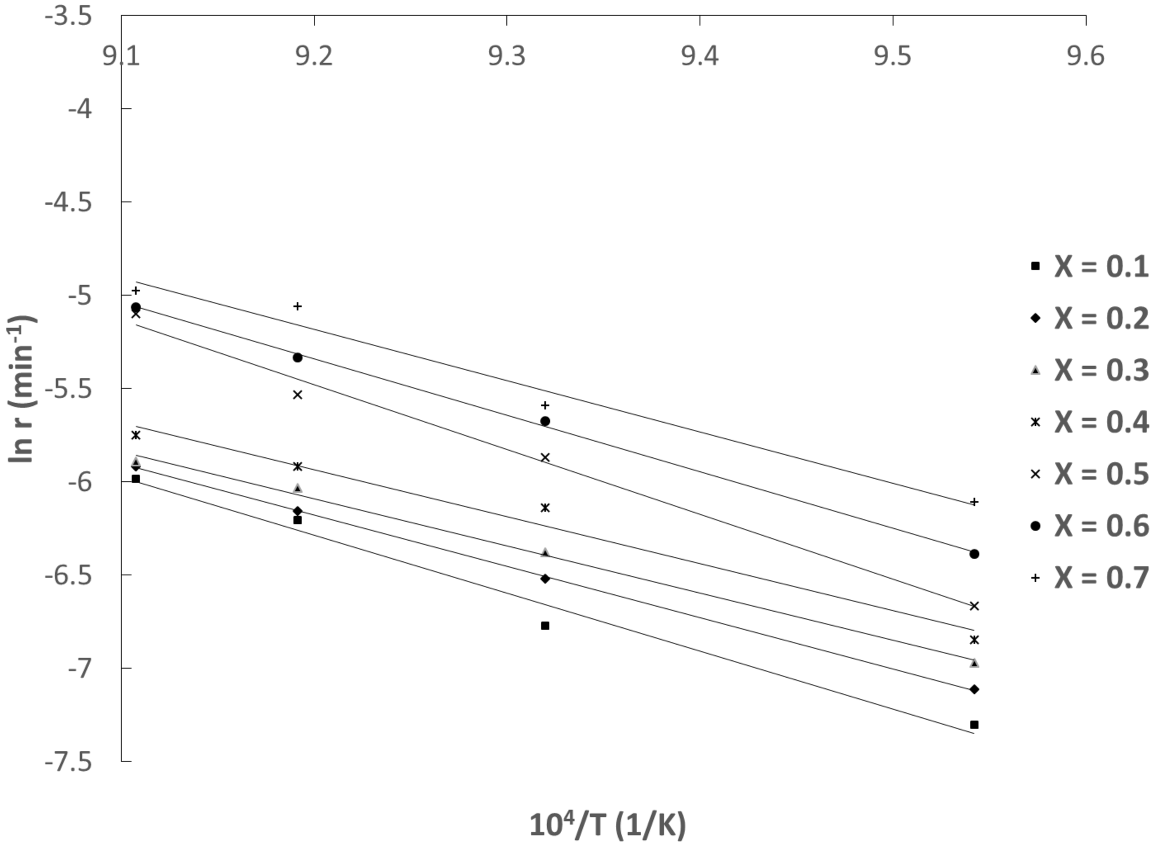


Figure C4. Arrhenius plots for gasification of C-SWSA with CO_2 at different conversion values

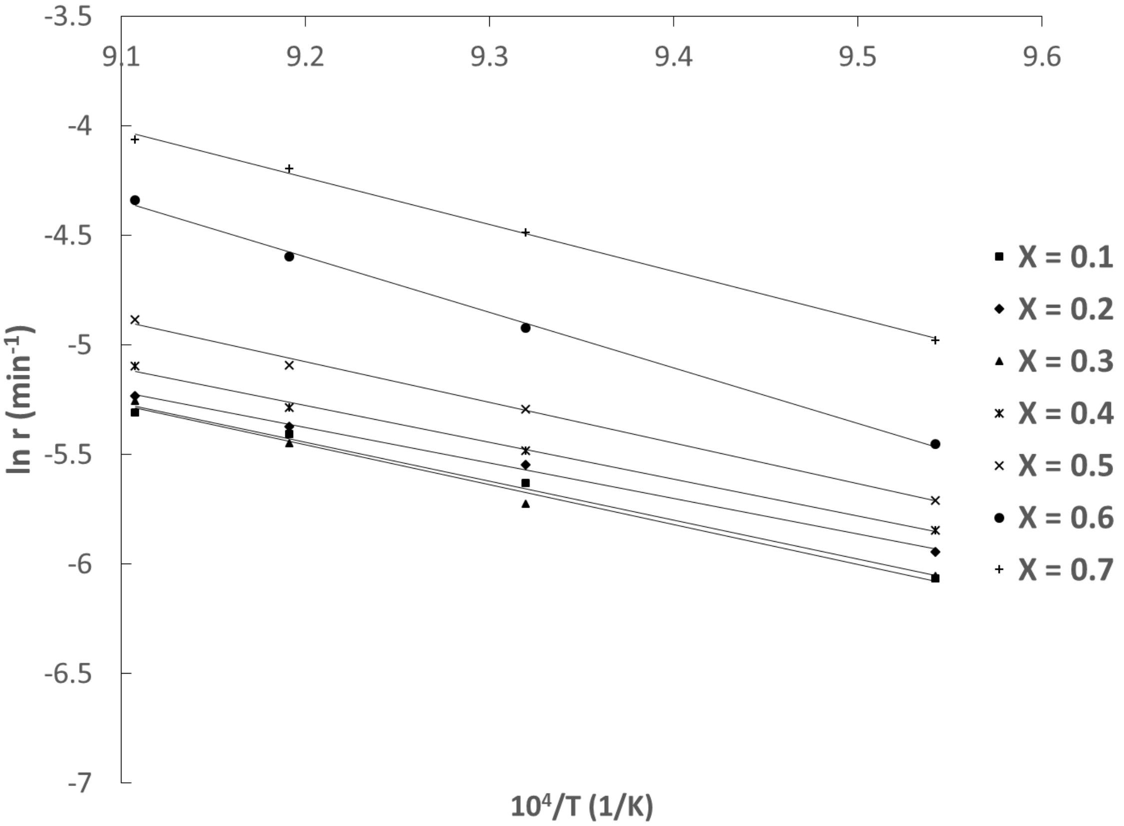


Figure C5. Arrhenius plots for gasification of C-SWFA with CO_2 at different conversion values

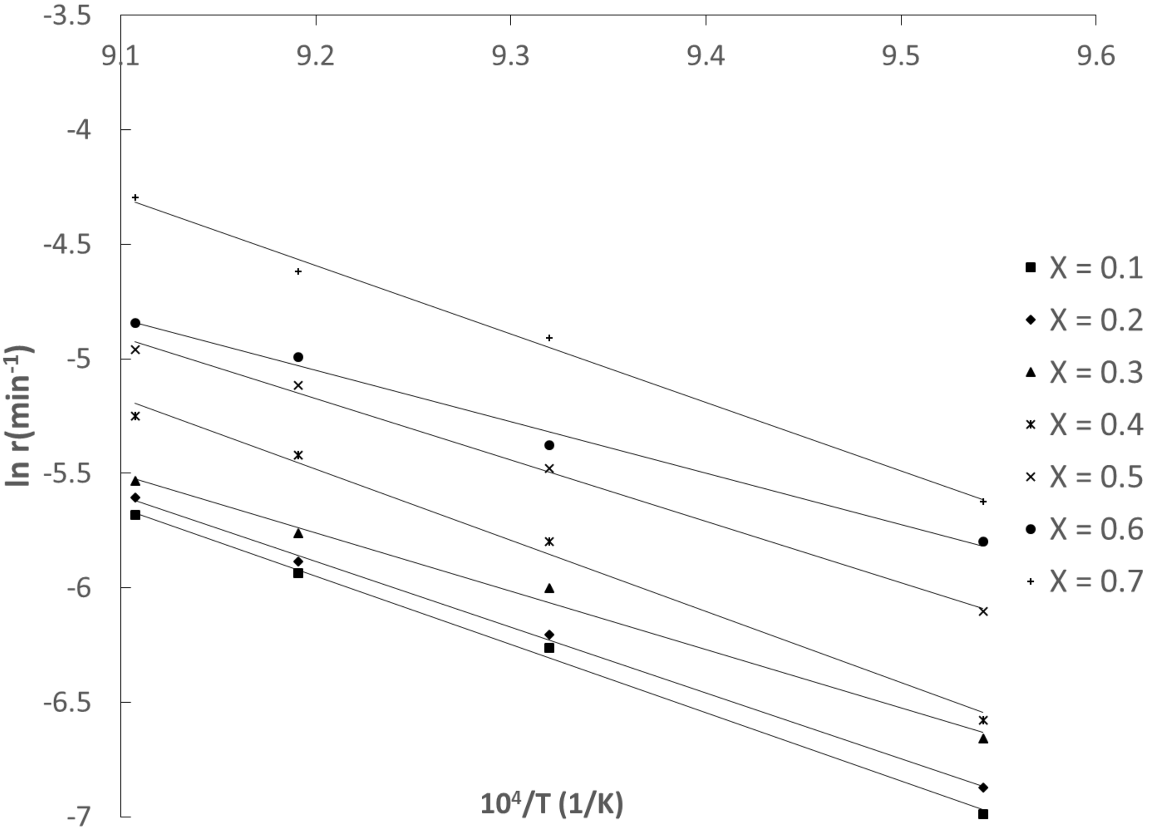


Figure C6. Arrhenius plots for gasification of C-SWCA with CO_2 at different conversion values

Appendix C

C1 Abstracts from conferences attended

C1.1. Institutions

[1] Forestry and Forest Products Research Centre, Council of Scientific and Industrial Research (CSIR), Durban, South Africa

[2] School of Chemical Engineering, University of KwaZulu-Natal, Howard College Campus, Durban, South Africa

[3] Universidad de Málaga, Andalucía Tech, Dpto. de Ingeniería Química, Facultad de Ciencias, Campus de Teatinos s/n 29071 Málaga, Spain

C1.2. 2013 TAPPSA National Conference and Exhibition, 22-23 October 2013, Durban, South Africa – Poster Presentation

Precipitation and valorisation of lignin in South African Kraft mill process liquors

Mpho NAMANE[1,2], Bruce B. SITHOLE[1,2], Deresh RAMJUGERNATH[2]

Abstract

Worldwide, the pulp and paper industry is in decline due to a number of factors such as higher production costs, the growing utilization of electronic media that compete with print media and books, and pressure for the industry to be more environmentally sustainable. The yield in kraft mills is about 50%; a major obstacle observed in attempting to increase production in many Kraft mills is a bottleneck in the recovery unit operations. One way to off-load the bottleneck is to divert the excess black liquor and use it to collect lignin by precipitation.

The aims of the current project are to develop effective and economic methods or technologies for isolation of relatively pure lignin from Kraft mill liquors resulting from chemical pulping of woods in South Africa. In order to realise the proposed aim, the investigation will focus on the following -:

- Explore the best method/s for precipitation and purification of lignin from Kraft mill liquor (mainly black liquor).
- Characterization of the obtained lignin.
- Generation of valuable chemicals by utilising methods such as reactive pyrolysis, synthesis, catalysis, etc.

Studies will be done to compare a collection of lignin from strong and weak black liquors.

C1.3. 10th International Conference on Renewable Resources and Biorefineries, 4-6 June 2014, Valladolid, Spain – Poster Presentation

Precipitation and characterisation of lignin obtained from South African kraft mill black liquor

Mpho NAMANE[1,2], Bruce B. SITHOLE[1,2], Deresh RAMJUGERNATH[2]

Abstract

The global depletion of fossil fuel resources, with a consequent increase in cost, has opened up opportunities for the investigation of renewable resources as an alternative source of carbon. The pulp and paper industry processing streams present new opportunities in the biorefinery field, where products other than cellulose can be obtained, and thereby adding value to the mill production and at the same time assisting in relieving the bottleneck experienced in the recovery boiler. Black liquor, which is a by-product of Kraft pulping, contains valuable materials such as lignin which can further be extracted for valorisation. Lignin is the second most abundant biological material after cellulose. During the last few decades, lignin has been investigated as the main alternate carbon resource for future fuels, chemicals, and materials; due to its rich carbon content, as well as being seen as the most underutilised carbon source. The aim of this study was to find an efficient method for extract lignin from Kraft black liquor. Black liquor obtained from a Kraft mill was analysed for solids content (~15%), ash (~10%), and total lignin content (~50%) prior to lignin isolation experiments. Lignin isolation was performed by acid precipitation utilising 6 M sulphuric acid, followed by centrifugation which resulted in the approximate recoveries of 83% of the lignin sample. The lignin obtained was qualitatively characterised for structural features using Fourier transform infrared spectroscopy, as well as ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy. These characterisation techniques gave insight on the heterogeneity and nature of the syringyl and guaiacyl composition of the lignin. Size exclusion chromatography provided information on the molecular weight distribution of the lignin, Mw ~ 188 KDa, and the polymer was found to have a dispersity, Đ = 1.036 cm^{-3} $g^{-}1$, illustrating a polymer with uniform molecular weight. Pyrolysis gas-chromatography mass-spectrometry analysis provided a general output of typical degradation compounds that could be obtained from the lignin sample, which was typical of a hardwood lignin.

C1.4. International Conference on Chemical Thermodynamic and The South African Institute of Chemical Engineer, 27 July – 1 August 2014, Durban, South Africa – Oral Presentation

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Mpho NAMANE[1,2], Bruce B. SITHOLE[1,2], Deresh RAMJUGERNATH[2]

Abstract

The global depletion of fossil fuel resources, with a consequent increase in cost, has opened up opportunities for the investigation of renewable resources as an alternative source of carbon. The pulp and paper industry processing streams present new opportunities in the biorefinery field, where products other than cellulose can be obtained, and thereby adding value to the mill production and at the same time assisting in relieving the bottleneck experienced in the recovery boiler. Black liquor, which is a by-product of Kraft pulping, contains valuable materials such as lignin which can further be extracted for valorisation. Lignin is the second most abundant biological material after cellulose. During the last few decades, lignin has been investigated as the main alternate carbon resource for future fuels, chemicals, and materials; due to its rich carbon content, as well as being seen as the most underutilised carbon source. The aim of this study was to find an efficient method for extract lignin from Kraft black liquor. Black liquor obtained from a Kraft mill was analysed for solids content (~15%), ash (~10%), and total lignin content (~50%) prior to lignin isolation experiments. Lignin isolation was performed by acid precipitation utilising 6 M sulphuric acid, followed by centrifugation which resulted in the approximate recoveries of 83% of the lignin sample. The lignin obtained was qualitatively characterised for structural features using Fourier transform infrared spectroscopy, as well as 1H and 13C nuclear magnetic resonance spectroscopy. These characterisation techniques gave insight on the heterogeneity and nature of the syringyl and guaiacyl composition of the lignin. Size exclusion chromatography provided information on the molecular weight distribution of the lignin, Mw ~ 188 KDa, and the polymer was found to have a dispersity, Đ = 1.036 cm-3 g-1, illustrating a polymer with uniform molecular weight. Pyrolysis gas-chromatography mass-spectrometry analysis provided a general output of typical degradation compounds that could be obtained from the lignin sample, which was typical of a hardwood lignin.

Keywords: Black liquor, lignin, kraft, precipitation, valorisation

C1.5. 1st International Workshop on Biorefinery of Lignocellulosic Materials, 9-12 June 2015, Córdoba, Spain – Oral Presentation

Extended Abstract:

Characteristics of lignin precipitated with organic acids as a source for valorisation of carbon products

Mpho NAMANE[1,2,3], Francisco J. GARCÍA-MATEOS[3], Bruce B. SITHOLE[1,2], Deresh RAMJUGERNATH[2], José RODRÍGUEZ-MIRASOL[3] and Tomás CORDERO[3]

Abstract

The biorefinery concept prescribes that the biomass should be utilised in its entirety to produce high-value chemicals and materials, as well as energy. Lignin is the second most abundant carbon material and a by-product of multiple lignocellulosic biomass derived industries. Its richness in carbon appropriates it for far more than the industry is currently utilising it for, therefore production of high-value products (and energy) from lignin could be a significant step towards appreciating the biorefinery concept. Hardwood (HW) and softwood (SW) lignin obtained from a South African kraft mill black liquor was precipitated with sulphuric and organic acids. Recovery of lignin after precipitation was achieved by an improved stepwise centrifugal washing methodology, which improved the recovery time as compared with straightforward filtration after precipitation. The sulphur content varied between species, with SW organic acid precipitated samples showing the lowest sulphur content. Thermogravimetric analysis (TGA) of the HW and SW lignin samples in air revealed differences in the main degradation region of the TG curve. The strength of the acids appeared to play an important role in the thermal degradation of the lignin samples, that is the weaker organic acid samples showed greater mass losses compared with sulphuric acid. TGA analysis under nitrogen showed carbon yields acceptable for the lignin samples to be considered biomass. SEM micrographs showed swelling in the lignin chars, however, all char samples revealed differences in morphology of their structure showing that different precipitation media, would produce different carbon structures, thus different valorisation products.

The biorefinery concept prescribes that the biomass should be utilised in its entirety to produce high-value chemicals and materials, as well as energy. Lignin is the second most abundant biopolymer and a by-product of multiple lignocellulosic biomass derived industries. Its richness in carbon appropriates it for far more than the industry is currently utilising it for, therefore production of high-value products (and energy) from lignin could be a significant step towards appreciating the biorefinery concept. Hardwood (HW) and softwood (SW) lignin obtained from a South African kraft mill black liquor was precipitated with sulphuric and organic acids. Recovery of lignin after precipitation was achieved by an improved stepwise centrifugal washing methodology, which improved the recovery time as compared with straightforward filtration after precipitation. The sulphur content varied between species, with SW organic acid precipitated samples showing the lowest sulphur content. Thermogravimetric analysis (TGA) of the HW and SW lignin samples in air revealed differences in the main thermal decomposition region of the TG curve. The strength of the acids appeared to play an important role in the thermal degradation of the lignin samples, that is the lignin precipitated with the weaker organic acid showed greater mass losses compared with sulphuric acid precipitated ones. TGA under nitrogen showed carbon yields acceptable for all the lignin samples. SEM micrographs showed swelling in the lignin chars, however, all char samples revealed differences in morphology of their structures showing that different precipitation acid media, would produce different carbon structures, thus different valorisation products.

I. INTRODUCTION

Lignin polymer is fast becoming the centre of much research in the biorefinery space, where it is envisaged as a potential alternative to fossil fuel resources (1,2). The polymer occurs naturally in plants, it is the second most abundant biopolymer, as well as the most underutilised carbon material for valuable products. One way to obtain lignin is by precipitation from the black liquor of kraft process. In the current kraft mill, black liquor is incinerated (gasified in some cases) in the recovery boiler to recover cooking chemicals, as well as use lignin's high heating value to provide energy for the mill. The capacity of the recovery boiler for black liquor is limited, thus resulting in a bottleneck that in turn impacts on the efficacy of the pulping process. Partial removal of lignin at this stage of the process would be a way to salvage the situation. Lignin has classically been isolated from black liquor by acid precipitation, specifically sulphuric acid, and most recently carbon dioxide (3,4). These two methods of precipitation have their drawbacks, although they work, that is, the former has been shown to release environmentally unfriendly gases, as well as disturb the sulphur balance in the mill, and the latter not being able to completely precipitate lignin from black liquor (5). Since only acidification of black liquor is needed to precipitate lignin, other acids can also be considered. This could include organic acids with a premise that they would be a greener alternative to sulphuric acid, as well as perform the work more efficiently that carbon dioxide. Organic acids are also not costly and are nontoxic. Polycarboxylic acids have been shown to increase the mechanical properties of polymers by crosslinking hydroxyl groups (6,7). This characteristic could also be beneficial for lignin valorisation into carbon fibres and activated carbon because polymer stability is essential for pre-treatment steps (8,9).

The objective of the current work was to investigate the thermal behaviour of lignin samples precipitated from kraft black liquor with sulphuric acid, and three organic acids (formic, acetic, and citric acid). The purpose of utilising organic acids was to consider the type of lignin that can be obtained could possibly be more ‘greener’ than that conventionally precipitated with sulphuric acid. The characteristics of each lignin samples were examined by elemental analysis (EA), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). Finally, the lignin samples were carbonised and the features of the products studied with scanning electron microscopy (SEM).

II. EXPERIMENTAL

Lignin Isolation

Hard- and softwood black liquor samples were obtained from a kraft mill in South Africa, and stirred for 3 hours to obtain homogeneity in the bulk samples. Lignin was isolated by acid precipitation (with sulphuric, formic, citric or acetic acids). The general precipitation and recovery procedure is as follows for all acids used in this study; approximately 500 mL of black liquor sample was taken from the bulk sample, and 6M each of the acid solution (per different experiment) was added to the black liquor drop-wise while stirring until pH of approximately 9. The solution was left stirring for 1 hour to allow for particle growth. The precipitation was completed by further acid addition until pH of 4, and stirring for another hour. Lignin was recovered from the solution by centrifugation. The recovered lignin was subsequently washed with acid-water in a decreasing acid gradient a number of times (or until the supernatant was clearer), each time utilising a centrifuge to recover the washed precipitate. Finally, lignin was recovered by filtration with a Buchner funnel under vacuum suction.

Characterization

The lignin samples were first dried over a long period of time and elemental analysis (CHNS/O) was performed on a Thermo Scientific Flash 2000 instrument. TG experiments for all lignin samples were performed using a thermobalance equipment from CI Electronics. The initial sample weight was constantly adjusted to approx. 10-12 mg and a continuous gas (air or nitrogen) flow at a rate of 150 mL/min (STP). The temperature signal for the controller was measured by means of a chromelalumel thermocouple placed inside the reaction tube. The sample weight loss was continuously recorded in a microcomputer data acquisition system to obtain the TG and DTG curves. The heating rate of 10 °C/min was used in all the experiments.

III. RESULTS AND DISCUSSION

All four different lignin precipitated with sulphuric (SA), formic (FA), acetic (AA), and citric acid (CA) showed behaviour typical of a general TG profile, even though each difference were observed for each lignin (Figure D1). Three main regions were generally observed for each TG profile. Subtle differences were observed in the TG profiles of HW- Acetic and Citric acid precipitated lignin samples, where there was a region prior to the 'final decay' which showed another steep weight loss. The TG profiles for HW lignin samples precipitated with SA and FA showed lower weight loss due to moisture, approx. 7%, while their AA and CA counterparts showed higher weight losses, 17% and 31% respectively. Following the loss of weight due to moisture, all samples exhibit the majority of the weight being lost up until temperatures of around 700 °C. In this region SA and FA, lignin samples displayed weight losses of about 90%, whereas AA and CA had lower values of around 65% and 50% weight loss in the second region.

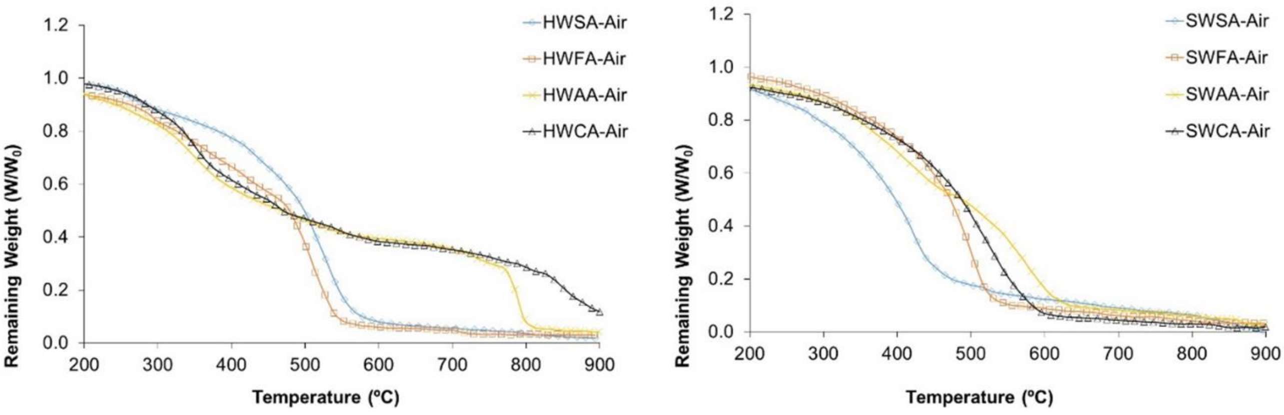


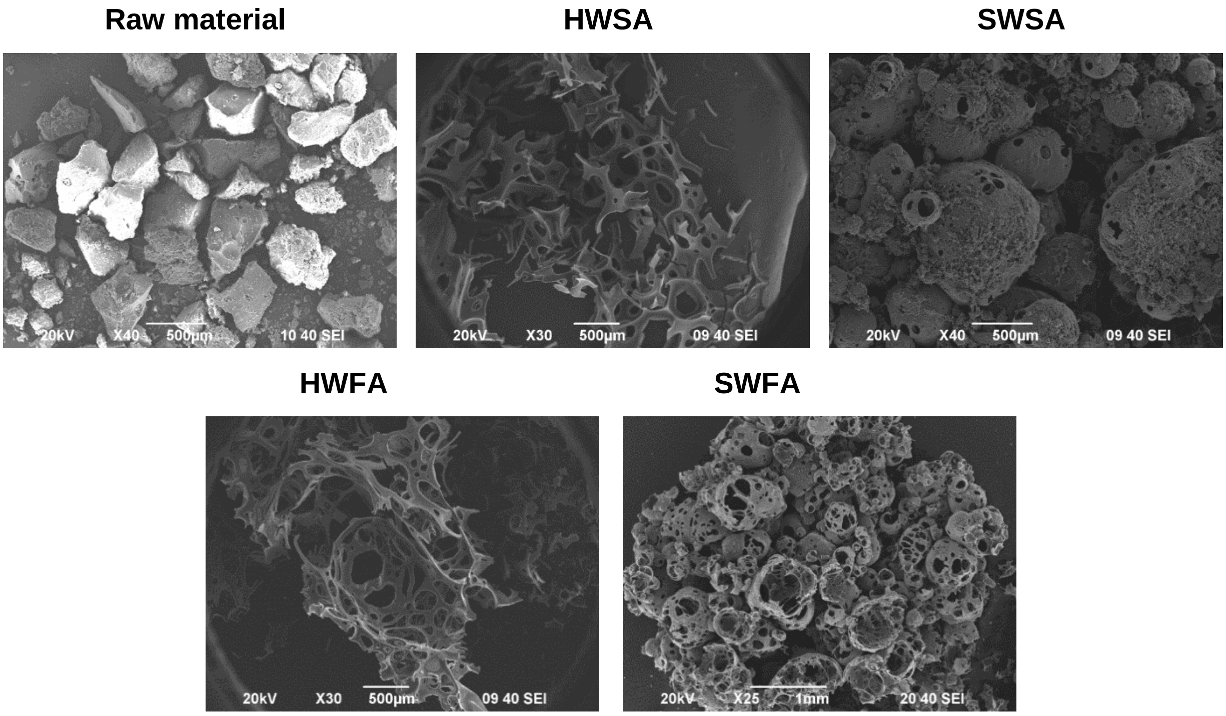
Figure D1. Representation of the TG curves (dry basis), performed in air, for hardwood (left) and softwood (right) lignin samples, precipitated with four acids.

Data of immediate analysis (fixed carbon, volatile matter, ash content and humidity) could be obtained from TG experiments performed in nitrogen or air environment. The fixed carbon and char yields from these experiments were considered to be good values for future processing of the samples into valuable carbon products (Table D 1) (10,11).

Sample	**% Volatile matter**	**%Fixed Carbon**	**% Yield**
HWSA	69.82	28.59	30.17
HWFA	63.26	33.91	36.73
HWAA	64.35	31.89	35.64
HWCA	61.26	35.91	38.73
SWSA	66.86	33.13	33.13
SWFA	73.82	23.67	26.17
SWAA	67.24	30.70	32.75
SWCA	59.42	39.64	40.57
CKL	75.02	12.36	24.97
Alcell	66.43	33.56	33.56

Table D2. TGA data obtained under a nitrogen atmosphere for HW and SW lignin samples to represent the volatile matter, fixed carbon and the carbonisation yield for different acid precipitated samples.

The obtained char samples were observed under a SEM (only four samples represented here) (Figure D2). In comparing the raw lignin sample with the carbonised samples, different swelling patterns were observed. HWSA, HWFA, as well as Alcell lignin, showed a ribbon-like structural pattern under the microscope. All the SW samples and HWCA show a commonly observed expansion of the lignin samples, where cracks and cavities were observed on the samples' micrographs. The volume of these swollen lignin has been observed to be four times higher than the initial volume, as well as that this increase in volume represents a plastic deformation by cavitation (12).



Raw material

HWSA

SWSA

HWFA

SWFA

Figure D2. SEM micrographs comparing the raw material with the carbonised samples

IV. CONCLUSIONS

Sulphur content was shown to be less in the weaker organic acid precipitated samples compared with that of sulphuric acid. Hardwood lignin samples precipitated with sulphuric and formic acid revealed lower moisture content compared with acetic and citric acid samples. Sulphuric and formic acid precipitated lignin samples displayed higher decomposition in the main region of the TG curve, while acetic and citric acid samples showed less. The fixed carbon and char yields observed from the carbonised lignin showed that the samples in this work are good biomass for further processing into valuable compounds.

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VI. REFERENCES

1. H. Wallmo, M. Wimby, A. Larsson. “Increase production in your recovery boiler with LignoBoost - Extract valuable lignin for biorefinery production and replacement of fossil fuels”. Tappi Engineering, Pulping and Environmental Conference; 11-14 Oct **2009**.
2. Ragauskas, M. Nagy, D.H., C. Eckert, J Hallett, C. Liotta. “From wood to fuels: Integrating biofuels and pulp production”. *Industrial Biotechnology* 2, 55-65 **2006**.
3. P. Tomani. “The LignoBoost process”. *Cell Chem Technol* 44, 53-58 **2010**.
4. R. Alen, P. Patja, E. Sjostrom. “Carbon dioxide precipitation of lignin from pine kraft black liquor”. *Tappi J* 62, 108-110 **1979**.
5. M. Gilarranz, F. Rodriguez, M. Oliet, J. Revenga. “Acid precipitation and purification of wheat straw lignin”. *Separ Sci Technol* 33,1259-1377 **1998**.
6. N. Reddy, Y. Yang. “Citric acid cross-linking of starch films”. *Food Chem* 118, 702-711 **2009**.
7. D. Wyrzykowski, E. Hebanowska, G. Nowak-Wiczk, M. Makowski, L. Chmurzynski. “Thermal behaviour of citric acid and isomeric aconitic acids”. *J Therm Anal Calorim* 104, 731-735 **2011**.
8. J. Rosas, R. Berenguer, M. Valero-Romero, J. Rodríguez-Mirasol, T. Cordero. “Preparation of different carbon materials by thermochemical conversion of lignin”. *Front Mater* 1, 1-17 **2014**.
9. R. Ruiz-Rosas, J. Bedia, M. Lallave, I. Loscertales, A. Barrero, J. Rodrıguez-Mirasol, T. Cordero. “The production of submicron diameter carbon fibers by the electrospinning of lignin”. *Carbon* 48, 696-705 **2010**.
10. F. Kifani-Sahban, A. Kifani, L. Belkbir, A. Zoulalian, J. Arauzo, T. Cordero. “A physical approach in the understanding of the phenomena accompanying the thermal treatment of lignin”. *Thermochim Acta* 298, 199-204 **1997**.
11. J. Rodriguez-Mirasol, T. Cordero, J.J. Rodriguez. “Preparation and characterization of activated carbons from eucalyptus kraft lignin. *Carbon* 31, 87-95 **1993**.
12. S. Sebbahi, A. Ahmido, F. Kifani-Sahban, S. El Hajjaji, A. Zoulalian. “Preoxidation and activation of the lignin char: Carbonization and oxidation. *J Eng*, 1-9 **2014**.