Characterization of Spruce Xylan and Its Potential for Strength Improvement

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Licentiate Thesis

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I dedicate this thesis to
my husband Marcus,
for his constant support and unconditional love.

这份半博论文也献给我亲爱的爸爸妈妈，感谢你们对我的养育之恩
ABSTRACT

Xylan dissolved during kraft cooking and later redeposited on fibre surfaces has been shown to give higher pulp yield and better strength properties. This is economically interesting from an industrial point of view. Many studies have been done to investigate xylan behaviour during kraft cooking, to discover the xylan-cellulose attachment mechanism, to find the optimal xylan retention or adsorption process, and to discover relations between xylan structure and strength enhancement. Most of them have concentrated on hardwood xylan. However, softwoods are the major raw materials for the pulp industries in the northern hemisphere. Earlier studies have shown that the xylan characteristics, rather than simply the amount of xylan, influence the strength-enhancing effect of xylan. To obtain optimal utilization of spruce xylan as a strength enhancer, it is essential to know what the beneficial xylan characteristics are and how cooking conditions affect the characteristics.

In this study, kraft cooking of spruce chips was performed under varied cooking conditions and the xylan in the black liquor was precipitated and characterized. It was found that dissolved spruce xylan had a much higher amount of bound lignin compared to previous studies on xylan dissolved from hardwoods. Increased cooking temperature increased the dissolution rate of xylan. The lower alkali charge and higher ionic strength of the cooking liquor resulted in a lower amount of dissolved xylan. Apart from the effect of the amount, cooking conditions also affected substitution of dissolved xylan. Higher temperature and higher ionic strength led to a lower amount of MeGlcA, while the MeGlcA amount of dissolved xylan was preserved during lower alkali cooking.

By distinguishing how different cooking conditions affect the characteristics of the xylan dissolved in the black liquor, xylans with different structures were designed to study their effects on pulp strength, that is, the addition of black liquors with certain known xylan characteristics in the kraft cooking process. It was found that the best effect of xylan on tensile strength occurred when the xylan penetrated some distance into the subsurface of the fibre wall. Both low molecular weight and high degree of substitution lowered the tendency of xylan to aggregate, which enabled the dissolved xylan to penetrate some distance into the exposed fibre surface. Upon beating, this xylan was exposed, thus facilitating improvement of fibre-fibre joint formation, which led to increased tensile strength.
SAMMANFATTNING

Man har sedan länge känt till att xylan löser sig alkalisk kokvätska för att senare under koket återutfällas på fiberytan. I industriell skala har man kunnat konstatera att återföring av svartlut från kok av björk till kok av barrved förbättrar barrvedsmassans dragstyrkeeegenskaper. Mycket forskning har ägnats björkxylan eftersom detta vedslag har unikt mycket xylan, även i jämförelse med andra lövträd. Man har sett att mer xylan på massafibrerna inte alltid leder till förbättrade styrkeegenskaper utan xylan med vissa egenskaper kan vara bättre än större mängd xylan med andra egenskaper. Xylanets molekylvikt och andel av uronsyragrupper har visat sig vara av vikt. Gran innehåller endast ca 8-10% xylan, mot björkens 30%, vilket gör det intressant att undersöka om denna vedens egna styrkekemikalie skulle kunna utnyttjas effektivare. Den grundläggande frågeställningen i denna avhandling är hur ska det gransxylan som återutfälls på fibrerna se ut för att ge optimal dragstyrka.


LIST OF PAPERS

This thesis is a summary of the following papers:

I  Characterisation of dissolved spruce xylan in kraft cooking
Zheng Li Jansson, Elisabet Brännvall

II  Designing spruce xylan for higher tensile strength
Daniel Tavast, Zheng Li Jansson, Elisabet Brännvall
In manuscript

III  Effect of kraft cooking conditions on the chemical composition of
the surface and bulk of spruce fibers
Zheng Li Jansson, Elisabet Brännvall
In manuscript

Results from some of the above papers have been presented on the following occasions:

PIRA 3rd Biennial Fibre Engineering, Barcelona, 25–26 May 2011
Characterisation of dissolved spruce xylan in kraft cooking.
Oral presentation by Brännvall, E.

EWLP 12th European Workshop on Lignocellulosics and Pulp, Espoo, 27–30 August 2012
Effect of xylan structure on tensile strength
Oral presentation by Tavast, D.

2nd Avancell Conference, Chalmers University of Technology, Göteborg, 2–3 October 2012
Optimal utilization of softwood xylan
Oral presentation by Tavast, D.

Ekmandagarna, Stockholm, 22–23 January 2013
Bättre utnyttjande av vedråvara på massasidan, kvalitetssförbättringar
Oral presentation by Tavast, D.
ABBREVIATIONS

AGX  arabinoglucuronoxylan
AX   arabinoxylans
DMAC N,N-dimethylacetamide
DPₙ number–average degree of polymerization
EA   effective alkali
Gal  galactose
GAX  (glucurono)arabinoxylans
Glc  glucose
GX   glucuronoxylan
HexA 4-deoxyl-β-L-threo-hex-4-enopyranosyluronic acid
HX   heteroxylans
LCC  lignin-carbohydrate complexes
Man  mannose
MeGlcA/UA 4-O-methyl-α-D-glucuronic acid
MeIdoA 4-O-methyl-β-L-idopyranosyluronic acid
Mᵢw weight–average molecular weight
ML   middle lamella
NaCl sodium chloride
NaOH sodium hydroxide
Na₂S sodium sulphide
P    primary wall
SEC size exclusion chromatography
SRº Schopper-Riegler value
WL   white liquor
X    homoxylans
Xyl  xylose
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1 INTRODUCTION

1.1 HEMICELLULOSES AND NATIVE XYLAN

Every year billions of tons of hemicelluloses are biosynthesized by plants using solar energy, carbon dioxide, and water. They are heterogeneous polysaccharides, which are soluble in alkali. Glucose (Glc), mannose (Man), galactose (Gal), and xylose (Xyl) are commonly found in the backbone chains of hemicelluloses. They form six-member rings (pyranose, see Fig. 1) and glycosidic linkages between rings by the reactions of 1-hemiacetal with 4-hydroxyl group.

![Fig. 1. Main constituents of hemicelluloses.](image)

All hemicelluloses possess side chains, including acetyl groups, pentoses (β-D-xylose, α-L-arabinopyranose, α-L-arabinofuranose), hexoses (β-D-glucose, β-D-mannose, α-D-galactose), hexuronic acids (β-D-glucuronic acid, α-D-4-O-methylglucuronic acid, α-D-galacturonic acid), and deoxyhexoses (α-L-rhamnose, α-L-fucose) (Ortwin 1994); see Fig. 2. These branched structures of hemicelluloses certainly inhibit the formation of hydrogen bonds. Hemicelluloses are therefore amorphous and much more accessible to hydrolytic attack compared to cellulose. Generally, hemicelluloses are named after their different types of monosaccharide residues. Abbreviations and designations (α, β, D, L) have been introduced for sugar units to indicate formulas and distinguish stereochemical configurations.
As plant cell wall structural components, hemicelluloses are more abundant in secondary walls. They are incorporated in the package of cellulose chains (Fengel 1970). It is proposed that interfaces between 'elementary fibrils' (3 nm in diameter) are formed by less ordered cellulose chains and hemicelluloses, and microfibrils (average 25 nm in diameter) are surrounded by a matrix of lignin and hemicelluloses. It has been suggested by Salmen and Olsson (1998) that glucomannan is closely associated with cellulose, and xylan with lignin. More studies show that the hemicelluloses are also integrated with pectin polysaccharides (Caffall and Mohnen 2009) and lignin (Lawoko et al. 2005) by cross-linking. Cell wall molecular arrangement patterns are thus complex.

Xylans are hemicelluloses generally constructed with β-(1,4)-D-Xylp or β-(1,3)-D-Xylp backbones and a certain degree of substitution with different distribution ratios. They may be found as glucuronoxylan (GX) in hardwood, arabinoglucuronoxylan (AGX) in softwood, homoxyxylans (X) in algae, arabinoxylans (AX) in cereal grains, heteroxylans (HX) in cereals and seeds, and (glucurono)arabinoxylans (GAX) in rice and corn (Ebringerova and Heinze 2000). The xylan content in softwoods is 7–10% of wood, while in hardwoods it is approximately 15–30% (Sjöström 1993). GX in hardwood often contains one (1→2)-linked -4-O-methyl-α-D-glucuronic acid (MeGlcA) per 8–20 xylose units and acetyl groups at C-2 and C-3; see Fig. 3. AGX in softwood is often substituted with α-L-arabinofuranose at C-3 every 8–9 xylose units and (1→2)-linked MeGlcA every 5–6 xylose units; see Fig. 3 (Teleman 2011). The molar mass of xylan reported in the literature varies depending on species, isolation method, and analytical approaches. In an investigation by Jacobs and Dahlman (2001), it was shown that GX from birch and aspen and AGX from spruce and pine have rather similar
degrees of polymerization. The average numbers of xylose units per xylan molecule (DP\textsubscript{n}) are 84–108 and 89–120, respectively.

![Representative structure of hardwood glucuronoxylan (above) and softwood arabinoglucuronoxylan (below).](image)

### 1.2 Kraft Cooking and Processed Xylan

Chemical pulping relies mainly on chemical reactants and heat energy to soften, dissolve, and degrade lignin and to leave behind most of the cellulose and hemicelluloses. This is achieved by treating the wood chips at an elevated temperature in a solution containing the pulping chemicals, until a certain degree of delignification is reached. The process is referred to as cooking.

Kraft pulping has become the dominant chemical pulping process by the production of high strength chemical pulp and the innovation of chemical recovery. It can be used for all kinds of wood, for example, softwood (pine, spruce, etc.) and hardwood (birch, eucalypt, etc.). This process can be performed either in batch or in continuous digester. The cooking liquor is a mixed solution of sodium hydroxide (NaOH) and sodium sulphide (Na\textsubscript{2}S). After cooking, wood chips are discharged from the digester, whereby the delignified chips are disintegrated into individual fibres, the so-called pulp. The small, uncooked fibres are called shives.

The aim of kraft pulping is to remove lignin, which can be seen as the glue holding the fibres together. Lignin is found at high concentrations in the middle lamella. The native lignin is a polymer of coniferyl alcohol (guaiacyl), sinapyl alcohol (syringyl), and p-coumaryl alcohol, connecting through
different types of C-O-C and C-C linkages. It is ‘coloured’, complex, and hydrophobic. The active cooking chemicals, hydroxide (OH) and hydrogen sulphide ions (HS), work as nucleophiles in bond cleavage, converting lignin molecules into small alkali-soluble fragments. However, they are not completely selective towards lignin. Carbohydrates, primarily hemicelluloses, are also chemically attacked and dissolve to some extent.

During kraft cooking, the whole xylan molecules can directly dissolve in the pulping liquor before further degradation (Axelsson et al. 1962). The dissolution of birch and eucalyptus xylan in kraft cooking is fast at the beginning of the cook. The maximum amount of xylan dissolved in the cooking liquor appears early in the cook, whereas afterwards, the amount steadily decreases (Danielsson and Lindström 2005). The maximum concentration of dissolved pine xylan, however, is obtained much later in the cook, after cooking for 3 hours, according to Simonson (1963). Xylan dissolution might be restricted by the lignin-carbohydrate complex (LCC). After xylan has been separated from the plant matter, its solubility is affected by its structures, such as molecular weight ($M_w$) and branching. Higher molecular weight will decrease solubility. Decreasing of arabinofuranose substituents makes xylan less soluble in water (Andrewartha et al. 1979). Linder et al. (2003) suggest that xylan chains have a tendency to self-associate. They exist in solution as both single molecules and aggregates. The aggregates are formed by the interaction of unsubstituted regions and hydrophobic connection between covalently bonded lignin and xylan. The dissolved xylan molecules may later redeposit on fibre surfaces. (Yllner and Enström 1956, 1957; Clayton and Stone 1963).

At the same time, xylan is degraded during kraft cooking. Acetyl side groups are rapidly cleaved through hydrolysis, forming carboxylic acids and alcohols. The glycosidic linkages are hydrolysed by alkali. The end sugar units are cut off by the peeling reactions, and the newly exposed reducing ends undergo ‘secondary’ peeling reactions. The shortening of xylan chains can be stopped by its substituents. For example, the substituent at 3-position favours β-elimination from the open aldehyde and forms metasaccharinic acid to prevent peeling reactions (Gellerstedt 2009). The MeGlcA substituents on the xylan backbone can be cleaved off or undergo reactions, for example, be converted to its epimer with an opposite configuration of C1, so-called 4-O-methyl-β-L-idopyranosyluronic acid (MeIdoA) (Johansson and Samuelson 1977; Teleman et al. 1996), or eliminate methoxyl group as methanol, forming 4-deoxyl-β-L-threo-4-enopyranosyluronic acid (HexA) (Clayton 1963; Johansson et al. 1977; Teleman et al. 1995); See Fig. 4. MeGlcA, MeIdoA, and HexA are stable enough to be detected as substituents of dissolved xylan in the black liquor. A 50% decrease in molecular weight of dissolved birch xylan during kraft cooking (Danielsson and Lindström 2005) and a quite stable molecular weight of dissolved eucalyptus xylan (Lisboa et al. 2005) have been reported.
1.3 PAPER STRENGTH AND ATTACHED XYLAN

Dewatering of the fibre suspension (drainage process) followed by pressing and drying form a network of fibres, the so-called laboratory sheet or industrial paper web. Improvement in paper strength is important for end-product benefits and machine performance. For example, the tensile strength specifies how well the paper can withstand tensile forces on its passage through a printing press. The paper strength is influenced by the properties of fibres and the strength of the fibre network (Page 1969). Different raw materials give different fibres. Longer fibres generally improve the strength, as they more easily entangle with each other; thin-walled fibres are more collapsible, and therefore give higher tensile strength compared to thick-walled fibres. Fibre deformations, such as curls, have a negative effect on tensile index (Mohlin et al. 1996). A greater bonded area and stronger specific bonding strength contribute to network strength.

Bonding is increased by beating. Beating induces the loosening of the fibre wall (delamination, internal fibrillation) and external fibrillation, exposes the secondary layer, and allows water to be adsorbed by the molecules. This results in a larger surface area of beaten fibres. Fibres swell and become more flexible (McIntosh 1967, Page and De Grace 1967). The degree of swelling also depends on the chemical composition of the fibres. It is promoted by hemicelluloses, but inhibited by lignin. Compared to never-dried fibres, dried fibres swell less on rewetting and will require more beating energy to obtain a certain tensile strength. Densification of the paper network is due to the improvement in bonding obtained by beating, since more contact points between the fibres are created, and they become more densely packed in the sheet. At a specific sheet density, higher tensile strength
predicts stronger bonding strength. From a different angle, if comparing sheets at the same tensile strength, a lower density is favourable, as raw materials consumption is less, and in addition, the higher bulk would give higher tensile stiffness of the sheet.

The redeposition of dissolved xylan molecules on fibre surfaces during kraft cooking contributes to the strength between fibres in the paper network (Sjöberg et al. 2004; Danielsson and Lindström 2005, 2009). It has been proposed that the attachment of an irreversible, water-swollen xylan layer to cellulose is driven by an increase of inherent entropy and van der Waals interactions (Paananen et al. 2004). The adsorption of xylan on fibre surfaces increases the water affinity of the surface, which increases the surface swelling of fibres. During drying, capillary forces draw highly swollen fibre surfaces together. More flexible fibres will be able to adapt their shape to the neighbouring fibres and create more fibre-fibre joints (Wågberg 2004). The mechanism of xylan contribution to paper strength is not totally clear. The fibre surface is rough and contains pits; thus, the two contacting cellulose fibres are partly jointed (Wågberg 2004). The tails of a single xylan molecular are able to diffuse, entangle, and penetrate across the interface of two contacting fibres (McKenzie 1984). The xylan aggregates adsorbing onto the fibre surface offer a larger contact area.

Xylan structure plays an important role in xylan-cellulose attachment and paper strength improvement. Danielsson and Lindström (2005) found that the addition of birch xylan with higher molecular weight is more efficient at enhancing softwood pulp strength than the addition of xylan with lower molecular weight. In a study on kraft cooking of eucalyptus with the addition of eucalyptus xylan, it was concluded that the amount of redeposited xylan was not the determining factor for pulp strength enhancement (Danielsson and Lindström 2009). In that study, it was also seen that a higher molecular weight of the xylan in black liquor doesn’t necessarily lead to higher pulp strength. It seems that the characteristics of the redeposited xylan, such as degree of substitution (contributing to total charges), and amount of lignin bound to the xylan, also affect the pulp strength.
1.4 OUTLINE OF THE THESIS WORK

1. Characterize dissolved spruce xylan; study how cooking conditions affect xylan structure.
   The parameters in the kraft cooking studied were
   • Cooking temperature
   • Alkali concentration profile
   • Ionic strength
   • Cooking time
   The xylan characteristics studied were
   • Dissolved amount in black liquor
   • Molecular weight
   • Degree of substitution
   • Aggregation with lignin

2. Study how cooking conditions affect chemical compositions of pulp surface and bulk.

3. Investigate paper tensile strength; study how xylan characteristics affect paper strength.
   The external xylans used in exchange cooking studies were birch xylan and spruce xylan.
2 MATERIALS AND METHODS

2.1 KRAFT COOKING FOR XYLAN CHARACTERIZATION

To study the xylan structural changes during kraft cooking, steel autoclaves with a capacity of 3l were used. During cooking, autoclaves were rotated and heated in a polyethylene glycol bath. The rotation was around the horizontal axis, and the autoclaves were maintained at a slight tilt during rotation to enable circulation of liquid inside. It was possible to remove one autoclave from the bath while others continued for longer cooking time. Heat for the PEG bath was provided by the steam. It took approximate 10 min to heat up the PEG bath to the desired temperature of 157°C or 167°C. The autoclaves were then mounted into the PEG bath, and the recording of the cooking time started. Cooking was stopped after different times, from 50 to 250 min, by placing and cooling the autoclaves in a water bath.

The spruce chips used in the study were industrial chips obtained from the Södra mill Värö. The birch chips were obtained from birch logs chipped in a laboratory chipper at Innventia, Stockholm. In each autoclave cook, 300 g (oxygen dried) chips were charged and the lid was mounted. The air was removed by 30 min vacuum suction. The white liquor was sucked into the autoclave by the vacuum created inside. The white liquor was prepared from stock solutions of NaOH and Na₂S, and diluted with deionized water, so as to reach a liquor-to-wood ratio of 4 l/kg. [Na⁺] was increased by addition of NaCl. The temperature, alkali charge, and ionic strength were adjusted (see Table 1), to investigate their effects on xylan structure.

Table 1. Variable cooking conditions

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<td>Reference</td>
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<td>1,46</td>
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<tr>
<td>High T</td>
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<td>1,46</td>
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<td>Low [OH⁻]</td>
<td>157</td>
<td>1,0</td>
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<tr>
<td>High [Na⁺]</td>
<td>157</td>
<td>1,2</td>
<td>0,26</td>
<td>2,50</td>
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</table>
2.2 ISOLATION OF XYLAN FROM BLACK LIQUOR

The xylan in the black liquor was precipitated by acid neutralization according to Axelsson et al. (1962), except that acetone was used in the final washing step instead of ethyl ether. The precipitation was performed on the same day after cooking. First, the black liquor was separated from the chips, and different amounts of black liquor were collected, for example, 300–450 ml in the case of spruce and 250–300 ml in the case of birch. Next, an equal volume of acetic acid was added to the black liquor under mixing. This will change the pH of the solution to pH 5. Then, the solution was poured into ethanol, which has three times the volume of solution. Finally, the mixture was placed in a refrigerator at a temperature of 4°C and left for 16–24 hours while the precipitate formed.

The supernatant was decanted off, and the precipitate was washed twice with an ethanol:water 2:1 mixture, three times in pure ethanol and finally three times with acetone. After each washing step, the precipitate and washing liquor mixture was centrifuged using a centrifuge Potofix 32A at a rotor speed of 4 000 rpm for 20 min. After a total of 8 washes, the precipitate was dried in a desiccator under vacuum to remove acetone. The dry solid content was determined on an IR balance, Mettler PM 460.

2.3 XYLAN CHARACTERIZATION METHODS

2.3.1 Xylan amount

Determination of Klason lignin in black liquor precipitate was carried out in parallel experiments. Precipitate samples of 250 mg ×2 were treated separately with 3 ml 72% H₂SO₄ in the desiccator under vacuum for 60 min. After 84 ml water was added, the sample was placed in the autoclave at 125°C for another 60 min. After sulphuric acid hydrolysis, the insoluble solid part was washed, dried, and gravimetrically determined as Klason lignin.

The filtrate part containing monosaccharide mixture was used for carbohydrate analysis. Samples went through reduction reaction with potassium-borate-hydride and acetylation reaction with acetic anhydride. They were converted into alditol acetates prior to gas chromatography (GC) analysis (Theander and Westerlund 1986). The GC analysis was performed on a Hewlett-Packard HP-6890 chromatograph, equipped with column BP X70 (12 m × 0.32 mm × 0.25 µm). Helium gas was used as the carrier gas at a flow rate of 0.9 ml/min. The inlet temperature was 230°C and the detector was 250°C.

The amount of xylan in the precipitate from black liquor was calculated in the unit gram per litre. xylan (g/l) = (%xylose + %arabinose) × C_{BL} (g/l). The percentage of different monosugars was obtained from carbohydrate analysis. The precipitate from black liquor P_{BL} (g/l) was assumed to
be composed of lignin and carbohydrates. With the lignin part removed, the remaining precipitate was carbohydrates $C_{BL}$ (g/l). $C_{BL}$ (g/l) = $P_{BL}$ (g/l) − $P_{BL'}$ (g/l) × Klassen lignin%

2.3.2 Precipitate aggregate

To extract the precipitate, the sample was wrapped in a filter paper, tied, and placed in an extraction thimble. After weighing, the extraction thimble was placed in the chamber of a Soxhlet extractor. The chamber was connected to a condenser and a boiling flask. A 9:1 1,4-dioxane:water solution was used as extraction solvent. The heat was adjusted to reach four solvent cycles per hour, and the extraction was continued for 18 hours. Under continuous treatment, co-precipitated lignin compounds not linked to xylan were dissolved into a warm solvent. The amount of free lignin was determined as the weight loss after extraction.

2.3.3 Xylan uronic acids content

The 4-O-methyl-α-D-glucuronic acid content was quantified using methanolysis and gas chromatography as described by Li et al. (2007).

2.3.4 Xylan molecular weight

The molecular weight of xylan was analysed by size exclusion chromatography (SEC) according to molecular hydrodynamic size. As preparation, the xylan sample was dissolved in 1.9 ml of 8% LiCl /N,N-dimethylacetamide (DMAC) solution under 80°C for two hours and then left at 4°C for 5 days with mild magnetic stirring. The sample was diluted to 0.5% LiCl/DMAC solution by the addition of 28.4 ml DMAC and filtered through a 0.45 µm poly(tetrafluorethylene) filter before SEC characterization. The SEC system consists of a degasser (DGU-20A), a liquid chromatograph (LC-20AD), a column oven (CT-20A) equipped with a Rheodyne 7725i fixed-loop, and a RID-10A refractive index detector. The sample was introduced by 100 µl injection and distributed in four Mixed-A-20 columns connected in series and a guard column. As a mobile phase, 0.5% LiCl/DMAC was used at a flow rate of 0.5 ml/min. Pullulan standard with different molecular weight was used for calibration.

2.4 MECHANICAL PEELING

Fifty grams of pulp (dry weight) was divided into 9 portions. For each portion, 2 litre distilled water was added to obtain a certain consistency before disintegration with PTI Disintegrator (model no. 95568, the same as used in ISO 5263) at 100 000 resolution. After disintegration, the pulp slurry was mildly impacted for 5 min in a NAF water jet defibrator at a water pressure of 1.8 bars. Pulp fibre
walls were divided into two fractions: central layers (bulk) and surface layers (fines, around 10%). Bulk part was collected by sieve PA 71, while fines passed through sieve PA 71 and were collected by another sieve PA 75.

2.5 EXCHANGED KRAFT COOKING FOR XYLAN SORPTION

After xylan characterization, it was discovered how cooking conditions affect xylan structure and xylan concentration in black liquor. Based on the results, four different black liquors with specific xylan structure were chosen for sorption studies. They were used to replace half the cooking liquor in an exchange cook. The exchange cook was performed in a laboratory digester with steam-controlled temperature and a forced circulation system. See Fig. 5.

![Fig. 5. Flow of exchange cook.]

In total, seven exchange cooks were performed in this study. In each cook, 500 g oxygen dried chips were placed in the digester with a mounted lid. Five minutes presteaming at 15 bars was performed before white liquor was pumped into the digester. This was to remove air from wood pores to facilitate diffusion of liquid. The white liquor was prepared in the following concentration: $[\text{OH}^-] = 1.25\text{ mol/l}$, $[\text{HS}^-] = 0.26\text{ mol/l}$, $[\text{Na}^+] = 2.5\text{ mol/l}$. The liquor-to-wood ratio was 4 l/kg. The cooking temperature was 157°C, which was reached by 1°C/min ramping from 100°C. Circulation started from 100°C. For all seven exchange cooks, the cooking proceeded for 120 min, at which time half the black liquor was extracted.
Liquid replacement: After 120 min, circulation was stopped. For reference cook 1 (Ref-no exchange), there was no liquor replacement during the stop. For the other six cooks, 1l of cooking liquor was removed and replaced by 1l exchange liquor during the stop. As reference cook 2 (Ref-WL), exchange liquor used white liquor with the following concentration: \([\text{OH}^-] = 0.3\ \text{mol/l}, [\text{HS}^-] = 0.26\ \text{mol/l}, [\text{Na}^+] = 2.5\ \text{mol/l}\). For cooks 3, 4, 5, and 6, the exchange liquors used the black liquors produced the day before the exchange in steel autoclaves; see Table 2. They were stored in plastic bottles squeezed to remove, presumably, air before storage at 4°C overnight and returned to room temperature before use. OH concentration of four black liquors was adjusted to 0.3 M by adding NaOH or diluting with water. Ion strength and sulphidity between exchange liquors were not compensated for. For cook 7, the exchange liquor used white liquor with birch xylan dissolved in it. All the replacements were done in 10–20 min, and temperature was increased to 157°C again without ramping. After replacement, cook was continued at 157°C for 48 min. See Table 2.

Table 2. Information about black liquors used as exchange liquors.

<table>
<thead>
<tr>
<th>Cooking conditions for production of black liquors used as exchange liquors</th>
<th>Residual alkali and xylan characteristics in black liquor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °C</td>
<td>Time min</td>
</tr>
<tr>
<td>157</td>
<td>150</td>
</tr>
<tr>
<td>167</td>
<td>200</td>
</tr>
<tr>
<td>157</td>
<td>50</td>
</tr>
<tr>
<td>167</td>
<td>50</td>
</tr>
</tbody>
</table>

2.6 HANDSHEETS PREPARATION AND TENSILE STRENGTH

The pulp was wet disintegrated and beaten with a PFI-mill (ISO 5264) at different revolutions (500, 1000, 2000, and 5000). Drainability (SchoPper-Riegler value SR°) was determined according to ISO 5267-1:1999. Handsheets were made with the Rapid-Köthen sheet dryer (ISO 5269-2:2004). The thickness and structural density were determined according to SCAN-P 88:01 method. The tensile strength was tested with a Frank Tensile Tester (horizontal TS, mod. 81502) (ISO 5270:1999, ISO 1924-2).
3 RESULTS AND DISCUSSION

3.1 EFFECT OF COOKING CONDITIONS ON DISSOLVED XYLAN

Kraft cooking of spruce chips was performed under different conditions. The reference cooking was carried out at a cooking temperature of 157°C and at a cooking liquor charge of \([\text{OH}^-] = 1.2 \text{ M} \) and \([\text{HS}^-] = 0.26 \text{ M}\). The ionic strength of the cooking liquor was \([\text{Na}^+] = 1.46 \text{ M}\). Cooks were also performed at higher ionic strength, using the same cooking conditions as the reference cooks, except that \([\text{Na}^+]\) was increased to 2.5 M, at lower alkali charge, \([\text{OH}^-] = 1.0 \text{ M}\), and at higher temperature, 167°C. The cooking time was varied between 50 and 250 min. For comparison, kraft cooking was performed on birch chips at 157°C, \([\text{Na}^+] = 1.46 \text{ M}, [\text{OH}^-] = 1.2 \text{ M}, \) and \([\text{HS}^-] = 0.26 \text{ M}\). The dissolved xylan in the black liquors was precipitated and characterized.

3.1.1 Effects of \([\text{OH}^-]\), \([\text{Na}^+]\), cooking temperature, and time on the amount of dissolved xylan

![Fig. 6. Xylan concentration in the black liquors obtained under different kraft cooking conditions.](image)

Fig. 6 shows the amount of xylan in black liquor. As expected, a higher amount of xylan was found in black liquors of birch kraft cooking, 11–13 g/l compared to maximum 4 g/l for spruce cooks. The rate of dissolution increased at higher temperature. Higher ionic strength or lower alkali charge in the cooking liquor slowed down the dissolution. By monitoring the amount of dissolved xylan in black liquor as a function of the degree of delignification, it can be seen (Fig. 7) that the amount of dissolved xylan obtained was quite similar when cooking at 157°C and 167°C. Lower alkali charge or higher
ionic strength, however, resulted in a lower amount of xylan dissolved at a given degree of delignification.

![Graph of Xylan concentration in black liquor at a certain degree of delignification under different cooking conditions.](image)

**Fig. 7.** Xylan concentration in black liquor at a certain degree of delignification under different cooking conditions.

Xylan was the predominant polysaccharide part of the precipitate, with the relative amount of 72–82% , depending on cooking conditions under which the black liquors were produced; see Table 3. However, the precipitate consisted of lignin also. In Fig. 8, the percentage of Klason lignin in precipitate is shown. The precipitate from birch black liquors consisted of only 10% lignin, whereas in the case of spruce, the lignin portion of the precipitate constituted from 30% up to 72%. Earlier studies have shown a lignin portion in hardwood black liquors of 4–18% in birch black liquor (Axelsson et al. 1962; Danielsson 2007), 12–22% in eucalyptus black liquor (Danielsson and Lindström 2009), and 9–22 % in acacia black liquor (Ginting 2009). The lignin content of precipitate from black liquor of pine kraft cooking has been reported to be only 5–10% (Engström et al. 1995). The precipitation procedure used in their study differed, however, from the one used in this thesis. The main solvent they used was dioxane, whereas ethanol was used in this investigation.
Table 3. Carbohydrate composition and amount of Klasson lignin in the precipitate.

<table>
<thead>
<tr>
<th>Cook</th>
<th>Time, min</th>
<th>Arabinose (rel %)</th>
<th>Xylose (rel %)</th>
<th>Mannose (rel %)</th>
<th>Galactose (rel %)</th>
<th>Glucose (rel %)</th>
<th>Klasson lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>157°C</td>
<td>50</td>
<td>15,3</td>
<td>57,7</td>
<td>4,8</td>
<td>13,5</td>
<td>8,8</td>
<td>30,1</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>12,3</td>
<td>57,9</td>
<td>4,9</td>
<td>14,8</td>
<td>9,0</td>
<td>51,9</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>11,1</td>
<td>59,8</td>
<td>4,1</td>
<td>16,1</td>
<td>8,9</td>
<td>54,2</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>12,1</td>
<td>57,3</td>
<td>3,7</td>
<td>19,2</td>
<td>7,6</td>
<td>64,2</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>12,1</td>
<td>60,3</td>
<td>2,5</td>
<td>19,0</td>
<td>6,1</td>
<td>67,9</td>
</tr>
<tr>
<td>157°C</td>
<td>50</td>
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<td>69,3</td>
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<td>8,8</td>
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<td>13,2</td>
<td>4,6</td>
<td>63,4</td>
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<tr>
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<td>61,4</td>
<td>1,9</td>
<td>17,8</td>
<td>5,1</td>
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<td>1,7</td>
<td>17,0</td>
<td>5,2</td>
<td>64,2</td>
</tr>
<tr>
<td>157°C</td>
<td>100</td>
<td>12,4</td>
<td>66,7</td>
<td>2,6</td>
<td>11,9</td>
<td>6,4</td>
<td>58,7</td>
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<tr>
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<tr>
<td>167°C</td>
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<td>55,3</td>
<td>2,6</td>
<td>28,6</td>
<td>7,2</td>
<td>62,4</td>
</tr>
</tbody>
</table>

Fig. 8. The amount of lignin present in the xylan precipitate from black liquor obtained under different kraft cooking conditions.

3.1.2 Fractions of free lignin and LCC in xylan aggregate

The large amount of lignin in the precipitate gave rise to the question whether the lignin in the precipitate was covalently bound to xylan. Westbye et al. (2007) have suggested that agglomerates of lignin molecules might form inclusion complexes with dissolved xylan, that is, some lignin might be co-precipitated with xylan without being covalently bound to the xylan. In order to test this, the xylan precipitate was extracted with a water and dioxane mixture. Free lignin compounds not linked to xylan were dissolved into warm solvent, and the amount was determined as weight loss. In Fig. 9, the ratio
of Klason lignin and xylan in the extracted precipitate is shown. The amount of bound lignin increased as cooking proceeded. Tamminen et al. (1995) have shown that lignin-carbohydrate complexes (LCC) exist in black liquor. They proposed that the arabinose substituents of xylan form a cross-link to the lignin molecule. Since arabinose substituents are much more common in softwood xylan, the higher amount of lignin in spruce xylan precipitate might be explained by this fact. Eriksson et al. (1980) have shown that lignin is linked to xylan by ether bonds to the arabinose unit.

Fig. 9. The fractions of free lignin, xylan, and LCC in the precipitate from black liquors obtained from the reference cooking group.

3.2 COOKING CONDITIONS AND XYLAN STRUCTURE

3.2.1 Effects of [OH⁻], [Na⁺], cooking temperature, and time on molecular weight of xylan

Higher temperature during the cook led to faster reduction of the xylan molecular weight; see Fig. 10. The $M_w$ of dissolved spruce xylan seemed to reach a maximum value after a certain cooking time and decreased afterward, as the delignification proceeded. In contrast to this, the $M_w$ of birch and eucalyptus xylan (Danielsson et al. 2005, 2009) as well as acacia xylan (Ginting 2009) has been shown to consistently decrease upon prolonged cooking time. According to Fig. 11, a maximum in molecular weight was obtained at around kappa number 70. It has been shown that the pore size of the fibre wall increases as the degree of delignification increases (Andreasson et al. 2003). Therefore, a plausible explanation could be that the larger xylan molecules were not able to dissolve into black liquor, because they were previously entrapped in the fibre wall. As the fibre wall was further delignified, the creation of voids in the fibre wall enabled larger molecules to be removed. However, as the cooking
continued, the dissolved xylan molecules in the black liquor were degraded by the alkaline hydrolysis and the peeling reactions, causing the decrease in the molecular weight.

Fig. 10. The molecular weight of the dissolved xylan in black liquor, obtained under different kraft cooking conditions.

Fig. 11. The molecular weight of the dissolved xylan in black liquor, obtained at a certain degree of delignification under different cooking conditions.
3.2.2. Effects of [OH\textsuperscript{-}], [Na\textsuperscript{+}], cooking temperature, and time on xylan substituents

4-O-methyl-α-D-glucuronic acid content in black liquor xylan decreased with prolonged cooking time; see Fig. 12. The trend was more or less similar under different cooking conditions. Cooking at higher temperature and higher [Na\textsuperscript{+}] led to a lower amount of MeGlcA in dissolved xylan, while cooking at lower [OH\textsuperscript{-}] led to a higher amount of MeGlcA.

![Fig. 12. MeGlcA content of the dissolved xylan in black liquors obtained under different kraft cooking conditions.](image)

Softwood xylan was substituted with arabinose units. As seen in Fig. 13, the arabinose content of the xylan remained unaltered over the cooking period, suggesting that the degree of arabinose substituents remained the same in the dissolved xylan. There was a slight tendency, however, for cooking at a higher temperature to result in a lower degree of arabinose substituents.

![Fig. 13. Arabinose content of the dissolved xylan in black liquors obtained under different kraft cooking conditions.](image)
3.3 EFFECTS OF COOKING CONDITIONS ON THE CHEMICAL COMPOSITION OF FIBRE BULK AND SURFACE

3.3.1 Xylan amount
Relocation of xylan takes place during kraft cooking (Dahlman et al. 2003). Xylan dissolves into cooking liquor from the fibre wall and later readso rbs onto the fibre surface. As expected, the amount of xylan was higher on the fibre surface compared to the fibre wall; see Fig. 14. As cooking was prolonged, there was a slight tendency for the amount of xylan on the fibre surface to decreased. The different cooking conditions studied did not seem to affect the proportion of xylan on the fibre surface at a given degree of delignification. The xylan fraction in the fibre wall seems to be fairly constant through the kappa number range investigated.

![Fig. 14. Xylan portion of carbohydrate part on fibre surface (unfilled symbols) and fibre bulk (filled symbols) as a function of kappa number.](image)

3.3.2 Lignin amount
The lignin content on the surface was approximately three times as high as that on the fibre wall; see Fig. 15. A higher lignin on the fibre surface has also been reported in several studies (Laine et al. 1994; Heijnession et al. 1995; Buchert et al. 1996; Westermark 1999; Fardim and Duran 2001). However, cooking at a higher temperature led to a smaller difference between the lignin content on the surface and in the fibre wall. The rate of delignification appeared to be similar at the fibre surface and fibre wall.
Fig. 15. Lignin amount on fibre surface (unfilled symbols) and fibre bulk (filled symbols) as a function of cooking time.

Since the different cooking conditions led to different delignification rates, the lignin content on the fibre surface and fibre wall is shown also as a function of kappa number; see Fig. 16. At a given kappa number it is apparent that cooking at a higher temperature or with lower alkali charge results in less lignin on the fibre surface.

Fig. 16. Lignin amount on fibre surface (unfilled symbols) and fibre bulk (filled symbols) as a function of kappa number.

### 3.3.3 Glucomannan amount

No difference in the amount of the other hemicellulose present in spruce, glucomannan, on the fibre surface compared to the fibre wall, can be concluded from Fig. 17.
3.4 EXCHANGE LIQUOR REPLACEMENT AND XYLAN SORPTION

Black liquor exchange cooks were carried out in a circulation digester. Sorption of xylan with specific characteristics onto fibers was done by replacing half of the cooking liquor at a later cooking stage with black liquor containing dissolved xylan of known characteristics. In this study, effect of molecular weight and degree of substitution of re-adsorbed xylan on tensile strength was investigated. As it is not possible to vary molecular weight or uronic acid content independently, factorial experiments were performed. Four black liquors were manufactured to obtain xylan with four different molecular weight and uronic acid content combinations. The selection of factor’s high and low level was relatively. In Table 4, the xylan characteristics in these black liquors are shown.

Table 4. Designed xylan structure in exchange black liquors

<table>
<thead>
<tr>
<th>Xylan characteristics in exchange black liquor</th>
<th>Factorial design</th>
</tr>
</thead>
<tbody>
<tr>
<td>UA / [µmol/g xylan]</td>
<td>Mₘ / [kDa]</td>
</tr>
<tr>
<td>66</td>
<td>10.6</td>
</tr>
<tr>
<td>12</td>
<td>6.3</td>
</tr>
<tr>
<td>517</td>
<td>8.6</td>
</tr>
<tr>
<td>188</td>
<td>9.2</td>
</tr>
</tbody>
</table>

3.4.1 Pulp yield

Exchange cooks were carried out under the same cooking conditions, and liquid replacement was performed between two predetermined cooking times, 120 min and 48 min. The pulps produced by
exchange cooks all had a kappa number around 27; see Table 5. The reference cook, Ref-WL, where half the spent cooking liquor was replaced with white liquor, resulted in 1.3% less yield compared to the reference cook where no exchange of liquor had taken place, Ref-no exchange cook. This was expected, since exchanging half of the cooking liquor with white liquor removed half the amount of the dissolved xylan, resulting in a lower amount of xylan being redeposited on the fibre surfaces. Exchanging half the cooking liquor with white liquor containing dissolved birch xylan gave approximately the same pulp yield as in the case of Ref-no exchange. Exchanging half the cooking liquor with different black liquors containing spruce xylan all resulted in lower yields. It can be hypothesized that the added spruce xylans had a lower tendency to redeposit compared to the ‘original’ xylan, and consequently, lower yields were obtained compared to the no-exchange cook.

Table 5. Pulp kappa number, pulp yield, track of xylan, and residual alkali of variable exchange process

<table>
<thead>
<tr>
<th>Exchange cook</th>
<th>Kappa number</th>
<th>Screened yield [%]</th>
<th>[OH-]_end [mol/l]</th>
<th>Add in xylan [g/l]</th>
<th>Xylan in black liquor (after 48 min cooking time) [g/l]</th>
<th>Readesorbed xylan/added in xylan [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref-WL</td>
<td>29.2</td>
<td>47.5</td>
<td>0.22</td>
<td>0</td>
<td>0.71</td>
<td>–</td>
</tr>
<tr>
<td>Ref-no exchange</td>
<td>28.6</td>
<td>48.8</td>
<td>0.20</td>
<td>0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>UA 517 M_w 8600</td>
<td>27.6</td>
<td>46.2</td>
<td>0.25</td>
<td>1.15</td>
<td>1.05</td>
<td>70</td>
</tr>
<tr>
<td>UA 188 M_w 9200</td>
<td>26.4</td>
<td>45.2</td>
<td>0.23</td>
<td>3.15</td>
<td>1.38</td>
<td>78</td>
</tr>
<tr>
<td>UA 66 M_w 10600</td>
<td>27.3</td>
<td>47.0</td>
<td>0.19</td>
<td>2.22</td>
<td>1.25</td>
<td>76</td>
</tr>
<tr>
<td>UA 12 M_w 6300</td>
<td>28.1</td>
<td>45.7</td>
<td>0.24</td>
<td>1.46</td>
<td>1.02</td>
<td>79</td>
</tr>
<tr>
<td>Birch</td>
<td>28.7</td>
<td>48.5</td>
<td>0.24</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
3.4.2 Influence of adsorbed xylan on pulp drainability

The measurement of Schopper-Riegler number (SR°) is one of the most common pulp dewatering tests. Drainability is affected by the amount of fines and the degree of beating. The development of pulp drainage resistance SR° is shown in Fig. 18. At the same PFI revolutions (the same beating energy input), the pulps obtained from the Ref-no exchange cook and cooks where half the cooking liquor was exchanged with white liquor containing birch xylan had noticeably lower SR° compared to other pulps.

![Fig. 18. SR° as a function of beating.](image)

3.4.3 Influence of adsorbed xylan on pulp tensile strength

In Fig. 19, the development of tensile strength upon beating is seen. The pulps lightly beaten, at 500 PFI revolutions, where the original xylan was exchanged with birch xylan, gave the best strength improvement. However, as beating proceeded, at 5000 PFI revolutions, the pulp that adsorbed spruce xylan with the highest uronic acid content displayed the best tensile strength. Adsorbing birch xylan, which had started off so promisingly, showed no strength improvement at the higher beating levels.
In Fig. 20, the tensile index as a function of sheet density is shown. It is even more apparent from this figure that at a lower degree of beating, adsorbing of birch xylan onto the fibres was pronouncedly better than was adsorbing spruce xylan, from a tensile strength perspective. Compared at any certain sheet density above 700kg/m³, the pulp adsorbing spruce xylan with the highest uronic acid content had a higher tensile index than the other pulps. In other words, it had higher bonding strength at a given degree of bonding.

Fig. 19. Tensile index development upon PFI beating.

Fig. 20. Tensile index vs. sheet density.
The solubility of xylan is affected by the degree of substitution. Xylan molecules containing few uronic acid groups will either redeposit on available fibre surfaces or aggregate with other xylan molecules. A high number of acid groups on the xylan chain, on the other hand, would therefore both keep the molecules dissolved in the liquor and prevent them from aggregating. It can be hypothesized that these free floating xylan molecules have been able to penetrate pores on the fibre surface. Free xylan molecules have a gyration radius below 10 nm (Danielsson 2007), and the pore radius of an unbleached softwood kraft pulp is 22 nm (Maloney et al. 1998). As beating creates more surface area, that is, external fibrillation, the xylan is, so to speak, activated, resulting in improved tensile strength. On the other hand, it can be assumed that xylan aggregates deposited on the fibre surface might be rubbed off the fibres during beating.

The number of fibres taking part in the stress transfer will also affect the strength of a paper. Since tensile strength is measured as tensile index, the tensile strength is indexed by the grammage, g/m², of the paper. Making paper from a pulp with higher yield would therefore mean that a sheet with a certain grammage would contain fewer fibres. The pulps in this present study had somewhat different yields, and to determine whether any strength differences are due to the amounts of fibres, the tensile strength at a given density was extrapolated from Fig. 20. As can be seen in Fig. 21, no correlation between the tensile strength, at a sheet density of 700 kg/m³, and yield can be seen.

Fig. 21. Tensile index vs. yield at a sheet density of 700 kg/m³.
4 CONCLUSIONS

- The dissolution rate of spruce xylan during kraft cooking was slower compared to the dissolution rate of birch xylan.

- Dissolved spruce xylan had a higher amount of bound lignin, from 30% up to 72%. This is much higher than what has been reported earlier for dissolved hardwood xylan. Birch xylan has been reported to contain only 10% lignin, and eucalyptus xylan 15–20% lignin.

- The molecular weight of the dissolved xylan depended on the degree of delignification of the wood matrix. Delignification of the wood matrix down to kappa number approximately 80 increasingly enabled larger xylan molecules to dissolve into the black liquor. Further delignification led to a degradation of the dissolved xylan molecules.

- The ionic strength of the cooking liquor affected the amount of xylan dissolved as well as the uronic acid content of the xylan. Higher ionic strength gave less dissolved xylan and lower uronic acid content.

- Increased temperature increased the dissolution rate of xylan from the wood matrix as well as the degradation rate of the molecular weight of the dissolved xylan. However, at the same degree of delignification of the wood matrix, temperature had no effect on the amount dissolved or the molecular weight of the dissolved xylan.

- The composition of the fibre surface was affected by the cooking conditions. At a certain kappa number, the lignin content was higher, if the cook had been performed at a lower temperature or higher ionic strength.

- The strength-enhancing effect of xylan depended on its chemical structure.

- When xylan with a very high content of uronic acid was deposited on the fibres, the tensile strength was improved at higher degrees of beating.
5 Future Work

Dissolved xylan in the black liquor of kraft cooking from other plant raw materials can be studied to characterize xylan structure under different cooking conditions.

Strength properties, in addition to tensile strength can be investigated.

The structure of the sheets with different xylan content can be studied using SEM.

It would also be interesting to use analytical tools to determine the degree of fibrillation and how the xylan characteristics affect this.
First of all I would like to thank my supervisors, Professor Mikael E Lindström and Assistant Professor Elisabet Brännvall, for giving me the opportunity to do this work, and their scientific guidance.

I am deeply grateful to Elisabet Brännvall for all the time you put into my work. Your knowledge of pulp and paper and key insights into this project have steadily directed me throughout my work. And thanks so much for carefully reading this thesis. I have received so many valuable comments and motivating questions.

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7 REFERENCES


