THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

On the Course of Kraft Cooking

The impact of ionic strength

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[Left: wood meal. Right: wood residues after cooking experiments.]

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ABSTRACT

Kraft pulping is the dominant process currently used to produce chemical pulps, and has been applied for more than 130 years. A large number of studies have been conducted to gain a better understanding of the delignification kinetics as well as the reactions of the wood components being dissolved during the cooking process. Nevertheless, these remain far from being well understood in detail due to the very complicated chemistry and morphology of wood.

The main goal of this work is to further increase knowledge of kraft cooking. The focus here is to investigate the influence of ionic strength on the kinetics of kraft cooking. Kraft cooks of wood meal from Scots pine (*Pinus silvestris*) were performed in a small-scale flow-through reactor. This equipment was employed to minimize resorption phenomena and the additional degradation of the wood components dissolved in the hot cooking liquors during the course of delignification. In addition, it was possible to adjust the concentration of the ions (Na^+, CO_3^{2-} and Cl^-) in the cooking liquor at any given time during the cook.

The results obtained show that the rates of delignification and xylan removal in the flow-through kraft cooks decreased significantly when the ionic strength/sodium ion concentration in the cooking liquor was increased, while the removal rate of glucomannan was virtually unaffected by the level of the ionic strength. The reaction rates of hexenuronic acid were found to increase with increasing ionic strength. When $[Na^+]$ was altered at a given time during the kraft cook, the effect on both the rate of xylan removal and delignification was quite similar, even though some differences could be noted. Analyses of lignin precipitated from black liquors showed that the molecular weight of the lignin dissolved decreased with increasing ionic strength in the cooking liquor. Furthermore, a very wide molecular weight distribution was found for dissolved lignin fragments. The content of carbohydrates present in precipitated lignin was found to increase with cooking time and decrease with increasing ionic strength. The results indicate the possibility of the existence of several types of lignin-carbohydrate complexes. The findings suggest that the solubility and/or mass transport of wood polymers mainly govern the overall rate of kraft delignification at the fibre wall level.

Keywords: flow-through kraft cooking; ionic strength; sodium ion concentration; kinetics; delignification; lignin; xylan; carbohydrate removal; hexenuronic acids; molecular weight distribution.

List of publications

This thesis is based on the following papers, referred to by Roman numerals in the text, which are appended.

I. **Impact of ionic strength on delignification and hemicellulose removal during kraft cooking in a small-scale flow-through reactor**
Binh T. T. Dang, Harald Brelid, Tobias Köhnke and Hans Theliander
Nordic Pulp & Paper Research Journal, 28(3), 358-365, 2013

II. **Effect of sodium ion concentration profile during softwood kraft pulping on delignification rate, xylan retention and reactions of hexenuronic acids**
Binh T. T. Dang, Harald Brelid, Tobias Köhnke and Hans Theliander
Nordic Pulp & Paper Research Journal, 29(4), 604-611, 2014

III. **The impact of ionic strength on the molecular weight distribution (MWD) of lignin dissolved during softwood kraft cooking in a flow-through reactor**
Binh T. T. Dang, Harald Brelid, and Hans Theliander
Holzforschung, 70(6), 495-501, 2016

IV. **Carbohydrate content of black liquor and precipitated lignin at different ionic strengths in flow-through kraft cooking**
Binh T. T. Dang, Harald Brelid, and Hans Theliander
Manuscript

V. **About structural changes of lignin during kraft cooking and the kinetics of delignification**
Cecilia Mattsson, Merima Hasani, Binh Dang, Maxim Mayzel, and Hans Theliander
Holzforschung, 71(7-8), 545-553, 2017

Parts of this work have also been presented at the following conferences:

I. **The effect of ionic strength on the kinetics of the kraft pulping of softwood**
Binh T. T. Dang, Harald Brelid, and Hans Theliander
In: Conference proceedings, 11th European Workshop on Lignocellulosics and Pulp
Hamburg, Germany, August 16-19, 2010, pp 313-316
(Poster presentation)

II. **Different sodium ion concentration profiles during kraft cooking - Impact on delignification and carbohydrate removal**
Binh T. T. Dang, Harald Brelid, and Hans Theliander
In: Conference proceedings, 16th International Symposium on Wood, Fibre and Pulping Chemistry
Tianjin, China, June 8-10, 2011, pp 641-645
(Poster presentation)

III. **Molecular weight distribution of lignin during flow-through kraft cooking of Scots pine**
Binh T. T. Dang, Harald Brelid, and Hans Theliander
In: Book of abstracts, 4th Avancell conference – Creating Value from the Swedish Forest Resources
Gothenburg, October 8-9, 2013, pp 23-25
(Poster presentation)

IV. **What do we know regarding the kinetics of delignification in kraft cooking?**
Binh T. T. Dang, Harald Brelid, and Hans Theliander
14th European Workshop on Lignocellulosics and Pulp
Autrans, France, June 28-30, 2016
(Oral presentation, by Hans Theliander)

Contribution report

The author of this thesis has made the following contributions to these articles:

I. Main author. Responsible for planning the experimental outline; performing experimental work; interpreting the results; writing the article with the support of the co-authors.

II. Main author. Responsible for planning the experimental outline; performing experimental work; interpreting the results; writing the article with the support of the co-authors.

III. Main author. Responsible for planning the experimental outline; performing experimental work; interpreting the results; writing the article with the support of the co-authors.

IV. Main author. Responsible for planning the experimental outline; performing the majority of experimental work; interpreting the results; writing the article with the support of the co-authors. A part of the carbohydrate analyses was carried out by Ms. Lena Fogelquist.

V. Active in planning the experimental outline. Did not perform NMR analysis. Joint effort made in interpreting the results and writing the article.

List of abbreviations

ATR-IR	Attenuated total reflectance - infrared
BL	Black liquor
CL	Cooking liquor
DMSO	Dimethyl sulphoxide
GPC	Gel permeation chromatography
HexA	Hexenuronic acids
H	High level of sodium ion concentration: $[Na^+] = 3.00$ mol/kg solvent
IS	Ionic strength
L	Low level of sodium ion concentration: $[Na^+] = 0.52$ mol/kg solvent
LCCs	Lignin-carbohydrate complexes
M	Medium level of sodium ion concentration: $[Na^+] = 2.00$ mol/kg solvent
MeGlcA	4-*O*-methylglucuronic acids
MWD	Molecular weight distribution
MW	Molecular weight
M_w	Weight average molecular weight
NMR	Nuclear magnetic resonance
PL	Precipitated lignin
WR	Wood residues

Contents

1. Introduction

Wood pulp is produced mainly by either chemical or mechanical treatment or processes combining the two. Mechanical pulping involves wood being disintegrated into fibres by grinding or refining, and the resulting pulp yield is thus high. In chemical pulping, the majority of the lignin is degraded and removed from the wood material in the presence of active chemicals in order to liberate the fibres: since carbohydrates are also removed to a certain extent, the pulp yield is consequently quite low. However, the main benefits of chemical pulping are that stronger paper can be produced and that most of the lignin can be removed, which facilitate a stable white paper. Chemical pulp is generally produced using two methods: kraft (sulphate) pulping or sulphite pulping.

Kraft pulping has become the predominant process for producing chemical pulp worldwide. The kraft pulping process produces a strong pulp and most wood species may be used as raw material. It does, however, have one critical drawback: a low pulp yield, due to the loss of carbohydrates. The pulp yield in a softwood kraft pulp mill producing unbleached pulp is about 45-55%, depending of the type of pulp produced (Sjöström 1993). The pulp yield becomes one of the key economic factors, since the cost of wood dominates the total production cost of a kraft pulp mill. An improvement in the selectivity of kraft pulping, i.e. a reduction of carbohydrate losses, would not only lead to an increased yield and, as a consequence, improve the utilization of wood, but also make it possible to control the composition of the pulp produced and its properties. Furthermore, such an improvement would also involve less organic material being released from the wood into the black liquors at a given degree of lignin removal: the load on the washing, evaporators and recovery boiler could thereby be reduced, improving both the economics of the process and sustainability.

The kraft pulping process has been used in the pulp industry for more than a century. It is, therefore, not surprising that a vast number of scientific studies dealing with various steps of the kraft process can be found in the literature. Many of these publications deal with kraft cooking, which is the heart of the kraft process. It can be stated that the mechanisms of the main chemical reactions are well understood. The gross behaviour regarding process conditions, and the resulting quality of the pulp, are also well established. However, despite the fact that a large number of investigations have already been conducted to improve and increase knowledge of both the delignification kinetics and the reactions of dissolved wood components during kraft cooking, these are still not well understood in all detail. For more detailed optimization of the process, deeper knowledge regarding the overall kinetics of the different wood components is therefore necessary. This is a demanding task, since the chemistry and morphology of wood are very complicated; furthermore, the kraft cooking operation involves not only heat and mass transfer but also heterogeneous reactions.

1.1 Objectives

The key objective of this work was to increase understanding of kraft cooking kinetics. The work has focused on how ions (Na^+, CO_3^{2-}, Cl^-) not directly involving in the main reactions influence the reaction kinetics of lignin and carbohydrate removal during flow-through kraft cooks of Scots pine. A small-scale flow-through reactor was used in order to minimize resorption phenomena and the additional degradation of wood components dissolved in the hot cooking liquor. Additionally, it was possible to adjust the chemical composition of the cooking liquor during the flow-through kraft cooks. Wood meal was chosen to minimize the influence of mass transport phenomena.

1.2 Outline of the thesis

This work is based on five papers, all of which are appended. The main findings from these five investigations are presented and discussed in this thesis. Following the introduction in Chapter 1, Chapter 2 provides a brief fundamental background of the components of softwood, the kraft pulping process and some findings from the literature of the reactions kinetics of lignin in kraft pulping. The materials and methods employed are described in Chapter 3 in some detail; the main results of the investigations are in reported Chapter 4, along with their interpretation and discussions. Finally, the main conclusions drawn are presented in Chapter 5.

2. Background

A brief background of the chemical composition and structure of softwoods, as well as the kraft pulping operation, is presented in this section together with some more detailed information from previous studies on the kinetics of kraft cooking.

2.1 The components of softwood

2.1.1 Cellulose

Cellulose is the most abundant biopolymer in nature and is one of the main constituents of wood. It is a linear homo-polysaccharide consisting of β-D glucose units linked together with 1→4-glucosidic bonds (Figure 2.1). The number of anhydroglucose units in the cellulose chain defines its degree of polymerization. The polymerization degree of cellulose varies according to the origin of the raw material, but is about 10 000 in native wood (Sjöström 1993). In most softwoods, the amount of cellulose varies between 37-43% of dry wood weight (Sjöström, Alén 1999).

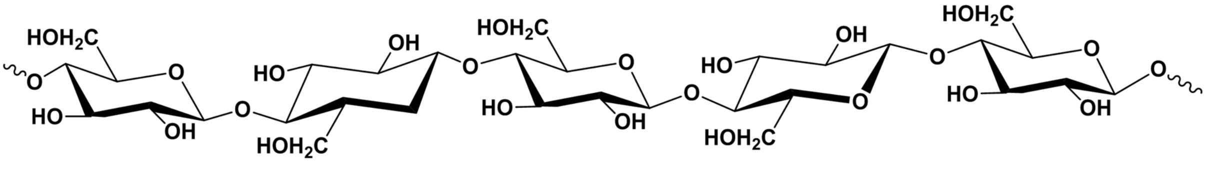

Figure 2.1. The structure of cellulose

The cellulose molecules form strong intra and intermolecular hydrogen bonds through equatorially placed hydroxyl group (OH); there are also axial strong hydrophobic interactions between the molecules, which stabilize aggregated bundles of molecules known as microfibrils. These microfibrils have regions where the cellulose chains are highly ordered (crystalline cellulose) and less ordered (amorphous cellulose). Cellulose microfibrils build up fibrils and, finally, cellulose fibres (Sjöström 1993).

2.1.2 Hemicelluloses

In contrast to cellulose, hemicelluloses are hetero-polysaccharides that consist of several different sugars. Hemicelluloses are amorphous, and have a degree of polymerization lower than that of cellulose. In softwoods, the amounts of hemicelluloses vary according to species and range normally from 20 to 30% of the dry wood weight (Sjöström, Alén 1999). The main hemicelluloses in softwoods can be classified into one of two categories, based on the constituents of their backbone.

The first group is (galacto)glucomannan, which is comprised of (1→4)-linked β-D-mannopyranose and β-D-glucopyranose, units to form a backbone with (1→6)-linked α-D-galactopyranose units as substituents, see Figure 2.2 (Fengel, Wegener 1984; Sjöström 1993). The content of (galacto)glucomannan in normal softwood is about 15-20% of the dry wood weight. (Galacto)glucomannan may be divided into two types that differ in galactose content: glucomannan, with a low content of galactose (galactose:glucose:mannose, 0.1:1:4), and galactoglucomannan, with a high content of galactose (galactose:glucose:mannose, 1:1:3). (Galacto)glucomannan is partially acetylated and, on average, one *O*-acetyl group per 3-4 hexose units is linked to the C-2 and/or C-3 positions in the backbone (Sjöström 1993; Sjöström, Alén 1999).

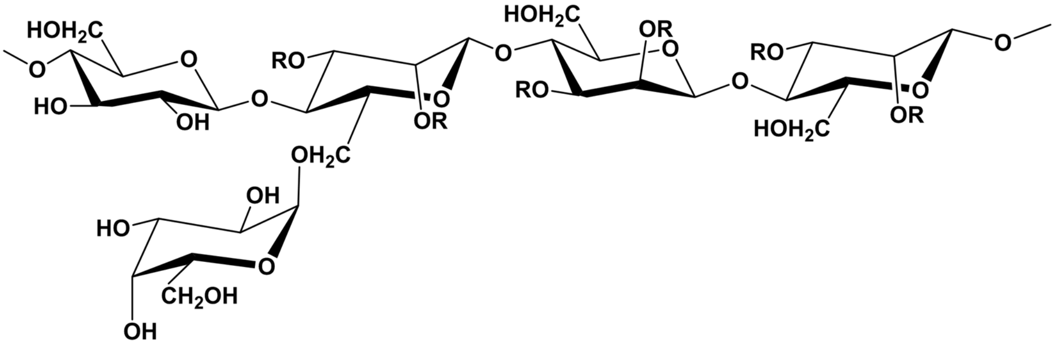

Figure 2.2. Partial structure of (galacto)glucomannan. R=H or CH_3CO

The second major hemicellulose in softwoods is arabinoglucuronoxylan, which has a backbone consisting of (1→4)-linked β-D-xylopyranose units: these are substituted with one α-L-arabinofuranose unit per 8-9 xylose units at C-3 and one 4-*O*-methyl-α-D-glucuronic acid group per 5-6 xylose units at C-2, see Figure 2.3. The content of arabinoglucuronoxylan in normal softwoods may range from 5-10% of the dry wood weight (Sjöström 1993; Sjöström, Alén 1999).

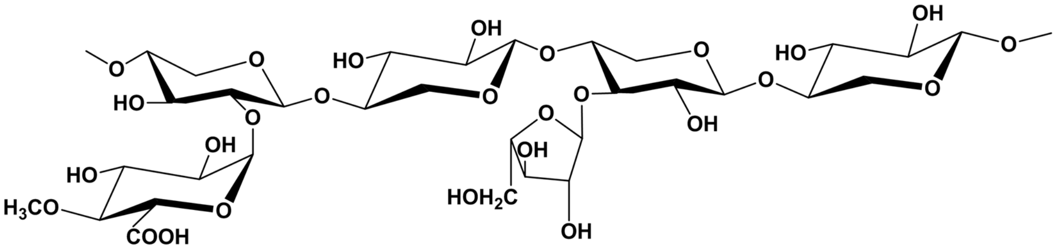

Figure 2.3. Principal structure of arabinoglucuronoxylan

2.1.3 Lignin

Another main component of softwood is lignin, which is an amorphous complex polymer. It consists mainly of three basic units: coniferyl alcohol, *p*-coumaryl and sinapyl alcohol, see Figure 2.4 (Heitner et al. 2010). The structure of lignin is formed primarily by these three basic units that are linked together by several different kinds of bonds, where the most common type is the β-aryl ether bond (β-O-4). Other common linkages present in lignin are α-O-4, 4-O-5 and C-C linkages (5-5, β-5, β-β and β-1). The proportions of the three basic units affect the chemical reactivity of the lignin. The lignin in softwoods is mainly composed of coniferyl alcohol units; the content of lignin varies according to species, ranging from 25-33% of the dry wood weight (Sjöström, Alén 1999).

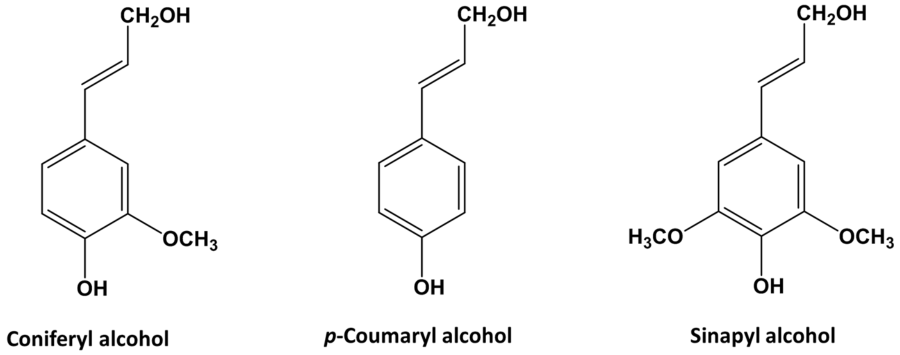

Figure 2.4. The basic units forming the lignin structure

2.2 The structure of wood

Wood is comprised of highly ordered longitudinal and radial wood cells. Softwoods have two basic types of cells: tracheids and ray cells. Tracheids orientated in the longitudinal direction are the dominant cell types (approx. 90-95% of total cell volume) (Sjöström 1993). A schematic diagram of the structure of a wood cell wall is presented in Figure 2.5 (Agarwal 2006). As can be seen, it has various layers: a primary wall (P), a secondary wall (S1, S2 and S3) and a warty layer (W). These layers differ in both structure and chemical composition.

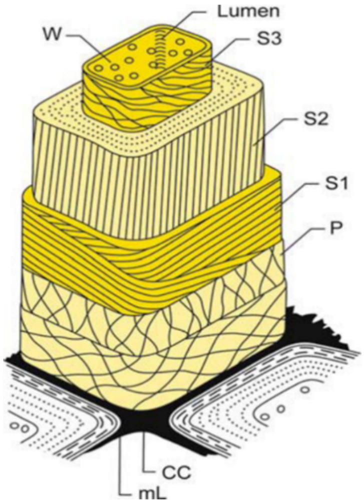

Figure 2.5. Schematic diagram of a wood cell wall (Agarwal 2006, reprinted with permission)

The primary wall (P) is a thin layer with a thickness of 0.1 - 0.2 μm and forms the outer layer of the cell. It consists of cellulose fibrils that are embedded in a matrix of hemicelluloses, lignin and pectin; they form a random network. The secondary wall is comprised of three layers: a thin outer layer (S1), a thick middle layer (S2) and a thin inner layer (S3). These layers, which are composed of parallel cellulose fibrils embedded in hemicelluloses and lignin, are organized in a plywood-type of structure in which the orientation of the cellulose fibrils differ. The S1 layer is between 0.2 and 0.3 μm thick and has 3 - 4 lamellae. The S2 layer is approx. 1 μm thick in earlywood and 5 μm in latewood, with lamellae in that may vary from 30 to 40 in the former to more than 150 in the latter. The thin S3 layer, which is approx. 0.1 μm thick, has several lamellae (Sjöström 1993; Sixta 2006).

The middle lamella (ML) is located between the cells and functions as a binder substance between them. The middle lamella is a thin region, being a mere 0.2 - 1.0 μm thick. The lignin content is about 60% in the middle lamella region (ML + P) and about 20% in the secondary wall. Nevertheless, approx. 63 - 74% of the total lignin in wood is located in the secondary wall: not only is this the thickest layer, it also contains 90% of the cellulose and 70-80% of the hemicelluloses (Sjöström 1993; Sixta 2006).

2.3 The kraft pulping process

2.3.1 General description

The kraft pulping process has been utilized for more than 130 years and is currently the dominant method used to produce chemical pulps; a simplified scheme of the process is shown in Figure 2.6. In principle, wood chips are subjected to an alkaline solution, in which hydroxide ions (OH^-) and hydrosulphide ions (HS^-) are the active cooking ions, at a temperature of 150°C-170°C (Sjöström 1993). The lignin is degraded and removed from the wood material, thereby facilitating the liberation of fibres suitable for paper production. After cooking, the resulting pulp is subjected to washing in several steps and, if a white product is required, bleaching is applied. A pulp mill that is integrated with a paper machine uses the pulp directly to produce paper; a stand-alone pulp mill dries and ships the pulp produced to paper mills. The heart of the kraft pulping process is kraft cooking, where the majority of the lignin is removed and the fibres are liberated. The kraft cook can be conducted either batch-wise or in a continuous way.

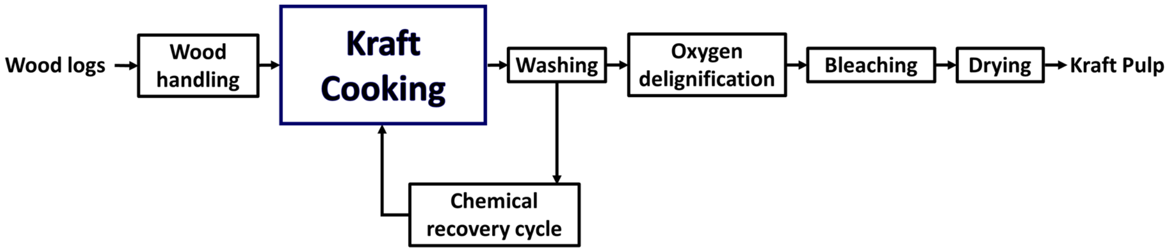

Figure 2.6. A simplified scheme of the kraft pulping process

The favourable reaction during kraft cooking is that lignin is degraded into smaller fragments and made more soluble, and finally dissolved in the cooking liquor. At the end of the kraft cook, more than 90% of the lignin in the wood material has been removed, although this depends on the cooking conditions applied. However, unfavourable reactions between carbohydrates and active cooking ions also occur: more than 20% of the carbohydrates, mainly hemicelluloses, are removed during softwood kraft cooking (Sjöström 1977).

2.3.2 Lignin and carbohydrate reactions

Lignin reactions

The various lignin reactions that occur during kraft cooking can be divided into two categories, namely degradation and condensation reactions. The former, which result in the cleavage of lignin structures, are desirable: the latter, which lead to the formation of alkali-stable linkages, are not (Sjöström 1993; Gullichsen et al. 2000). A large number of investigations regarding the reactions of lignin model compounds have clarified the features of the main chemical reactions (e.g. Gierer 1980; 1985) as being:

- Cleavage of the α and β-aryl ether bonds in phenolic structures
- Cleavage of the β-aryl ether bonds in non-phenolic structures
- Demethylation reactions
- Condensation reactions

The β-aryl ether bond is the dominant type of linkage in lignin structures in both softwoods and hardwoods. Cleavage of this linkage therefore contributes significantly to the degradation of lignin. The main cleavage routes are described schematically in Figures 2.7 and 2.8.

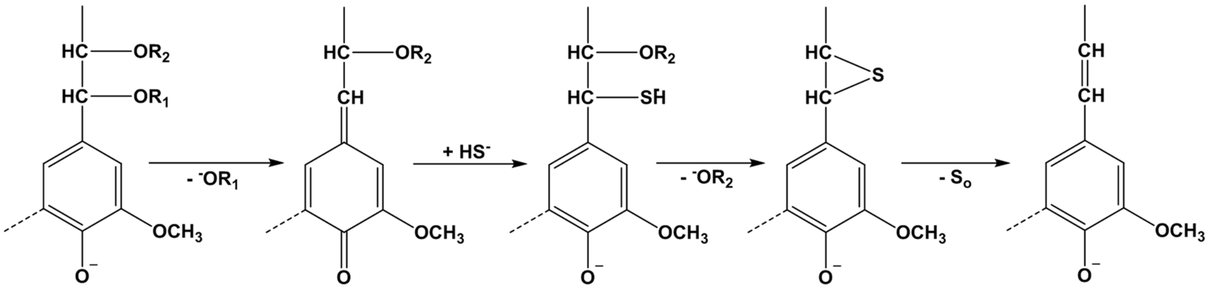

Figure 2.7. The cleavage routes of a β-aryl ether bond in phenolic structures under kraft cooking conditions (Gierer 1980; 1985).

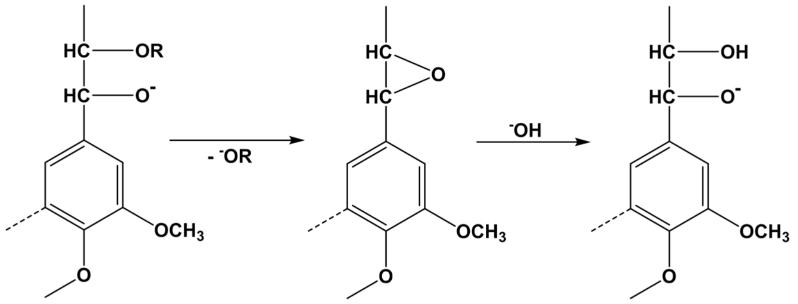

Figure 2.8. The cleavage routes of a β-aryl ether bond in nonphenolic structures under kraft cooking conditions (Gierer 1980; 1985).

Carbohydrate reactions

Two major carbohydrate reactions occur under kraft cooking conditions: peeling reactions and alkaline hydrolysis reactions (Sjöström 1993), as established by several studies (see e.g. Sjöström 1977; Knill, Kennedy 2003; Sixta 2006). Schematic diagrams of these can be seen in Figures 2.9 and 2.10, respectively.

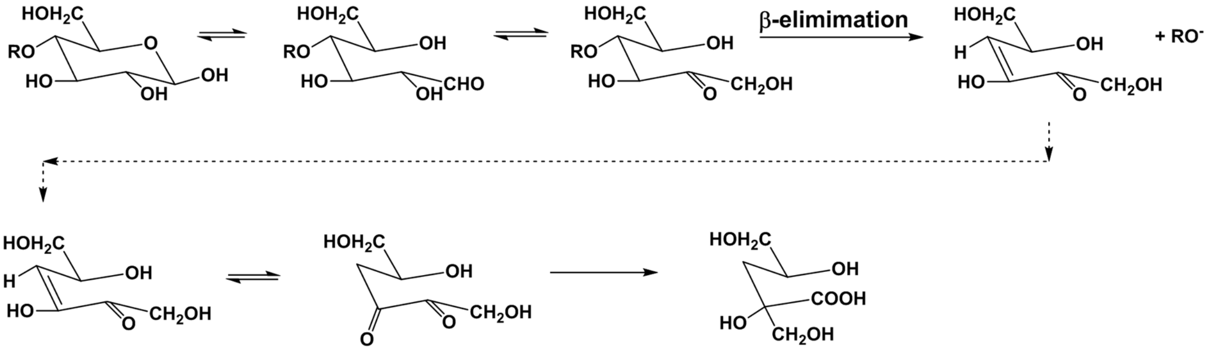

Figure 2.9. Mechanism of the peeling reaction under kraft cooking conditions (Sixta 2006).

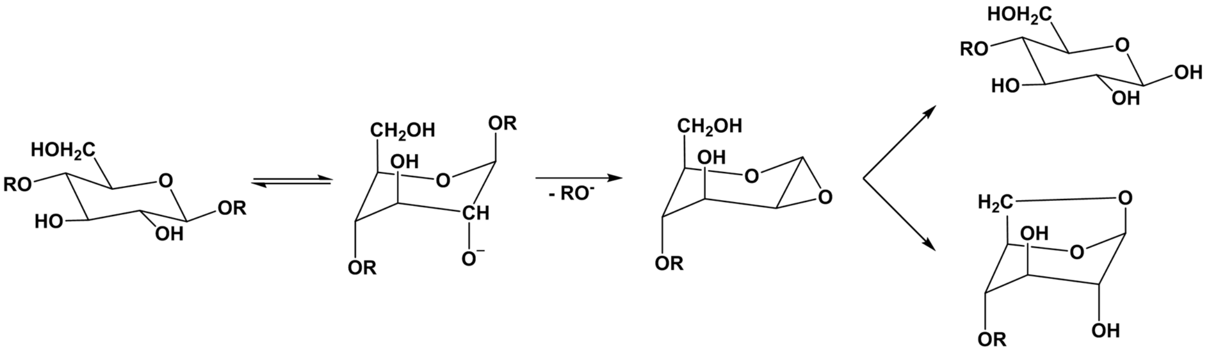

Figure 2.10. Alkaline hydrolysis under kraft cooking conditions, where R = cellulose chain (Sixta 2006).

2.4 Reaction kinetics of lignin

The most important stage of the kraft pulping process takes place in the digester, where lignin is degraded and dissolved. The reaction between the components of the wood and the active ions in the cooking liquor is a heterogeneous operation since wood chips are solid material. The active ions must therefore be transferred to reaction sites in the wood chips; the reaction products have to be transferred to the surface of the chips before diffusing into the cooking liquor. Consequently, the overall course of lignin and carbohydrate reactions in a two-phase solid/liquid system during a kraft cook can be described as following the following stages:

i. Mass transfer of active chemical ions from bulk phase to the surface of the wood chip
ii. Mass transfer of active chemical ions from the surface of the chip to the reaction sites (pore structure and cell wall)
iii. Reactions and dissolution of wood components
iv. Mass transfer of the dissolved wood components from the reaction sites to the surface of the chip
v. Mass transfer of the dissolved wood components from the surface of the chip to the bulk phase

The overall delignification operation is very complex due to the fact that wood is a very complex composite of different components having very different properties and reactivity. Several publications regarding the kinetics of the kraft delignification can be found in the literature. In one of the most common models, known as the “three phase model”, it has been assumed that the system is homogenous and, in most cases, the heating-up period has also been ignored. The three phase model consists of an initial phase, a bulk phase and a residual phase (e.g. Wilder, Daleski 1965; Kleinert 1966; Kleppe 1970; LéMon, Teder 1973; Teder, Olm 1981). The delignification has often been considered as being a first order reaction or close to first order, with respect to the remaining lignin content in wood (Wilder, Daleski 1965; Kleppe 1970; LéMon, Teder 1973; Teder, Olm 1981). In the rapid initial phase, approx. 15-25% of the lignin originally present in the wood is dissolved. The majority of the lignin, i.e. approx. 60-70%, is removed during the bulk phase and roughly 10-15% of the lignin reacts according to residual phase kinetics (Wilder, Daleski 1965; Gierer 1980; Chiang et al. 1990). Delignification during the residual phase of the kraft cook is slow and the selectivity is poor. Consequently, the kraft cook must be interrupted when the residual phase is reached in order to maintain a high level of yield and quality.

The overall reaction rate of delignification and the removal of carbohydrate observed do not depend on the reaction kinetics alone, as described above. The mass transport of the reacting chemicals, as well as the solubility and the mass transfer of the reaction products, influence the overall reaction rate, too (Bogren et al. 2007). The heat transfer and the temperature at the reaction site should also be taken into account when considering the overall delignification rate.

A significant number of publications dealing with how the overall delignification rate is influenced by the process conditions, such as cooking temperature, active ion concentrations and dimensions of the wood chips, can be found in the literature; a short summary of the influence of these variables follows.

2.4.1 Dimension of the wood chip

The overall reaction rate of the wood components during the kraft cook is influenced by transport steps involving both the active ions in the cooking liquor and reaction products. The importance of mass transport phenomena is reflected by the influence that the dimensions and shape of the wood chip have on the delignification rate. Several investigations dealing with the influence of the dimensions of the chip on the delignification rate in kraft cooking can be found in the literature (Larocque, Maass 1937; Hatton, Keays 1973; Hatton 1978; Akhtaruzzaman, Virkola 1979a, b, c; Akhtaruzzaman et al. 1980). Hatton and Keays (1973) reported that a chip thickness of 3 mm was the optimal size for kraft cooking. Akhtaruzzaman and Virkola (1979a) reported that the transport of chemicals into the wood chip is a combination of penetration and diffusion, and that the diffusion rate is almost the same in all three of the chip’s structural directions during kraft cooking. However, they found the thickness to be the most critical of the three dimensions with respect to delignification (Akhtaruzzaman, Virkola 1979a; b). An increase in the dimensions of the wood chip was seen to have a retarding effect on delignification, with the thickness having a more pronounced impact than the length (Akhtaruzzaman, Virkola 1979c). According to Akhtaruzzaman et al.

(1980), the rate of delignification in the bulk phase decreases significantly with increased thickness of the chip, while an increase in length has a relatively smaller influence.

2.4.2 Temperature

The dependence of the delignification rate on temperature during kraft cooking has been reported in a large number of publications: it has been shown that the delignification rate increases with a rise in cooking temperature (Lusby, Maass 1937; Wilder, Daleski 1965; Teder, Olm 1981; Gustafson et al. 1983; Chiang et al. 1990; Lindgren, Lindström 1996). The influence of the cooking temperature on the delignification rate is low in the initial part of the kraft cook (Kondo, Sarkanen 1984), becoming more pronounced in the main part of the cook (Wilder, Daleski 1965; Teder, Olm 1981; Chiang et al. 1990; Lindgren, Lindström 1996). This effect on the delignification rate in the latter part of the kraft cook seems to be lower than in the main part (Teder, Olm 1981).

2.4.3 Concentration of hydroxide ions

According to Lusby and Mass (1937), the concentration of hydroxide ions in the cooking liquor plays an important role in the removal of lignin. Wilder and Daleski (1965) reported that the rate of delignification in the initial phase of the kraft cook is almost unaffected by the concentration of hydroxide ions, but becomes more significant in the latter part (Wilder, Daleski 1965; Kleinert 1966; LéMon, Teder 1973; Chiang et al. 1990; Lindgren, Lindström 1996). It has been found that an increase in the concentration of hydroxide ions increases the delignification rate of the kraft cook (Bogren et al. 2007).

2.4.4 Concentration of hydrosulphide ions

The presence of hydrosulphide ions in the kraft cooking liquor enhances the degradation reaction rate of lignin (Sjöström 1993). The reaction path involving the breakage of the phenolic β-*O*-4 bond is fast (see Figure 2.7). The delignification rate in the main part of the kraft cook increases when the concentration of hydrosulphide ions in the cooking liquor is increased (LéMon, Teder 1973; Lindgren, Lindström 1996; Bogren et al. 2007). In the residual phase, on the other hand, the delignification rate of kraft cooking is almost unaffected by the concentration of hydrosulphide ions (Teder, Olm 1981; Lindgren, Lindström 1996).

2.4.5 Dissolved components of wood

The components of wood, i.e. lignin and carbohydrates, undergo chemical reactions during kraft cooking that lead to the formation of a large number of different organic compounds, referred to as dissolved wood components, in the cooking liquor. The influence these dissolved wood components have on the delignification rate has been investigated far less than the variables mentioned previously. It has been shown that dissolved wood components have a positive influence on the rate of delignification during the early part of the kraft cook and a negative effect during the latter part (Sjöblom 1996). Blixt and Gustavsson (2000) reported that the dissolved lignin has a positive influence on the delignification rate in the bulk phase in normal cooks. According to Sjödahl et al. (2004), the yield at a given kappa number increases when an addition of dissolved wood components (in the form of industrial black liquors) is made to a softwood kraft cook. During the main part of the kraft cook, the delignification rate increases as the concentration of the dissolved kraft lignin in the cooking liquor increases (Bogren et al. 2007).

2.4.6 Ionic strength/concentration of sodium ions

The industrial white liquor used in kraft cooking digesters is comprised of active ions (OH^- and HS^-) with sodium (Na^+) and potassium (K^+) as the counter ions; other anions commonly present are CO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$ and Cl^-. The impact of non-reacting ions is often referred to as effects caused by greater ionic strength, and is often measured as the concentration of sodium ions, $[Na^+]$. In laboratory investigations, sodium chloride is often used to achieve the industrial level of $[Na^+]$ even though only a minor amount of NaCl is present in industrial white liquors (Ulmgren 1997).

Several studies have reported that an increase in the ionic strength/sodium ion concentration has impacts on the delignification rate of the kraft cook (e.g. Lusby, Mass 1937; Lémon, Teder 1973; Teder, Olm 1981; Sjöström 1999; Sjödahl et al. 2004; Bogren et al. 2007; 2009b). LéMon and Teder (1973) reported that a decrease in ionic strength in the cooking liquor increases the delignification rate in the bulk phase of pine chips slightly. Moreover, the rate of delignification in the final residual phase has been found to decrease as the concentration of sodium ions in the cooking liquor increases (Teder, Olm 1981). According to Gustavsson et al. (1997), an increase in ionic strength leads to an increase in the residual phase lignin in the kraft cooking of spruce chips. Furthermore, Bogren et al. (2009b) reported that additions of different inactive sodium salts (i.e. sodium salts with anions that do not react with the constituents of wood) have different impacts on the kinetics of kraft cooking: the addition of NaCl, Na_2CO_3 and Na_2SO_4 were all seen to retard the delignification rate, with NaCl having the greatest effect. The dissolution rate of xylan decreases when the ionic strength is increased (Gustavsson, Al-Dajani 2000; Jansson, Bränvall 2011), while the degradation rate of cellulose and glucomannan is not affected by ionic strength (Gustavsson, Al-Dajani 2000).

An increase in ionic strength has been found to promote the aggregation of lignin molecules (Lindström 1979; Garver, Callaghan 1991). It has been shown that the aggregation of kraft lignin in alkaline solutions containing high concentrations of sodium chloride increases when the temperature is increased (Norgren et al. 2001). Furthermore, results show that concentrations of hydroxide ions and metal ions affect the stability of kraft lignin solutions under cooking conditions (Norgren et al. 2002). These findings could, at least partly, explain why a higher ionic strength during the kraft cook, i.e. a higher concentration of sodium ions, requires a higher H-factor (a higher temperature or a prolonged cooking time) to reach a certain kappa number. According to Bogren et al. (2009b), the main reason for the decrease in delignification rate at high ionic strength is that the solubilization of lignin fragments decreases with increasing ionic strength in the kraft cook, especially when the concentration of hydroxide ions becomes low at the end of the cook.

2.5 Hexenuronic acids

The formation and degradation of hexenuronic acids (HexA) in kraft pulps has been an important issue in the pulp industry. The formation of HexA leads to an increase in chemical consumption in the bleaching stages. Several investigations have been conducted to study the formation and degradation of HexA during kraft cooking of different wood materials (Clayton 1963; Johansson, Samuelson 1977; Buchert et al. 1995; Teleman et al. 1995; Gustavsson, Al-Dajani 2000; Bogren et al. 2008; Bogren et al. 2009b). It has been proposed that the formation and degradation of HexA are affected by the cooking temperature as well as the concentration of hydroxide and hydrosulphide ions. Ionic strength has been reported to have a certain impact on the formation and degradation of HexA (Gustavsson, Al-Dajani 2000; Bogren et al. 2008; Bogren et al. 2009b). Gustavsson and Al-Dajani (2000) showed that the degradation rate of HexA increases at higher ionic strength. Bogren et al. (2008 and 2009b) showed that the rates of both formation and degradation increase at higher ionic strengths. The given main explanation for the increase in reaction rates is that a higher [Na^+] in the cooking liquor increases the concentration of hydroxide ions in the fibre wall in accordance to the Donnan equilibrium theory.

3. Materials and Methods

3.1 Materials

Sapwood meal of Scots pine (*Pinus silvestris*) was used as the substrate for all cooking experiments and was produced in a Wiley mill equipped with a sieve (<1mm). The wood meal was stored at room conditions before cooking in order to maintain a uniform moisture content: its dry content was approx. 92%.

3.2 Experiments

3.2.1 Equipment

A small-scale flow-through reactor was employed to perform all cooking experiments during which the composition of the cooking liquor could be altered at a maintained cooking temperature. A schematic diagram of the flow-through reactor is presented in Figure 3.1. The flow-through reactor was a column (300x7.8mm ID, SS) with coils of piping both before the inlet and after the outlet for heating and cooling the liquor, respectively (Figures 3.1 and 3.2). The cooking liquor was pumped through the reactor by a high pressure pump; a valve was used at the end of the system to control the pressure (cf. Borgen et al. 2009a).

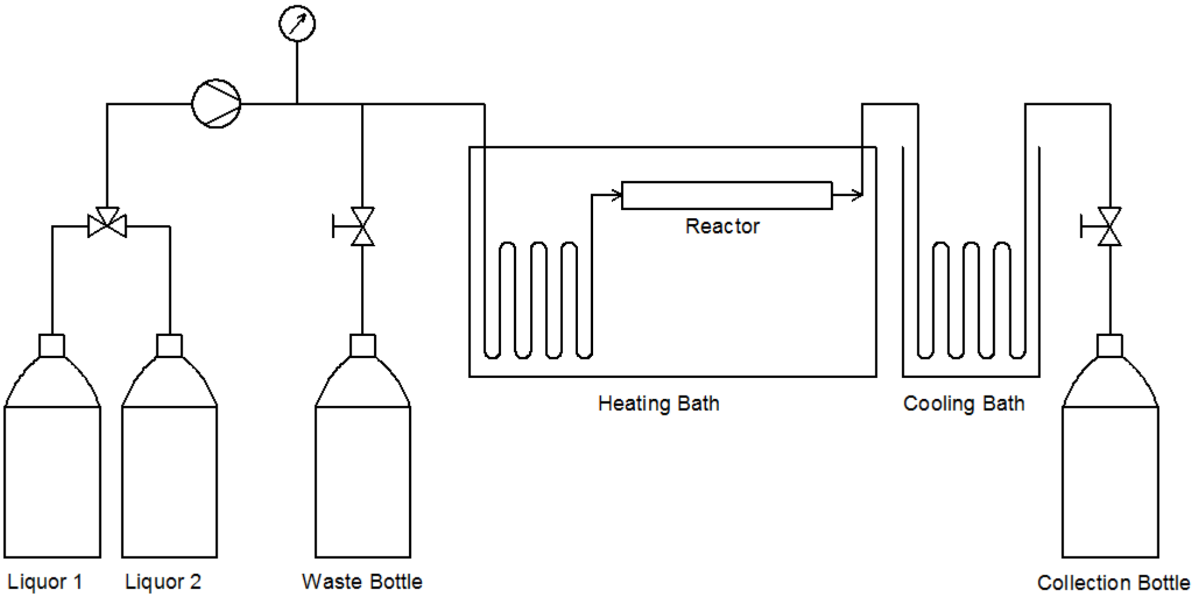

Figure 3.1. A schematic diagram of the small-scale flow-through reactor used

Figure 3.2. Image of the small-scale flow-through reactor used

3.2.2 Cooking liquors

In this study, the cooking liquors were prepared from analytical grade Na_2S which was dissolved in deionized water. Either sodium carbonate or sodium chloride was added to the cooking liquor when the concentration of sodium ions was to be controlled. The concentration of sodium ions in the cooking liquor was varied between 0.52 and 3.00 mol/kg solvent; the concentrations of hydroxide and hydrosulphide ions were set to 0.26 mol/kg solvent and kept constant during all kraft cooks.

3.2.3 Cooking experiments

Approximately 4 g (dry weight) of wood meal was put in the small-scale flow-through reactor and packed carefully to ensure the flow rate through the bed that was thus formed was even. The cooking liquor was pumped continuously through the reactor during the cooking process. The cooking liquor (approx. 3-4 free column volumes) was pumped through the reactor at room temperature before cooking began in order to ensure good impregnation. The flow rate was set to 10 ml/min during the first 12 min of cooking. It was then lowered to 8 ml/min and, after 22 min of cooking, set to 2.5 ml/min. This procedure was used to minimize the change in $[OH^-]$ during the initial phase of the kraft cook, where the alkali consumption is relatively fast. After 10 min of cooking, the level of $[OH^-]$ in the outlet of the column had decreased by approx. 20%: after 15 min of cooking and onward, it was virtually the same in both the outlet and the inlet (cf. Borgen et al. 2009a). The temperature was set to 115˚C at the beginning of the cook and then increased to a maximum cooking temperature, which was kept constant during the rest of the cook, see Figure 3.3.

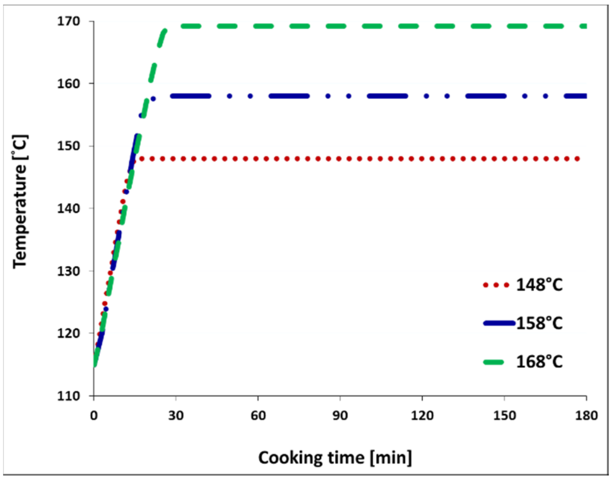

Figure 3.3. Temperature profiles during the kraft cooking experiments

The experiments were divided into two parts. In the first, trials were performed in which the concentration of the sodium ions was kept constant during cooking at three levels of concentration (0.52, 2.00 and 3.00 mol/kg solvent) at the three maximum temperatures 148˚C, 158˚C and 168˚C. The concentration of sodium ions was adjusted by adding either Na_2CO_3 or NaCl. In the second part, experiments were conducted at a maximum temperature of 158˚C and the concentration of the sodium ions was varied during cooking, which was done by taking two different routes, see Figures 3.4 A and B. The $[Na^+]$ was changed at two different points during the cooking process: the first took place after 30 min and the second after 60 min. In the latter, the $[Na^+]$ was varied between 0.52 and 3.00 mol/kg solvent during kraft cooking and adjusted by the addition of Na_2CO_3. The experimental conditions employed are shown in Table 3.1.

Table 3.1 Cooking conditions used in the two experimental series with constant and varied amounts of $[Na^+]$.

Series	**Initial compositions mol/kg solvent**			**Temperature (°C)**	**Salts added**	**Exchanged time (min)**	**$[Na^+]$ mol/kg solvent**
	$[OH^-]$	**$[HS^-]$**	**$[Na^+]$**				
$[Na^+]$ const.							
S1 - LLL	**0.26**	**0.26**	**0.52**	**158°C**	**No**	**-**	**-**
S2 - MMM	**0.26**	**0.26**	**2.00**	**158°C**	**Na_2CO_3**	**-**	**-**
S3 - HHH	**0.26**	**0.26**	**3.00**	**158°C**	**Na_2CO_3**	**-**	**-**
S4 - MMM	**0.26**	**0.26**	**2.00**	**158°C**	**NaCl**	**-**	**-**
S5 - HHH	**0.26**	**0.26**	**3.00**	**158°C**	**NaCl**	**-**	**-**
S6 - LLL	**0.26**	**0.26**	**0.52**	**148°C**	**No**	**-**	**-**
S7 - LLL	**0.26**	**0.26**	**0.52**	**168°C**	**No**	**-**	**-**
$[Na^+]$ varied							
S8 - LHH	**0.26**	**0.26**	**0.52**	**158°C**	**Na_2CO_3**	**30**	**0.52→3.00**
S9 - LHL	**0.26**	**0.26**	**0.52**	**158°C**	**Na_2CO_3**	**30;60**	**0.52→3.00→0.52**
S10 - HLL	**0.26**	**0.26**	**3.00**	**158°C**	**Na_2CO_3**	**30**	**3.00→0.52**
S11 - HLH	**0.26**	**0.26**	**3.00**	**158°C**	**Na_2CO_3**	**30;60**	**3.00→0.52→3.00**

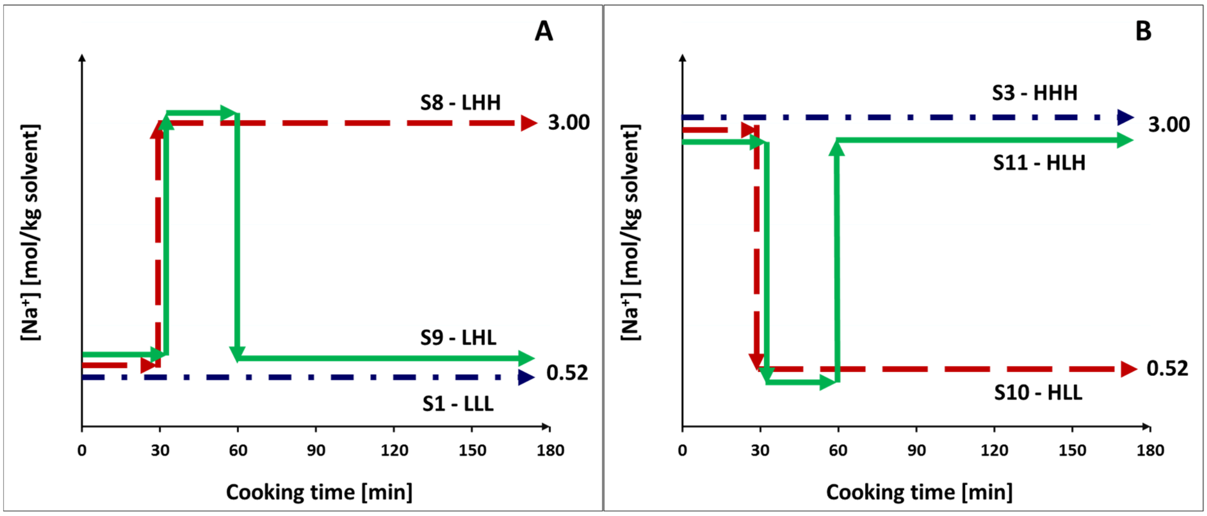

Figure 3.4. Profiles of the concentration of sodium ions in the second part of the experiments. L = low level of $[Na^+]$ (0.52 mol/kg solvent) and H = high level of $[Na^+]$ (3.00 mol/kg solvent).

Wood residues (WR)

The experiment was halted after a pre-determined cooking time and the solid wood residues were suspended in approx. 300 ml de-ionized water, dewatered in a glass filter and washed with approx. 700 ml de-ionized water. The wood residue was then dried in an oven at a temperature of 105˚C to obtain constant weight.

Black liquors (BL)

Eight fractions of BL of some kraft cooks were collected as a function of cooking time (0-10, 10-20, 20-40, 40-60, 60-90, 90-120, 120-150 and 150-180 min) during flow-through kraft cooking.

Lignin precipitated from black liquors

Some cooking series were selected to isolate lignin dissolved in black liquors. Lignin dissolved in the black liquor fractions was separated by acid precipitation, using sulphuric acid (95-97% w/w), at a pH of 2.5 at room temperature and the sample was agitated. The resulting suspensions were placed in a freezer at -18˚C and left overnight. Once the suspensions had been thawed at room temperature, the precipitated lignin in the samples was collected by filtration on a glass filter, subsequently washed with approx. 100 ml of acidic water at a pH of 2.5 and then dried in a desiccator containing P_2O_5 at 50˚C for a period of 24 h.

3.3 Analytical methods

3.3.1 Wood residues (Papers I-II)

The samples of solid wood residues taken after the cooking experiments were analysed for yield, Klason lignin content, acid-soluble lignin, carbohydrate composition and HexA content.

Lignin content

The Klason lignin content was determined by using acid precipitation and hydrolysis according to Theander and Westerlund (1986). Approx. 200 mg (dry weight) of wood residues was weighed and mixed with 3 ml H_2SO_4 72% in a glass tube (125 ml). The mixture was stirred for a few minutes with a round glass rod and evacuated for 15 min. The sample was kept at 30˚C in a water bath for 60 min before 84 gram deionised water was added and the sample was placed in an autoclave at 125°C for 60 min. Following hydrolysis, the slurry was filtered and the resulting filtrate was diluted up to 100 ml in a volumetric flask. The solid residue remaining after filtration and drying, denoted as Klason lignin, was measured gravimetrically.

The acid-soluble lignin content in the filtrate was measured using UV spectroscopy at a wavelength of 205 nm. The content was calculated by assuming an absorptivity constant of 110 $dm^3\ g^{-1}\ cm^{-1}$ (Lin, Dence 1992).

Carbohydrate content

The carbohydrate composition of wood residues was determined by analysis of the filtrate obtained after the acid hydrolysis, see above. The filtrate after hydrolysis was diluted and fucose was added as an internal standard for the following analysis. The concentrations of neutral monosaccharides in the filtrate were analysed by using a high-performance anion exchange chromatography instrument (CarboPac^{TM} PA1 column, Dionex, Sunnyvale, CA, USA) with pulsed amperometric detection. The data was evaluated using the software Star Chromatography Workstation, System Control Vers. 5.50 (Varian). The contents of xylan, glucomannan and cellulose were calculated from the carbohydrate analysis using the assumptions and corrections presented by Wigell et al. (2007), see Appendix B.

HexA content

The content of HexA in wood residues was determined by using a mild acid hydrolysis (Jiang el al. 2001). The sample (approx. 0.5 mg dry weight of the wood residues) was mixed with 30 ml acid solution (H_2SO_4) at pH of 1.5. The sample was evacuated for 30 min before being put into an autoclave at 125°C for 120 min. After hydrolysis, the sample was filtered and the resulting filtrate diluted up 100 ml in a volumetric flask. The HexA content was measured by analysing the degradation products, 5-formyl-2-furoic acid and 2-furoic acid, that were obtained after acid hydrolysis (cf. Bogren et al. 2008).

3.3.2 Black liquors (Paper IV)

Samples of BL fractions taken from some of the cooking series were analysed for carbohydrate content using acid hydrolysis (Theander, Westerlund 1986). The filtrate obtained after acid hydrolysis was diluted and fucose was added as an internal standard for the following analysis.

Chromatographic separation, using high performance anion exchange chromatography with pulse amperometric detection (HPAEC-PAD) and a gold reference electrode, was used to determine the concentrations of neutral monosaccharides. The analyses were carried out on a Dionex ICS-5000 HPLC system equipped with Dionex CarboPac PA1 columns (guard column 2x50 mm, pre-column 2x50 mm and separation column 2x250 mm). The software used for analysing the data was Chromeleon 7, Chromatography Data System software, Vers. 7.1.0.898.

3.3.3 Lignin (Papers III-IV-V)

Molecular weight distribution (MWD)

The samples of preciptated and dried lignin were dissolved in dimethyl sulphoxide (DMSO) containing 10 mM LiBr, and the molecular weight distribution was determined by a gel permeation chromatography (GPC) system (PL-GPC 50 Plus Integrated instrument system equipped with both RI and UV detection, Polymer Laboratories, Varian Inc.). Two PolarGel-M columns (300x7.5 mm) and a PolarGel-M guard column (50x7.5 mm) were employed. DMSO containing 10 mM LiBr was used as an eluent. The flow rate was 0.5 ml/min and the separation was carried out at 50°C. The calibration was performed by means of ten pullulan standards with an M_w of 708, 375, 200, 107, 47.1, 21.1, 11.1, 5.9, 0.667 and 0.180 kDa. Data was evaluated using the software Cirrus GPC Vers. 3.2.

Carbohydate analysis

The carbohydrate composition of the precipitated lignin samples were analysed after acid hydrolysis (Theander, Westerlund 1986). The filtrate after acid hydrolysis was diluted and fucose was added as an internal standard for the following analysis. Chromatographic separation, using high-performance anion exchange chromatography with pulse amperometric detection (HPAEC-PAD) and a gold reference electrode was used to determine the relative compositions of sugars. The analyses were performed on a Dionex ICS-5000 HPLC system equipped with Dionex CarboPac PA1 columns (guard column 2x50 mm, pre-column 2x50 mm and separation column 2x250 mm). The software used for analyzing data was Chromeleon 7, Chromatography Data System software, Vers. 7.1.0.898.

Nuclear magnetic resonance (NMR)

Five precipitated and dried samples of lignin (0-10, 10-20, 20-40, 40-60 and 60-90 min) collected from the reference cooking series ($[Na^+]$ = 0.52 mol/kg solvent) were analyzed by ^{13}C and ^{1}H NMR spectroscopy. These samples were dissolved in DMSO-d_6, with 1 drop of pyridine-d_5 being added to the sample (60-90 min) in order to obtain a homogenous solution. Experimental setups and instrumentations are described in detail in the appended paper (Paper V).

3.4 Kinetic model describing the formation and degradation of HexA

The model presented by Bogren et al. (2008) describing the change in the content of 4-*O*-methylglucuronic acids (MeGlcA) and HexA during kraft cooking was used in the present work. It assumes that the degradation of MeGlcA proceeds via the formation of HexA which, in turn, is removed from the xylan backbone (Johansson, Samuelson 1977; Bogren et al. 2008). Furthermore, the model assumes that MeGlcA is distributed homogeneously along the xylan backbone, which has been shown to be the case for softwood xylan (Lindquist, Dahlman 1998). For more details of the model, see Appendix C.

4. Results and Discussion

4.1 Initial cooking trials at different temperatures

Flow-through kraft cooking trials at three different levels of temperature were performed in the small-scale flow-through reactor. The concentrations of hydroxide and hydrosulphide ions were set to 0.26 mol/kg solvent. The [OH^-] may be considered to be on the lower side if one compares with industrial conditions. However, the [OH^-] drops rapidly at the beginning of the kraft cook in industrial cooking, whereas the decrease in [HS^-] is not that large (Sjöström 1993). This means that the concentrations of hydroxide and hydrosulphide ions are often on similar levels during the majority of the kraft cook.

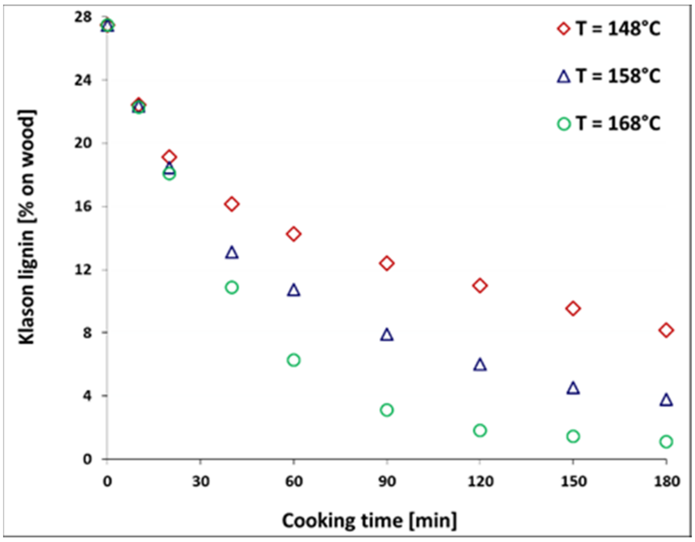

Figure 4.1. Klason lignin content of the wood residues vs. cooking time of kraft cooks performed in the small-scale flow-through reactor at different temperatures. [OH^-] = 0.26 mol/kg solvent; [HS^-] = 0.26 mol/kg solvent; [Na^+] = 0.52 mol/kg solvent (without the addition of surplus sodium salts).

Figure 4.1 shows the Klason lignin content of the wood residues versus cooking time. As expected, the results obtained show that the kraft delignification rate has a strong dependence on temperature. It should be noted that during the period of time in which the temperature was raised to a pre-determined cooking temperature (up to about 20 min of cooking, see Figure 3.3), the degree of delignification rate was quite similar at the three different levels of temperature (Figure 4.1).

These first trials showed that the experimental procedure could be considered as giving consistent results. Furthermore, it was decided that the cooking temperature in the further trials should be set to 158°C, the cooks performed with constant levels of $[OH^-]$ and $[HS^-]$ (0.26 mol/kg solvent), and focus placed on the impact of Na_2CO_3 and NaCl on the course of kraft cooking.

4.2 Ionic concentrations of cooking liquors and fibre walls

Wood meal was digested in the small-scale flow-through reactor in which the particles of wood are assumed to be surrounded by liquid with a constant concentration of ions. The cooking liquor used had the same concentrations of $[OH^-]$ and $[HS^-]$ at different levels of $[Na^+]$, which was controlled by the addition of either Na_2CO_3 or NaCl. As maintained by the Donnan equilibrium theory, an increase in the concentration of sodium ions in the cooking liquor will lead to an increase in the concentration of anions in the fibre wall (Pu, Sarkanen 1991; Motomura et al. 1998; Bogren et al. 2008). In this investigation, the concentration of ions in the fibre wall phase was calculated as a function of the concentration of these ions in the liquor by applying the Donnan equilibrium theory. According to the findings of Bogren et al. (2008), the concentration of fixed anionic charges in the fibre wall polymers was set to 1.06 mol/kg fibre wall solvent. The concentration of ions in the cooking liquor and those calculated in fibre wall phase are presented in Table 4.1 (see Appendix A for the calculation procedure).

Table 4.1 shows that the concentrations of hydroxide and hydrosulphide ions in the fibre wall increase considerably when the $[Na^+]$ in the cooking liquor is increased from 0.52 to 2.00 mol/kg solvent for both cases (CO_3^{2-} and Cl^-), but that there is only a minor increase in the concentration of these ions when $[Na^+]$ increases from 2.00 to 3.00 mol/kg solvent. However, there is a significant increase in ionic strength in the fibre wall phase. The ionic strength in the fibre wall will be on a higher level when sodium ions are added in the form of Na_2CO_3 than of NaCl. The estimated data in Table 4.1 also indicates that the divalent ions (CO_3^{2-}) give a somewhat higher concentration of $[OH^-]$ and $[HS^-]$ in the fibre wall phase than monovalent ions (Cl^-). Although the data in Table 4.1 is a relatively rough estimation, it indicates the relative differences between the various cases.

Table 4.1. Estimated concentrations of the diffusible ions in the liquor and fibre wall phases

Bulk phase mol/kg solvent				**Fibre phase mol/kg solvent**				
$[Na^+]_{Bulk}$	$[OH^-]_{Bulk}$	$[HS^-]_{Bulk}$	$[CO_3^{2-}]_{Bulk}$	$[Na^+]_{Fibre}$	$[OH^-]_{Fibre}$	$[HS^-]_{Fibre}$	$[CO_3^{2-}]_{Fibre}$	I_{Fibre}*
0.52	0.26	0.26	0.00	1.28	**0.11**	0.11	0.00	**0.75**
2.00	0.26	0.26	0.74	2.46	**0.21**	0.21	0.49	**2.42**
3.00	0.26	0.26	1.24	3.42	**0.23**	0.23	0.95	**3.84**
$[Na^+]_{Bulk}$	$[OH^-]_{Bulk}$	$[HS^-]_{Bulk}$	$[Cl^-]_{Bulk}$	$[Na^+]_{Fibre}$	$[OH^-]_{Fibre}$	$[HS^-]_{Fibre}$	$[Cl^-]_{Fibre}$	I_{Fibre}**
0.52	0.26	0.26	0.00	1.28	**0.11**	0.11	0.00	**0.75**
2.00	0.26	0.26	1.48	2.60	**0.20**	0.20	1.14	**2.07**
3.00	0.26	0.26	2.48	3.58	**0.22**	0.22	2.08	**3.05**

* Estimated ionic strength in the fibre wall phase: $I_{Fiber} = ½ ([OH^-]_{Fibre} + [HS^-]_{Fibre} + [Na^+]_{Fibre} + 4*[CO_3^{2-}]_{Fibre})$

** Estimated ionic strength in the fibre wall phase: $I_{Fiber} = ½ ([OH^-]_{Fibre} + [HS^-]_{Fibre} + [Na^+]_{Fibre} + [Cl^-]_{Fibre})$

Figure 4.2 shows the pulp yield versus the degree of delignification at different concentrations of sodium ions in kraft cooks of Scots pine performed in the small-scale flow-through reactor. As can be seen in Figure 4.2A, the pulp yield at a certain degree of delignification is not affected very much by the ionic strength/sodium ion concentration in the cooking liquor, or by variations in the concentration profile of the sodium ions during flow-through kraft cooking as shown in Figure 4.2B. This result could lead to the conclusion being drawn that the relatively large effects the addition of inactive ions, in the form of Na_2CO_3 and NaCl, have on the ionic strength and alkalinity of the fibre wall (see Table 4.1) do not affect the overall reaction pattern during cooking. However, as will be shown in the following parts of this work, the ionic strength of the cooking liquor is in fact a major influential factor with respect to certain aspects of behaviour of the wood polymers during kraft pulping and kraft cooking kinetics.

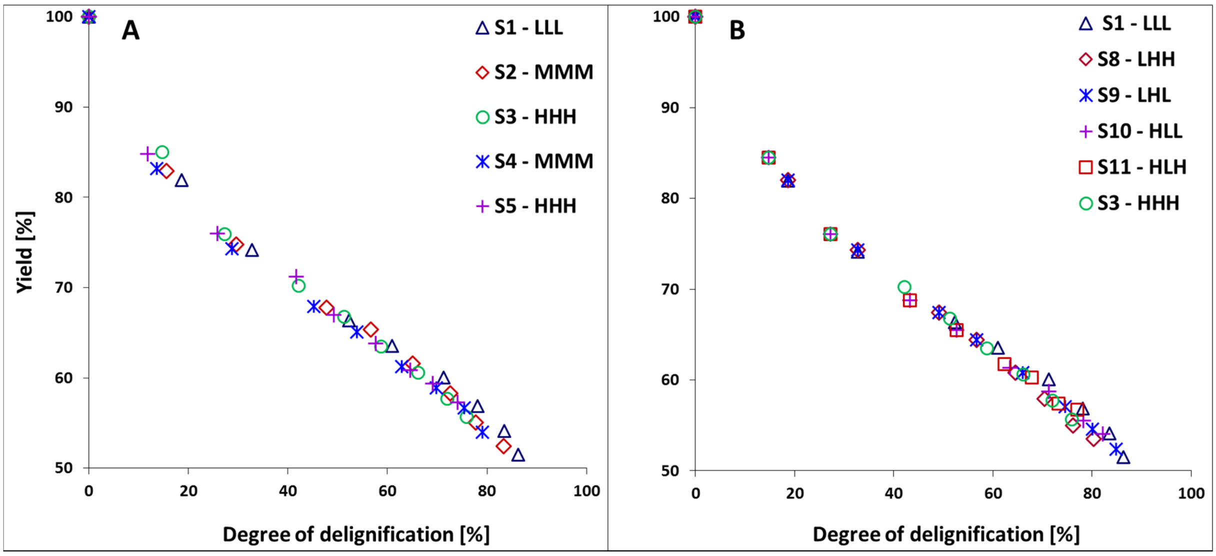

Figure 4.2. Pulp yield vs. degree of delignification of the kraft cooks performed in the small-scale flow-through reactor. [OH$^-$] = 0.26 mol/kg solvent; [HS$^-$] = 0.26 mol/kg solvent; T = 158°C; L = low level of [Na$^+$] (0.52 mol/kg solvent); M = middle level of [Na$^+$] (2.00 mol/kg solvent); H = high level of [Na$^+$] (3.00 mol/kg solvent).

4.3 Formation and degradation of HexA

The 4-*O*-methylglucuronic acid groups (MeGlcA) present as substituents along the xylan chains undergo reactions to form hexenuronic acid side groups (HexA) under alkaline cooking conditions. The HexA groups formed are removed gradually from the xylan backbone since they are alkali-labile (e.g. Clayton 1963; Johansson, Samuelson 1977; Buchert et al. 1995; Teleman et al. 1995). The rates of formation and degradation of HexA have been shown to be affected strongly by temperature, the alkalinity of the cooking liquor and ionic strength (Bogren et al. 2008).

Figure 4.3 illustrates the influence of different levels of [Na$^+$] on the formation and degradation of HexA during flow-through kraft cooking. The experimental data of the HexA content in xylan (symbols) is shown, along with lines representing the results acquired from calculations of the contents of MeGlcA and HexA. The lines are obtained by using a model describing the kinetics of the formation and degradation of HexA as described by Bogren et al. (2008) in combination with the experimental values of the HexA content of the S1, S2, S3, S4 and S5 series. Despite the fact that this model is relatively simple, it predicts the trends of the contents of MeGlcA and HexA quite well (Paper I).

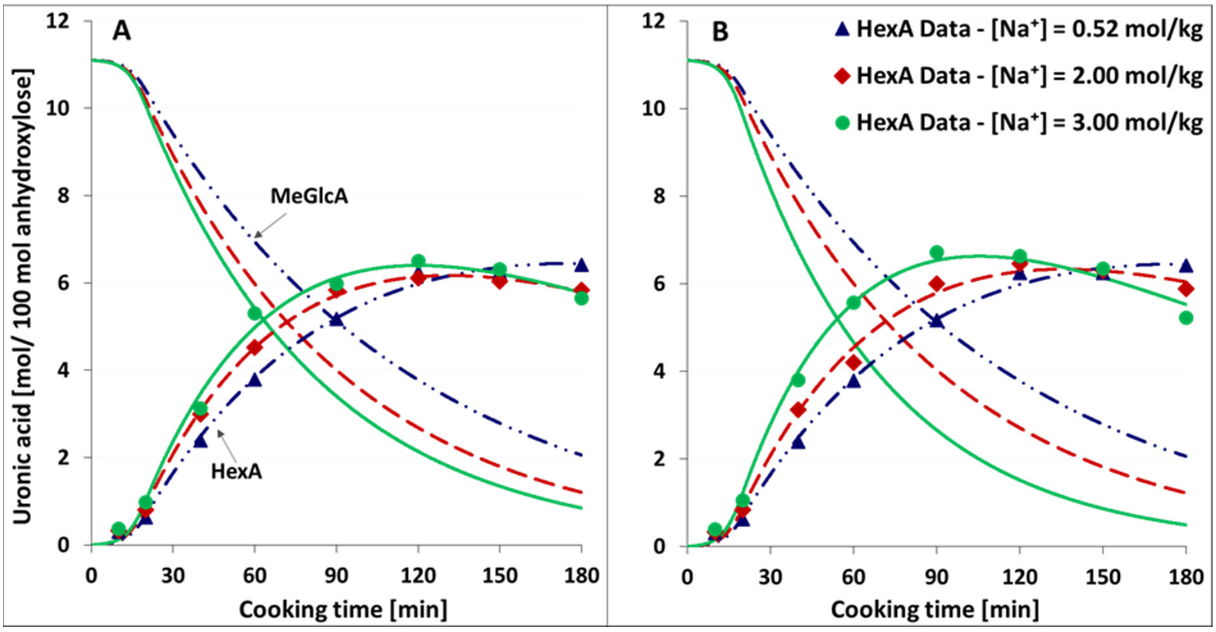

Figure 4.3. The effects additions of sodium salts have on MeGlcA and HexA in xylan during flow-through kraft cooking: A) Na_2CO_3; B) NaCl. The predicted content of MeGlcA is included in the figures. The lines correspond to the modelled content of HexA and MeGlcA. $[OH^-]$ = 0.26 mol/kg solvent; $[HS^-]$ = 0.26 mol/kg solvent; T=158°C.

The rates of transformation of MeGlcA into HexA increased when the $[Na^+]$ in the cooking liquor was increased, as can be seen in Figure 4.3; a similar tendency was observed for the additions of both Na_2CO_3 and NaCl. Bogren et al. (2008) suggested that the reason for the increase in reaction rates is due mainly to the increase in the concentration of $[OH^-]$ in the fibre wall at higher levels of $[Na^+]$ because of the Donnan equilibrium effect as described in Table 4.1 (cf. Pu, Sarkanen 1991; Motomura et al. 1998).

In the second part of the experiments, the $[Na^+]$ profile was changed at a certain time during the cooking process; the influences these variations had on the HexA content of the wood residues are shown in Figure 4.4. Here, series S8-LHH, S9-LHL, S10-HLL and S11-HLH, in which the profile of $[Na^+]$ in the cooking liquor was varied during flow-through kraft cooking (see also Figure 3.4), are compared with series S1-LLL and S3-HHH, where the $[Na^+]$ was kept at a constant level throughout the entire cook. In this part, the lines shown in Figure 4.4

representing the modelled content of HexA were obtained from the model as described above. The model was fitted to the experimental values of the HexA content in order to estimate the parameters K_1 and K_2 in the model, see Appendix C. The parameters were estimated using 36 experimental data points obtained from 36 individual kraft cooks from the S1, S3, S8, S9, S10 and S11 series; the temperature rise was also taken into account (Paper II).

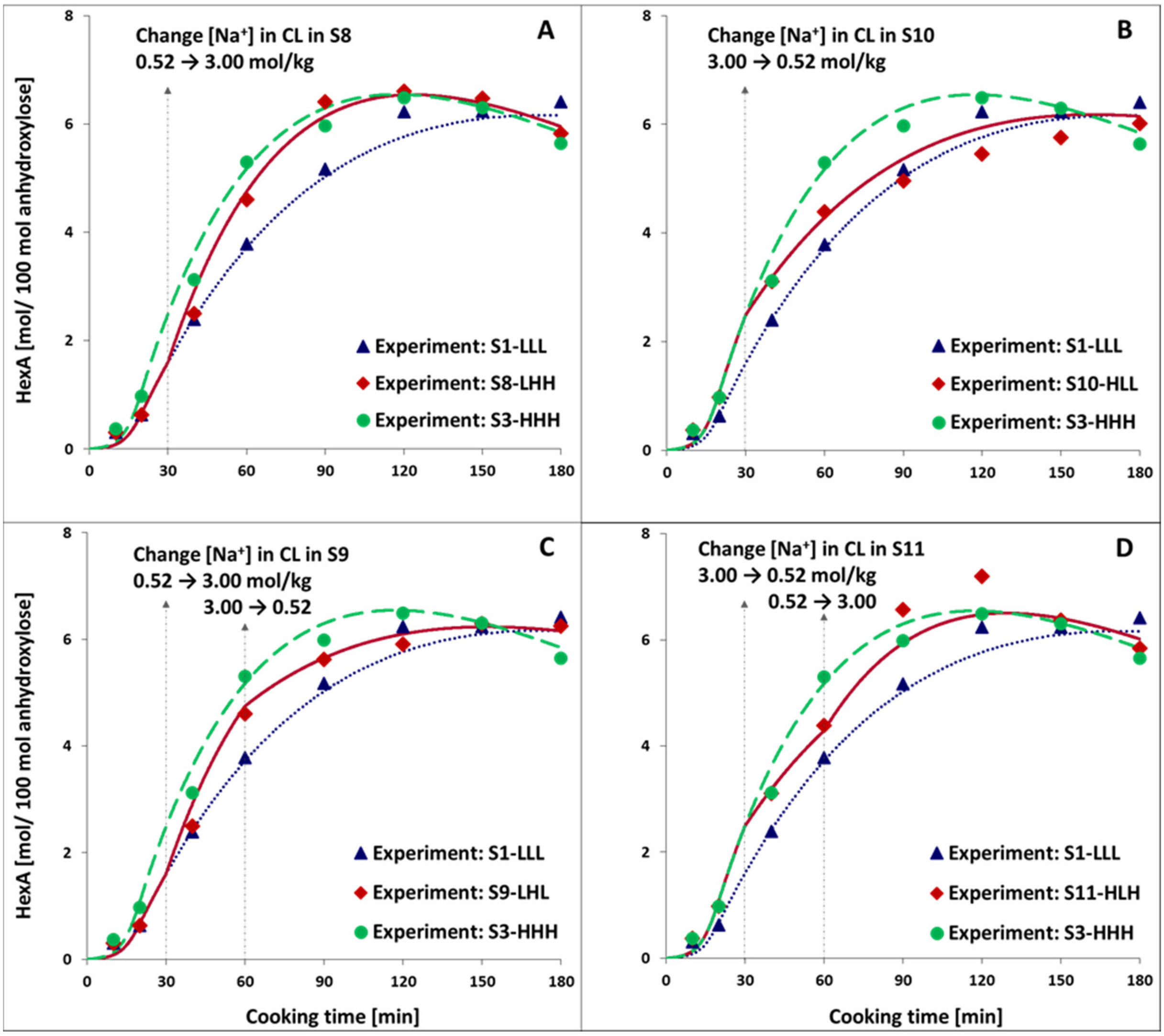

Figure 4.4. The effects that varying [Na^+] have on the content of HexA in xylan during flow-through kraft cooking, [OH^-] = 0.26 mol/kg solvent; [HS^-] = 0.26 mol/kg solvent; T=158°C. The lines correspond to the modelled contents of HexA. [Na^+] concentration was controlled by addition of Na_2CO_3. L = low level of [Na^+] (0.52 mol/kg solvent); H = high level of [Na^+] (3.00 mol/kg solvent).

A comparison of the experimental data and the model shown in Figure 4.4 indicates that the reaction kinetics of HexA adapt to the variations of [Na^+] in the cooking liquor. Bogren et al. (2008) suggested that the reaction rate of HexA reflects the [OH^-] at the reaction sites in the fibre wall. The rapid response in the formation and degradation of HexA when the profiles of [Na^+] were varied during the flow-through kraft cook therefore indicate a fast change in [OH^-] in fibre wall due to changes in the [Na^+] in the cooking liquor.

4.4 Influence of sodium ion concentration on lignin and carbohydrates

4.4.1 Klason lignin in wood residues and molecular weight distribution of dissolved lignin

The dependence on [Na^+] of the delignification rate and the M_w of the dissolved lignin precipitated from BL during flow-through kraft cooking is shown in Figures 4.5 and 4.6, respectively. It is evident that the [Na^+] in the cooking liquor has a significant impact on both the content of Klason lignin in the wood residues and the M_w of lignin dissolved in BL. An increase in the [Na^+] of the cooking liquor leads to a large decrease in the overall delignification rate as well as a decrease in the molecular weight of the dissolved lignin. The effect on the M_w of the dissolved lignin is more pronounced at the end of the kraft cook (Figure 4.6).

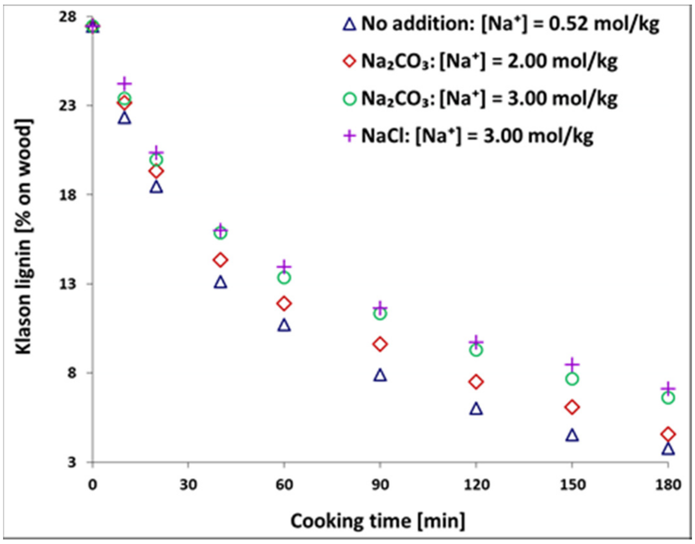

Figure 4.5. The effect [Na^+] has on the content of Klason lignin in wood residues during flow-through kraft cooking. [OH^-] = 0.26 mol/kg solvent; [HS^-] = 0.26 mol/kg solvent; T = 158°C.

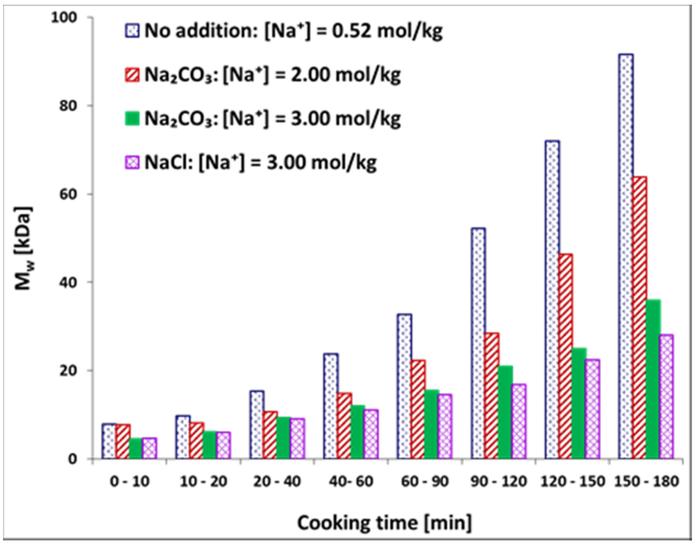

Figure 4.6. The effect of [Na^+] on the M_W of the lignin dissolved in BL during flow-through kraft cooking. [OH^-] = 0.26 mol/kg solvent; [HS^-] = 0.26 mol/kg solvent; T = 158˚C.

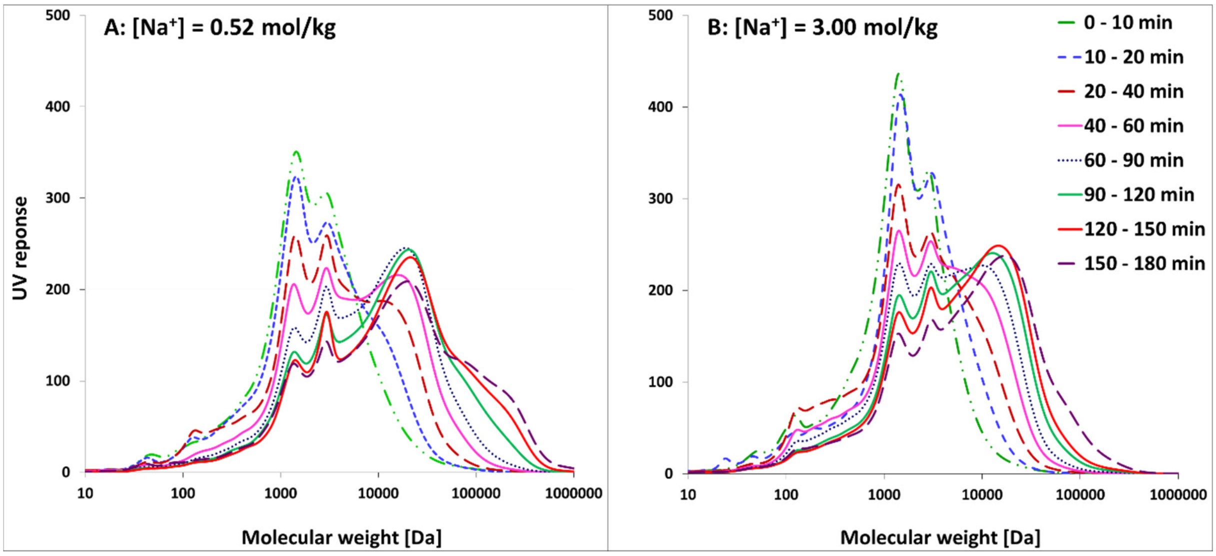

Figure 4.7. Chromatograms of the two series at constant levels of [Na^+] during flow-through kraft cooking. [OH^-] = 0.26 mol/kg solvent; [HS^-] = 0.26 mol/kg solvent; T = 158˚C. [Na^+] was controlled by the addition of Na_2CO_3. The data has been baseline corrected.

MWD profiles of the dissolved lignin samples precipitated from BL, obtained from two cooking series at a constant [Na^+] during kraft cooking, are shown in Figure 4.7. As can be seen from Figures 4.6 and 4.7, the molecular weight of the dissolved lignin fractions increases with increasing cooking time: this result is in agreement with earlier publications (McNaughton et al. 1967; Gellerstedt, Lindfors 1984; Robert et al. 1984; Sjöholm et al. 1999a, b; Pakkanen, Alén 2012). It is obvious that there is a clear shift towards a larger molecular weight with increasing cooking time, and that the fractions of dissolved lignin with a low M_w gradually decrease while those with a larger M_w increase. The wide distribution of molecular weight was observed for all of the fractions of dissolved lignin, see Figure 4.7.

Figures 4.8 and 4.9, respectively, exemplify the change in the content of Klason lignin in the wood residues and the M_w of the lignin dissolved when the profile of [Na^+] in the cooking liquor was varied during flow-through kraft cooking, see also Figure 3.4. Closer examination shows that there is a correlation between the change in [Na^+] concentration and the delignification rate as well as of the M_w of lignin released.

In the case of cooking series S8-LHH, where the [Na^+] in the cooking liquor was increased from 0.52 to 3.00 mol/kg solvent after 30 min of cooking, the retarding effect on the delignification rate and the decrease in the M_w of the dissolved lignin was observed immediately after altering the [Na^+] (Figures 4.8A and 4.9A). After exchanging [Na^+], both the delignification rate and the M_w of the dissolved lignin followed the same trend as series S3-HHH, where the [Na^+] was kept constant at a high level (3.00 mol/kg solvent) during the whole cook. Also, in the reverse case, where cooking began at a high level of [Na^+] that was lowered after 30 min of cooking (i.e. S10-HLL), the impact that decreasing [Na^+] from 3.00 to 0.52 mol/kg solvent had on the delignification rate and the M_w of the dissolved lignin was also seen (Figures 4.8B and 4.9B). In this particular case, however, the delignification rate not only responds less promptly but also shows a certain delay before the effect of the decrease in [Na^+] becomes significant. A similar tendency was also seen for the M_w of the dissolved lignin. After the exchange point at 30 min of cooking, the delignification rate and M_w of dissolved lignin also followed kinetics similar to those of series S1-LLL, with cooking at a constant low level of [Na^+] during kraft cooking, see Figures 4.8B and 4.9B.

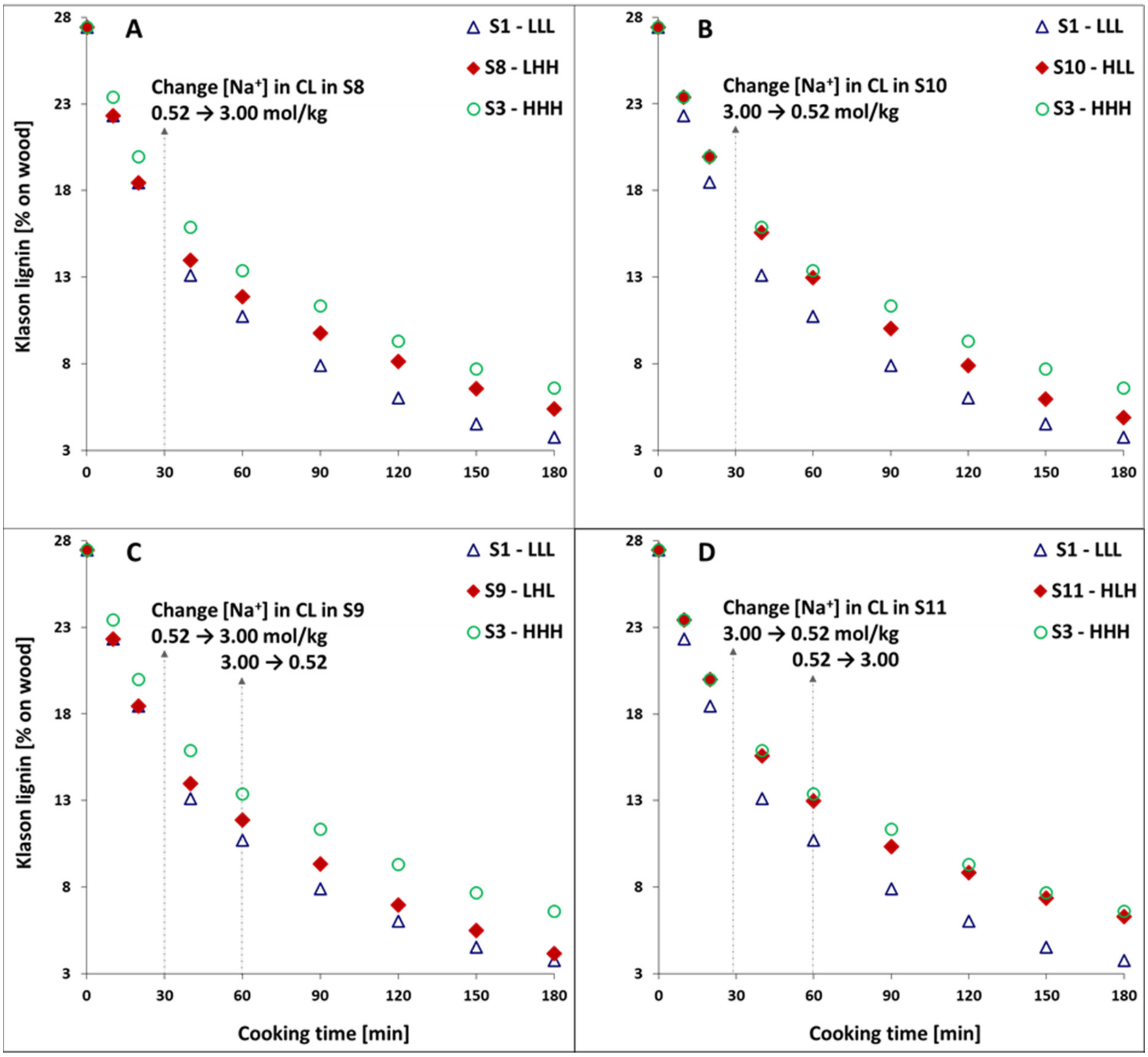

Figure 4.8. The effect that varying the [Na$^+$] has on the Klason lignin content of wood residues during flow-through kraft cooking. [OH$^-$] = 0.26 mol/kg solvent; [HS$^-$] = 0.26 mol/kg solvent; T=158°C. [Na$^+$] was controlled by the addition of Na_2CO_3. L = low level of [Na$^+$] (0.52 mol/kg solvent); H = high level of [Na$^+$] (3.00 mol/kg solvent).

Figures 4.8C, D and 4.9C, D show the impact that [Na$^+$] had on both the delignification rate and the M_w of the dissolved lignin when its concentration was altered at two times during the kraft cook: S9-LHL and S11-HLH, see also Figure 3.4. Rigorous inspection reveals that the results obtained from series S9-LHL and S11-HLH are obviously in agreement with the results obtained in series S8-LHH and S10-HLL.

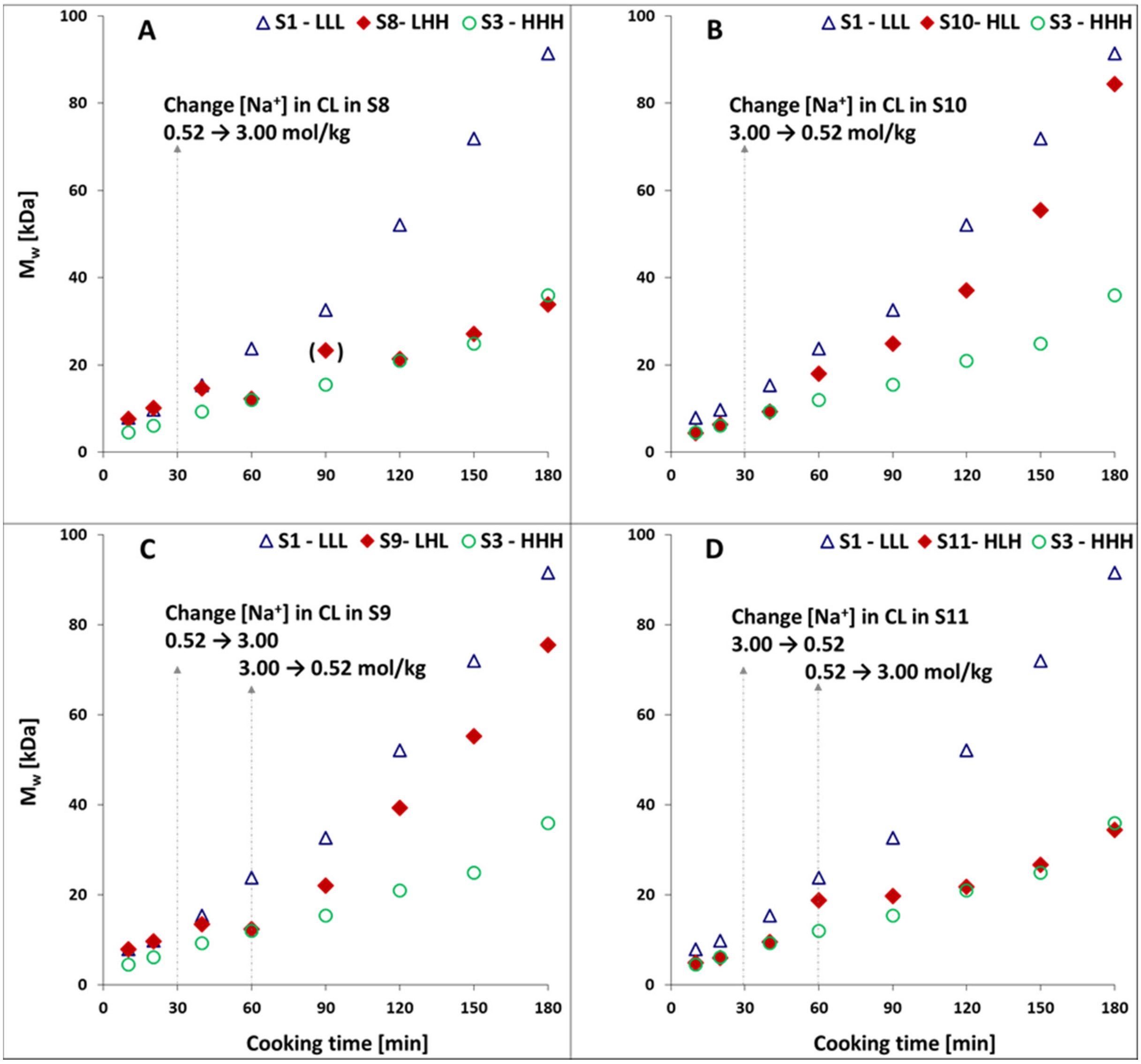

Figure 4.9. The effect that varying the [Na^+] has on the M_w of the samples of dissolved lignin precipitated from BL during flow-through kraft cooking. [OH^-] = 0.26 mol/kg solvent; [HS^-] = 0.26 mol/kg solvent; T=158°C. [Na^+] was controlled by the addition of Na_2CO_3. L = low level of [Na^+] (0.52 mol/kg solvent); H = high level of [Na^+] (3.00 mol/kg solvent).

4.4.2 Carbohydrates in precipitated lignin (PL) (Paper IV)

It is known that there are small amounts of various kinds of carbohydrates present in the lignin precipitated from BL when it is acidified. In this work, black liquor samples collected at different times were acidified to a pH of 2.5 and the carbohydrate content of the precipitates was investigated after acid hydrolysis. The total content of anhydrosugars (arabinose, xylose, galactose, glucose and mannose) and the amounts of individual monosaccharides in hydrolysed PL samples taken at different times and different levels of [Na^+] during kraft cooking are shown in Figures 4.10 and 4.11, respectively.

It can be seen in Figure 4.10 that each PL sample contained some carbohydrates: arabinose, xylose, galactose, glucose and mannose were all detected (Figure 4.11). Although the dominant sugar detected was generally xylose, the hydrolysed PL samples were also rich in arabinose, galactose, and glucose. A minor amount of mannose was detected, while a rather high amount of glucose was found, particularly at the end of the cooking series without the addition of sodium salts (Figure 4.11A). The overall results regarding carbohydrates found in the PL samples concur with earlier reports (Tamminen et al. 1995; Niemelä et al. 2007; Balakshin et al. 2003).

Figure 4.10 shows that the total content of monosaccharides in hydrolysed PL increases at prolonged cooking time and decreases as the [Na^+] in the cooking liquor increases; this decrease is more pronounced at the end of the flow-through kraft cook. Figure 4.11 shows that increasing the [Na^+] had a similar effect on the sugars xylose, arabinose and galactose, whereas no clear trend was seen for glucose. In general, the amount of arabinose, galactose and xylose in hydrolysed PL increases with increasing cooking time, but decreases with increasing amounts of [Na^+] in the cooking liquor (Figure 4.11). It is apparent from Figures 4.6, 4.10 and 4.11 that the dissolved fragments of lignin with a high M_w have a high content of sugars; this is particularly clear at prolonged cooking times and low levels of [Na^+].

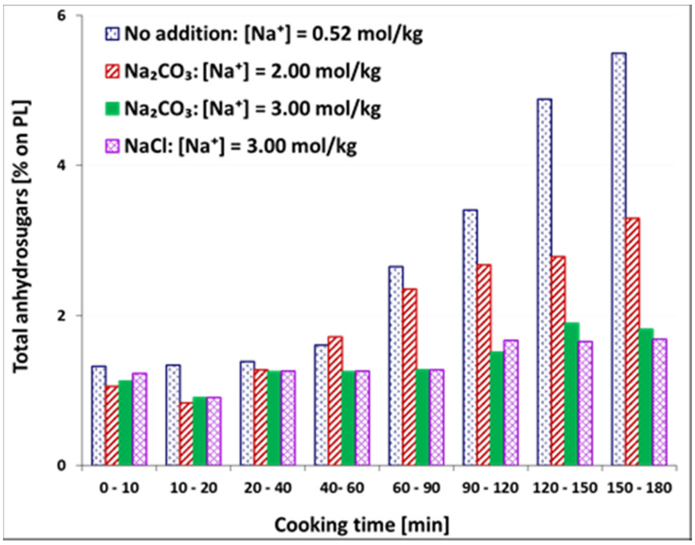

Figure 4.10. The total sugar content of PL during flow-through kraft cooking. $[OH^-]$ = 0.26 mol/kg solvent; $[HS^-]$ = 0.26 mol/kg solvent; T=158°C.

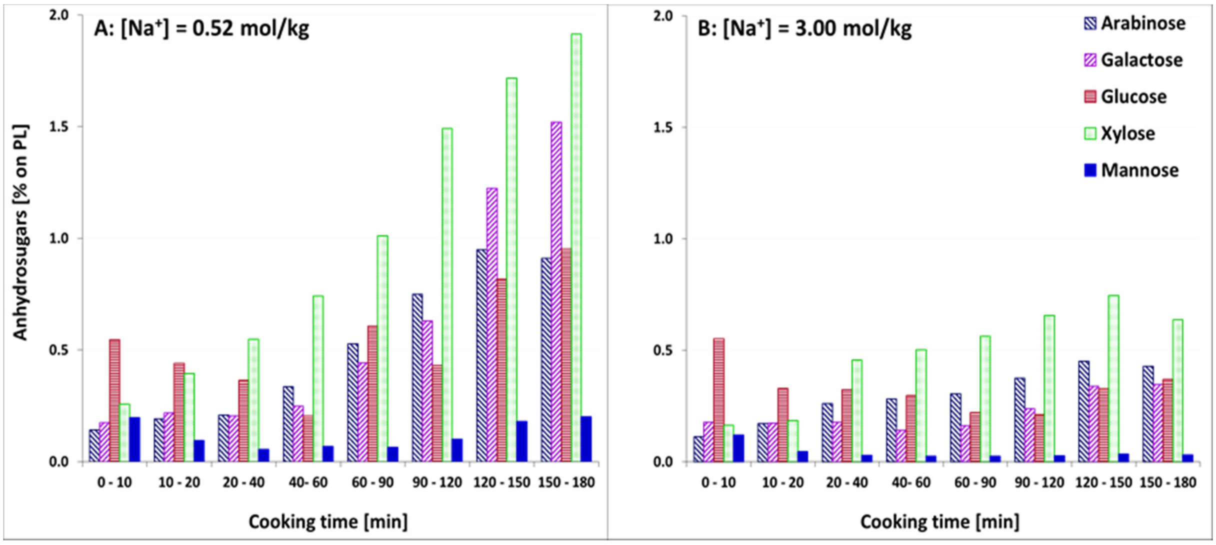

Figure 4.11. The effect $[Na^+]$ has on the content of anhydrosugars in PL during flow-through kraft cooking. $[OH^-]$ = 0.26 mol/kg solvent; $[HS^-]$ = 0.26 mol/kg solvent; T=158°C. $[Na^+]$ was controlled by the addition of Na_2CO_3.

The MWD of four PL samples are given in Figure 4.12. The UV signal measured at a wavelength of 280 nm relates to the concentration of lignin; the RI signal is affected by the concentrations of both polysaccharides and lignin. The figure shows that the UV profiles are very similar to the RI profiles. It may, however, be difficult to discern possible differences between these two profiles since the contents of carbohydrates in the PL samples are quite small (approx. 5% at most, see Figure 4.10). Nevertheless, the data obtained indicates that lignin and carbohydrates exist in the outlet of the separation column at the same time, which reveals the potential existence of lignin-carbohydrate complexes (LCCs): these results concur with earlier findings (Simonson 1963; 1969; Fengel, Przyklenk 1975; Eriksson, Lindgren 1977; Eriksson et al. 1980; Lawoko et al. 2005; 2006). Furthermore, Eriksson et al. (1980) suggested that all types of sugar units could be linked to lignin. Lawoko et al. (2006) reported that lignin was linked through covalent linkages to all of the major polysaccharides (i.e. (galacto)glucomannan, arabinoglucuronoxylan, cellulose and pectin) in the cell walls of spruce wood. The results obtained here therefore indicate that lignin could be linked to the various carbohydrates present in residues of Scots pine (Figures 4.10 and 4.11).

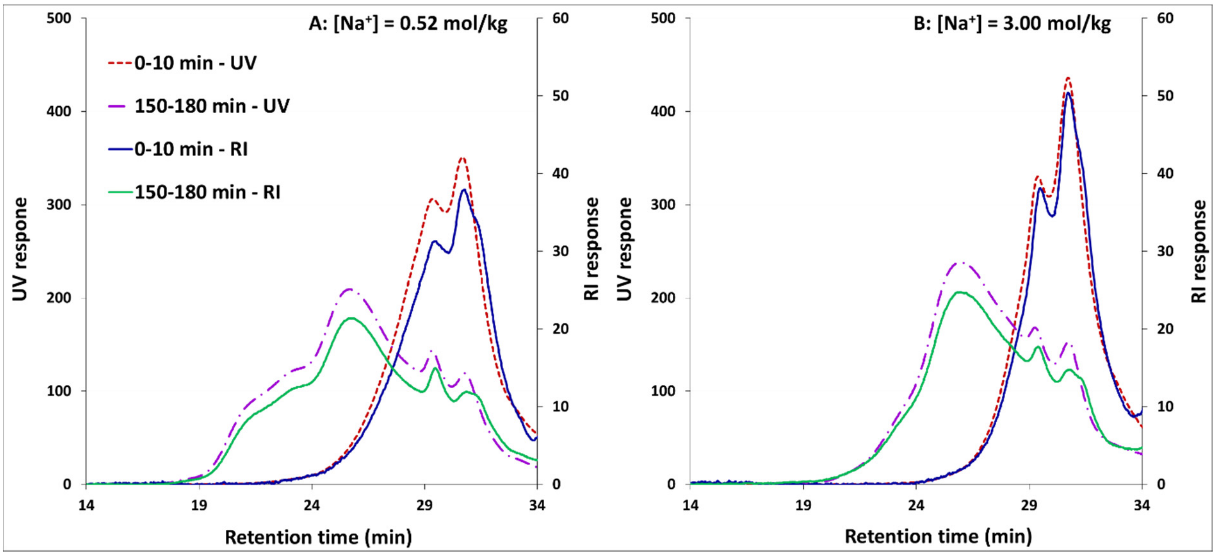

Figure 4.12. Chromatograms of samples of dissolved lignin precipitated from black liquors during flow-through kraft cooking. [OH^-] = 0.26 mol/kg solvent; [HS^-] = 0.26 mol/kg solvent; T=158°C. [Na^+] was controlled by the addition of Na_2CO_3. The data has been base line corrected.

4.4.3 Xylan retention (Papers I and II)

The influence of the ionic strength/sodium ion concentration on the content of xylan in wood residues is illustrated in Figure 4.13. It shows that the removal rate of xylan decreased when the sodium salts were added to the cooking liquor. In general, a considerable increase in the content of xylan was observed when the [Na^+] was increased from 0.52 to 2.00 mol/kg solvent, but was less pronounced when the [Na^+] was increased from 2.00 to 3.00 mol/kg solvent.

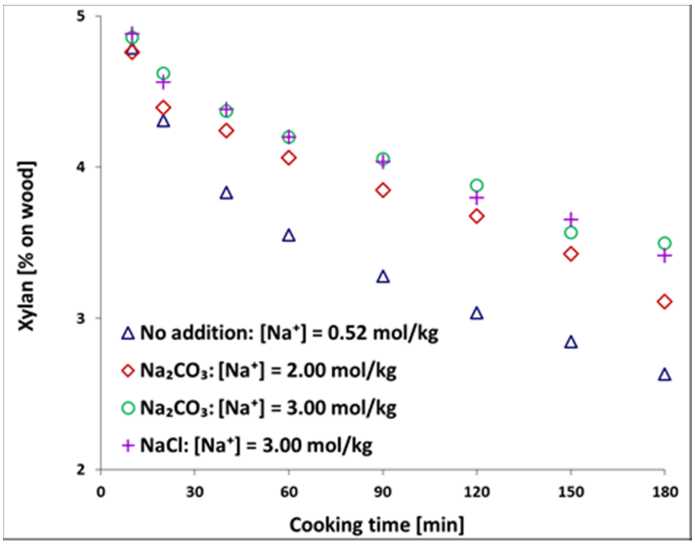

Figure 4.13. The effect $[Na^+]$ has on the content of xylan in wood residues during flow-through kraft cooking. $[OH^-]$ = 0.26 mol/kg solvent; $[HS^-]$ = 0.26 mol/kg solvent; T = 158˚C.

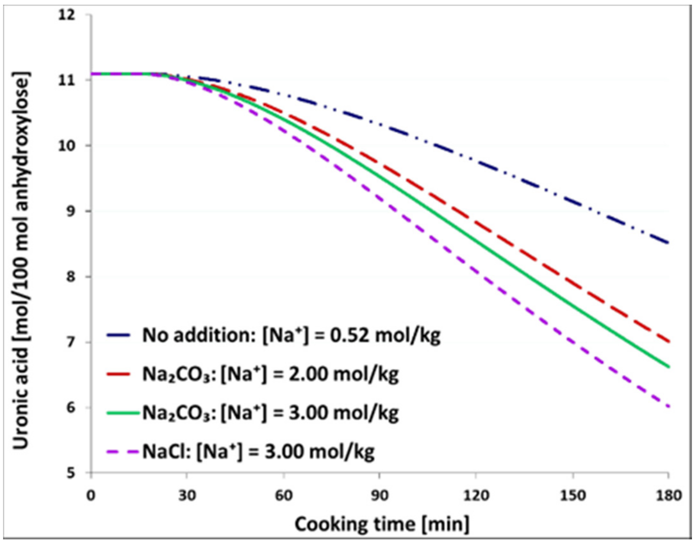

Figure 4.14. The effect $[Na^+]$ has the content of uronic acid in xylan during flow-through kraft cooking. $[OH^-]$ = 0.26 mol/kg solvent; $[HS^-]$ = 0.26 mol/kg solvent; T = 158˚C. The content of uronic acid was estimated using the model for the formation and degradation of HexA in combination with experimental data obtained for the content of HexA from S1, S2, S3, and S5 series, see Section 4.2.

It is known that the solubility of xylan depends on its molecular structure: it decreases, for instance, when the degree of substitution of the uronic acids on the xylan backbone is reduced (Axelsson et al. 1962; Clayton 1963). Furthermore, the solubility of xylan has been reported to increase with increasing amounts of $[OH^-]$ (Hansson, Hartler 1969), but decrease with increasing ionic strength (Köhnke et al. 2010; Ribe et al. 2010; Jansson, Brännvall 2011). Figure 4.14 exemplifies the influence of [Na$^+$] on the estimated content of uronic acids in xylan during flow-through kraft cooking. It shows that the estimated content of uronic acids in xylan decreased when [Na$^+$] was increased. Consequently, a decrease in the removal rate of xylan when the [Na$^+$] in the cooking liquor was increased may be due not only to a decrease in the solubility of xylan caused by an increase in ionic strength but also to the decrease in the degree of substitution of uronic acids on the xylan backbone.

Figure 4.15 shows the behaviour of the xylan when the [Na$^+$] was changed at a particular cooking time (see Figure 3.4). As can be seen in Figure 4.15A, the removal rate of xylan decreased rapidly when the [Na$^+$] in the cooking liquor was increased from 0.52 to 3.00 mol/kg solvent at 30 min of cooking (S8-LHH). Although the influence of [Na$^+$] on the removal rate of xylan when the [Na$^+$] was decreased from 3.00 to 0.52 mol/kg solvent (S10-HLL) was also observed, this effect was quite delayed, see Figure 4.15B. In general, it can be said that the results from series S9-LHL and S11-HLH imply that the influence of [Na$^+$] on the removal rate of xylan is instant when [Na$^+$] is increased and delayed when it is decreased (Figures 4.15C and 4.15D).

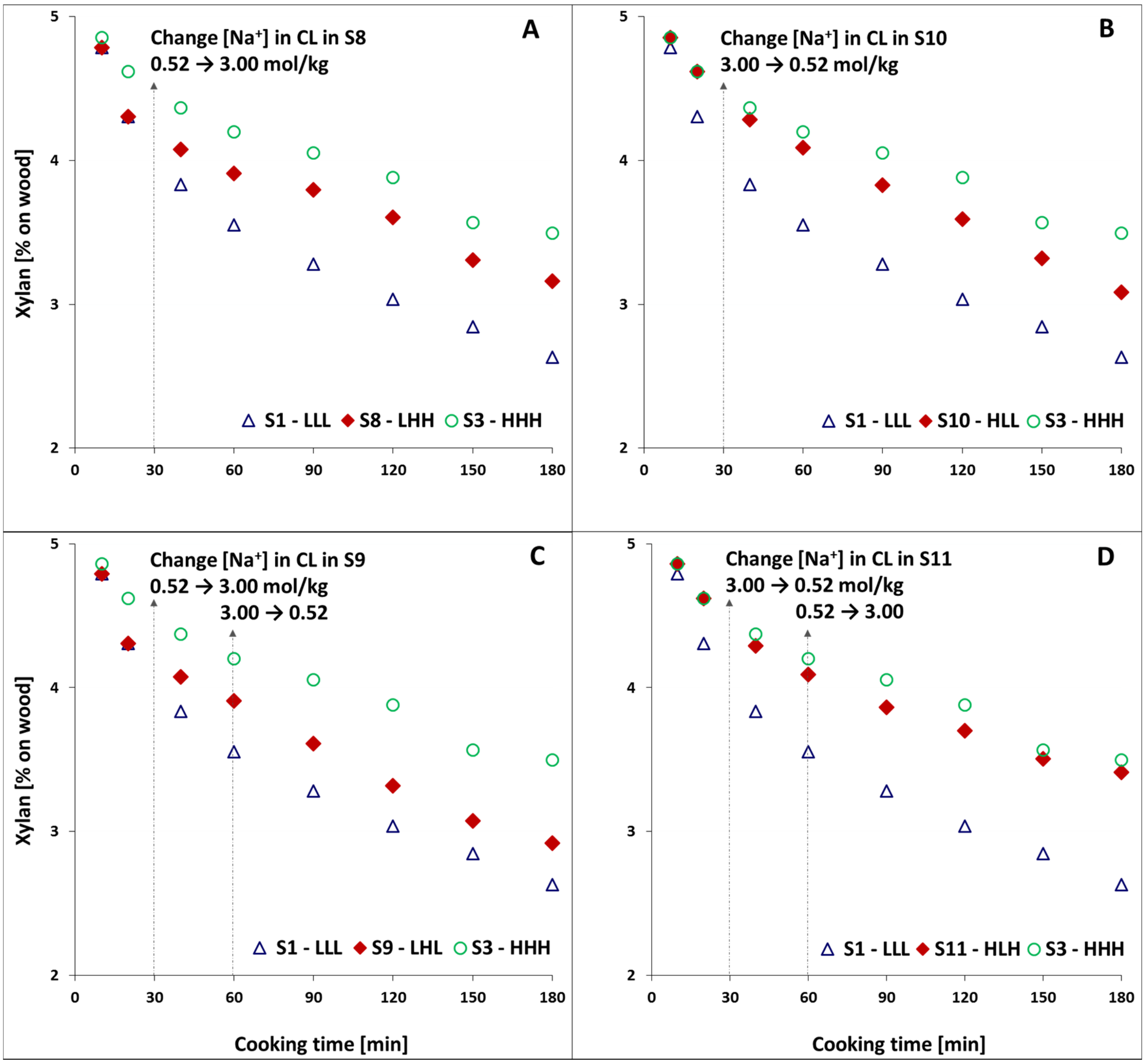

Figure 4.15. The effect that varying [Na^+] has on the content of xylan in wood residues during flow-through kraft cooking. [OH^-] = 0.26 mol/kg solvent; [HS^-] = 0.26 mol/kg solvent; T=158°C. [Na^+] was controlled by the addition of Na_2CO_3. L = low level of [Na^+] (0.52 mol/kg solvent); H = high level of [Na^+] (3.00 mol/kg solvent).

It should be pointed out that the behaviour of xylan is quite similar to that of lignin, see Section 4.4.1 (Figures 4.5 and 4.13). However, a close analysis of the data implies that an increase in [Na^+] gives a higher retention of xylan in wood residues with a given content of Klason lignin (Figure 4.16). The reason for this is probably related to the extent to which an increase in [Na^+] influences the solubility of both xylan and lignin. Accordingly, the results indicate that the dissolution of xylan is impeded more by a high [Na^+] than lignin solubilisation is.

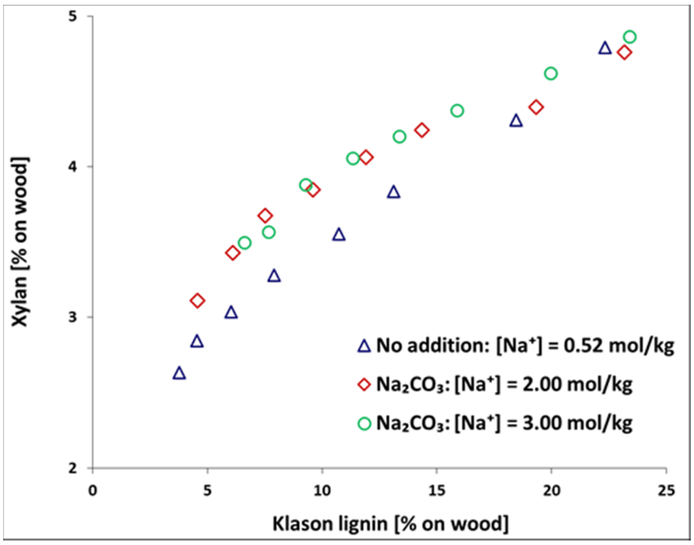

Figure 4.16. The effect [Na^+] has on xylan vs. content of Klason lignin in wood residues during flow-through kraft cooking. [OH^-] = 0.26 mol/kg solvent; [HS^-] = 0.26 mol/kg solvent; T = 158°C.

4.4.4 Glucomannan retention

The dependence of the retention rate of glucomannan on the concentration of sodium ions in the cooking liquor during the flow-through kraft cook is presented in Figure 4.17.

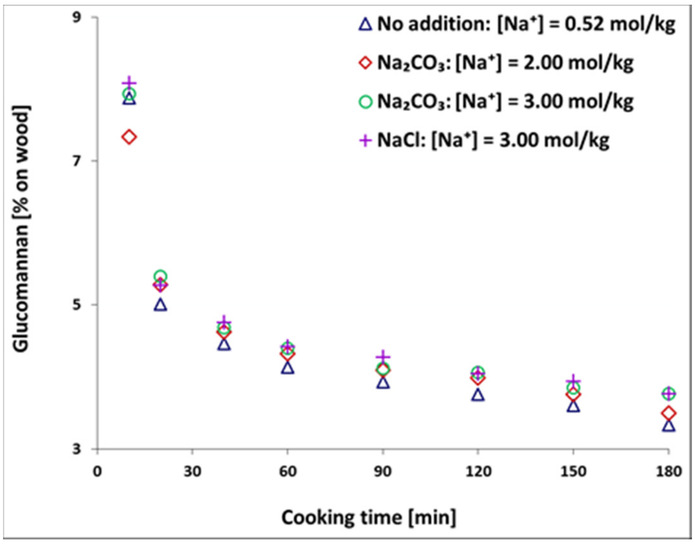

Figure 4.17. The effect [Na^+] has on the content of glucomannan in wood residues during flow-through kraft cooking. [OH^-] = 0.26 mol/kg solvent; [HS^-] = 0.26 mol/kg solvent; T = 158°C.

The content of glucomannan in wood residues decreases rapidly during the period of temperature rise: Figure 4.17 shows that approx. 70% of the glucomannan was removed after 20 min of cooking. The reason for the loss of glucomannan is mainly due to the peeling reactions that take place in the heating-up period (Sjöström 1993). The data obtained shows that retention of the glucomannan was almost unaffected by the addition of sodium salts even though the glucomannan yield is somewhat higher at an elevated concentration of sodium ions.

4.5 Comparison between Na_2CO_3 and NaCl

Figures 4.5, 4.6, 4.10, 4.13 and 4.17 show that Na_2CO_3 and NaCl have a very similar influence on the removal rate of wood components, lignin and carbohydrates as well as on the MWD of the lignin dissolved in BL. However, closer examination reveals that there is a slight difference between Na_2CO_3 and NaCl. For example, it can be seen in Figure 4.5 that the retarding effect of NaCl on the delignification rate is somewhat more extensive than that of Na_2CO_3 (Paper I). Figure 4.6 shows that the M_w values of lignin fragments released from the NaCl series is somewhat lower than that of Na_2CO_3 and that this is more pronounced at the end of the flow-through kraft cook (Paper III). The reason for this is still unclear: the different anions may affect the dissolution and aggregation of lignin molecules in black liquors in different ways (Norgren, Edlund 2003; Bogren et al. 2009b).

4.6 NMR results

Five black liquor samples taken at different times during cooking of the reference series ($[Na^+] = 0.52$ mol/kg) were acidified and the lignin in each one was precipitated. These lignin samples were then analysed using NMR methods. The data obtained from 2D NMR spectroscopy shows that the percentage of β-O-4′ and β-5′ linkages found in the dissolved kraft lignin was lower in the first sample taken (0-10 min), and is thereafter quite stable between 20 and 90 min of cooking during the cook, as reported in Table 4.2. The table also shows that a reference sample of LignoBoost™ kraft lignin was found to have a similar range of these linkages. This result implies that the main reactions that cleave these linkages in the lignin structure occur rapidly in the early part of the kraft cook, and that the structure of the dissolved lignin with respect to chemical bonds remains quite stable during the latter part of the kraft cook (20-90 min) even though the concentration of the active ions ($[OH^-]$ and $[HS^-]$) was kept constant. The data obtained from ATR-IR measurements supports the NMR results showing that the structures of the various fractions of dissolved lignin are similar (Paper V).

Table 4.2. Percentage of kraft lignin structures detected by 2D NMR and ^{1}H NMR in kraft lignin precipitated from black liquors taken from flow-through kraft cooks and LignoBoost™ kraft lignin taken from a conventional kraft cook (for details, see Paper V).

Structure	**Fractions of precipitated kraft lignin**					**LignoBoost™ kraft lignin (%)**
	0-10 (%)	**10-20 (%)**	**20-40 (%)**	**40-60 (%)**	**60-90 (%)**	
2D NMR						
β–O–4′ (CH$_\alpha$)	5	10	10	12	9	7
β–5′ (CH$_\alpha$)	5	9	11	12	8	10
^{1}H NMR						
β–O–4′ (CH$_\alpha$)	11	11	12	13	13	9

4.7 General discussion

Delignification

It is known that the overall delignification rate of the kraft cook is influenced by the variables: temperature, dimensions of the wood chip and composition of the cooking liquor (hydroxide ions, hydrosuphide ions, and the inorganic/organic ions present in the cooking liquor). Furthermore, the kinetics of kraft delignification are generally described based on the assumption that the kraft cooking system is a homogeneous operation, describing the delignification as a first order reaction or close to it.

The main hypothesis of this work was that the solubility of lignin molecules and mass transport phenomena exert an influence on the overall kinetics of kraft delignification.

The experimental trials undertaken were performed in a flow-through reactor that minimizes both the resorption of lignin and the additional degradation of the wood's components dissolved in the hot cooking liquor. Wood meal was used as a substrate to eliminate mass transport phenomena on the level of the chip size.

In an early study on the formation and degradation of HexA (Paper II), the results obtained indicated that the diffusion of (OH^-) into the fibre wall is quite fast. The mass transport of active cooking ions is, therefore, unlikely to have an impact on the kinetics of kraft delignification at the level of the fibre wall.

An investigation that was undertaken recently regarding the structural changes in lignin shows that the chemical bonds in dissolved lignin were quite stable after 20 min of kraft cooking (Paper V).

Furthermore, it was found that the molecular size of the lignin dissolved during kraft cooking increased when the cooking time was increased (Paper III). As described above, the chemical bonds in dissolved lignin are virtually stable after 20 min. The increase in the molecular weight of dissolved lignin at longer times is likely due to the fact that larger lignin molecules need more time to be transferred out of the fibre wall. Consequently, the mass transport of lignin is an important factor that must be taken into account when describing the overall kinetics of delignification in a kraft cook.

It should be noted nevertheless that the lignin molecules must be solubilized before they can be transported out of the fibre wall. It was found that the ionic strength/sodium ion concentration influenced both the delignification rate and the molecular weight of the dissolved lignin: the former was retarded rapidly and the latter decreased rapidly when the ionic strength of the cooking liquor was increased (Papers I and III). It should also be observed that the concentration of the active cooking ions ($[OH^-]$ and $[HS^-]$) in the fibre wall increases when the $[Na^+]$ in the cooking liquor is increased, in accordance with the Donnan equilibrium theory, and that the ionic strength in the fibre wall will increase, too (see Table 4.1). Therefore, the decrease in the solubility of lignin caused by the increase in ionic strength is likely to be a main reason for the decrease in the overall rate of delignification that was observed. An increase in the concentration of the active ions in the fibre wall, on the other hand, does not seem to have any major effect on the overall rate of delignification.

The rate of delignification and the molecular weight of the dissolved lignin increased when the ionic strength was decreased by reducing the amount of Na_2CO_3 added to the cooking liquor. However, the change observed after the amount of [Na^+] was decreased was slower than for the reverse case, i.e. when it was increased (Papers II and III). A reason that can be suggested for this is that when the ionic strength is increased, the smaller ballast ions are transported rapidly into the fibre wall; the lignin molecules go from a "soluble state" to an "in-soluble state" due to the higher ionic strength of the fibre wall. The response of the lignin molecules is fast, and the overall rate of delignification that is observed decreases immediately. When the ionic strength is decreased, it can be assumed that the rate of the mass transport of the ballast ions out of the fibre wall is about the same rate as the reverse case, and the lignin molecules of high molecular weight become solubilized. However, these lignin molecules have a low diffusive mass transport rate and the response of lignin is therefore slower.

In summary, it is suggested that the decrease in the overall rate of delignification at high ionic strength and the impact of the ionic strength on the molecular weight of the dissolved lignin are mainly due to the solubility effect combined with mass transport phenomena. It can thus be concluded that solubility and mass transport phenomena control the overall rate of kraft delignification mainly at the level of the fibre wall.

The relationship between lignin and xylan

It was found that an increase in the amount of IS/[Na^+] decreases the rate of delignification as well as the removal rate of xylan, and that the patterns of lignin and xylan are very similar (see Figures 4.5 and 4.13). The results obtained also show the behaviour of both xylan and lignin to be generally similar when the profile of [Na^+] was varied during flow-through kraft cooking, if Figure 4.8 is compared to Figure 4.15 (Papers I and II). A close relationship has been reported between the rate of delignification and the removal of xylan during alkaline cooking of softwoods (Matthews 1974; Wigell et al. 2007; Bogren el al. 2007). It is suggested that this close relationship is due to a decrease in the solubility of both lignin and xylan caused by an increase in ionic strength. However, the behaviour that is similar for both xylan and lignin may in fact also be due to the existence of linkages between lignin and xylan in the wood residues of Scots pine (LCCs).

5. Concluding remarks

The findings of this work provide further understanding of the overall rate of delignification as well as the carbohydrate losses that occur in Scots pine. The results that were obtained in this work suggest that the solubility and/or mass transport are the main factors governing the overall rate of kraft delignification at the level of the fibre wall.

The main findings of this work are summarised thus:

- The overall rate of delignification in the kraft cooking of Scots pine decreased significantly when the ionic strength/sodium ion concentration of the cooking liquor was increased. The negative influence of the ionic strength on the overall delignification rate can be explained by solubility and mass transport phenomena.

- The removal rate of xylan during the flow-through kraft cook of Scots pine decreased at an elevated ionic strength/sodium ion concentration whilst the retention rate of glucomannan was almost unaffected by the concentration level of the sodium ion. The decrease in the removal rate of xylan can be explained partly by the solubility of xylan and partly by the lignin-xylan covalent bonds. The behaviour of xylan generally follows that of lignin.

- The molecular weight distribution of the lignin dissolved in the black liquor during flow-through kraft cooking increased at prolonged cooking times but decreased when the ionic strength/sodium ion concentration in the cooking liquor was increased. The dissolved lignin fragments were found to have a very wide molecular weight distribution; as the cooking time was increased, the percentage of lignin fragments with a low M_w decreased gradually, whilst those with a greater M_w increased.

- Regarding carbohydrates present in precipitated lignin: the amount of carbohydrates present in the precipitated lignin increased when the cooking time was increased, but decreased when the ionic strength/sodium ion concentration of the cooking liquor was increased. The results indicate the possible presence of various linkages between the lignin and carbohydrates in Scots pine.

- The rates of the formation and degradation of HexA are affected significantly by the ionic strength/sodium ion concentration of the cooking liquor. The behaviour of HexA when the $[Na^+]$ profile was varied during the flow-through kraft cook indicated a fast change in the concentration of hydroxide ions in the fibre wall due to the change in the concentration of the sodium ions in the cooking liquor.

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8. Appendix

A. Calculation of the concentration of ions in the fibre wall

The concentration of the ions in the fibre wall at equilibrium given in Table 4.1 was estimated as a function of the bulk concentration by applying the Donnan equilibrium theory (Pu, Sarkanen 1991; Motomura et al.1998; Bogren et al. 2008). The concentration of the fixed anionic charges in the fibre wall was set at C = 1.06 mol/kg fibre wall solvent, according to Bogren et al. (2008). The estimation of the concentration of ions in the fibre wall at equilibrium was based on the following equations (Motomura et al. 1998; Bogren et al. 2008):

Case: addition of Na_2CO_3

$$[Na^+]_F + [H^+]_F - 2*[CO_3^{2-}]_F - [OH^-]_F - [HS^-]_F - C = 0 \qquad [1]$$

Case: addition of NaCl

$$[Na^+]_F + [H^+]_F - [Cl^-]_F - [OH^-]_F - [HS^-]_F - C = 0 \qquad [2]$$

The ratio of the concentration of ions in both the bulk (B) and fibre wall (F) phases is presented by:

$$Y = [Na^+]_F / [Na^+]_B \qquad [3]$$

$$Y = [OH^-]_B / [OH^-]_F \qquad [4]$$

$$Y = [HS^-]_B / [HS^-]_F \qquad [5]$$

$$Y = [Cl^-]_B / [Cl^-]_F \qquad [6]$$

$$Y^2 = [CO_3^{2-}]_B / [CO_3^{2-}]_F \qquad [7]$$

B. Calculation of the carbohydrate content

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

i. The amount of sugars analysed was corrected for the acid hydrolysis yield.

ii. Xylan was calculated as the sum of xylan and arabinan. All arabinan measured is included in xylan.

iii. (Galacto)glucomannan was calculated as the sum of the mannan, galactan and part of the glucan. The molar ratio between the mannose and glucose in the (gaclacto)glucomannan was assumed to be 3.5:1 (Meier 1958). All the galactan measured is included in the (galacto)glucomannan; the acetyl groups are not included.

iv. Anhydrosugars were calculated from sugar monomers by the withdrawal of water (multiplied by 0.90 in the case of hexosans and 0.88 in the case of pentosans).

v. Cellulose was calculated as the content of glucan after withdrawal for the contribution of glucan to (galacto)glucomannan.

$$\text{Xylan} = \text{Xylose} + \text{Arabinose}$$

$$\text{(Galacto)glucomannan} = \text{Galactose} + (1 + [1/3.5])*\text{Mannose}$$

$$\text{Cellulose} = \text{Glucose} - (1/3.5)*\text{Mannose}$$

The analyses were summed up in a mass balance based on the assumption that the carbohydrates were comprised of cellulose, (galacto)glucomannan and xylan, which were calculated as described above.

C. Model describing the content of HexA in wood

Estimations of the total uronic acid content and the modelled content of MeGlcA and HexA were based on the model for the kinetics of the formation and degradation of HexA as described by Bogren et al. (2008).

$$d[\text{MeGlcA}]/dt = -k_1[\text{MeGlcA}][\text{OH}^-]_F \qquad [8]$$

$$d[\text{HexA}]/dt = k_1[\text{MeGlcA}][\text{OH}^-]_F - k_2[\text{HexA}][\text{OH}^-]_F \qquad [9]$$

$$k_1 = A_1 e^{-E_{a1}/RT} \qquad [10]$$

$$k_2 = A_2 e^{-E_{a2}/RT} \qquad [11]$$

The estimations of K_1 and K_2 in the second part of the experiments were based on the equations:

$$d[\text{MeGlcA}]/dt = -K_1 e^{-E_{a1}/RT}[\text{MeGlcA}] \qquad [12]$$

$$d[\text{HexA}]/dt = K_1 e^{-E_{a1}/RT}[\text{MeGlcA}] - K_2 e^{-E_{a2}/RT}[\text{HexA}] \qquad [13]$$

$$K_1 = A_1[\text{OH}^-]_F \qquad [14]$$

$$K_2 = A_2[\text{OH}^-]_F \qquad [15]$$

Abbreviations

- [MeGlcA]: content of 4-*O*-methylglucuronic acid (mol/ 100 mol anhydroxylose).
- [HexA]: content of hexenuronic acid (mol/ 100 mol anhydroxylose).
- $[\text{OH}^-]$: content of hydroxide ion (mol/kg solvent).
- $[\text{MeGlcA}]_0$: the initial content of 4-*O*-methylglucuronic acids taken from the experimental data of Bogren et al. (2008).
- The activation energy used was: E_{a1} = 122 kJ/mol and E_{a2} = 126 kJ/mol, according to Bogren et al. (2008).