THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Equilibrium of Lignin Precipitation

The Effects of pH, Temperature, Ion Strength and Wood Origins

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CHALMERS UNIVERSITY OF TECHNOLOGY

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ABSTRACT

The kraft process is the predominant method for producing pulp in Scandinavia. However, the material efficiency in modern kraft pulp mills for pulp production is only 40−55% and the final product consists mainly of cellulose. A novel process called “LignoBoost” has been introduced recently for extracting lignin from alkaline black liquor. The separated lignin can either be utilized as solid fuel or raw material of other value-added products such as carbon fibre or phenols, which is one step towards a combined pulp and biorefinery process. The LignoBoost process consists of four major steps: precipitation, filtration, re-dispersing and final washing. Whilst filtration and washing have already been investigated extensively, more knowledge needs to be gained of the precipitation step.

In this work, lignin precipitation was performed by the acidification of black liquor at various process conditions, namely pH, temperature and ion strength, and the influences exerted by these parameters on the equilibrium of lignin precipitation were investigated. Carbohydrate analysis was performed on the precipitated solid and lignin-lean liquor, and the average molecular weight of the precipitated lignin was determined. The content of the functional groups (i.e. phenolic and methoxyl) in the precipitated lignin was analyzed and, finally, new parameters in a given model from a previous study for estimating the precipitation yield of lignin were provided and evaluated.

The results show that the precipitation yield of lignin increases with decreasing pH and temperature and/or with increasing ion strength of the black liquor used. The concentration of carbohydrates in lignin decreases with decreasing pH or with increasing temperature, and that an increasing amount of lower molecular weight lignin is precipitated at a higher precipitation yield. Furthermore, it was found, for the experimental conditions chosen, that the precipitation pH has a much stronger influence than the temperature and the ion strength on the precipitation yield and the average molecular weight of the precipitated lignin. According to ^{1}H and ^{13}C NMR spectra analysis, the content of phenolic and methoxyl groups in the precipitated lignin increases with increasing precipitation yield.

Keywords: LignoBoost process, lignin precipitation, black liquor, molecular weight of lignin, ^{1}H and ^{13}C NMR spectra of lignin, carbohydrate analysis

List of publications

This thesis is based on the studies presented in following papers:

I. **Investigation and characterization of lignin precipitation in the LignoBoost process**

Weizhen Zhu, Gunnar Westman and Hans Theliander

Accepted and in press in *Journal of Wood Chemistry and Technology*

II. **The changes of lignin molecular weight and carbohydrates during lignin precipitation from black liquor**

Weizhen Zhu and Hans Theliander

In manuscript, to be submitted

Results relating to this work have also been presented at the following conference:

Equilibrium of lignin precipitation

Weizhen Zhu and Hans Theliander
(Poster presentation)

In: Conference proceedings. 16th International Symposium on Wood, Fibre and Pulping Chemistry, Tianjin, China, June 8-10, 2011, pp 195-199

Contents

1. INTRODUCTION AND OBJECTIVES

1.1 Introduction

The forest industry accounts for approximately 3% of the Swedish gross domestic product (GDP) and 10-12 % of the total employment, sales and added-value products within Swedish industry (Skogsindustrierna, 2010). Sweden is also the second largest combined exporter of pulp, paper and sawn wood products in the world (Skogsindustrierna, 2010). The Swedish pulp and paper industry, in particular, is the third largest in Europe and more than 85% of the pulp and paper production is exported to other countries (Skogsindustrierna, 2010). As a consequence, the pulp and paper industry plays a very important role in the Swedish economy.

The predominant pulping process in Sweden is the kraft process. In 2010, the amount of kraft pulp produced was 8.2 million metric tons, which was approximately 65% of the total amount of pulp produced in Sweden (Skogsindustrierna, 2010). Additionally, the tendency in the past few years has been that the percentage of mechanical pulp in the total amount of pulp produced has decreased (Skogsindustrierna, 2012).

A schematic diagram of the kraft pulping process is illustrated in Figure 1.1. Firstly, the wood chips are treated with steam and impregnated with cooking liquor. The active ions in the cooking liquor are hydroxide and hydrosulphide ions but other ions, such as carbonate and sulphate, are also present in the solution. The counter ions are mainly sodium and, to some extent, potassium. The impregnated wood chips are digested in either a batch or a continuous digester at an elevated temperature. The primary aims of digestion are to degrade the lignin in wood chips and to separate the fibres in the chips. At alkaline condition, phenolic groups on the lignin are formed during digestion but some condensation reactions (forming carbon-carbon bond) of lignin units take place and larger lignin fragments are formed. During digestion, some of the cellulose and hemicelluloses are degraded and dissolved, which decreases the cooking yield. After digestion, the solution that consists of dissolved organic material, inorganic compounds and spent cooking chemicals is called “black liquor”. This black liquor is now separated from the pulp in the “brown-stock washing” department and the washed pulp can either be used in various packaging products in its unbleached form or transferred to the bleaching plant and be used to produce bleached pulp. The black liquor is then fed to an evaporation plant where most of the water is evaporated and the dry solid content (DS) is increased from approx. 15 % to 70 %. Following evaporation, the black liquor is combusted in a recovery boiler where heat and electricity are generated and cooking chemicals are recovered.

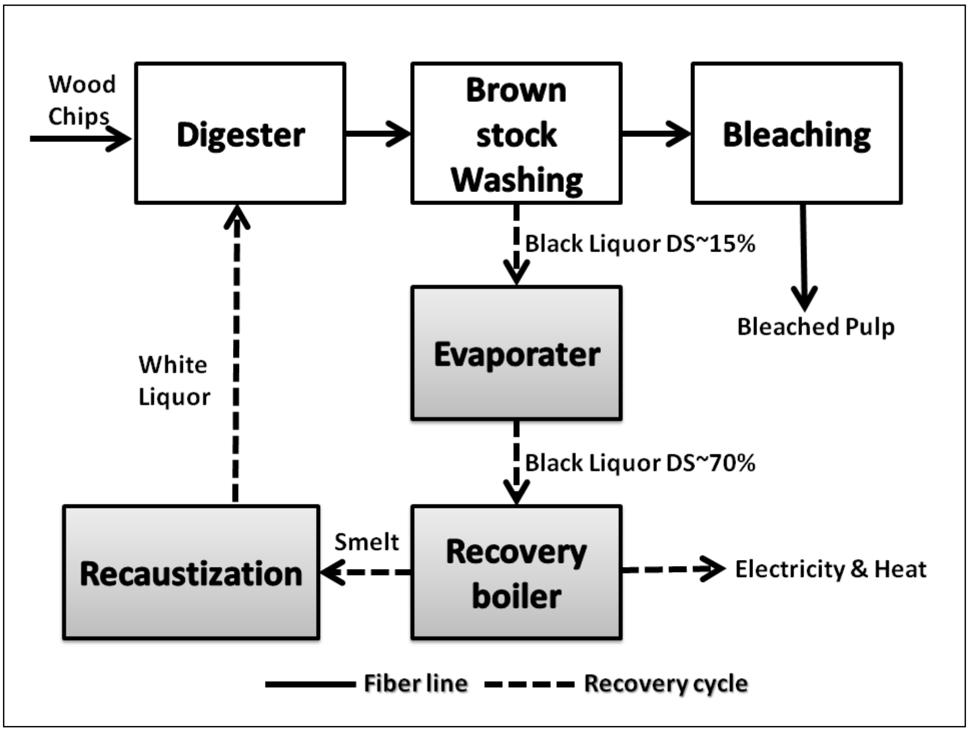


Figure 1.1 Schematic diagram of the kraft pulping process.

In fact, during the kraft process, the wood material yield is only approx. 40-55 % and, so far, only cellulose has been utilized efficiently in the production of materials. The black liquor, which contains most of the dissolved organic compounds, is incinerated to recover the latent heat in the organic compounds as well as the inorganic cooking chemicals. Lignin is the major constituent of the organic components in black liquor and is of great interest for various material applications, such as carbon fibres (Sudo and Shimizu, 1992, Gellerstedt *et al.,* 2010) and phenolic-based chemicals. Furthermore, extracting a renewable material such as lignin from black liquor may be considered as being a step towards converting the pulp mill into a biorefinery, and thereby improve the total material yield of the mill. Moreover, since lignin is the greatest contributor to the heating value of black liquor, the heat load of recovery boiler will be decreased if a certain amount of lignin is extracted from black liquor: this is beneficial for pulp mills where the capacity of the recovery boiler limits the overall production rate of pulp (Wallmo *et al.*, 2009c). In the case of a greenfield plant, a smaller recovery boiler can be designed and constructed.

1.2 Objectives

This thesis focuses on the fundamentals of lignin precipitation in black liquor and, more specifically, the apparent equilibrium in the lignin precipitation step. The aim of this study is to investigate the influences of some important process parameters, namely pH, temperature and ion strength on the equilibrium of lignin precipitation. The influences of these process parameters on the molecular weight as well as the content of the functional group (phenolic and methoxyl) of the precipitated lignin are also investigated.

1.3 Outline

Chapter 2 provides background information of black liquor together with a brief introduction of the chemical and physical chemistry of lignin; the novel process “LignoBoost” is also introduced. In Chapter 3, the experimental work and analytical methods are described and the results are presented in Chapter 4. The main findings are summarized in Chapter 5 and, finally, some proposals for future work are presented in Chapter 6.

2. BACKGROUND

2.1 Black liquor

Black liquor is a process stream obtained from the digestion/washing departments in the chemical pulping process. It is an aqueous solution consisting of organic residues such as lignin, polysaccharides, carboxylic acids and extractives, as well as the spent cooking chemicals used in the process. The chemistry and properties of black liquor are directly correlated to these components. The organic materials in black liquor have a latent heat that can be recovered during combustion in a recovery boiler, with lignin being the major constituent. The chemical and elemental compositions of a typical kraft black liquor are shown in Table 2.1 and Table 2.2, respectively.

Table 2.1 Chemical species found in kraft black liquors from north American wood species (Frederick, 1997).

Chemical species in kraft black liquor	Content (%)
Alkali lignin	30–45
Carbohydrate degradation products	
-Hydroxyl acids	25–35
-Acetic acid	5
-Formic acid	3
Extractives	3–5
Methanol	1
Sulphur	3–5
Sodium	15–20

Table 2.2 Typical elemental composition of virgin black liquor from Scandinavian wood species (Gullichsen and Fogelholm, 1999).

Elemental composition	Content (%)			
	Softwood (pine)		Hardwood (birch)	
	Typical	Range	Typical	Range
Carbon	35.0	32–37	32.5	31–35
Hydrogen	3.6	3.2–3.7	3.3	3.2–3.5
Nitrogen	0.07	0.04–0.11	0.1	0.14–0.2
Oxygen	33.9	33–36	35.5	33–37
Sodium	19.0	18–22	19.8	18–22
Potassium	2.2	1.5–2.5	2.0	1.5–2.5
Sulphur	5.5	4–7	6.0	4–7
Chlorine	0.5	0.1–0.8	0.5	0.1–0.8
Inert	0.2	0.1–0.3	0.2	0.1–0.3

The proportion of the organic and inorganic components in black liquor varies from mill to mill due to the natural variations of the organic constituents in wood species and the cooking conditions of each particular mill. The properties of black liquor therefore differ in different pulp mills and even within the same mill. One important property of black liquor is that it contains several chemical species that act as buffers, e.g. H_2S (pK_a 13–13.5), Na_2CO_3 (p$K_a \approx$ 10.2), phenolic groups (pK_a 9.4–10.8)/carboxyl groups (p$K_a \approx 4.4$) on lignin and other organic acids.

2.2 The separation of lignin from black liquor

2.2.1 The advantages of lignin extraction from black liquor and the future of biorefineries

Vast quantities of lignin (more than 70 million metric tons per year) are produced in the kraft pulping industry worldwide. However, more than 99% is burned in the chemical recovery boiler and is not recovered for other industrial applications (Pye, 2008). The extraction of lignin makes it possible to transform the dissolved lignin into a solid fuel which can be used internally in a pulp mill as a replacement for the fuel oil consumed in the lime kiln, or be sold to other industries. Furthermore, the extracted lignin can be used as a raw material for other value-added products, e.g. carbon fibres, dispersants, binders and chemicals (such as phenols and benzene) which require lignin with a high level of purity. In some cases, it is of great benefit to withdraw a certain amount of lignin if it acts as a limit in the mill production lines: the production of pulp is, in some cases, limited by the heat load (black liquor throughput) of the recovery boiler. Lignin is the major contributor to the overall heating value of the black liquor, so the extraction of lignin can lower the heating value of black liquor and, consequently, increase the production of pulp.

The separation of lignin from black liquor creates new opportunities for a further conversion of the modern kraft pulp mill into a biorefinery. The pulp and paper industry can therefore remain competitive by creating new revenues and diversifying its products and markets. Some other examples of these opportunities are the separation of extractives from bark, the removal of xylan from black liquor, ethanol fermentation and the gasification of biomass (Axegård, 2007).

2.2.2 Lignin separation methods

Several techniques are available for the separation and purification of lignin from black liquor. These techniques are based on the changes of lignin solubility, the differences between the molecular weight/size of lignin or a combination of both. The criteria used for the separation methods are, firstly, that lignin should be isolated with a high yield, secondly, the isolated lignin should be free from contaminants and, thirdly, the procedure should be simple and easy to perform (Lin, 1992).

(I) Precipitation

Extracting lignin from black liquor by means of acidification has been commercialized for a long period of time. In 1942, in the United States, the Westvaco Company (now MeadWestvaco Corporation) started to produce lignin from black liquors obtained from the kraft process; it is still one of the dominant suppliers of lignin products derived from kraft black liquor, with an estimated annual production of 27000 metric tons (Pye, 2008, Gellerstedt *et al.*, 2012). Kraft lignin was also sold by Borregaard LignoTech in 1994. In recent decades, the successful lignin extraction process called "LignoBoost", which will be discussed further in Section 2.2.3, has been introduced and a demonstration plant has been established in Sweden to produce large amount of lignin (1–1.2 metric tons per hour) from black liquor. The first commercial operation was started by Domtar in the United States in early 2013.

There are a number of studies related to lignin precipitation by acidification to be found in the literature. In 1872, a method in which carbon dioxide is injected into hot black liquor was patented (Tessie du Motay, 1872). The aim here was to separate the “impurities” to obtain a pure liquor which could be recaustified and reused. Later, in 1910, another patent by Hough (1910) was published that proposed a method of using acidification to precipitate lignin and resin in the spent liquors (black liquor) from the production of alkaline pulp. The precipitated solution was filtered at high temperature in order to improve the dead-end filtration. Alén *et al.* (1979) published a paper on the precipitation of lignin. They studied lignin precipitation from softwood black liquor by introducing carbon dioxide gas and found that when the pressure was increased the carbonation time was markedly shortened and the yield was higher. They also reported the strong influence of the dry solid (DS) content of the black liquor on the precipitation yield: the highest yield of precipitated lignin was obtained with a DS content of 27-30% for softwood black liquor and 30-35% for hardwood black liquor (Alén *et al.*, 1985). Uloth and Wearing (1989a and 1989b) compared the lignin recovered from three different separation procedures: 1) acid precipitation using sulphuric acid/chlorine dioxide generator waste acid (GWA), 2) carbon dioxide precipitation and 3) ultrafiltration. The conclusion was that, when compared to ultrafiltration, lignin precipitation through acidification provided a higher amount of lignin at a lower estimated cost.

Öhman and Theliander (2006 and 2007) have published some papers dealing with kraft lignin precipitation, filtration and washing procedures. They pointed out that the precipitation pH and temperature are important factors that influence filtration properties. They also concluded that the yield was approximately the same for precipitation using strong acid and carbon dioxide. Wallmo *et al.* (2007) used carbon dioxide to precipitate lignin from black liquor and found that the chemical composition of black liquor affected the total amount of hydrogen ions needed for acidification. They also found that the precipitation yield increased with decreasing temperature and increasing DS content of black liquor (Wallmo *et al.*, 2009a). In a later paper, they investigated the influences of mixing speed and hemicellulose content on the filtration properties of black liquor. Among other things, the results showed that the mixing speed affected the rate at which the pH was decreased to above 10.5, and that hardwood black liquor contained a higher concentration of hemicellulose and a higher average specific filtration resistance in the first filtration step (Wallmo *et al.*, 2009b).

Changing the ion strength of lignin solutions is another alternative for lignin precipitation. Villar *et al.* (1996) found that alcohol-calcium solutions were good precipitation agents that can recover 90% of the lignin with good filtration properties. Moreover, Sundin (2000) also precipitated lignin in an alkaline solution by the addition of electrolyte: it was shown that the critical coagulation concentration of the metal cation increased, in most cases, with increasing pH but decreased with increasing valency of the metal cation.

(II) Ultrafiltration

Separating lignin from black liquor by membrane ultrafiltration has also been suggested, and a few studies (Tanistra and Bodzek, 1998, Holmqvist *et al.*, 2005, Jönsson *et al.*, 2008) have been published. These studies showed that ultrafiltration may be considered as a technically feasible method for the production of kraft lignin. However, when compared with acidification, this technique involves higher capital and operating costs. Nevertheless, ultrafiltration is still an interesting option for separating the lignin fraction with a defined molecular weight distribution (Toledano *et al.*, 2010a).

(III) The combination of precipitation and ultrafiltration

A combination of precipitation and membrane filtration was investigated by Wallmo *et al.* (2009b). It was found that the filtration resistance of precipitated lignin from hardwood black liquor was improved considerably when the concentration of hemicelluloses was lowered prior to precipitation by ultrafiltration.

2.2.3 The LignoBoost process

As mentioned earlier, lignin precipitation by the acidification of black liquor is not a new technique; the lignin extracted from a traditional, single-stage, dewatering/washing process has a relatively low DS content and high ash content. It also results in severe problems with a complete or partial plugging of the filter cake and/or the filter media. The case of virtually complete plugging results in an extremely low flow of wash liquor through the cake, and a partial plugging of the filter cakes results in high levels of impurities in the lignin. Consequently, the novel two-stage washing/dewatering process called "LignoBoost" (Öhman *et al.*, 2007a, Öhman *et al.*, 2007b, Theliander, 2008, Tomani, 2010), which extracts lignin efficiently from black liquor, was designed. Using this process it is possible to separate lignin with a low ash content and a high DS content for large-scale industrial production (see Figure 2.1).

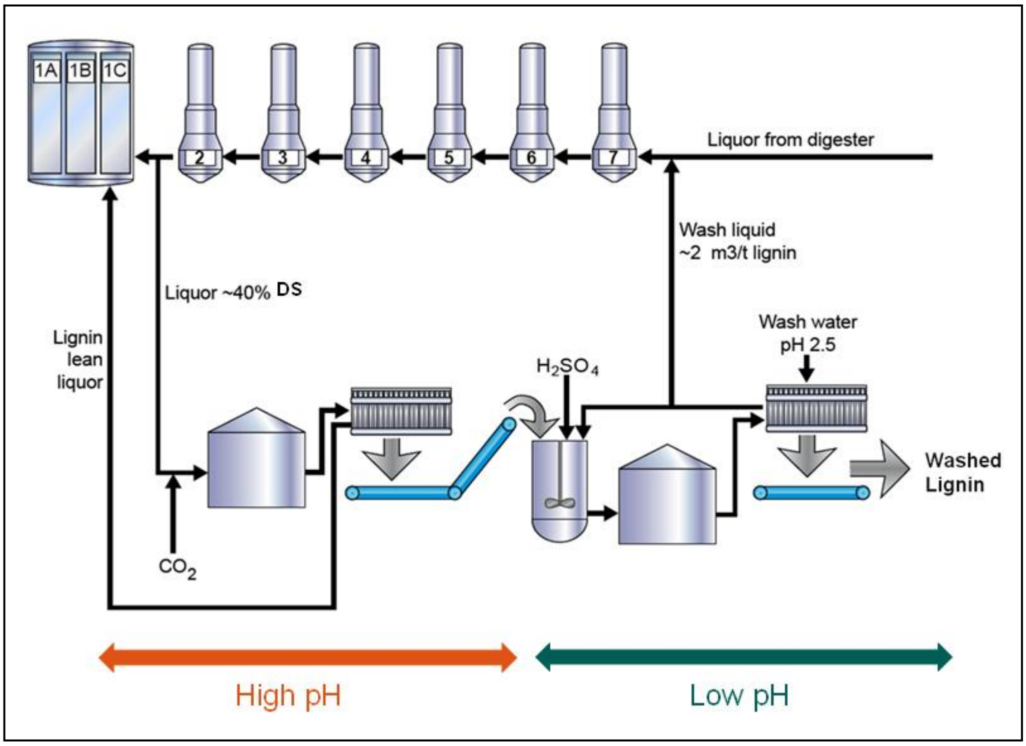


Figure 2.1 Schematic diagram of the LignoBoost process (Wallmo *et al.*, 2009c). (Courtesy of Metso.)

In the LignoBoost process, a stream of black liquor is taken from the evaporation plant; the lignin in it is precipitated by acidification (CO_2 is preferred) and then filtrated. The difference between this and the single-stage lignin separation process is that instead of washing the lignin immediately after filtration, the filter cake is re-dispersed and acidified in the re-slurry tank (Öhman *et al.*, 2007a). When the filter cake is re-dispersed, the temperature is kept equal to that of the final washing liquor and the pH is decreased to approximately the same as the final pH of the washing liquor so that the concentration gradients of the hydrogen ions during the washing stage are minimized. Therefore the change in pH and, consequently, the change in lignin solubility take place mainly in the slurry and not in the filter cake during the final washing stage. Although gradients of ion strength are still present, the dilution process in the re-slurrying stage minimizes these changes. The resulting slurry is then filtered and washed by displacement washing.

The major advantages of the LignoBoost process can be regarded as being (Tomani, 2010):

- Higher yield of lignin
- Lower ash and carbohydrate content and a higher DS content of the lignin

- Lower investment costs due to reductions in the size of the filter area and the volume of acidic washing
- Lower operational costs due to a reduction in the amount of sulphuric acid necessary

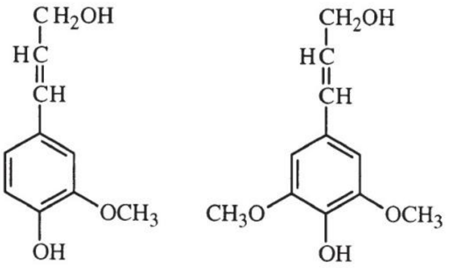
2.3 Lignin and its chemistry

2.3.1 Native lignin

After cellulose, lignin is the second most abundant polymeric organic substance and the most abundant aromatic renewable material on the planet. It is a three-dimensional, heterogeneous polymer that “adheres” fibres in the middle lamella and the fibrils in the cell wall together. The unique mechanical properties of wood are derived partially from the presence of lignin. The biological function of lignin is to provide woody biomass with stiffness, hydrophobicity and resistance to bacterial degradation (Henriksson, 2008).

Softwood contains 26-32% (spruce approx. 27%) and hardwood contains 20-26% (birch approx. 22%) of lignin. Around 70% of softwood (spruce) lignin and 60% of hardwood (birch) lignin are found in the secondary cell wall. The remaining lignin in softwood is present between the fibres, i.e. in the middle lamella and cell corners (Sjöström, 1993).

The building blocks of the lignin structure are phenylpropane units, which are shown in Figure 2.2. The guaiacyl propane unit is the most abundant unit found in native softwood lignin while syringyl propane is the most common unit in native hardwood lignin. The phenylpropane units are joined together both with C-O-C (ether) and C-C linkages: the ether linkage is the dominating type, accounting for about two thirds of the total linkages (Sjöström, 1993). The types of linkage and their approximate proportion are shown in Table 2.3. The functional groups of lignin, such as phenolic and methoxyl groups, also affect the reactivity of lignin strongly, so it is of great interest to study these groups. The amount of functional groups present in lignin is given in Table 2.4.



(1) (2) (3)

Figure 2.2 The building units in lignin: (1) guaiacyl propane, (2) syringyl propane, (3) p-hydroxyphenyl propane (Adler, 1977).

Table 2.3 The types of linkages connecting the phenylpropane units in lignin and their approximate proportions (Sjöström, 1993).

Linkage type	Dimer structure	Percentage of the total linkages (%)	
		Softwood lignin	Hardwood lignin
β-O-4	Arylglycerol-β-aryl ether	50	60
α-O-4	Noncyclic benzyl aryl ether	2–8	7
β-5	Phenylcoumaran	9–12	6
5-5	Biphenyl	10–11	5
4-O-5	Diaryl ether	4	7
β-1	1,2-Diaryl propane	7	7
β-β	Linked through side chains	2	3

Table 2.4 The functional groups in lignin per 100 C_6C_3 units (Sjöström, 1993).

Functional group	Softwood lignin	Hardwood lignin
Methoxyl	92–97	139–158
Phenolic	15–30	10–15
Benzyl alcohol	30–40	40–50
Carbonyl	10–15	

The possible linkages that can be expected between the lignin monomers are illustrated in Figure 2.3, which shows a random, cross-linked, amorphous network of softwood lignin. The hardwood lignin differs mainly in the methoxyl group content. It is important to emphasize that this proposed model does not depict the actual structure of lignin: it serves, instead, as a tool in order to visualize the linkages and functional groups in lignin.

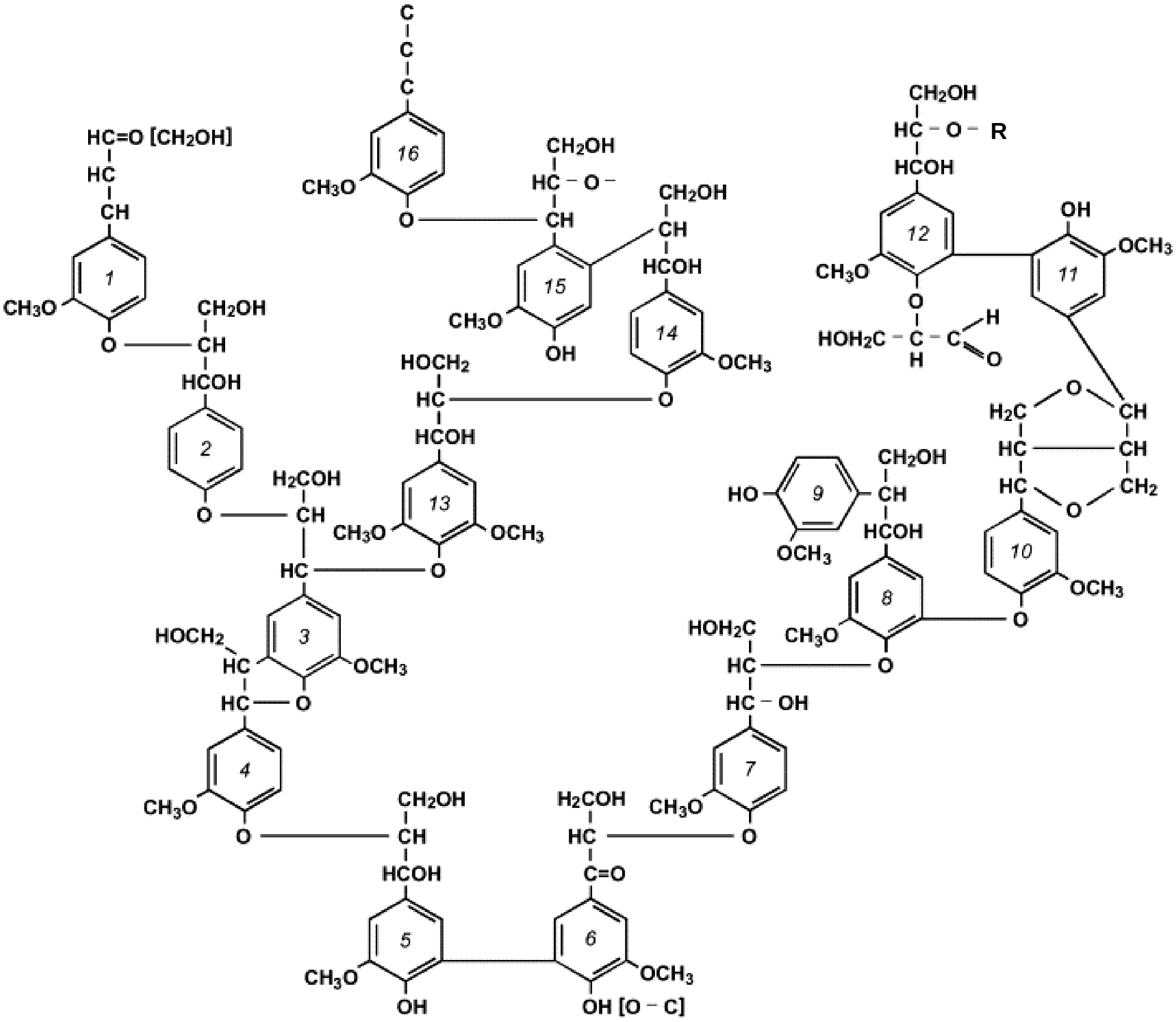


Figure 2.3 A representation of the hypothetical linkages and functional groups of native softwood lignin (Adler, 1977).

2.3.2 Lignin-carbohydrate complex

Hemicellulose is another major component of the cell wall of wood. Chemical bonds have been reported between lignin and hemicelluloses: these covalently bonded complexes are often termed as “lignin-carbohydrate complex” (LCC). The α-position of the phenylpropane unit is, in most cases, the connection point between lignin and hemicellulose. These linkages can be of the ester or ether type, with the latter being more common and much more stable (Sjöström, 1993). The principal hemicellulose in softwood is galactoglucomannan (GGM), which accounts for approx. 20% of the dry material, whilst xylan is the main hemicellulose in hardwood and varies in content within the limits of 15-30% of the dry wood.

During kraft pulping, it is assumed that the network of lignin and hemicelluloses disintegrates, and that smaller LCC fragments are formed which then dissolve in the black liquor (Lawoko *et al.,* 2004). This was also the hypothesis by Tamminen *et al.* (1995), who reported that LCC was present in black liquor and that it was likely that xylan was cross-linked to lignin molecule by the arabinose substituent (Eriksson *et al.*, 1980). It has also been found that xylan is preferentially linked to a rather linear type of lignin with a predominance of alkyl-aryl ether structure, whereas the lignin linked to GGM is more branched and/or cross-linked (Lawoko et al., 2004, Gellerstedt et al., 2012). As a result, the xylan-lignin bond is much easier to degrade and dissolve in the pulping process. However, GGM is degraded more extensively than xylan which is only partially degraded, after the peeling and alkaline hydrolysis reactions that occur during kraft pulping, (Sjöström, 1993).

2.3.3 Lignin reactions during kraft pulping

The predominant reaction that occurs in lignin during kraft pulping is the cleavage of its phenolic β-O-4 linkages, which results in the formation of new phenolic groups. This fragmentation causes a large decrease in the molecular weight of lignin, and the degraded lignin becomes more hydrophilic as a result of the introduction of the new phenolic groups.

The reaction of the phenolic β-O-4 structures being cleaved in the kraft process is shown in Figure 2.4. The reaction proceeds by the reaction of the hydrosulphide ion with lignin, which yields a benzyl thioalcohol structure. The thiol group on the α-carbon can attack the β-carbon atom in a nucleophilic reaction to form an episulphide intermediate and a new phenolic end-group. The episulphide structure is not stable and elemental sulphur is discharged to form polysulphide. In a competing reaction, the quinone methide can lose the hydroxymethyl group and be converted into an alkali-stable enol ether structure (Gellerstedt and Lindfors, 1987). The quinone methide can also undergo lignin condensation reactions (Gierer, 1970) and side chain reduction reactions (Gellerstedt and Robert, 1987). In addition, condensation between lignin and the polysaccharide peeling intermediate, and the resulting formation of LCC, have also been reported (Gierer and Wännström, 1984).

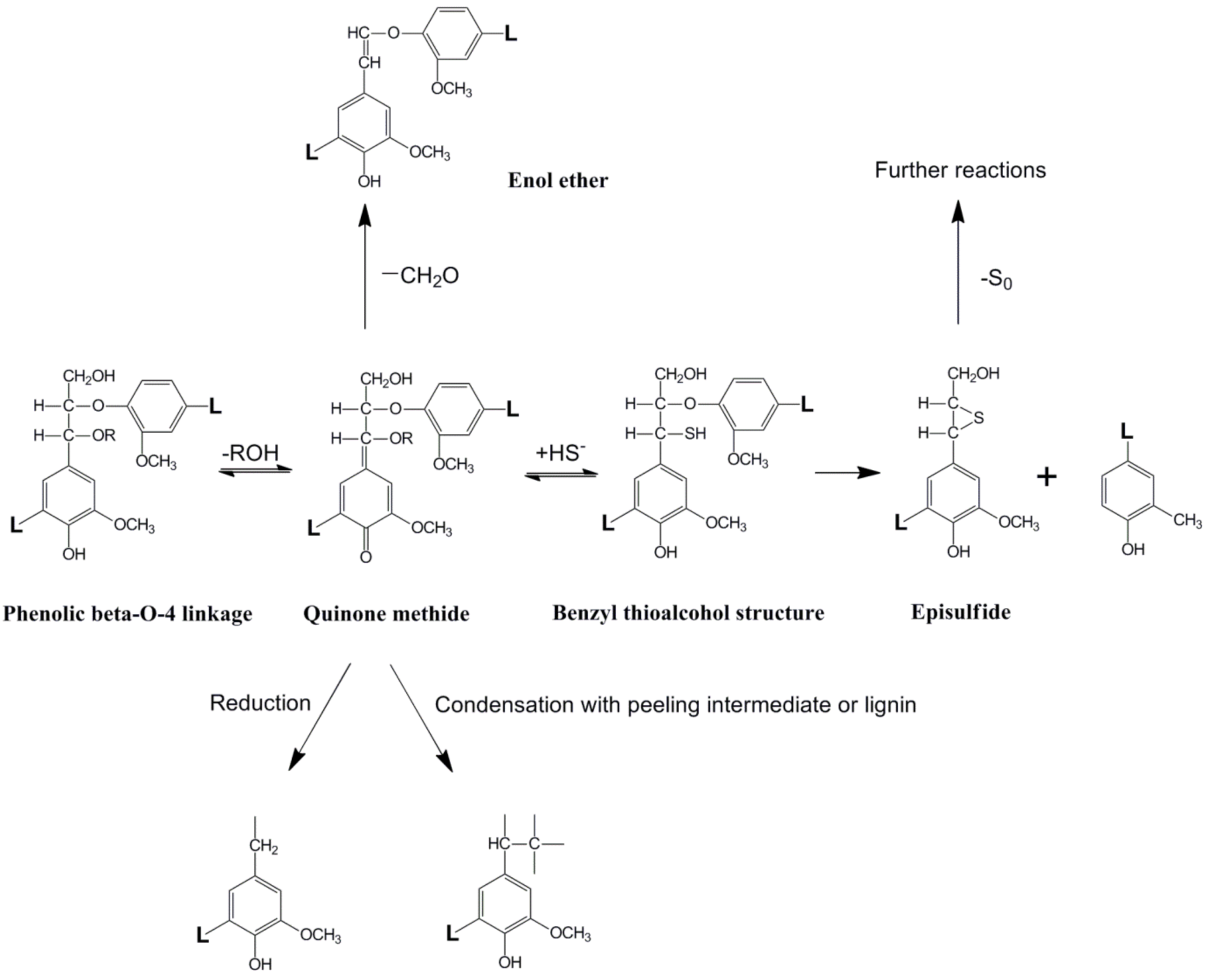


Figure 2.4 Reactions of phenolic β-O-4 structures in kraft cooking. **L** denotes a lignin residue.

For non-phenolic β-O-4 structures, the cleaving of β-aryl ether linkages involves the attack of an ionized α-hydroxyl (or a γ-hydroxyl) group (Chakar and Ragauskas, 2004). An epoxide structure is formed together with a new phenolic end-group (see Figure 2.5).

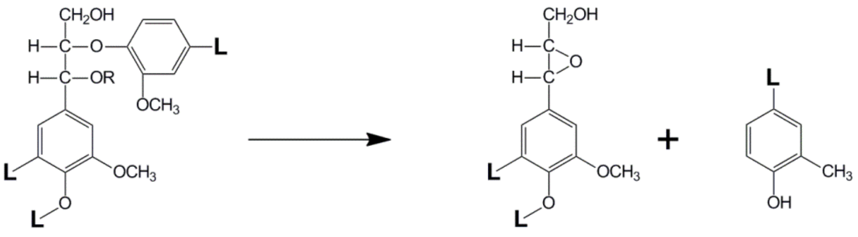


Figure 2.5 Reactions of non-phenolic β-O-4 structures in kraft cooking. **L** denotes a lignin residue.

After kraft pulping, the average molecular weight of hardwood lignin was reported to be lower than that of softwood kraft lignin (Goring, 1971): this is due to the higher content of β-aryl ether linkages in hardwood lignin (Larsson and Miksche, 1971, Sjöström, 1993) and the fact that these ether linkages are heavily degraded during kraft pulping. Moreover, the smaller amount of C-C bonds between the syringyl units (Labidi *et al.*, 2006) and the lack of reactive positions (C_5 positions) in the aromatic nuclei for condensation reactions (Mörck *et al.*, 1988) also lead to the relative lower molecular weight of hardwood kraft lignin.

2.3.4 Mechanisms of the precipitation and growth of lignin particles

(I) The pK_a of lignin

Lignin contains weakly acidic groups, namely phenolic and carboxyl groups. The mechanism of lignin precipitation (solidification) in the alkaline region can be regarded as a protonation of ionized phenolic groups on the lignin molecule. The equilibrium of dissociation of phenolic groups on lignin can be written symbolically as:

$$\mathbf{L}\text{-OH} \leftrightarrow \mathbf{L}\text{-O}^- + \text{H}^+ \tag{2.1}$$

where L is the lignin molecule and –OH is the phenolic group on the benzene ring of the lignin phenylpropane unit. The dissociation constant (K_a) of a phenolic group is written as a quotient of the activities of {L-OH}, {L-O$^-$} and {H$^+$}:

$$K_a = \frac{\{\text{L}-\text{O}^-\}\{\text{H}^+\}}{\{\text{L}-\text{OH}\}} \tag{2.2}$$

if it is assumed that the protonated lignin is in solid phase and the activity of solid lignin is unity (1). The activity coefficients of the ions (L-O$^-$ and H$^+$) are also assumed to be unity (1). Eq. 2.2 can be simplified as:

$$K_a = [\text{L-O}^-][\text{H}^+] \tag{2.3}$$

The logarithmic constant, pK_a, which is equal to $-\log_{10} K_a$, is used more widely to describe the dissociation of a phenolic group. It has been found that the pK_a value is correlated to the temperature, ion strength and the solvent used (Ragnar *et al.*, 2000). The apparent pK_a of kraft lignin has also been found to be a function of the molecular weight of lignin (Rudatin *et al.*, 1989, Norgren and Lindström, 2000a).

(II) The mechanism of lignin precipitation

It has been suggested that lignin with a high molecular weight, behaves like a colloid in aqueous solutions (Marton, 1964, Lindströmn, 1979). Self-aggregation of the kraft lignin macromolecule and the precipitation of lignin have been reported in aqueous solutions at room temperature or at a slightly elevated temperature in the case of pH near, and below, the pK_a of the phenolic groups or at high ion strength (Norgren *et al.*, 2001, Norgren *et al.*, 2002). According to the DLVO theory (Shaw, 1993), the stability of kraft lignin in solution is an interplay of the attractive and repulsive forces. If the attractive forces, such as van der Waals and other hydrophobic forces, dominate then aggregation is favoured. If, on the other hand, repulsive electrostatic forces between the lignin molecules dominate, they provide stability to the lignin in the solution (Norgren *et al.*, 2001). Rudatin *et al.* (1989) proposed that the balance of these forces is influenced by the structural characteristics of lignin (mainly the functional groups), the conditions of the solution (such as the pH, temperature and ion strength) and the concentration of the lignin.

The precipitation of lignin by acidification can be described as follows: in alkaline condition lignin molecules are negatively charged due to the dissociation of the phenolic and carboxyl groups on the lignin. The lignin molecules repel one another by means of electrostatic interactions and the lignin is thus stable. When the pH is decreased, the hydrogen ions interact with the negatively-charged lignin and neutralize the charges on the molecular surface. The repulsive forces are reduced and, eventually, the precipitation of lignin occurs. The ζ-potential (zeta potential) could be used as an indicator to predict this precipitation (Wang and Chen, 2013). Figure 2.6 shows that, when the pH is decreased (i.e. more H^+ is introduced) to near or below the pK_a of the phenolic groups on the lignin, protonation of the phenolic groups occurs and that the zeta potential on the surface of the lignin molecule approaches zero. The lignin molecule thus becomes unstable and favours precipitation.

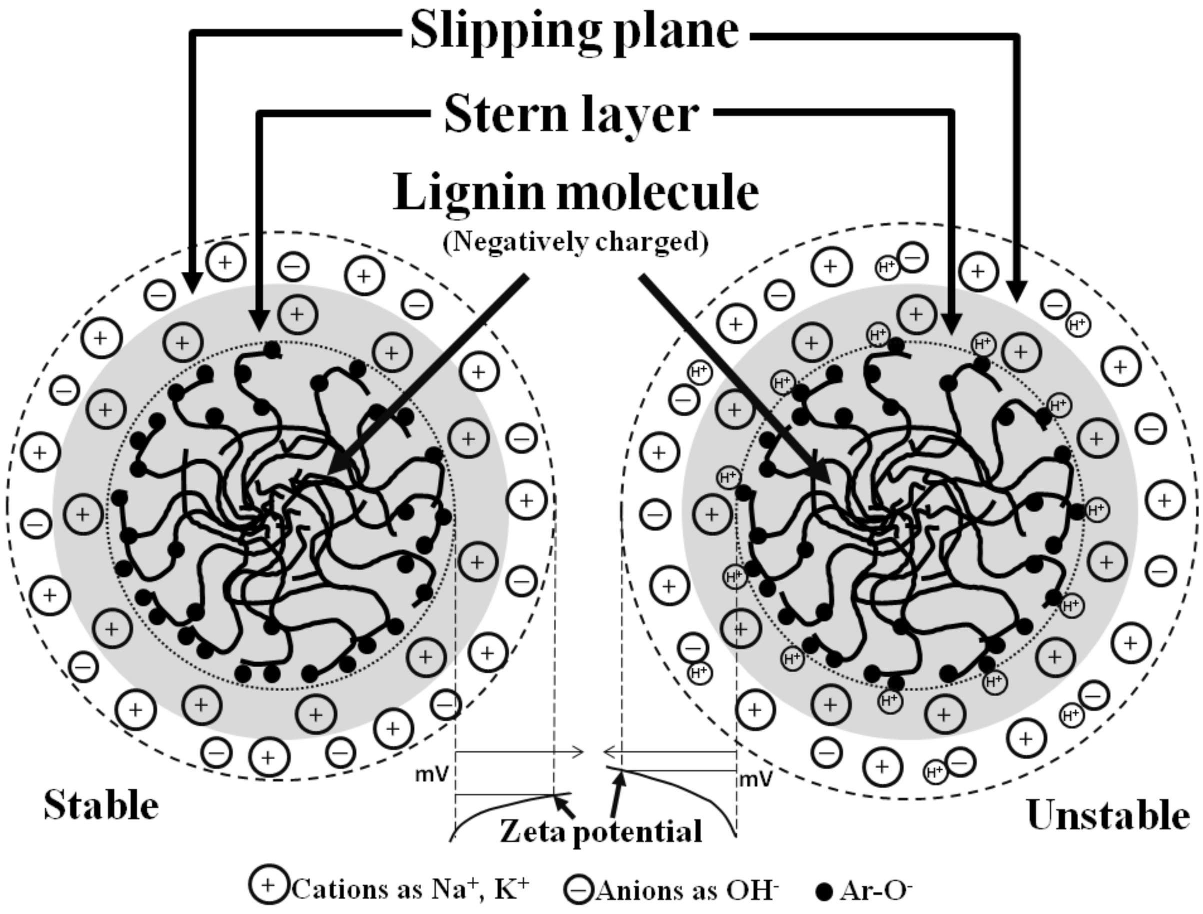


Figure 2.6 A suggested illustration of a stable and an unstable lignin molecule in black liquor.

(III) A hypothesis of the growth of lignin particles during precipitation

It is known that the solubility of a macromolecule decreases with increasing molecular weight: this is due to the small changes in the conformational chain entropy of large polymers during phase transition (Flory, 1953). Moreover, as mentioned earlier, lignin of high molecular weight has a higher apparent pK_a value than lignin of low molecular weight. So the larger lignin molecules, which have a lower solubility and higher pK_a values, are expected to coagulate first when the lignin becomes unstable (Norgren *et al.*, 2001).

The following hypothesis of the formation and growth of lignin particles has been proposed by Norgren *et al.* (2002 and 2007): Large lignin molecules, with structures that are described as cross-linked and spherical, can be considered as seed-points (i.e. nuclei) in the solution (see Figure 2.7(a)) and, when they lose stability, the lignin starts to self-aggregate and form particles, i.e. a nucleus of lignin molecules (Figure 2.7(b)). When these particles reach a certain critical volume, the low molecular weight fragments of lignin start to sorb onto the particle surface and the particles thus grow, both in size and number (Figure 2.7(c)). Rudatin *et al.* (1989) also stated that the presence of large kraft lignin macromolecules in solution facilitates the aggregation of smaller lignin fragments because more attractive sites are available for adsorption. The growing lignin particles aggregate to each other in a fractal manner and form cluster structures (Figure 2.7(d)) that grow larger and, finally, are precipitated (Figure 2.7(e)). Different densities of the cluster structures may be obtained depending on the rate of aggregation.

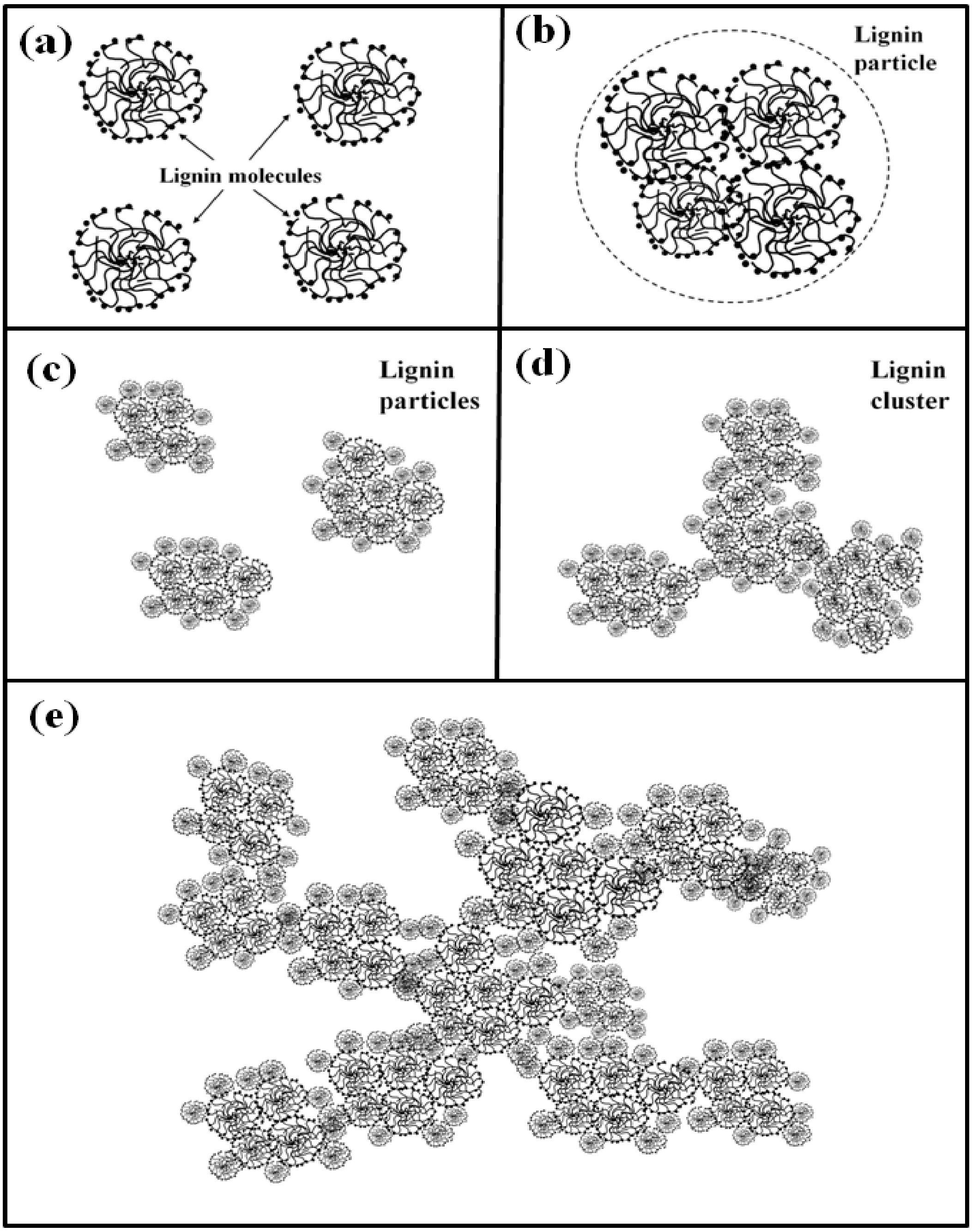


Figure 2.7 A suggested illustration of the formation and growth of kraft lignin particles during precipitation: a) large lignin macromolecules (seed points) are present in the solution; b) the formation of a lignin particle (nucleation); c) the growth of a lignin particle (in size and population); d) the formation of a lignin cluster; e) the growth of a lignin cluster.

3. MATERIALS AND METHODS

3.1 Precipitation and filtration of lignin

The black liquor used in this study was obtained from a batch kraft pulp mill that produces bleachable grade pulp in two fibre lines. The fractions of the wood used at the mill are approximately 1/3 softwood (a mixture of Scots pine and Norway spruce) and 2/3 hardwood (mainly birch). The black liquors from the two fibre lines are mixed prior to entering the chemical recovery department. The precipitation experiments were carried out on lab scale using the procedure proposed by Theliander (2010), see Figure 3.1.

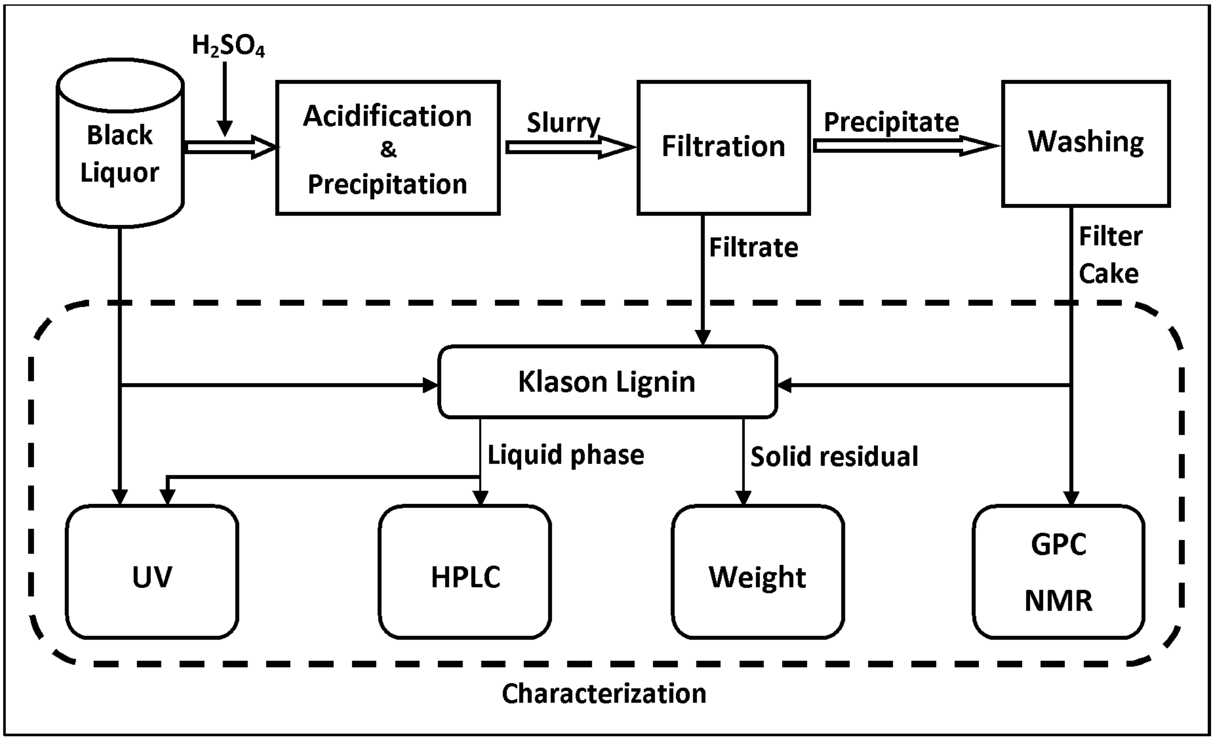


Figure 3.1 Schematic diagram of the black liquor acidification and filtration processes and the characterization units.

In Paper I, 200 g of black liquor were weighed and placed in a plastic bottle with a magnetic stirrer to enhance mixing when the bottle was shaken. A certain amount of sodium sulphate (Fisher Scientific, 99.5%) was added to the black liquor if a higher ion strength was required, when the original sodium content (63.5 g/kg black liquor) was increased by 10% or 20%. The bottle was closed with a lid and placed in a water bath for 1 hour in order to reach the target temperature, with the bottle being shaken well every 10 minutes. The temperature ranged from 45°C to 75°C. When the target temperature was reached, 6M sulphuric acid was added to the sample to reach the target pH. The pH measurement was performed at room temperature using a JENWAY Model 370 pH/mV Meter with temperature correction. The electrode used was an Epoxy bodied combination pH electrode (924 005) suitable for pH measurement between 10°C and 105°C. A three-point calibration at pH 7.00, 10.00 and 12.00 was performed before the measurements were made. The sample was then shaken every 10 minutes for a period of 1 hour to obtain an apparent equilibrium. When precipitation was complete, the sample was filtrated through a Büchner funnel with a filter paper (Munktell, 70 mm) and the filtrate was collected and stored in a gas tight bottle, ready for the lignin and carbohydrate concentrations to be determined. The filter cake (dark-coloured solid) was then washed with deionized water at pH 3 (sulphuric acid was used to adjust the pH) and, finally, dried at 105 °C for 8 hours. The detailed experimental parameters are given in Table 3.1.

Table 3.1 The experimental parameters of lignin precipitation in Paper I.

Temperature (°C)	Na Content	pH
45, 55, 65, 75	Original	~11, ~10.5, ~10, ~9.5
45, 55, 65, 75	Original + 10 %	~11, ~10.5, ~10, ~9.5
45, 55, 65, 75	Original + 20 %	~11, ~10.5, ~10, ~9.5

In Paper II, the experimental process was similar to that in Paper I. Some modifications were however made: 100 g sample of black liquor was used and the sodium content was increased by 5%, 10%, 15% and 20%. The temperatures investigated ranged from 45 °C to 80 °C and, in order to minimize the pH and ion strength gradients in the washing stage, the filter cake was washed with deionized water of the same pH and ion strength as in the precipitation process. This was to ensure that the precipitated lignin would not be re-dissolved in the wash water. The detailed experimental parameters are given in Table 3.2.

Table 3.2 The experimental parameters of lignin precipitation in Paper II. (The amount of salt added is calculated from the original concentration of sodium in the black liquor: 63.5 g/kg liq.)

Sample number	Approximate pH	Temperature (°C)	Ion strength addition	
			%	Salt (g)
1	11.5	45	0	0
2	11	45	0	0
3	10.5	45	0	0
4	10	45	0	0
5	9.5	45	0	0
6	10.5	55	0	0
7	10.5	65	0	0
8	10.5	75	0	0
9	10.5	80	0	0
10	10.5	65	5	0.98
11	10.5	65	10	1.96
12	10.5	65	15	2.94
13	10.5	65	20	3.92

3.2 Analytical Methods

3.2.1 Properties of black liquor

The total dry solids (TDS) content of the black liquor was determined according to the Tappi T650 om-09 method in which the sample was dried at 105 °C for 24 hours. The contents of sodium hydroxide and sodium sulphide were measured according to the Tappi T625 method. After wet combustion in a microwave oven, the sodium concentration of the black liquor was measured by atomic absorption spectroscopy (AAS) (Thermoscientific iCE 3000).

3.2.2 Klason lignin

Klason lignin is defined as the solid residual material obtained after a sample has been subjected to hydrolysis treatment with 72% sulphuric acid. The detailed method, which is presented by Theander and Westerlund (1986) can be summarized as follows: either 0.2 g of an oven-dried precipitated sample of lignin or 1.2 g of filtrated liquor is weighed and 3 mL of 72% sulphuric acid is added to the sample. The sample is then evacuated for 15 min and placed in a water bath at 30 °C for 1 hour. 84 g of deionized water is added to the sample and then heated to 125 °C in an autoclave for 1 hour. After hydrolysis, the sample is filtrated and the insoluble solid residue, which is referred to Klason lignin, is measured gravimetrically according to the Tappi T222 cm-00 method. The filtrate is then diluted to 100 mL in a volumetric flask. A solution that is 100 times weaker is prepared by diluting the concentrated sample and is used for UV measurement, which allows the content of the acid-soluble lignin to be calculated. Fucose is used as an internal standard for the following high performance liquid chromatography (HPLC) measurement. The solution is filtered through a 0.45 μm PVDF filter prior to being injected into HPLC.

3.2.3 Acid-soluble lignin

The concentration of acid-soluble lignin was measured based on the absorbance value determined by UV at a wavelength of 205 nm in a Specord 205, Analytik Jena. The absorption constant used was 110 $dm^3g^{-1}cm^{-1}$ (Dence, 1992) and the deviation of the results was estimated to be 0.9%.

3.2.4 Carbohydrate analysis

In Paper I, the HPLC instrument employed was a Varian Pro-Star HPLC equipped with an AutoSampler Model 410 and a Dionex Isocratic Pump IP20. The detector was an Electrochemical Detector, Varian Star 9080. The running system consisted of two Dionex columns: a pre-column CarboPac™ PA 1 (2×50 mm) and a main column CarboPac™ PA 1 (2×250mm). The software used was the Star Chromatography Workstation, System Control version 5.50 by Varian. A flow rate of 2 mL/min was applied to all samples, and the standard concentration of fucose was 40 mg/L. The estimated error for determination is about 6% based on the calibration curve of standard samples.

In Paper II, the analysis of monomeric sugars was performed using the Dionex ICS-5000 HPLC system equipped with CarboPac PA1 columns and run using NaOH, NaOH/NaAc (0.2

M) as eluents. An Electrochemical Detector was used for detection measurements. The software used was Chromeleon 7, Chromatography Data System, version 7.1.0.898.

The amounts of carbohydrates analyzed were corrected for the acid hydrolysis yield (Janson, 1974) which varies for different sugars; the values used were collected from experimental results reported by Wigell *et al.* (2007). The amounts of xylan and (galacto)glucomannan were calculated using the algorithm described in the Appendix.

3.2.5 Molecular weight and molecular weight distribution (MWD)

A Gel Permeation Chromatograph (GPC) provides a rapid way of obtaining information of the molecular weight of polymers. In this study, the dried precipitated lignin sample was dissolved in dimethyl sulphoxide (DMSO), with the addition of 10mM LiBr, to a concentration of 0.25 g/L. The resulting solution was then analyzed in a GPC to obtain the average molecular weight as well as the molecular weight distribution of the precipitated lignin.

The measurement was performed on a PL-GPC 50 Plus, Integrated GPC System from Polymer Laboratories (A Varian Inc. Company) equipped with a detection system consisting of a refractive index (RI) and Ultraviolet (UV) detector. The UV measurements were performed at a wavelength of 280 nm, which was generally associated with lignin, and the RI responses corresponded to both lignin and carbohydrates.

The system was equipped with two PolarGel-M (300×7.5mm) columns and a PolarGel-MGuard column (50×7.5mm). The mobile phase was DMSO with the addition of 10 mM LiBr, and the sample was injected via a PL-AS RT GPC Autosampler at a flow rate of 0.5 mL/min. The sample was analyzed using software Cirrus GPC version 3.2. Pullulan of 9 different molecular weights (708, 375, 200, 107, 47.1, 21.1, 11.1, 5.9 and 0.667 kDa) was employed for calibration (Polysaccharide Calibration Kit, PL2090-0100, Varian). The estimated error for determination is about 5% based on the calibration curve of standard samples. All the results obtained were baseline corrected.

3.2.6 Determination of functional groups

In Paper I, Nuclear Magnetic Resonance (NMR) was performed in order to analyze the content of functional groups in precipitated lignin. The samples were acetylated using the method proposed by Lundquist (1992b), in which the precipitated lignin (ca.100 mg) is acetylated with 1–2 ml of acetic anhydride/pyridine (1:1, v/v) at room temperature overnight in a 50-ml flask. Ethanol (25 ml) is added and, after 30 min, the solvents are removed via rotary evaporation. The repeated addition and removal (rotary evaporation) of ethanol (five to ten times) results in the removal of acetic acid and pyridine from the sample. Finally, the acetylated lignin is dried in a desiccator over KOH and P_2O_5.

(I) ^{1}H (proton) NMR spectra

A 50 mg acetylated lignin sample was dissolved in 0.8 mL $CDCl_3$ (99.8%, ALDRICH Chemistry) and ^{1}H NMR spectra were recorded at 25ºC on a Varian 400-MR 400 MHz spectrometer operating at 399.95 MHz for proton detection. Tetramethylsilane (TMS) was used as the internal reference. The lignin spectra were recorded with a 45° pulse angle, 5 s pulse delay, 1024 scans and 2.56 acquisition time. The resulting spectra were baseline corrected.

(II) ^{13}C (carbon) NMR spectra

A 50 mg acetylated lignin sample was dissolved in 0.5 mL DMSO-d_6 (99.8%, ARMAR Chemicals) and ^{13}C NMR spectra were recorded at 25ºC on a Bruker Avance III HD 18.8 T spectrometer operating at 201 MHz for ^{13}C detection. Tetramethylsilane (TMS) was used as the internal reference. The lignin spectra were recorded with an inverse-gated decoupling sequence, 90° pulse angle, 12 s pulse delay, 3200 scans and 1.36 acquisition time. The resulting spectra were baseline corrected.

4. RESULTS AND DISCUSSION

4.1 Black liquor characterization

Some important characteristics of the sample of black liquor are listed in Table 4.1. It can be seen that the content of acid-soluble lignin is rather high, which is probably because the black liquor used in this study consists of a high fraction of hardwood lignin. This finding is in agreement with earlier studies (Musha Y, 1974, Gellerstedt *et al.,* 2012).

Table 4.1 Some important characteristics of the black liquor sample.

Characteristics	**Content**
Dry Content (%)	33.2
Na (g/kg liq.)	63.5
K (g/kg liq.)	4.1
Lignin UV (g/kg liq.)	115.1
Lignin Klason (g/kg liq.)	88.9
Acid-soluble Lignin (g/kg liq.)	28.2
NaOH (g/kg liq.)	12.8
Na_2S (g/kg liq.)	13.2
Carbohydrates	
-Arabinose (g/kg liq.)	1.4
-Galactose (g/kg liq.)	2.2
-Glucose (g/kg liq.)	0.5
-Xylose (g/kg liq.)	4.7
-Mannose (g/kg liq.)	0.1

The buffer capacity of black liquor was studied in order to calculate the amount of hydrogen ions needed to lower the pH to a certain value. The titration curve with 1M HCl of the black liquor used is presented in Figure 4.1. The result, i.e. the shape of the plot curve, is in agreement with previous work (Wallmo *et al.,* 2009b). The curve can be roughly divided into three stages: neutralization of hydroxide ions, protonation of charged groups on the lignin molecule that make the lignin start to precipitate, and some buffering reactions (e.g. the hydrogen sulphide and the carbonate system) (Wallmo *et al.,* 2007). Naturally, these three stages overlap each other.

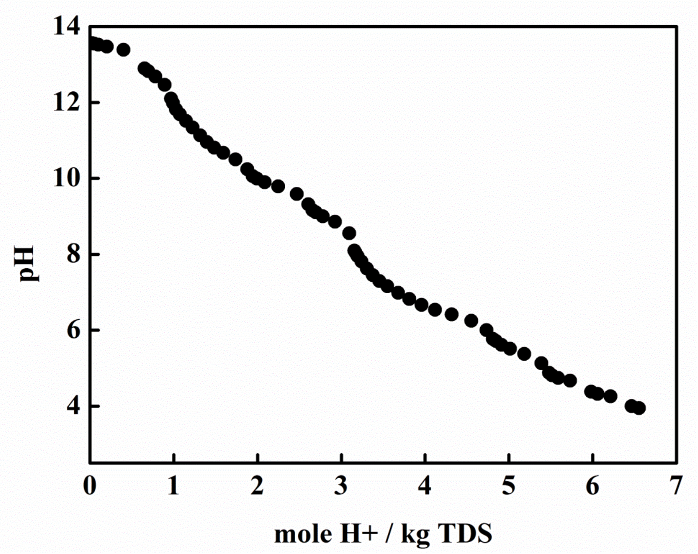


Figure 4.1 The buffer capacity of the black liquor sample.

4.2 Equilibrium of lignin precipitation in black liquor

4.2.1 Calculation of the precipitation yield

In this work, the precipitation yield of lignin was calculated using the following equation:

$$Yield = \frac{L_{BL}-L_F}{L_{BL}} \times 100\% \tag{4.1}$$

where *Yield* is in percentage (%), L_{BL} is the lignin concentration of the black liquor before precipitation and L_F is the lignin concentration of the lignin-lean filtrate after precipitation. The measurement of the lignin concentration was based on the measurement of the Klason lignin.

4.2.2 Equilibrium of lignin precipitation

The precipitation yield of lignin at different temperatures, pH and ion strengths is shown in Figure 4.2. It can be seen that the precipitation yield of lignin increases as the pH and temperature of the black liquor decrease and the ion strength of black liquor increases. These observations are in agreement with earlier investigation by Theliander (2010). The concentration of Klason lignin in the filtrate is also presented in Figure 4.2, which shows, as expected, that the content of Klason lignin in the filtrate decreases as the pH and temperature decrease and the ion strength increases.

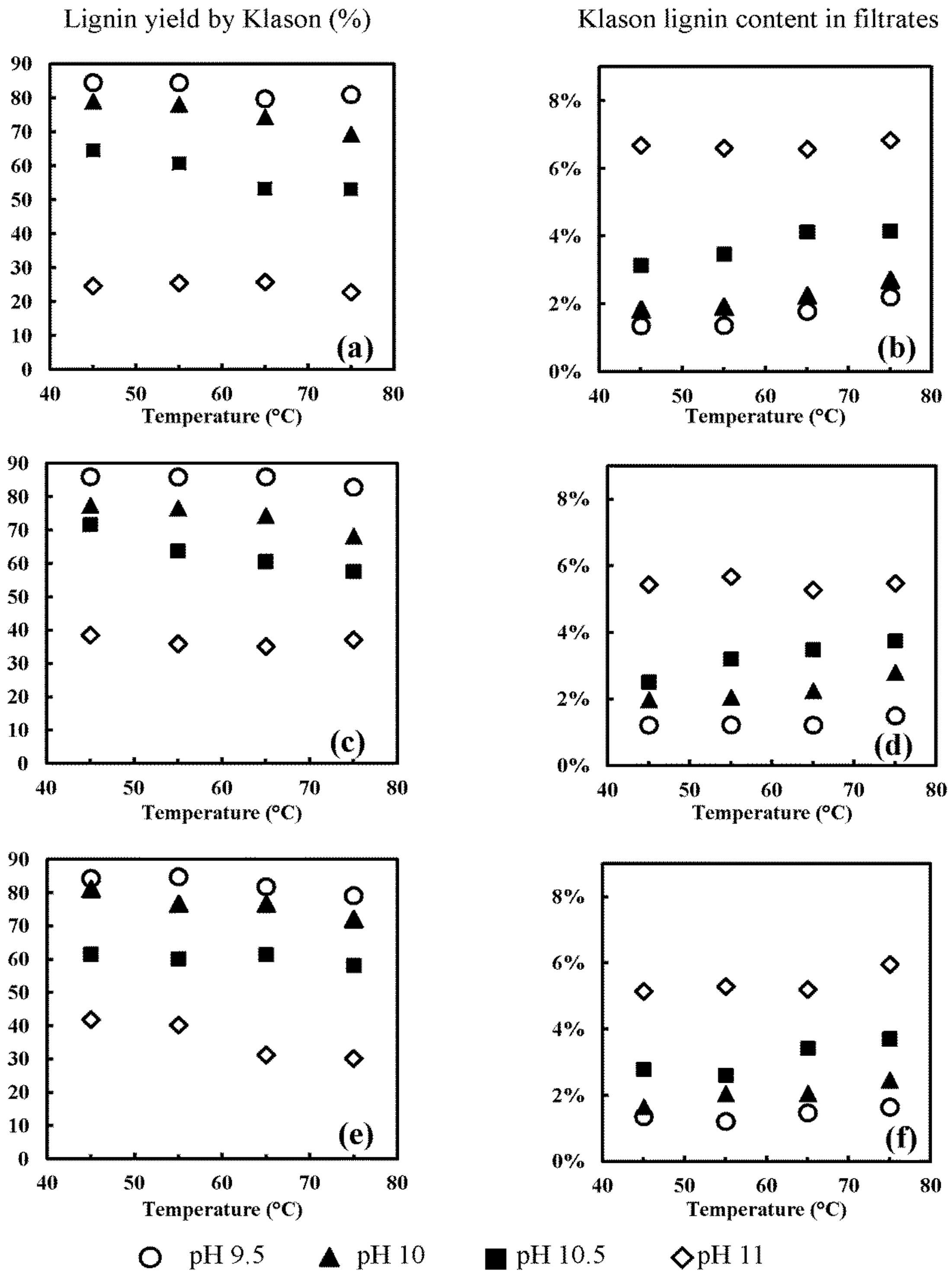


Figure 4.2 Precipitation yield of lignin and content of Klason lignin in filtrates at different pH, temperature and ion strength. (a) and (b): No extra sodium content introduced; (c) and (d): 10% extra sodium content introduced (sodium sulphate is added to the sample); (e) and (f): 20% extra sodium content introduced (sodium sulphate is added to the sample).

Figure 4.2 shows that a larger amount of lignin is precipitated at lower precipitation pH values in (a), (c) and (e). This is reasonable since more phenolic groups are protonated at a higher concentration of hydrogen ions (i.e. lower pH). The protonation of phenolic groups in lignin leads to a decrease in the electrostatic repulsion between lignin molecules (Gilardi and Cass, 1993, Sundin, 2000, Vainio *et al.,* 2004) and, consequently, the lignin molecules become less hydrophilic and the solubility of lignin is reduced. Rudatin *et al.* (1989) also claimed that the hydrogen bonding caused by phenolic-phenolic linkage or phenolic-ether linkage might play a role in the association of kraft lignin when the pH is decreased from 13 to 8.5.

Figure 4.2(a) shows that, at a certain precipitation pH (no extra salt added), there is a decrease in the precipitation yield with increasing temperature. This is in accordance with a previous study (Evstigneev, 2011) showing that the solubility of lignin increases with increasing temperature. The reason could be due to the pK_a value of kraft lignin being lower at higher temperatures, which indicates an increased dissociation of lignin phenolic groups and an improvement in the solubility of lignin. In addition, the repulsive electrostatic force is also enhanced by an increase in temperature since more thermal energy is being provided to the system (Lee *et al.,* 2012). However, the temperature has not influenced the yield as drastically as the pH in the range investigated. The reason could be that, at a higher temperature, the logarithm of the autoprotolysis constant of water, pK_w, is also lower. As shown in the equation (Norgren, 2001):

$$\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} = \frac{\alpha}{1-\alpha} = \frac{K_a}{K_w}[\mathrm{OH}^-] \tag{4.2}$$

where [HA] is the concentration of a protonated phenolic group and $[A^-]$ is the concentration of its corresponding base, at a certain pH, the net dissociation of lignin (α) is correlated to the quotient of K_a and K_w, and that K_w may prevent the dissociation of phenolic groups at a higher temperature (higher K_w).

Figure 4.2(c) and (e) also show that the precipitation yield of lignin is increased with an increase in the ion strength of the black liquor. This has also been found in an earlier study by Rutatin *et al.* (1989), which showed that increasing ion strength could promote the association of lignin molecules. This is because when the ion strength is increased, the charges on the lignin molecules are strongly screened and the electrostatic repulsion between them is reduced, which is unfavorable for the stability of lignin molecules (Norgren *et al.,* 2001).

4.3 Carbohydrate analysis

It is of interest to investigate hemicelluloses, and xylan in particular, since an earlier study has shown that they have a major impact on the filtration properties of black liquor during precipitation (Wallmo *et al.*, 2009b). As mentioned in Section 2.4.2, carbohydrates and lignin might link to each other as LCC in black liquor. The concentrations of the carbohydrates xylan and galactoglucomannan in the precipitated lignin (i.e. the filter cakes) and filtrates are listed in Table 4.2 and shown in Figure 4.3. It can be seen that, overall, the concentration of xylan is higher than that of GGM. This is because a high fraction of the black liquor used in this study is from hardwood and the main hemicellulose present in hardwood is xylan. Moreover, the majority of GGM is degraded during kraft pulping and only a trace amount is connected to the lignin after degradation.

Table 4.2 Concentrations of carbohydrates (xylan and galactoglucomannan (GGM)) in the filter cakes (precipitated lignin) and filtrates.

Sample	Precipitation yield of lignin (%)	Concentration of carbohydrates in the filter cake (g/kg TDS)		Concentration of carbohydrates in the filtrate (g/kg TDS)	
		Xylan	GGM	Xylan	GGM
1	3.2	53.7	11.7	14.5	5.4
2	32.1	24.5	5.0	12.7	5.4
3	58.5	21.0	3.9	12.5	5.8
4	70.9	15.4	2.8	11.8	5.8
5	83.1	15.1	2.9	11.3	5.9
6	58.9	17.2	3.4	13.3	5.8
7	50.6	15.5	3.7	16.8	5.6
8	47.5	11.8	3.8	17.3	5.8
9	46.1	10.1	4.0	18.0	5.7
10	53.9	14.2	3.8	18.4	6.4
11	55.3	13.0	3.2	15.9	5.6
12	61.1	16.1	3.8	15.0	5.4
13	70.3	16.0	3.6	11.9	4.4

In Figure 4.3(a) it can be observed that the concentration of xylan in the precipitated lignin decreases with decreasing pH. This is probably because, at a higher pH, the precipitates are mainly large lignin molecules that are degraded less during kraft pulping which, in turn, may result in their containing more lignin-carbohydrates linkages.

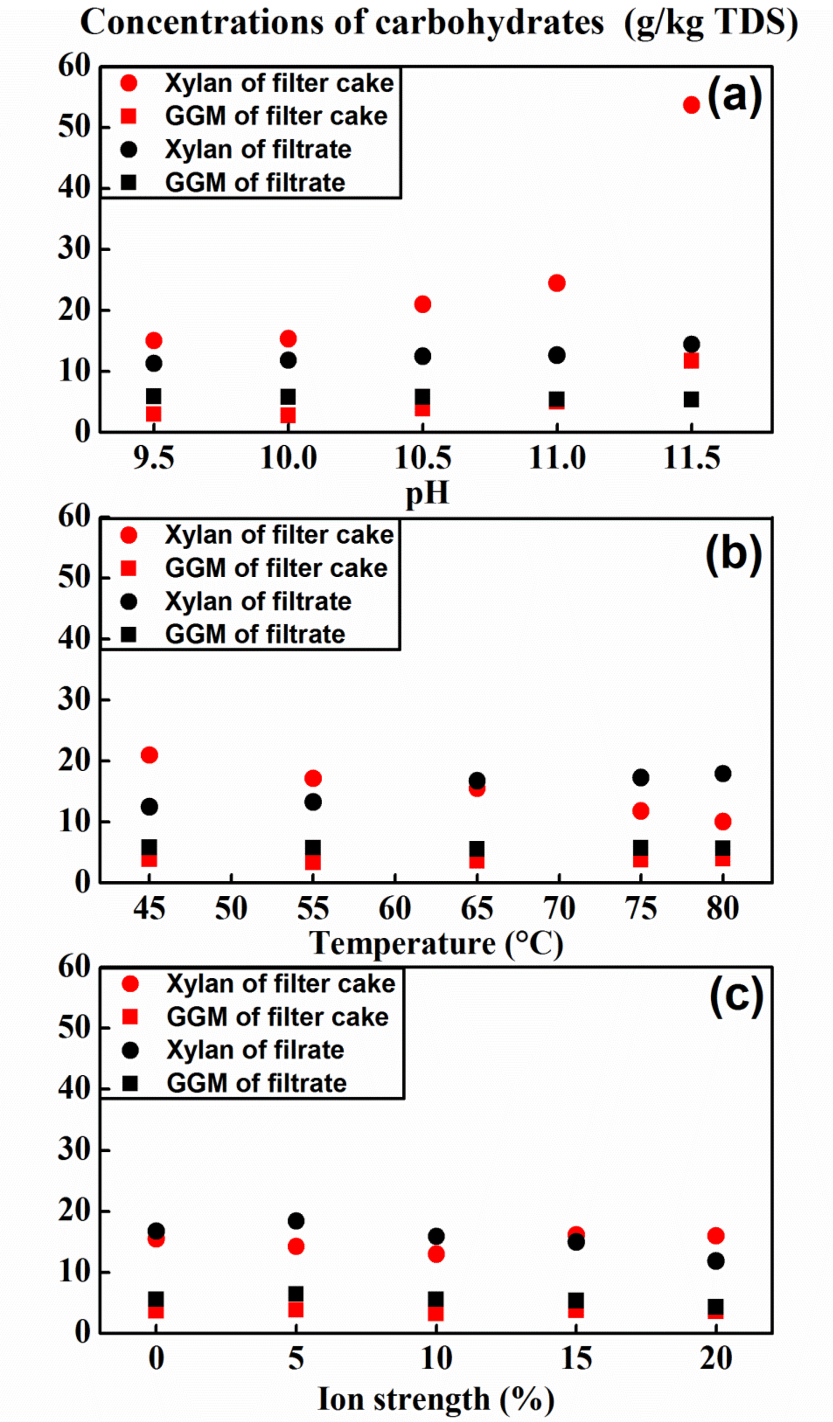


Figure 4.3 Concentrations of xylan and galactoglucomannan (GGM) (from Paper II) in the filter cakes (precipitated lignin) and filtrates at different precipitation conditions: (a) 45°C with no extra sodium added, (b) pH 10.5 with no extra sodium added, and (c) 65°C and pH 10.5.

At a constant pH of 10.5, the concentration of xylan increases slightly as the temperature decreases, see Figure 4.3(b). These results are contradictory to the results shown in Figure 4.3(a), the reason for this is not yet fully understood. It might be due to the distribution of LCCs, since the carboxylic groups on xylan have a lower pK_a than the phenolic groups on lignin, but this remains to be investigated.

It can also be seen from Figure 4.3 that the concentration ratio of lignin to GGM, both in the filter cakes and the filtrates, remains almost constant at different levels of pH, temperature and ion strength. This indicates that the amount of GGM linked to lignin is not affected by the molecular weight of lignin.

4.4 Molecular weight of lignin vs. precipitation equilibrium

The yield and average weight and number-molecular weight (Mw and Mn) of the precipitated lignin at different conditions are listed in Table 4.3 and shown in Figure 4.4.

Table 4.3 The yield and average weight and number-molecular weight (Mw and Mn) of the precipitated lignin.

Sample	Precipitation yield of lignin (%)	Mw of filter cake (Da)		Mn of filter cake (Da)	
		UV response	RI response	UV response	RI response
1	3.2	25598	22441	1638	12054
2	32.1	18116	17404	1329	9723
3	58.5	12307	14927	1241	8413
4	70.9	9870	12875	1088	9484
5	83.1	9340	12637	1047	8379
6	58.9	14203	16228	1436	9867
7	50.6	16068	18282	1432	11699
8	47.5	17143	18703	1538	9860
9	46.1	16324	17248	1510	7836
10	53.9	15171	17414	1311	11019
11	55.3	15147	17016	1295	10843
12	61.1	14623	16412	1453	8746
13	70.3	14584	16086	1457	10019

In Table 4.3 it can be seen that the Mw and Mn of most of the lignin samples are higher when measured by RI response than by UV response. This is probably because the calculation of molecular weight by RI response has neglected the small molecules which are below the low molecular weight limit (based on the molecular weight calibration). However, the Mw of samples 1 and 2 calculated by RI response are lower than those obtained by UV response. In Table 4.2 it can be seen that the concentration of carbohydrates in these two samples is rather high (especially sample 1) and the lignin yield is low.

The average molecular weight of lignin decreases with increasing precipitation yield, as shown in Figure 4.4, which indicates that an increasing amount of lower molecular weight lignin is precipitated at high precipitation yields. This finding can also be seen in the MWD of the precipitated lignin in Figure 4.6. It can be noted that there is a good general correlation between molecular weight and the parameters investigated. Although pH and temperature both seem to have a rather similar effect on the changes in the molecular weight of the lignin, ion strength shows a slightly different behaviour. Whether the latter is due to a relatively small change in ion strength (5-20% addition of sodium) or experimental errors is not known at this point. More details regarding the relationship between precipitation yield and the Mw of lignin under various conditions are presented in Figure 4.5.

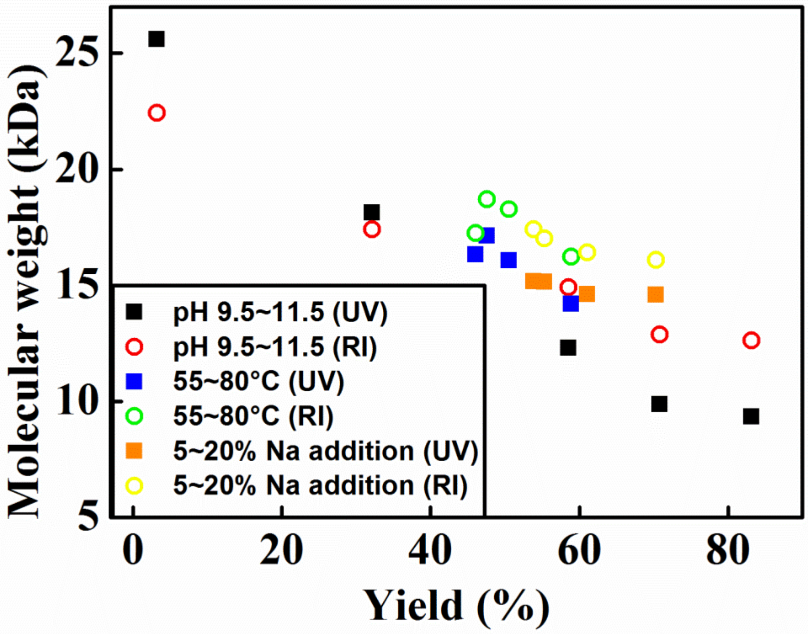


Figure 4.4 The weight-average molecular weight of precipitated lignin at different precipitation yields.

Figure 4.5(a) shows the Mw of precipitated lignin at 45°C at various pH levels but with no extra salt added. It shows that, at precipitation pH of 11.5 to 9.5, the Mw of precipitated lignin decreases substantially from approx. 25000 Da to 9000 Da. This can be interpreted as the apparent pK_a of lignin which is changing significantly with molecular weight. One reason for this is probably because the lignin of high molecular weight contains fewer phenolic groups, since it has not been degraded into smaller fragments during kraft pulping and therefore has a higher apparent pK_a value. Another reason could be the fact that the larger lignin molecule has a stronger attraction to hydrogen ions (Norgren and Lindström, 2000a, Norgren and Lindström, 2000b). A combination of these effects is also a plausible explanation.

It can be seen from Figure 4.5(b) and (c) that when the precipitation yield of lignin increases with decreasing temperature or increasing ion strength, the average molecular weight of precipitated lignin decreases. This is in agreement with previous findings that more smaller lignin molecules are precipitated at a higher yield.

The molecular weight distribution (MWD) of the samples at various conditions, based on RI and UV responses, are shown in Figure 4.6. It can be seen that the profiles of RI and UV responses are similar, which not only indicate that the lignin and carbohydrates exit the separation columns at the same time but also reveal the possible existence of LCC.

The results obtained confirm, once again, the findings discussed earlier in this section. As can be seen in Figure 4.6(a) and (d), there is a clear trend regarding the influence of pH on the MWD of the lignin. A weak trend corresponding to the influence of temperature can be found in Figure 4.6(b) and (e), which is in agreement with earlier data in this work. However, it is not possible to see a trend related to the influence of ion strength in Figure 4.6(c) and (f).

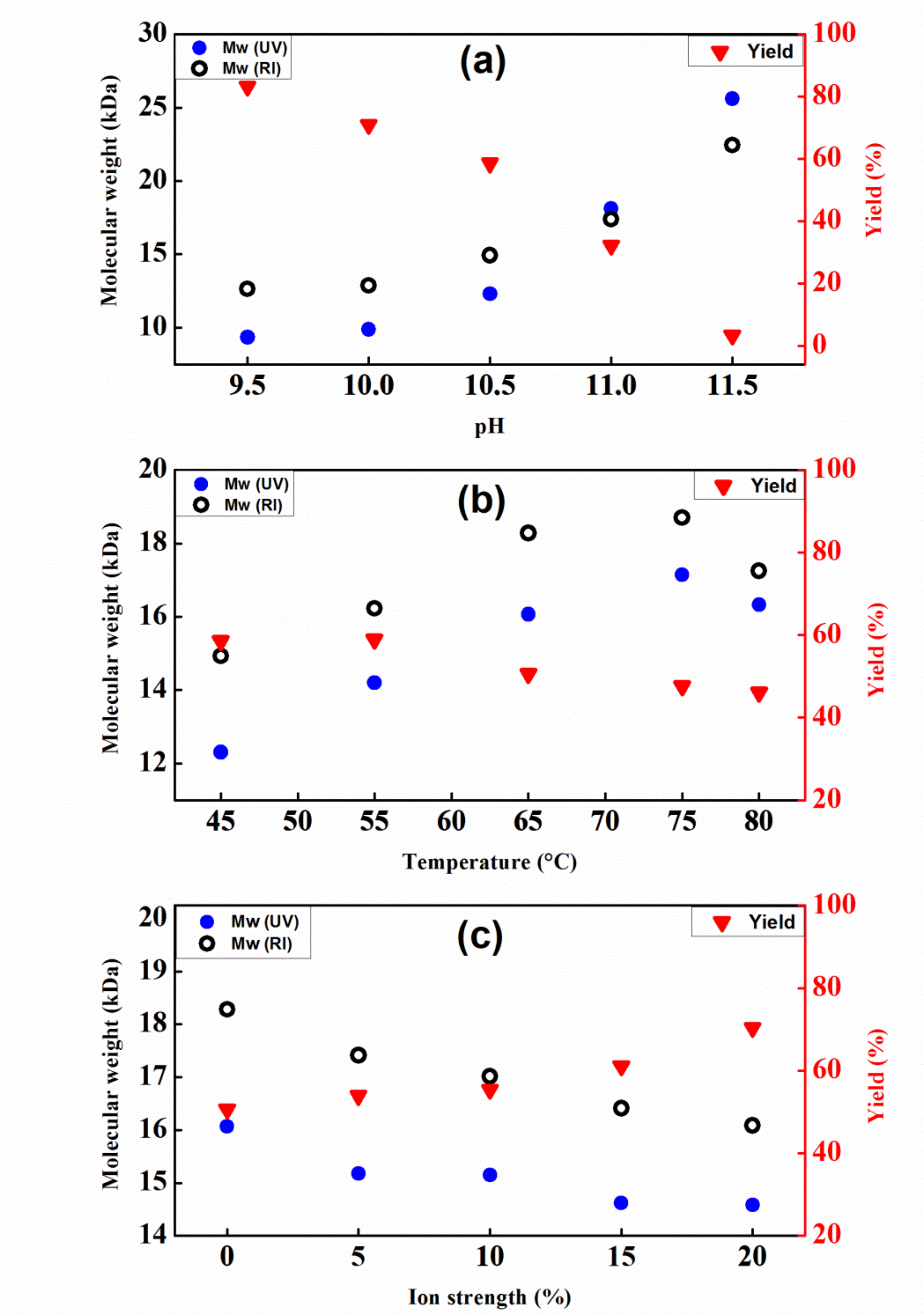


Figure 4.5 The weight-average molecular weight (Mw) of precipitated lignin and the precipitation yield of lignin at different precipitation conditions: (a) 45°C with no extra sodium added, (b) pH 10.5 with no extra sodium added and (c) 65°C and pH 10.5.

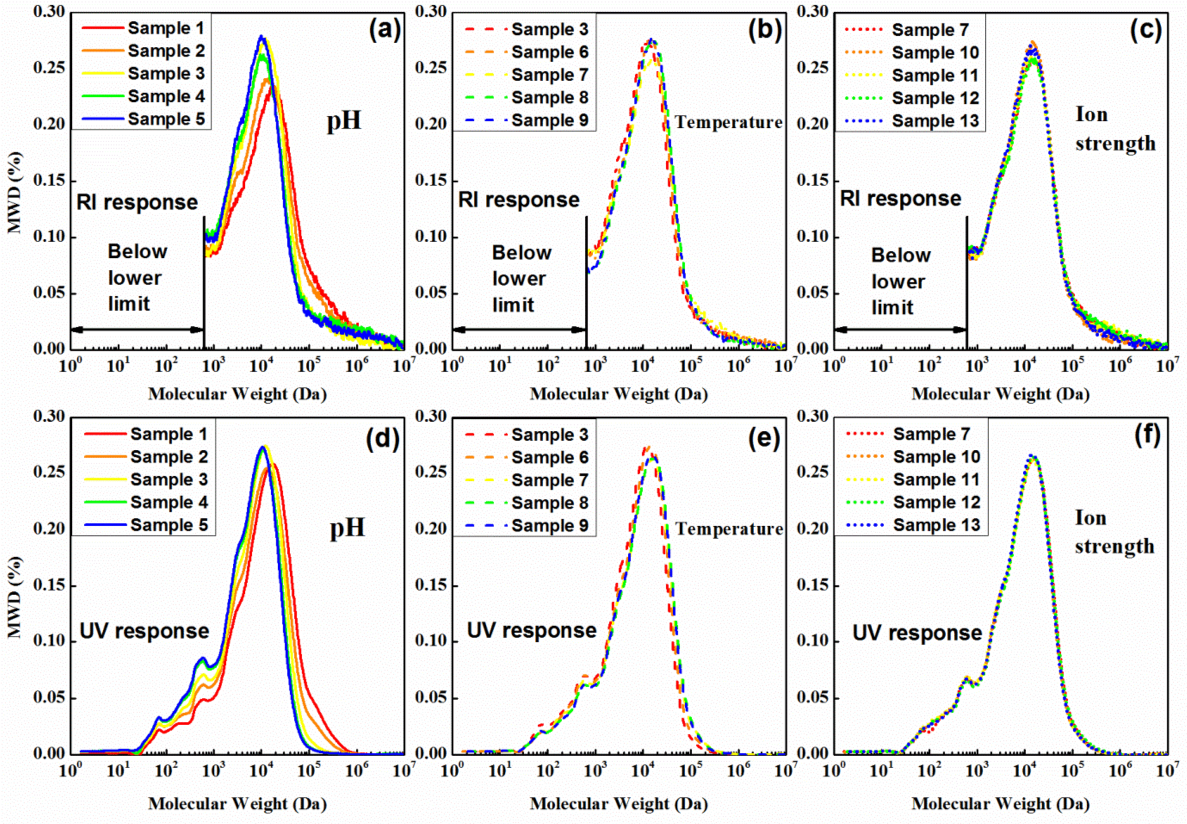


Figure 4.6 Molecular weight distributions (MWD) of precipitated lignin at different precipitation pH, temperature and ion strength.

4.5 NMR analysis of precipitated lignin

In Paper I, seven samples of precipitated lignin produced under different precipitation conditions were selected for NMR analysis. These samples were divided into two groups, as shown in Table 4.4. These seven samples were chosen in order to investigate the influence of process conditions on the amount of functional groups (phenolic and methoxyl groups) found on the lignin molecules. Samples 1, 2 and 3 represent the precipitated lignin at the highest, medium and lowest precipitation yield, respectively. Samples 4 to 7 represent the precipitated lignin at 65°C with no extra sodium added but with different levels of precipitation pH (i.e. 9.5, 10, 10.5 and 11).

Table 4.4 The samples of lignin from Paper I that were analyzed via NMR measurements.

Group	Sample number	Precipitation pH	Temperature (°C)	Increase in ion strength with addition of sodium (%)
A	1	9.5	45	20
	2	10	65	10
	3	11	75	0
B	4	9.5	65	0
	5	10	65	0
	6	10.5	65	0
	7	11	65	0

4.5.1 ^{1}H NMR

^{1}H NMR spectroscopy was used for the characterization of the functional groups in the kraft lignin precipitate. In this work, the precipitated lignin was analyzed as acetylated derivatives using $CDCl_3$ as the solvent. The peaks in the spectra shown in Figure 4.7 are broad: this is typical for the ^{1}H NMR spectra of lignin (Lundquist, 1992b, El Mansouri *et al.*, 2011) due to the stereochemical complexity and broad range of possible chemical environments (Donald, 2010). According to studies by Lundquist (1991, 1992a and 1992b), it is assumed that the chemical shifts at $\delta \approx 2.3$ originate from phenolic acetate, while those at $\delta \approx 3.8$ originate from methoxyl groups. The overlapping of signals makes it difficult to obtain an accurate quantitative calculation of the peak area of the functional group in the ^{1}H NMR spectra. However, if it is assumed that the proton signal of the aromatic ring at $\delta \approx 7$ corresponds to 2.5H/aromatic ring (Li and Lundquist, 1994) for kraft lignin, estimations of the ratio of aromatic ring/phenolic acetate and the ratio of aromatic ring/methoxyl groups can be made. The trends of these functional groups content can then be discovered.

It can be observed that the content of the phenolic acetate group decreases from samples 1 to 3 and from samples 4 to 7, i.e. when the precipitation yield decreases. Additionally, it was found that the average molecular weight of the precipitated lignin decreases with increasing yield, see Figure 4.5(a), which indicates that a greater amount of small lignin molecules is precipitated when the yield is higher. The conclusion can therefore be drawn that small lignin molecules have a greater content of phenolic groups content than large ones. This is most likely due to the fact that the small lignin molecules have been degraded more extensively during kraft cooking and that more phenolic groups have thereby been formed (Gellerstedt and Lindfors, 1984, Gellerstedt, 2008).

In Figure 4.7, the amount of the methoxyl group contained in the precipitated lignin in samples 1 to 3 and 4 to 7 seems to decrease with decreasing precipitation yield. According to the molecular weight data of lignin given in Table 4.3, it can be concluded that the content of the methoxyl group increases with decreasing molecular weight of the precipitated lignin. A possible reason for this is the higher syringyl/guaiacyl ratio of a degraded lignin of lower molecular weight, as observed by Mörck *et al.* (1986 and 1988). This has also been reported by Toledano *et al.* (2010b), who claimed that there was a high fraction of syringyl type lignin in the precipitated lignin of low molecular weight, whereas more guaiacyl lignin was found in lignin of high molecular weight. Moreover, hardwood lignin contains more syringyl units whereas softwood lignin has more of the guaiacyl type, so it can be assumed that the precipitated lignin with a low molecular weight contains more hardwood lignin and that with a high molecular weight contains more softwood lignin.

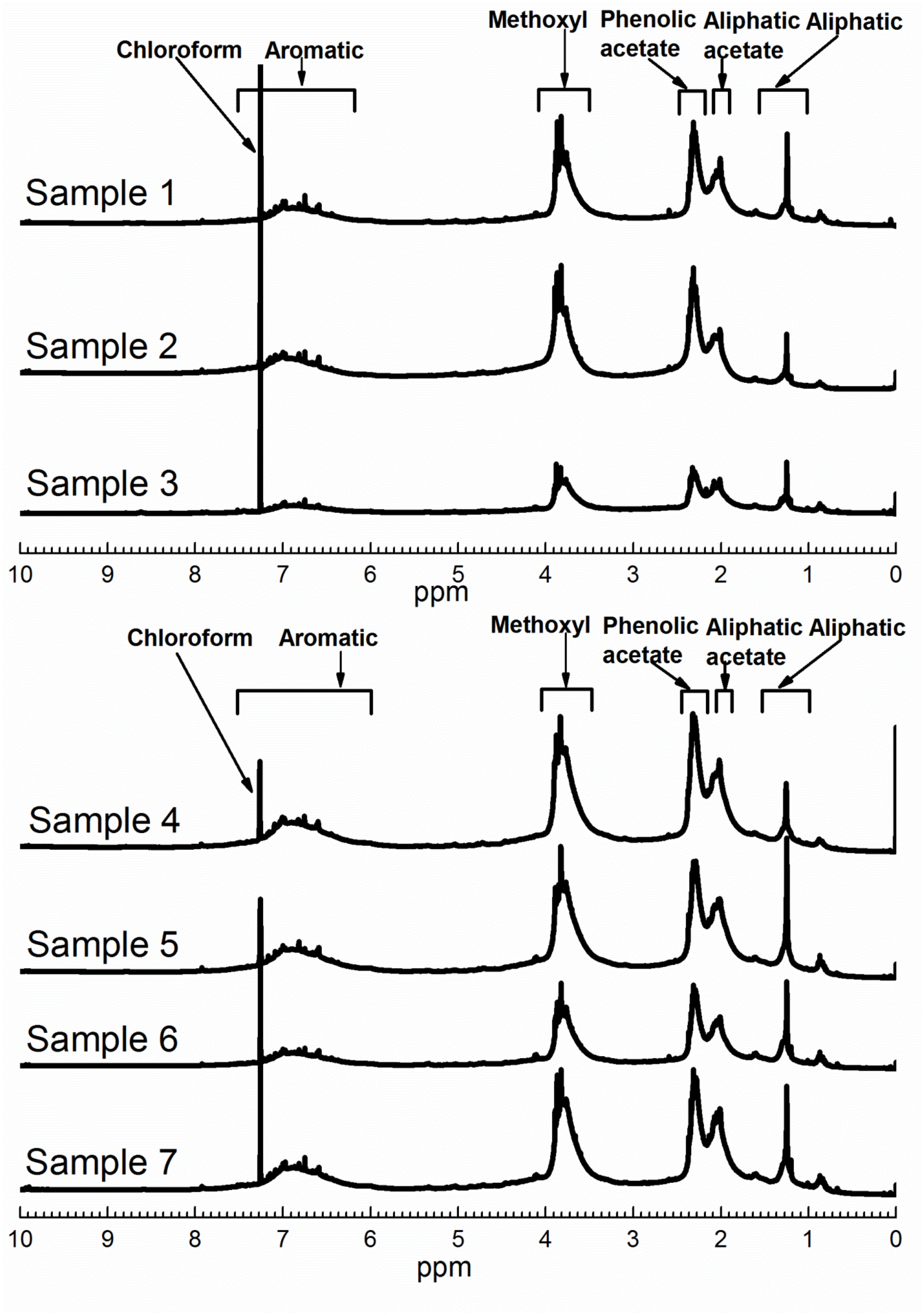


Figure 4.7 ^{1}H NMR spectra of the precipitated kraft lignin.

4.5.2 ^{13}C NMR

A quantitative analysis of the functional groups in lignin was obtained by ^{13}C NMR spectroscopy, see Figure 4.8. The chemical shift assignments were based on the literature (Mörck and Kringstad, 1985) and are summarized in Table 4.5 along with the integrated peak areas of the functional groups. The integrations were performed by calculating the integral of the aromatic region (102–160 ppm) and calibrating the integral value to 6.00, which represents an aromatic ring with 6 carbons. The integrated peaks of acetylated phenolic and methoxyl groups were therefore reported as carbon atoms per aromatic ring (Robert, 1992, Faix et al., 1994, Ralph and Landucci, 2010, Choi and Faix, 2011).

Table 4.5 Quantitative comparison (number of carbons/aromatic ring) of the functional groups in the samples of acetylated kraft lignin based on ^{13}C NMR spectra.

Group	Sample number	Acetylated phenolic groups	C_5 in non-etherified, aromatic C-C bond	C_5, aromatic C-H bond	Aliphatic C-O bond, C in β-O-4	Methoxyl groups	Mw from UV response
		Chemical shift range (ppm)					(Da)
		168.8–166	127–121	115–110	90–67	57.5–54	
A	1	1.2	0.36	0.42	0.48	1.62	8783
	2	1.02	0.42	0.42	0.42	1.5	10947
	3	0.84	0.42	0.36	0.42	1.38	13134
B	4	1.08	0.36	0.42	0.42	1.56	10309
	5	1.02	0.36	0.42	0.42	1.5	11675
	6	0.96	0.36	0.42	0.42	1.5	12278
	7	0.96	0.42	0.36	0.42	1.56	12521

In Table 4.5, it can be seen that the results for Group A (samples 1–3) show a clear decrease in the acetylated phenolic and methoxyl groups with increasing molecular weight of the lignin, which is in agreement with the results of the ^{1}H NMR analysis made in this study. However, there is no clear trend as to the amount of functional groups present in Group B (samples 4–7). This could be due to differences in the precipitation conditions, which results in the differences in the molecular weight of lignin being smaller and thereby leads to slight changes in the contents of acetylated phenolic and methoxyl groups.

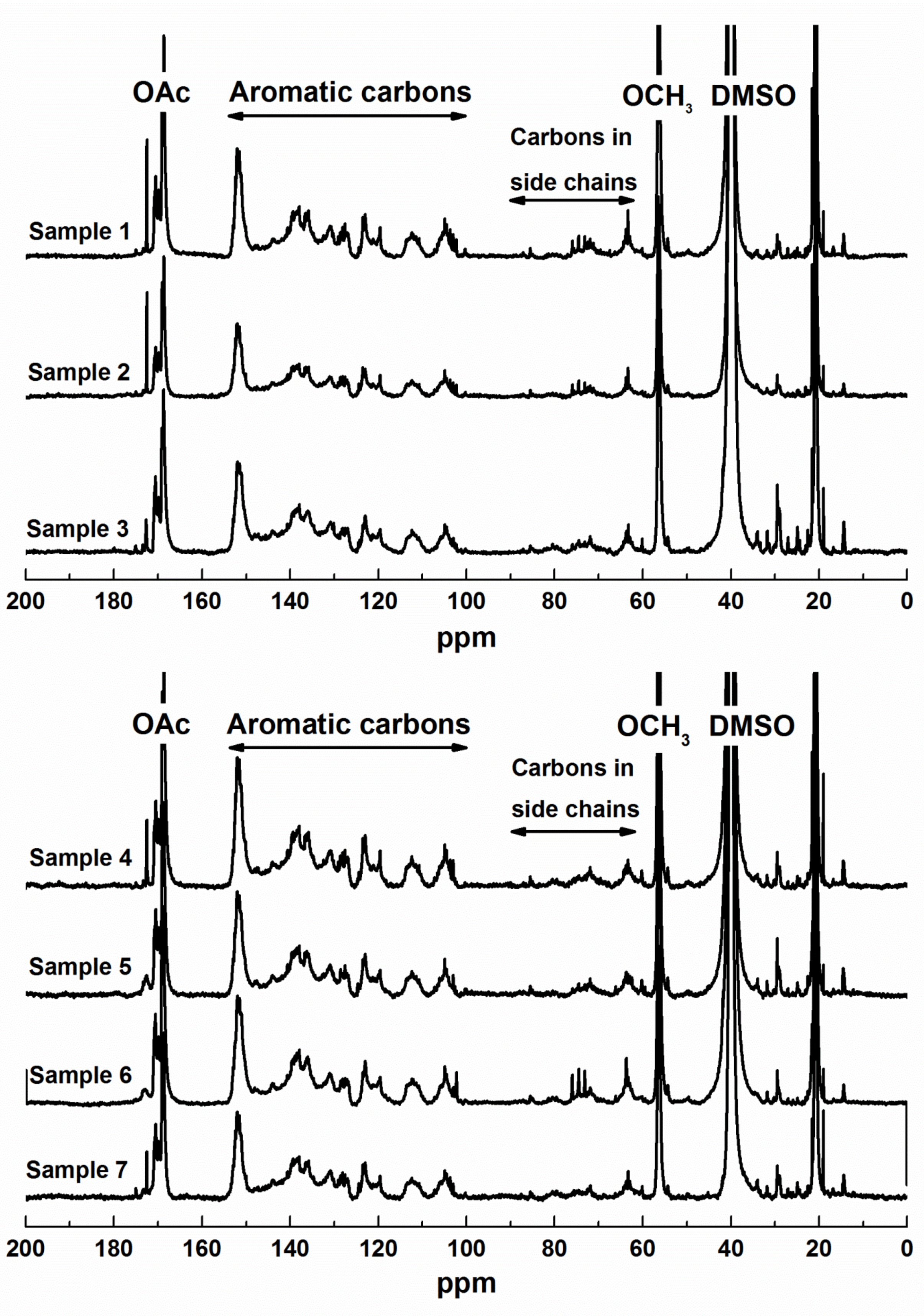


Figure 4.8 ^{13}C NMR spectra of the precipitated kraft lignin.

4.6 Modelling the equilibrium of lignin precipitation

Theliander (2010) developed a simple model (Eq.4.3) for estimating the precipitation yield of lignin that is valid for softwood black liquor:

$$Yield = a \times \exp\left(\frac{b}{T}\right)(\mathrm{H}^{+})^{c}(\mathrm{Na}^{+} + \mathrm{K}^{+})^{d} \tag{4.3}$$

where *Yield* is the precipitation yield of lignin (%), T is the temperature in Kelvin, H^{+} is the concentration of hydrogen ions (mol/L) and Na^{+} and K^{+} are the concentrations of sodium and potassium ions (g/kg liquor), respectively.

The result of fitting Eq. 4.3 to the experimental data presented in this work is shown in Figure 4.9(a), which is a plot of the estimated yield versus the experimental; Table 4.6 shows the estimated parameters *a*, *b*, *c* and *d*. The mathematical fitting was done in MATLAB using the *lsqcurvefit* function.

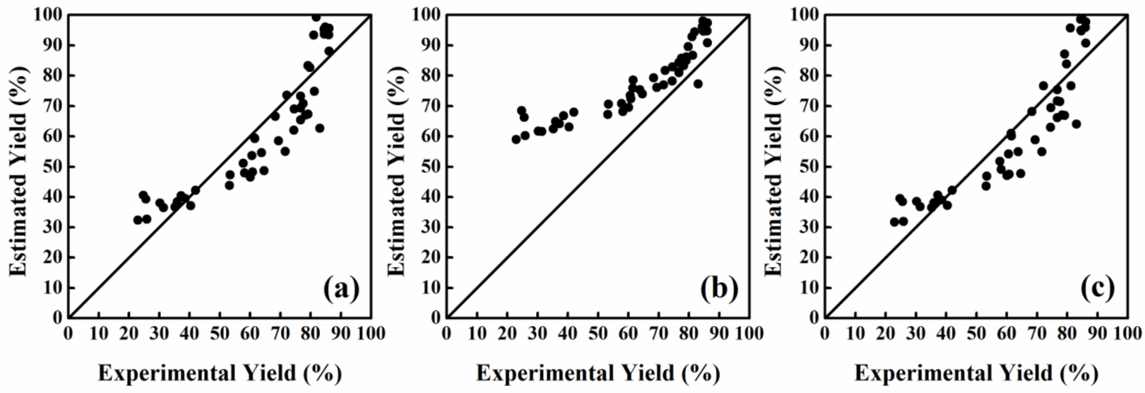


Figure 4.9 Estimated lignin yield versus experimental lignin yield through modification, using (a): the new fitting parameters from the present study; (b): the parameters of Theliander (2010) and (c): the fixed *b* from Theliander (2010) and fitting the other parameters from present study.

Table 4.6 Numerical values of the parameters in Eq. 4.3 valid for softwood black liquor (as applied in previous work by Theliander (2010) and the present study).

Parameters used	***a***	***b***	***c***	***d***	**Error (%)**
The present study	235	412	0.256	0.779	14.5
Work by Theliander	157	365	0.109	0.174	35.8
The present study with fixed *b*	184	365	0.266	0.931	14.6

In Figure 4.9(a) it is obvious that the error is not completely random: a small bending can be noticed, the reason for which is not known at present.

If the values of the parameters *a*, *b*, *c* and *d* obtained in this study are compared with those of Theliander (2010) it can be concluded that the numerical values of parameters *c* and *d* differ a lot, while the values of parameters *a* and *b* are similar (see Table 4.6). Parameter *b* may be interpreted as being proportional to an activation energy and the fact that these *b* values are similar indicates that the solidification mechanisms are similar. The influences of hydrogen ions (H^+) and ion strength are different if two studies are compared. One possible explanation may be that the origin of black liquor differs: A mixture of softwood/hardwood black liquor was used in this study whereas only softwood black liquor was used in Theliander's study.

In Figure 4.9(b) it can be seen that the yield is overestimated if the parameters from the previous study are applied to this study. This indicates that the precipitation yield of lignin from a black liquor containing both softwood and hardwood lignin is lower than the yield from a pure softwood black liquor under the same precipitation conditions. This is in agreement with Öhman *et al.*(2007c) who reported (using only one measuring point) that the hardwood black liquor had a lower precipitation yield of lignin than softwood black liquor.

Figure 4.9(c) and Table 4.6 show the results of the parameter *b* from the Theliander study and the values of parameters *a, c* and *d* estimated by fitting Eq. 4.3 to the experimental data obtained in the present study. When (a) and (c) in Figure 4.9 are compared with each other it is obvious that they are almost identical. Furthermore, Table 4.6 shows that there is only a small difference in the parameters *a*, *c* and *d* compared to when all four of the parameters are estimated. This indicates that the solidification mechanism may be independent of the types of lignin (i.e. protonation) but that the equilibrium constant differs between them.

5. CONCLUSIONS

- The precipitation yield of lignin increases when the precipitation pH and temperature decreases; increasing the ion strength of the black liquor is also seen to improve the yield. A mixed softwood/hardwood black liquor gives a lower yield than a softwood black liquor.
- The content of carbohydrates (most likely in the form of LCC) in the precipitated lignin decreases when the pH decreases or the temperature increases.
- The amount of lower molecular weight lignin increases as the precipitation yield increases.
- According to ^{1}H and ^{13}C NMR spectra analysis, the amount of methoxyl groups contained in the precipitated lignin increases when the precipitation pH decreases, indicating that the ratio between precipitated softwood and hardwood lignin decreases with decreasing pH. The amount of phenolic groups is found to increase with an increase in the precipitation yield.

6. FUTURE WORK

The present work has focused mainly on the equilibrium of lignin precipitation by studying the precipitation yield of lignin. The changes of the molecular weight of lignin during precipitation have also been investigated. In order to gain further knowledge of the formation of lignin particles during precipitation, and how the equilibrium may be improved from a kinetics perspective, it is suggested that the following are examined in more detail:

- Questions related to the formation and growth of lignin particles under various precipitation conditions, especially where pH, temperature and ion strength are concerned. The balance between the growth of lignin particles and their disintegration is also of interest.
- The kinetics of the growth and agglomeration of lignin particles: a study of the rate at which lignin aggregates are formed and the size they can reach. Modelling the rate of aggregation of lignin particles.
- Introducing surfactants or lignin of high molecular weight to act as boosters in the precipitation process.

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APPENDIX

Carbohydrate analysis

The contents of cellulose, (galacto)glucomannan and xylan were calculated after carbohydrate analysis by using the following assumptions/corrections:

The amounts of sugars analyzed were corrected for the acid hydrolysis yield. Anhydro sugars were calculated from sugar monomers by the withdrawal of water (multiplication by 0.88 in the case of pentosans and by 0.90 in the case of hexosans). Glucomannan was calculated as the sum of galactan, mannan and part of the glucan. The molar ratio between the mannose and the glucose in galactoglucomannan was assumed to be 3.5:1(Meier, 1958). All galactan measured was included in (galacto)glucomannan. Acetyl groups were, however, not included. Xylan was calculated as the sum of xylan and arabinan. All arabinan measured was included in the xylan. Cellulose was calculated as the content of glucan after withdrawal for the contribution of glucan to (galacto)glucomannan.

Cellulose = Glucose – (1/3.5) × Mannose

(Galacto)glucomannan = Galactose + [1+ (1/3.5)] × Mannose

Xylan = Xylose + Arabinose

The analyses were summed up in a mass balance under the assumption that the carbohydrates were divided into cellulose, (galacto)glucomannan and xylan, which were calculated as described above.