

High-yield Pulping of Scots Pine under Strongly Alkaline Conditions

Markus Paananen



High-yield Pulping of Scots Pine under Strongly Alkaline Conditions

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Abstract

The high price of raw material and the global and competitive pulp market is a combination that creates an additional challenge for the Nordic softwood pulping industry. During conventional kraft pulping, less than half of the raw material ends up in the pulp. In order to reduce carbohydrate losses while producing a bleachable-grade pulp, this work investigated different aspects that effect the degradation and dissolution behavior of Scots pine polysaccharides, as well as delignification. Emphasis was put on the effect of liquor alkali concentration and pulping temperature.

Under alkaline conditions, considerable polysaccharide losses occurred during the initial pulping or heating-up phase. Increases in the liquor alkali concentration at constant sulfidity provided substantially faster delignification. Pulp yield, on the other hand, was comparable regardless of alkali concentration due to the higher galactoglucomannan (GGM) and slightly lower arabinoxylan and cellulose content in the pulp.

The effect of polysulfide (PS) and anthraquinone (AQ) on carbohydrate preservation was investigated, with a special emphasis on the influence of liquor alkalinity and temperature. In the presence of PS, the influence of liquor alkali concentration on overall polysaccharide preservation was rather insignificant. However, the rate of delignification was considerably faster at higher liquor alkali concentrations, thus ensuring effective delignification even at 130°C. During high-alkali low-temperature polysulfide pulping (HALT-PS), carbohydrate losses were substantially reduced compared to conventional kraft processes at 160°C. In particular, the preservation of GGM and cellulose was improved, thus pulp yield in HALT-PS concept pulping was up to 7.2% higher. The viscosity of HALT-PS pulp was well preserved or even improved compared to reference kraft pulp due to the lower pulping temperature. Despite the high brownstock pulp kappa number of 50, the high-yield HALT-PS pulp was effectively delignified before bleaching. Therefore, pulp yield advantage and fiber strength were well-maintained in the fully bleached pulp. Pulping according to the HALT-PS concept would require additional black liquor (BL) treatment due to large amounts of unused alkali. In order to recycle and re-use the alkali-rich liquor fraction and thus support conventional chemical recovery, membrane filtration was effectively used to purify the BL from dissolved hemicelluloses and fragmented lignin.

Keywords alkaline hydrolysis, anthraquinone, degradation, dissolution, galactoglucomannan, high-alkali, high-yield, peeling, polysulfide, Scots pine, stopping, ultrafiltration

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Männyn korkeasaantoinen kuidutus vahvasti alkalisissa olosuhteissa

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Pohjoisen ilmastovyöhykkeen havupuuselluteollisuus kohtaa erityisiä haasteita puuraaka-aineen korkean hinnan, sekä sellu-, paperi- ja kartonkiteollisuuden murroksesta johtuvan tiukentuneen kilpailun takia. Peinteissä sulfaattiprosessissa alle puolet puuraaka-aineesta päätyy lopputuotteeseen eli selluun. Tämä työ tutkii olosuhteita jotka vaikuttavat pohjoisella ilmastovyöhykkeellä menestyvän metsämännyn (*Pinus sylvestris* L.) hiilihydraattien pilkkoutumiseen ja liukenemiseen, sekä delignifioitumiseen alkalisin prosessin aikana. Työ painottui erityisesti keittolipeän alkalipitoisuuden sekä keittolämpötilan vaikutukseen.

Alkalisissa olosuhteissa merkittäviä hiilihydraattihäviöitä tapahtuu jo keiton alkuvaiheessa ennen lopullisen keittolämpötilan saavuttamista. Perinteiseen sulfaattiprosessiin verrattuna korkeammalla keittolipeän alkalipitoisuudella aikaansaadaan huomattavasti nopeampi delignifioituminen. Massan keittosaanto säilyy kuitenkin käytännössä muuttumattomana korkeammasta galaktoglukomannaanisaannosta, ja hieman laskeneesta arabinoksyylaani- ja selluloosasaannosta johtuen.

Polysulfidin (PS) ja antrakinonin (AQ) vaikutusta hiilihydraattien säilyvyyteen tutkittiin eri alkali-pitoisuuksissa ja lämpötiloissa. PS-keitoissa keittolipeän alkalipitoisuuden vaikutus hiilihydraattien säilyvyyteen oli melko merkityksetön, delignifioituminen oli kuitenkin huomattavasti nopeampi korkeampaa alkalipitoisuutta hyödyntämällä. Tämä mahdollisti keittolämpötilan laskun, ja tehokkaan delignifioitumisen jopa 130°C lämpötilassa. Näissä olosuhteissa (korkea-alkalinen PS keittoliuos, matala lämpötila; HALT-PS), hiilihydraattien stabiilisuus parani huomattavasti verrattuna perinteiseen sulfaattiprosessiin 160°C lämpötilassa. Erityisesti galaktoglukomannaanin ja selluloosan retentio kasvoi merkittävästi, johtaen jopa 7.2%-yksikköä korkeampaan sellun saantoon. Kuvatulla prosessilla tuotettujen korkeasaantomassojen viskositeetti säilyi ja paikoitellen jopa nousi verrattuna perinteiseen sulfaattiprosessiin. Korkeasta ruskeanmassan kappaluvusta huolimatta (kappaluku 50), HALT-PS prosessilla tuotettu massa oli verrattain helppo valkaista, jolloin keiton saantoetu ja kuidun lujuus säilyivät myös täysin valkaistussa massassa. Korkea-alkalinen keittoprosessi vaatii erityisen mustalipean puhdistusprosessin korkean jäännösalkali-pitoisuuden takia. Keittolipeän membraanisuodatus käytettiin tehokkaasti puhdistamaan mustalipeää liuenneista hiilihydraateista sekä ligniinistä, joka mahdollistaisi keittolipeän kierrättämisen ja keittokemikaalien uudelleenkäytön.

Avainsanat alkalinen hydrolyysi, antrakinoni, galaktoglukomannaani, korkea alkalipitoisuus, liukeneminen, polysulfidi, pysäytysreaktio, päätepilkkoutuminen, ultrasuodatus

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Preface

The work summarized in this thesis was carried out in the department of Forest Products Technology at the Aalto University School of Chemical Technology during 2008 – 2009 and 2010 – 2015. This work was made possible by the funding and support of TEKES, FIBIC Ltd, and commercial corporations, including (in alphabetical order) Andritz, Kemira, Metsä Fiber, Metso, Stora Enso, and UPM. Your endless support throughout this study is cordially acknowledged.

Professor Herbert Sixta, you have guided me through a long journey, and you were always available to recalibrate my focus. Sometimes it is difficult to understand the vast experience and knowledge you possess in our field of science. You have my deepest gratitude.

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passionately pursued. My mother Leena and brother Kasper, I am forever grateful for your support throughout these years. And not to forget my “extended family,” Leena and Paavo - I now see the origin of Maija’s great characteristics. Laura, Jaakko, and your two energetic children Eemeli and Aada: You made me recognize what the most important thing in life is. Maija, your daily love and affectionate support mean everything to me.

Markus Paananen

Helsinki, 16th March 2016

List of publications

This doctoral dissertation consists of a summary of the following five publications, which from here on are referred to as Roman numerals in the text:

- I** **Paananen, M.**, Tamminen, T., Nieminen, K., Sixta, H. (2010) Galactoglucomannan stabilization during the initial kraft cooking of Scots pine. *Holzforschung*, 64:683—692.
- II** **Paananen, M.**, Liitiä, T., Sixta, H. (2013) Further insight into carbohydrate degradation and dissolution behavior during kraft cooking under elevated alkalinity without and in the presence of anthraquinone. *Industrial & Engineering Chemistry Research*, 52:12777—12784.
- III** **Paananen, M.**, Rovio, S., Liitiä, T., Sixta, H. (2015) Effect of hydroxide and sulfite ion concentration in alkaline sulfite anthraquinone (ASA) pulping – a comparative study. *Holzforschung*, 69:661—666.
- IV** **Paananen, M.**, Rovio, S., Liitiä, T., Sixta, H. (2015) Stabilization, degradation, and dissolution behavior of Scots pine polysaccharides during polysulfide (K-PS) and polysulfide anthraquinone (K-PSAQ) pulping. *Holzforschung*, 69:1049—1058.
- V** **Paananen, M.**, Sixta, H. (2015) High-alkali low-temperature polysulfide pulping (HALT) of Scots pine. *Bioresource Technology*, 193:97—102.

Author's contribution

- I** Markus Paananen carried out all experiments and the pulp and black liquor analyses, and wrote the introduction and experimental sections of the manuscript.
- II** Markus Paananen carried out all experiments and the pulp characterization, and wrote the manuscript as principal author. Tiina Liitiä and Stella Rovio performed the black liquor analyses.
- III** Markus Paananen carried out all experiments as well as pulp characterization, and wrote the manuscript as principal author. Tiina Liitiä and Stella Rovio performed the black liquor analyses.
- IV** Markus Paananen carried out all experiments as well as pulp characterization, and wrote the manuscript as principal author. Tiina Liitiä and Stella Rovio performed the black liquor analyses..
- V** Markus Paananen carried out all experiments as well as pulp and black liquor analyses and wrote the manuscript as principal author.

Related publications

Nieminen, K., Kuitunen, S., Paananen, M., Sixta, H. (2014) Novel insight into lignin degradation during kraft cooking. *Industrial & Engineering Chemistry Research*, 53:2614—2624.

Nieminen, K., Paananen, M., Sixta, H. (2014) Kinetic model for carbohydrate degradation and dissolution during kraft pulping. *Industrial & Engineering Chemistry Research*, 53:11292—11302

Nieminen, K., Testova, L., Paananen, M., Sixta, H. (2015) Novel insight in carbohydrate degradation during alkaline treatment. *Holzforschung*, 69:667—675.

List of essential abbreviations

2,5-DHPA	2,5-Dihydroxypentanoic acid
2-HBA	2-Hydroxybutyric acid
AGU	Anhydroglucose unit
ASA	Alkaline sulfite anthraquinone pulping process
AQ	9, 10- Anthraquinone
AHQ[•]	Partially oxidized anthrahydroquinone radical
AHQ²⁻	Fully reduced anthrahydroquinone
AX	Arabinoglucuronoxylan
B.A.R	Benzilic acid rearrangement reaction
BL	Black liquor
BLG	Black liquor gasification
CTO	Crude tall oil
D₀	First acidic bleaching stage in ECF bleaching sequence
D₁	Second acidic bleaching stage in ECF bleaching sequence
DP	Degree of polymerization
Eop	Alkaline extraction stage (with oxygen and peroxide) in ECF bleaching sequence
ECF	Elemental chlorine free
EDTA	Ethylenediaminetetraacetic acid
FT-OD	Flow-through oxygen delignification
G-L	Lignin-carbohydrate-complex enriched with glucomannan
GGM	Galactoglucomannan
GISA	Glucoisosaccharinic acid
HALT-PS	High-alkali low-temperature polysulfide pulping process
KL	Klason lignin (acid insoluble lignin)
L/W	Liquor-to-wood ratio (mL/g)
LA	Lactic acid
LCC	Lignin-carbohydrate-complex
MCC	Modified cooking concept
NBSK	Nordic bleached softwood kraft
O	Single stage oxygen delignification process
OD	Oxygen delignification process
OxO	Two-stage oxygen delignification process with inter-stage treatment
odw	Oven dry wood
P	Peroxide stage in ECF bleaching sequence
PS	Polysulfide
PSAQ	Polysulfide + 9, 10- anthraquinone
REG	Reducing end-group
S₀	Polysulfide charge, expressed as elemental sulfur amount
SET	Single electron transfer reaction
UF	Ultrafiltration
X-L	Lignin-carbohydrate-complex enriched with xylan
XISA	Xyloisosaccharinic acid

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References

1 Introduction and Outline of the Study

A steady increase in paper consumption, together with improvements in pulp bleaching and chemical recovery system, empowered the rise of chemical pulping industry in the 20th century (Sixta 2006). In the 21st century, alkaline pulping processes, and especially kraft process, is used to produce pulp for the needs of paper industry. Today, mature and well established pulping technology has ensured the built-up of even larger pulp mills (>1 million tons/year); locating mainly on areas with growing paper consumption and fast growing wood feedstock, such as Latin America and Asia. In Europe, on the other hand, paper consumption is slowly decreasing and the number of particularly smaller pulp mills is annually declining (CEPI 2014). European pulp mills that remain competitive in global market are characteristically larger, use softwood as raw material, and continuously pursue towards more efficient pulping processes.

Especially in Nordic countries, a substantial part of the overall production costs is related to softwood raw material (Kangas et al. 2014). Alkaline pulping is connected with major carbohydrate losses as a consequence of non-selective lignin removal. Approximately one third of the softwood carbohydrates are removed along with lignin; thus less than half of the dry raw material is transferred to brownstock pulp. Main polysaccharide losses originate from progressive end-wise degradation reaction (peeling); in which, the terminal monosaccharide unit is cleaved-off from the reducing end of polysaccharide chain via β -elimination. All polysaccharides undergo peeling reactions; nevertheless, especially galactoglucomannan (GGM) losses are extensive even before the final cooking temperature is reached. Peeling reactions are chemically terminated when the reducing end-group (REG) is converted into alkali-stable acidic end-group (stopping reaction). Both peeling and stopping are alkali dependent reactions, however, the rate of stopping reaction is increasing to the level of the peeling reaction by elevated base concentration (Lai & Sarkanen 1969). Furthermore, pulping liquor containing oxidants, such as polysulfide (PS) and 9,10-anthraquinone (AQ), effectively stabilize the REGs against peeling. At conventional pulping temperature around 150-170°C, polysaccharide chains are randomly depolymerized at substantial rate due to alkali-induced cleavage of glycosidic bonds, or alkaline hydrolysis (Lai & Sarkanen 1967). Following the polysaccharide chain scission, the newly formed REG undergoes further end-wise degradation (secondary peeling), thus contributing to additional carbohydrate losses.

According to current practice in producing bleachable grade softwood kraft pulp, approximately 90% of the initial lignin (corresponding to kappa number 30; κ -30), is removed in pulping and further delignification is obtained in the subsequent oxygen

delignification process (OD). Transition from pulping to OD is compulsory in order to maintain a good rate of delignification and to reduce the extent of carbohydrate chain depolymerization and loss reactions. Since the selectivity of lignin removal is generally better in OD than during the pulping stage, termination of pulping significantly above κ -30 would be even more advantageous in terms of carbohydrate preservation (Parthasarathy 1997). However, during a conventional two-stage OD process the kappa reduction is typically limited to around 60%, above which, delignification selectivity is again impaired.

As emphasized above, kraft pulping technology is well established, nonetheless, further needs and advances particularly in lowering production costs and recovering of the value-added wood by-products are acknowledged. Through a comprehensive experimental study, this thesis provides further understanding of the effect of pulping liquor composition and temperature on the behavior of softwood constituents. While producing bleachable grade pulp, the main objective was to demonstrate means that ensure a significant pulp yield increase in respect to conventional kraft pulping practice. Emphasis was put in wood fractionation and especially in kraft based pulping, which is the most relevant chemical pulping method worldwide.

Parallel to lignin removal, this thesis identifies the key factors that affect degradation and dissolution behavior of softwood polysaccharides under alkaline conditions. In **paper I**, initial kraft pulping kinetics were studied in order to provide fundamental understanding regarding initial delignification and rapid carbohydrate losses during heating-up phase. In order to minimize the changes in pulping liquor chemical composition and the effect of mass transfer, high liquor-to-wood ratio and wood meal was utilized, respectively. At constant sulfidity, the influence of liquor hydroxide ion concentration on the carbohydrate preservation was studied at 80-130°C, while underlining the peeling and stopping reactions of GGM. A similar experimental set-up was utilized also in **paper II**, however, the focus was transferred on polysaccharide behavior during bulk delignification phase at 130-160°C. In addition to **paper I**, black liquor was characterized in order to differentiate carbohydrate losses via dissolution and degradation.

Paper II also demonstrated preliminary attempts to increase pulp yield and accelerate delignification reactions during kraft pulping by utilizing oxidative additives, namely AQ. **Paper III**, on the other hand, introduced alkaline sulfite anthraquinone (ASA) process, which provides comparable fiber strength to kraft process. In this comparative study, ASA pulping is assessed in respect to kraft and kraft-AQ processes to elucidate the effect of sulfite anions in comparison to HS^- and anthrahydroquinone (AHQ^-) as strong nucleophiles, presented in **paper II**. The main emphasis of **papers II** and **III** was to

evaluate the effect of AQ on polysaccharide stabilization in respect to liquor chemical composition.

In **paper IV**, further improvement in the stability of polysaccharides was obtained using another oxidative agent, polysulfide (PS). PS was studied without and together with AQ (PSAQ) at conventional pulping temperature of 160°C and, in addition, at 130°C in order to prevent alkaline hydrolysis reactions. Again, the main focus was on the effect of cooking chemical concentration on the delignification and polysaccharide preservation kinetics.

Whereas **papers I - IV** utilized wood meal and elevated liquor-to-wood ratio to underline the essential pulping reactions, finally, **paper V** demonstrated the favorable conditions for carbohydrate preservation at conditions resembling industrial practice. In addition, unconventional approach for alkali recovery and extended oxygen delignification is presented, as a part of the scale-up demonstration. **Figure 1** illustrates the division of research areas according to **papers I-V**.

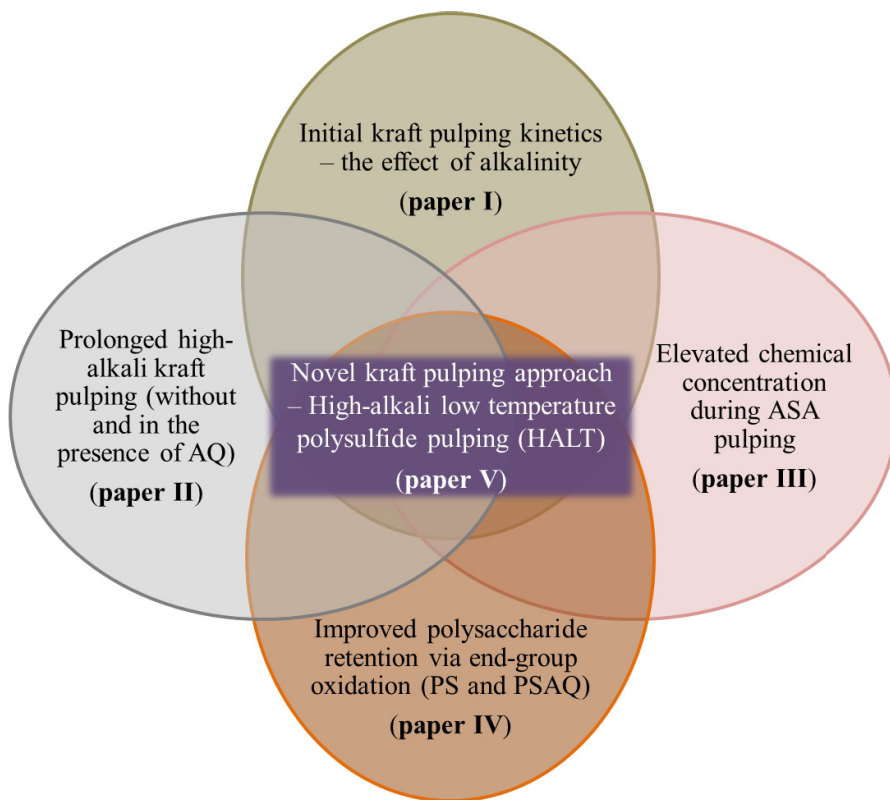


Figure 1 Research areas covered in this thesis and the outline of the published research articles.

2 The Structure of Softwood

2.1 Wood Ultrastructure

Before addressing the chemistry of pulping, it is important to understand the distinguishable hierarchical structures of softwood and its main constituents (**Fig. 2**). Softwood consists of tracheids or commonly fibers that are generally 2-4 mm long and oriented in the longitudinal direction of the stem. Fiber cell wall is built upon cellulose microfibril bundles (10-20 nm in width), being encapsulated in a complex lignin-hemicellulose matrix. Fiber cell wall can be further divided into distinctive layers, characterized by altering chemical composition, thickness and fibril orientation. Individual fibers are bound together by a highly lignified middle lamella (ML). The thin primary wall (P, 0.1-0.2 μm) is enriched with lignin and characterized by non-defined orientation of cellulose microfibrils. The secondary wall (S) is formed by three sublayers, thin outer (S_1) and inner layers (S_3), and a thick middle layer (S_2). According to growth time, S_2 layer thickness varies greatly, in a range of 1 μm (earlywood, fluid transport) and 5 μm (latewood, mechanical support). Microfibril orientation in the secondary cell wall is more organized than in primary wall; nonetheless, it varies within sublayers. In the S_1 and S_3 layers, microfibrils are oriented against the fiber axis in a range of 50-90°, whereas in S_2 layer the microfibril orientation is between 5° and 30°, with earlywood fibers having higher microfibril angles than latewood fibers. Accordingly, S_2 layer properties have a pronounced influence on the fiber stiffness. (Sjöström 1993)

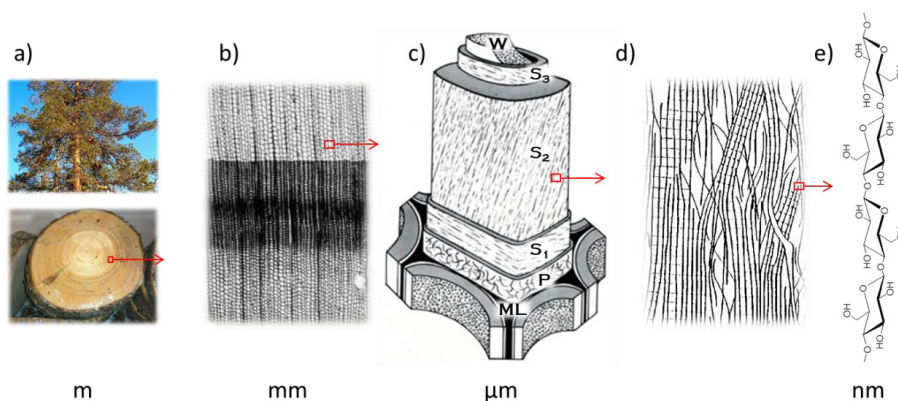


Figure 2 Hierarchical structure of softwood: **a)** individual tree and cross section of Scots pine (*Pinus sylvestris* L.), **b)** growth rings presenting earlywood (light) and latewood (dark), adapted from Schweingruber (2007) **c)** cell wall layers, adapted from Côte (1967) **d)** fringed fibril model of cellulose supramolecular structure, adapted from Hearle (1958). **e)** polymeric cellulose chain.

2.2 Chemical Composition

As a natural biocomposite, softwood fibers are chemically comprised of cellulose, galactoglucomannan (GGM), arabinoglucuronoxylan (AX), lignin, and extractives. Each component is associated with specialized purpose in the fiber cell wall functionality. Cellulose and hemicelluloses (GGM and AX) are basically supporting material for the cell wall (Sjöström 1993). Lignin, on the other hand, acts as adhesive that attaches everything together to form a rigid fiber. Extractives are considered non-structural constituents, although they are essential in the biological activities of the tree. In native softwood, AX and GGM show distinctively different structural localization in the fiber wall, GGM accompanying cellulose and AX in close connection with lignin (Salmén & Olsson 1998). Average softwood composition is presented in **Table 1**.

Table 1 The main components of softwood (Sjöström & Westermarck 1999).

Component	%, on dry wood
Cellulose	37-43
Galactoglucomannan	15-20
Arabinoglucuronoxylan	5-10
Lignin	25-33
Extactives	2-5

2.2.1 Cellulose

Cellulose is a linear homopolymer built of β -D-anhydroglucopyranose units, linked by β - (1 \rightarrow 4)-glycosidic bonds. Each anhydroglucose unit (AGU) has three hydroxyl group substituents attached to C₂, C₃, and C₆ carbon (**Fig. 3a**). Two adjacent AGUs form cellobiose, having a length of 1.03 nm (Fengel & Wegener 1989) and forming the repeating unit of cellulose chain. The native softwood cellulose chain consists of several thousands of repeating AGUs (chain length denoted as degree of polymerization, DP), reaching a length of few micrometers.

Cellulose has a strong tendency for intra- and intermolecular hydrogen bonding between the hydroxyl groups. Intermolecular bonds cause bundles of cellulose chains to aggregate into microfibrils, and further to fibrils. Fibrils are then enclosed with hemicelluloses and lignin to form the structure of fiber cell wall. Supramolecular structure of cellulose can be defined as a two-phase entity including low-ordered amorphous structures and high-ordered crystalline regions, as already illustrated in **Figure 2d**. Extensive intermolecular hydrogen bonding is observed in the crystalline domains, thus characterized by dense structure, strength, and swelling resistance. On the other hand, amorphous areas tend to be more accessible; therefore, degradative reactions of cellulose are predominantly taking place at these regions.

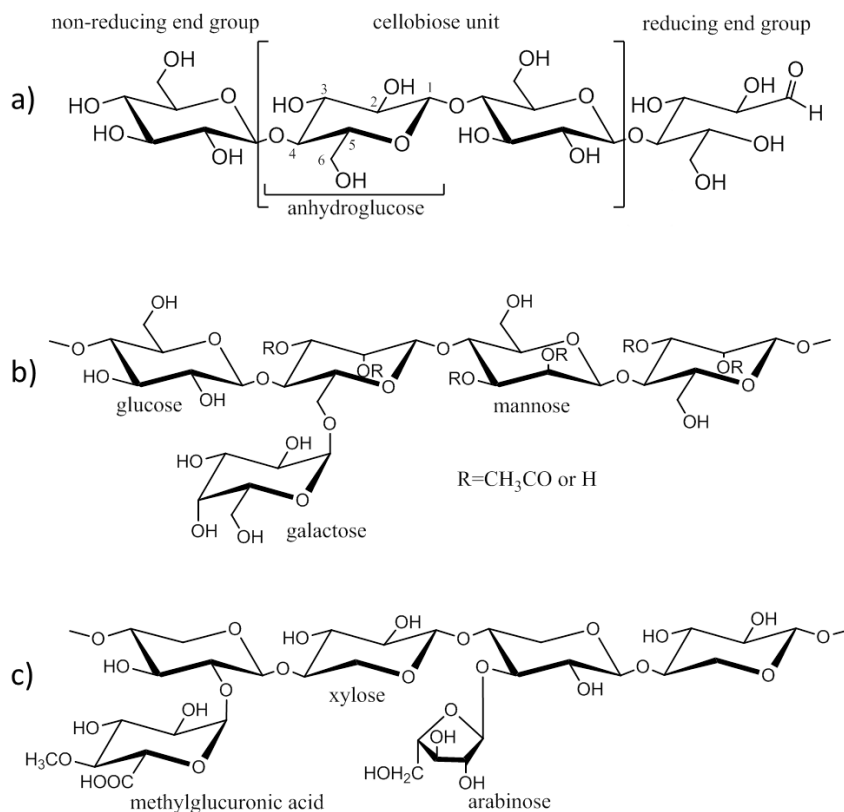


Figure 3 The partial structure of softwood **a)** cellulose, **b)** galactoglucomannan, and **c)** arabinoglucuronoxylan.

2.2.2 Galactoglucomannan

Hemicelluloses are heterogeneous polysaccharides that consist of different monosaccharide units. Structure of hemicelluloses is often considered to be amorphous although they arguably are oriented more or less in the same direction as the cellulose microfibrils (Stevanic & Salmén 2009). The principal hemicellulose in softwood and in Scots pine in particular, GGM, is built up of β - (1 \rightarrow 4) linked glucose and mannose monomers that alternate within the linear backbone (**Fig. 3b**). Mannose is partly substituted with α - (1 \rightarrow 6) linked galactose monomer, in a ‘galactose: glucose: mannose’ molar ratio of 1:1:3 (Sjöström 1993). In addition, roughly every third mannose unit contains an acetyl group in C₂ or C₃ position, corresponding approximately 6% of the total GGM amount (Alén 2000). The DP of native GGM is much lower than that of cellulose: in a range of 90-102 (Jacobs & Dahlman 2001).

2.2.3 *Arabinoglucuronoxylan*

The linear backbone of the minor softwood hemicellulose, AX, is built up of β - (1 \rightarrow 4) linked xylose units (**Fig. 3c**). The DP of softwood AX is considered rather similar to GGM, varying in the range of 89-120 (Jacobs & Dahlman 2001). Xylose units are partially substituted with α - linked 4-*O*-methyl-D-glucuronic acid (C₂ position) and L-arabinofuranose units (C₃ position) in a molar ratio of 8: 2: 1 corresponding ‘xylose: methyl-glucuronic acid: arabinose’ (Sjöström 1993).

2.2.4 *Lignin*

The structure of lignin is complex. Starting from the work of Anselme Payen in 1838 and later by Peter Klason in 1897 (Sjöström 1993), lignin structure as we know it today has been slowly unraveled. Still today, studying entities of native lignin is problematic due to the difficulties in isolating lignin without major fragmentation of its structure. Lignin is built up from phenyl propane precursor units: in case of softwood, mainly from coniferyl alcohol units. Precursor units are inter-linked with various bonding configurations. Approximately two thirds of the overall inter-linkages are ether type with numerous configurations, and the rest rather stable carbon-carbon bonds, as elucidated in **Figure 4**. The predominant bond type is the β -*O*-4 aryl ether bond, coupling roughly half of the precursor units in native softwood lignin. (Adler 1977)

3 Main Reactions of Polysaccharides and Lignin under Alkaline Conditions

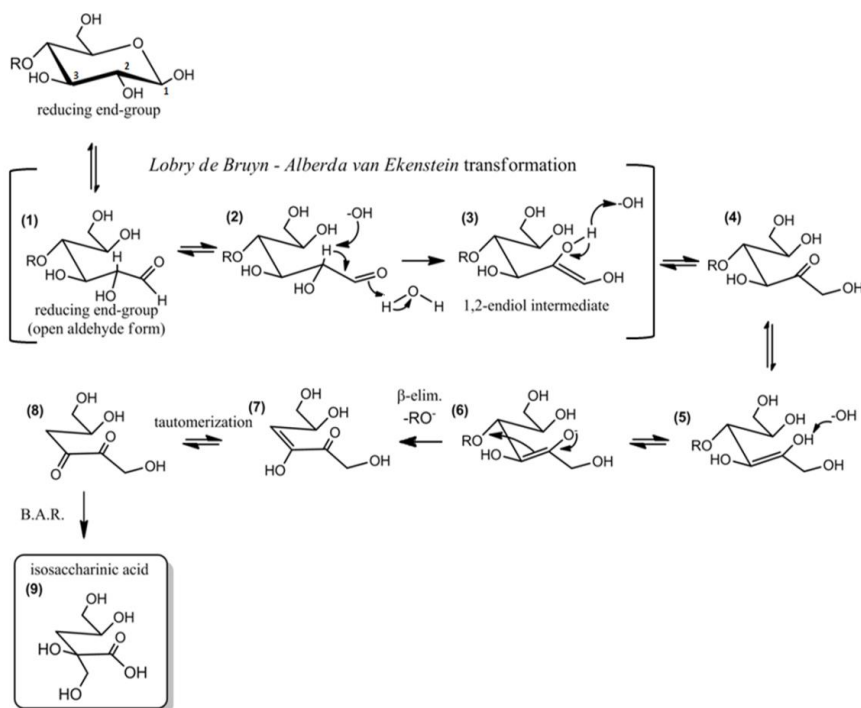
3.1 Polysaccharide Loss Reactions

No chemical pulping process is completely selective towards lignin, also undesirable polysaccharide losses occur parallel to delignification. Under alkaline conditions, the main carbohydrate degradation reactions are end-wise degradation (peeling) and random chain depolymerization (alkaline hydrolysis) followed again by end-wise degradation (secondary peeling).

3.1.1 Peeling - End-wise Degradation

All softwood polysaccharide chains contain reducing and non-reducing end-groups; accordingly, the number of REGs is practically inverse of polysaccharide chain length, or DP. Whereas the non-reducing end is considered stable under alkaline conditions, REGs are susceptible to peeling reactions. In peeling, the terminal monosaccharide unit is progressively cleaved-off from polysaccharide chain. Primary peeling reactions occur already during heating-up to final cooking temperature, thus, they cause major carbohydrate losses.

Monosaccharide units in cellulose and GGM chain (hexoses) are substituted by hydroxyl groups at C₂, C₃, and C₆ position; the most and the least reactive hydroxyl groups are found in C₂ and C₃ positions, respectively (Whistler & BeMiller 1958). As illustrated in **Scheme 1**, peeling reaction involves isomerization at C₂ that is initiated in enolization reaction known as Lobry de Bruyn – Alberda van Ekenstein transformation (Lobry de Bruyn & Alberda van Ekenstein 1895 and 1897; Speck 1958). Such rearrangement of the REG leads to formation of 1,2-endiol intermediate (**3**) and eventually a keto form (**4**). The keto form further undergoes an alkali assisted β -elimination reaction (**5-6**), resulting in the cleavage of the terminal monosaccharide unit and simultaneous formation of a new reducing end-group. Cleaved-off end-group (**7**) then rearranges to form isosaccharinic acid (**9**) or other hydroxy acids. In case of softwood, isosaccharinic acids formed from GGM or cellulose, and from AX are called glucoisosaccharinic and xyloisosaccharinic acids, respectively. Before the final cooking temperature is reached, over half of the GGM (9.5% odw) is lost via peeling while only 25% of the lignin (6.6% odw) is removed (Matthews 1974). Matthews also reported a notable cellulose loss during heating-up period (3.5% odw), whereas AX was found to be rather stable at lower temperature region.



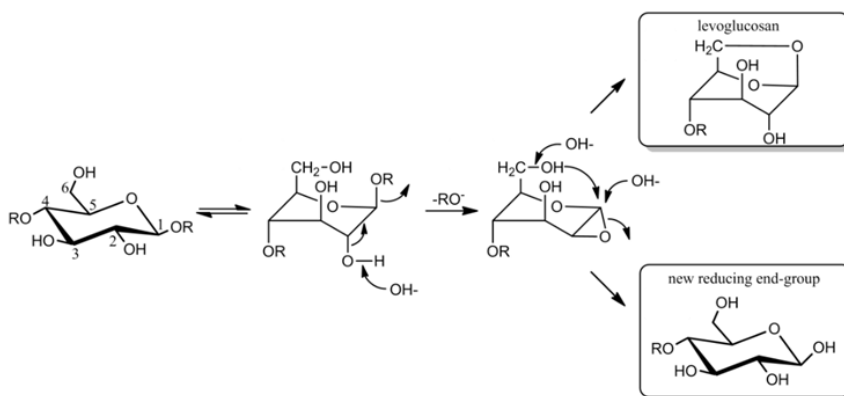
Scheme 1 End-wise degradation of cellulose. B.A.R. – benzilic acid rearrangement, adopted from Sixta et al. 2006.

3.1.2 Alkaline Hydrolysis - Random Chain Scission

Softwood polysaccharides are built of monosaccharide units interlinked with glycosidic bonds. Alkali induced cleavage of a glycosidic bond (alkaline hydrolysis) takes place at random chain position, therefore, it is independent of the polysaccharide DP, in contrary to peeling reactions. Every chain scission creates a new REG that is susceptible to further degradation (secondary peeling). A decrease in the polysaccharide chain DP renders especially hemicelluloses vulnerable towards dissolution. Whereas major polysaccharide losses via primary peeling occur already during initial pulping, alkaline hydrolysis followed by secondary peeling reactions becomes significant with increasing temperature (Lai & Sarkanen 1967). At conventional pulping temperatures around 160°C, carbohydrate degradation is increasingly proportional to the rate of alkaline hydrolysis reactions and the formation of new REGs.

Alkaline hydrolysis reaction is illustrated in **Scheme 2**. Under elevated temperature, conformational change ensures the ionization of hydroxyl group at C₂ position, which then attacks C₁ carbon resulting in a cleavage of the polysaccharide chain. In the subsequent reaction with hydroxide ion, the oxirane intermediate can further form a new

REG or, in an intramolecular reaction with ionized C₆ hydroxyl group, levoglucosan. (Sixta et al. 2006)



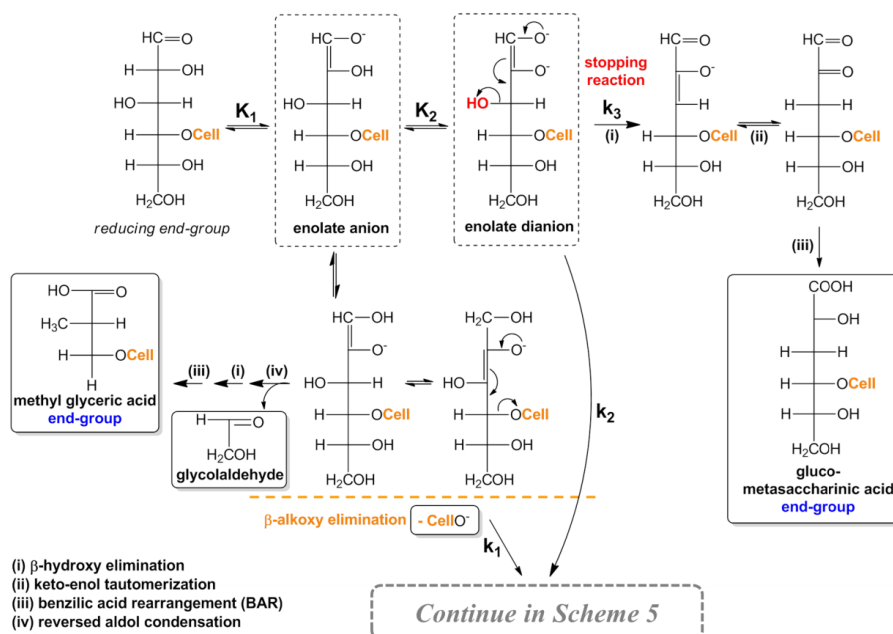
Scheme 2 Alkali-induced hydrolysis reaction, adopted from Sixta et al. 2006.

3.2 Stopping Reaction – Termination of Peeling

Degradative polysaccharide reactions can be terminated physically and chemically. Polysaccharide degradation is physically hindered or even terminated when highly ordered or otherwise inaccessible regions are reached. Chemically, peeling reactions are terminated in a stopping reaction, where the hydroxyl group in C₃ position is cleaved off by direct β -elimination, leading to a formation of alkali stable acidic end-group. Similar to peeling, also stopping reactions take place already at lower temperatures.

Peeling and stopping reactions are alkali dependent competing reactions that progress irrespective of hydrogen sulfide ion concentration (Kondo & Sarkanen 1984). According to **Scheme 3**, alkali dependent equilibrium exists between neutral reducing end-group, enolate anion and enolate dianion species, characterized by equilibrium constants K_1 and K_2 . Whereas the cleavage of terminal polysaccharide unit can take place through enolate anion (k_1) and dianion intermediate (k_2), stopping reaction leading to the formation of metasaccharinic acid end-group proceeds only after the β -elimination of C₃ hydroxyl group in enolate dianion (k_3) (Young et al. 1972). Young et al. (1972) determined the values for ionization constants, pK_1 and pK_2 , as 12.2 and 13.8, respectively. Accordingly, only sufficiently high alkali concentration ensures the termination of peeling of GGM and cellulose via competing stopping reaction to form a metasaccharinic acid end-group. On the other hand, an AX backbone is substituted by 4-*O*-methylglucuronic acid and arabinose side units in position C₂ and C₃, respectively. Under alkaline conditions, arabinose substituent in REG may be β -eliminated without isomerization. The formed end-group contains both keto and aldehyde functions, and can rearrange to alkali stable acidic end-group that prevents further peeling (Whistler & BeMiller 1958). In addition to

the pathway leading to the formation of metasaccharinic acid end-group, peeling reactions can be terminated by the formation of methyl glyceric acid, however, in lesser extent (Johansson & Samuelson 1974).



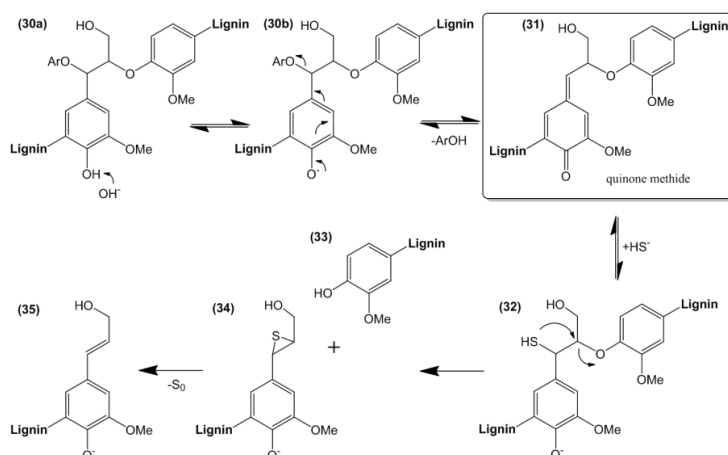
Scheme 3 Peeling and stopping of (1→4)-linked hexoses according to Young & Liss (1978).

Several studies have confirmed the alkali dependency of peeling and stopping reactions. According to Young & Liss (1978), the yield of GGM levels-off more rapidly at elevated alkali concentration. Based on the ratio of propagation and termination rate constants (k_p/k_s) at 100°C and around 1.0 M [OH⁻], they estimated that approximately 34 terminal GGM units are cleaved-off before stopping reaction takes place. Lai & Sarkanen (1969) studied amylose at 100°C, and found out that the rate of peeling reactions levelled-off at roughly 0.1 M [OH⁻], whereas stopping reaction rate continued to accelerate until approximately 1.5 M [OH⁻]. Green et al. (1977) reported that the rate of cellobiose peeling at 120°C levelled-off at 0.5 M [OH⁻].

3.3 Lignin

3.3.1 Fragmentation

In chemical pulping, individual fibers are liberated from wood matrix through dissolution of the middle lamella. Middle lamella comprises of lignin, which is readily insoluble due to its extensive inter-unit linking. Lignin removal, or delignification, is characterized by fragmentation of the lignin structures, and the formation of hydrophilic lignin moieties. Under alkaline conditions, cleavage of inter-linking lignin bonds progresses via interactions between electron-deficient lignin hubs and nucleophiles, like hydroxide ion (OH^-), hydrogen sulfide ion (HS^-), and sulfite ion (SO_3^{2-}). More than half of the inter-connecting linkages between lignin precursor units are of aryl-ether type (α -O-4 or β -O-4) (Fengel & Wegener 1989), and are thus great contributors to overall fragmentation. **Scheme 4** illustrates the cleavage of β -O-4 linkage in phenolic lignin. Initiated by the cleavage of adjacent aryl propane unit (**30**), phenolic lignin moieties are converted into quinone methide intermediates (**31**). In the presence of a strong nucleophile like HS^- ion, addition reaction to α -carbon results in a re-aromatization of the quinone methide (**32**). If ionized, the subsequent attack to β -carbon results in the cleavage of β -O-4 linkage (Gierer 1985) and the formation of new phenolic lignin structure (**33**). More drastic conditions are needed to cleave the β -O-4 linkage in non-phenolic lignin. The cleavage is initiated only when the α - or γ -hydroxyl group becomes ionized, followed by a nucleophilic attack to β -carbon and the cleavage of the β -O-4 linkage. Therefore, residual lignin is difficult to remove, especially in case of alkali depletion, characteristic to conventional pulping processes. Due to the complexity of lignin fragmentation, detailed review of various fragmentation pathways and intermediate products is presented elsewhere, e.g., Adler (1977) and Gierer (1985).



Scheme 4 Fragmentation of phenolic lignin in kraft pulping. Ar = arylpropane unit.

Adopted from Sixta et al. 2006.

3.3.2 Lignin Condensation and Lignin-Carbohydrate Complexes (LCCs)

Approximately 10% of the initial lignin amount is more difficult to remove under prevailing alkaline pulping conditions, and thus mainly associated with the residual lignin. Condensed structures refer to lignin moieties containing alkyl or aryl substituents at the C₅ or C₆ carbon of the aromatic ring (Chakar and Ragauskas 2004); in general, condensation reactions are characterized by the formation of inter-lignin carbon-carbon linkages that are increasingly difficult to fragment. Condensation reactions compete with fragmentation reactions; both involve a nucleophilic addition into quinone methide intermediate (component **(31)**, **Scheme 4**). Whether originating from the degradation of polysaccharides or lignin, pulping liquor contains a variety of nucleophiles that can initiate a condensation reaction.

Lignin and carbohydrates are not isolated entities in the complex wood ultrastructure, but form covalently linked networks called lignin-carbohydrate complexes (LCCs) (Lawoko 2005). Not until recently (Lawoko et al. 2003), quantitative characterization of LCCs has been impossible without significant destruction of the lignin-carbohydrate linkages. Although exclusive categorization of LCCs is not exactly unambiguous, main complexes in the softwood fiber wall have been distinguished. Whereas native softwood LCCs are more versatile and characterized by lignin-hemicelluloses-cellulose-pectin complexes, in kraft pulp, hemicellulose-lignin complexes dominate (Lawoko et al. 2005). Hemicellulose-lignin complexes can be further divided in LCCs enriched with glucomannan (G-L) and analogously LCCs enriched with xylan (X-L). According to the main hemicellulose component in the respective LCC, different delignification rates have been observed (Lawoko et al. 2004). Especially during extended pulping, G-Ls starts to dominate and residual lignin seems to be more recalcitrant towards removal, indicating lack of β -O-4 linkages as well as lignin condensation reactions (Lawoko et al. 2005).

3.4 Degradation Products in Black Liquor

In the course of pulping, spent cooking liquor (black liquor, BL) becomes gradually enriched with low-molar-mass hydroxy acids, as well as with dissolved wood components having larger molecular weight (lignin fragments and oligosaccharides). Even though lignin structure is extensively fragmented during pulping, it is mainly dissolved as a polymer. Therefore, the amount of monomeric lignin degradation products in BL is rather low; only approximately 6% of the dissolved lignin is found in monomeric form, consisting mainly of guaiacol, vanillin, acetovanillone, and dihydroconiferyl alcohol (Alén & Vikkula 1989). On the other hand, a significant amount of polysaccharides is transferred into low-molar-mass hydroxy acids, representing roughly

20% of the wood material (Malinen & Sjöström 1975). Following the progressive cleavage of terminal polysaccharide unit, end-groups are diverted into a complex mixture of hydroxy acids (**Fig. 5**) via isomerization, elimination and fragmentation reactions, as shown in **Scheme 5**.

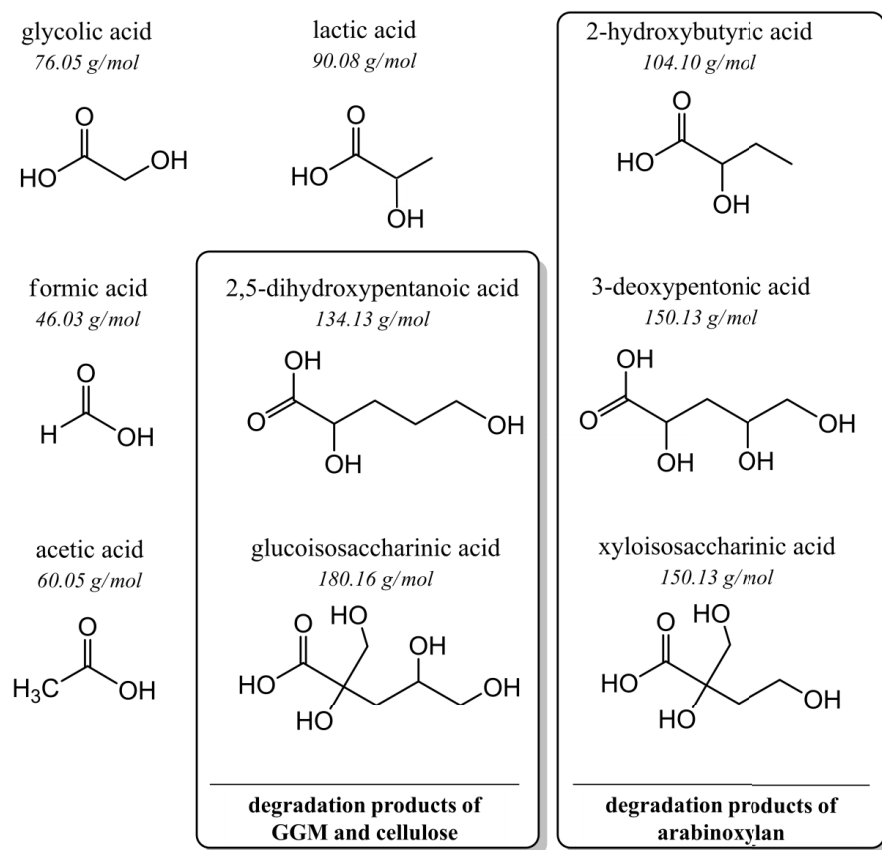
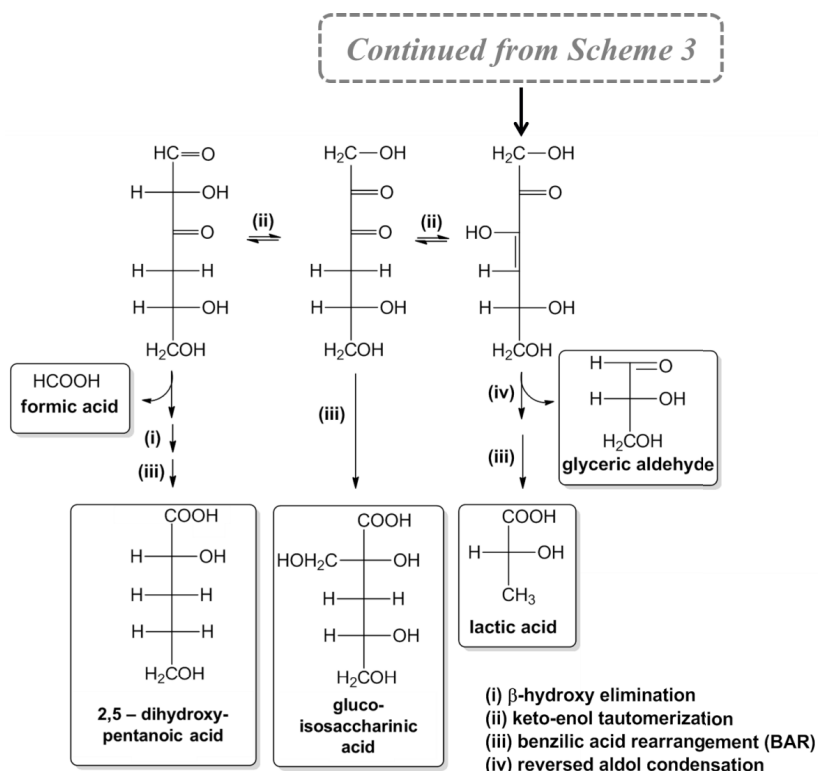


Figure 5 Main degradation products of carbohydrates in pine kraft black liquor according to Malinen & Sjöström (1975).



Scheme 5 The formation of the main hydroxy acids via fragmentation and rearrangement of the cleaved-off terminal cellulose unit, adopted from Sjöström (1977).

Hydroxy acid formation is rapid already during heating-up. Approximately 50 kg of acids (per ton of wood) is formed even before cooking temperature is reached, accumulating 150 kg acid amount towards the end of pulping (Pakkanen & Alén 2013). The composition of pine black liquor has been well characterized in numerous publications (Malinen & Sjöström 1975; Löwendahl et al. 1976; Sjöström 1977; Alén et al. 1985; Söderhjelm & Hausalo 1996; Rautiainen & Alén 2010). Composition of black liquor is presented in **Table 2**.

Table 2 General composition of pine kraft black liquor (Sjöström 1993).

Component	% of the organic material	kg/t adt pulp
Lignin	46	480
Hydroxy acids	30	320
Glucosaccharinic	10.5	110
Lactic	4.5	50
Glycolic	3	30
3,4-Dideoxypentonic	3	30
Xylosaccharinic	1.5	15
2-Hydroxybuturic	1.5	15
3-Deoxypentanoic	1.5	15
Others	4.5	55
Formic acid	8	85
Acetic acid	5	50
Extractives	7	70
Other	4	40

A significant amount of alkali is consumed in neutralization reactions of the acidic degradation products. Due to the fragmentation of C5, C6 sugars into C2, C3, and C4 units, approximately an average of 1.6 acid equivalents are formed in respect to one peeled-off terminal monosaccharide unit. Overall, the effective alkali consumption in softwood kraft cooking is approximately 150 kg NaOH/t wood, of which, 60-70% is consumed in reactions connected to carbohydrate degradation and neutralizing the hydroxy acids, 25-30% in delignification and neutralizing the lignin degradation products and 10% in neutralizing acetic acid and uronic acids (Sjöström 1993).

4 Kraft Pulping

A typical alkaline pulping process utilizes high temperature and elevated pH to soften the structure of lignin and to obtain a fiber swelling that ensures effective liquor diffusion, respectively. In order to liberate individual fibers from wood matrix, lignin is removed with hydroxide ions (OH^-) as such (soda process) or in the presence of strong nucleophiles, such as hydrogen sulfide ions (HS^- ; kraft) or sulfite ions (SO_3^{2-} ; alkaline sulfite). According to Food and Agriculture Organization of the United Nations Statistic Division (FAOSTAT), the annual production of wood based fibers was approximately 170 million air dry tonnes in 2014. More than 75% of these fibers was produced chemically, and primarily in a kraft process (over 90%).

4.1 General Characteristics of Kraft Pulping

4.1.1 Delignification Phases and the Predominant Reactions

In the related literature, the kraft process is traditionally divided into three consecutive phases in respect to characteristic delignification rate, namely initial (Olm & Tistad 1979), bulk (Lémon & Teder 1973) and residual delignification phase (Kleppe 1970; Teder & Olm 1981; Axegård & Wikén 1983; Lindgren & Lindström 1996). Even though the division according to the delignification degree is more ambiguous in case of carbohydrates, also carbohydrate reactions can be divided into initial reactions occurring already during heating-up phase, and slower reactions that require higher temperatures to become significant. Cooking temperature and cooking liquor composition have a profound influence on the extent and rate of all relevant reactions among softwood chemical components. Consequently, the characteristic features of initial, bulk, and residual delignification phase as listed below apply only on general level and exclusively to the conventional kraft pulping process (Sixta et al. 2006).

Initial delignification or heating-up phase (delignification degree below 20%)

- lignin removal is mainly associated with the dissolution of low-molar-mass lignin and the cleavage of β - and α -O-4 linkages in phenolic lignin units (Gierer 1980)
- extensive alkali consumption
- rapid deacetylation of GGM
- peeling reactions together with dissolution of the short chain length hemicelluloses leads to significant carbohydrate losses

Bulk delignification phase (delignification degree up to 90%, ~kappa number 30)

- the cleavage of β -O-4 linkages in phenolic units continue, however, the cleavage of β -O-4 linkages in non-phenolic lignin units becomes the reaction that determines the delignification rate (Gierer 1980)
- notable lignin condensation
- increased temperature accelerate the rate of alkaline hydrolysis reactions and depolymerize polysaccharides (formation of new REGs)
- step-wise degradation of polysaccharides via primary and secondary peeling reactions become significant

Residual delignification phase (delignification degree above 90%)

- residual lignin fraction is difficult to remove due to the enrichment of condensed lignin moieties and LCCs
- slow delignification, as the cleavage of carbon-carbon bonds determine the rate of delignification (Gierer 1980)
- owing to decelerated delignification rate and prolonged cooking, significant carbohydrate losses accumulate due to alkaline hydrolysis and subsequent peeling reactions as well as dissolution of the depolymerized hemicelluloses
- severe lignin condensation reactions

4.1.2 Active Cooking Components

As mentioned, the main active cooking components in kraft pulping are hydroxide ion (OH^-) and hydrogen sulfide ion (HS^-). During the preparation of synthetic kraft pulping liquor (white liquor), sodium hydroxide (NaOH) is dissociated to sodium and hydroxide ions according to reaction (1), whereas sodium sulfide (Na_2S) dissociates to sodium, hydroxide ions and hydrogen sulfide ions (2). According to equation (3), sulfidity can be used to define the relationship between hydrogen sulfide and hydroxide ions in caustic solution.



$$\text{Sulfidity} = \frac{2*[\text{HS}^-]}{[\text{HS}^-] + [\text{OH}^-]} * 100 \quad (3)$$

Further, the charge of active cooking components in respect to wood amount can be stated according to effective alkali (EA, expressed as % on wood), active alkali (AA), and again, sulfidity according to equations (4-6). Below, the amount of Na_2S is expressed as NaOH .

$$EA = NaOH + 0.5 * Na_2S \quad (4)$$

$$AA = NaOH + Na_2S \quad (5)$$

$$Sulfidity = 2 * \left(1 - \frac{EA}{AA}\right) * 100 \quad (6)$$

During conventional kraft process, both EA and sulfidity have a profound influence on the rate of delignification (**Fig. 6a**), whereas the pulp yield is mainly affected by the charge of alkali (**Fig. 6b**).

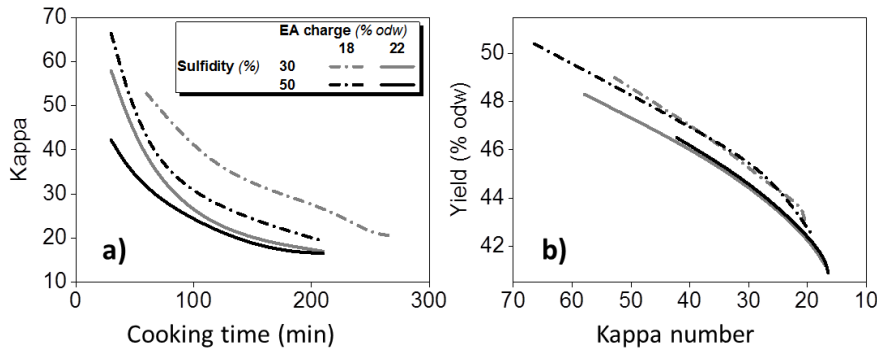


Figure 6 The effect of liquor alkalinity and sulfidity on **a)** kappa reduction and **b)** pulp yield at 170°C during kraft pulping of pine (heating from 80°C to 170°C in 90 minutes).

Data extracted from Pekkala (1986).

4.1.3 Modified Cooking Technologies

Today, the parameters that affect delignification selectivity during kraft pulping are rather well recognized. Low and uniform $[OH^-]$, high $[HS^-]$ especially during bulk delignification, and effective removal of dissolved lignin and low ionic strength in later cooking phase are emphasized in modified cooking concept (MCC) (Teder & Olm 1981; Johansson et al. 1984). Also, the influence of the so-called inactive ions (sodium cations and its counter anions) on lignin solubility and the Donnan equilibrium has been demonstrated by Bogren et al. (2009).

The principles of MCC are adapted in numerous commercial continuous cooking applications utilizing co- and countercurrent cooking stages and modifications in the alkali splitting and liquor circulation, such as Compact Cooking (Kvaerner) and Enhanced Alkali Profile Cooking (Andritz). These modifications have ensured the utilization of lower pulping temperature, as well as more even cooking chemical concentration throughout cook (IsoThermal Cooking and Extended Modified Cooking), providing moderate improvements to pulp yield and strength with less rejects and precipitated lignin. (Sixta et al. 2006)

Implementing the aforementioned principles ensures improved delignification selectivity to some extent. Nevertheless, these means do not significantly hinder the extensive carbohydrate losses that attribute the progressive cleavage of the terminal end-groups, and contribute to pulp yield losses of roughly 15% based on wood. Due to the significant carbohydrate losses, chemical pulping industry is seeking for novel next-generation pulping processes beyond “MCCs”. According to Brown (2014), next-generation processes are characterized by reduced input energy and effluent load, and probably most importantly, by significantly enhanced utilization of raw material, e.g., in terms of increased pulp yield.

4.2 Means to Improve Carbohydrate Preservation

Typical softwood material comprises 65-70% of carbohydrates. Owing to harsh alkaline conditions combined with elevated temperature, carbohydrate related yield loss during conventional pulping to κ -30 is approximately 20% on dry wood basis (odw); 4% attributed to cellulose, 13% to GGM and 3% to AX (Sjöström 1977). As already discussed in *Chapter 3.1 – Polysaccharide Loss Reactions*, extensive GGM losses relate to unhindered peeling reactions. On the other hand, the comparative stability of cellulose stems from its inter-hydrogen bonding, hydrophobic stacking and ordered supramolecular structures, and AX stability is due to the presence of 4-*O*-methylglucuronic acid (C₂ position) and arabinose (C₃) substituents that divert the end-group rearrangement towards stopping reaction.

Chemical modification of the REG provides additional stability towards peeling. Oxidation of the REG to carboxylic acid (aldonic acids), or reduction to alcohols (alditols) can effectively stabilize carbohydrates against (primary) peeling reactions, at least until new REGs are formed via alkaline hydrolysis reaction. Whereas reductive applications with, e.g., sodium borohydride (NaBH₄) are not considered economically attractive (Sixta et al. 2006), oxidative methods including AQ and/or PS have been used industrially. **Figure 7** presents the effect of pulping enhancers, PS and AQ, on delignification rate and pulp yield. Despite the undisputed benefits of AQ as a pulping selectivity enhancer, its future utilization seems unlikely due to the health concerns and the recent change in regulatory policy (Hart & Rudie 2014).

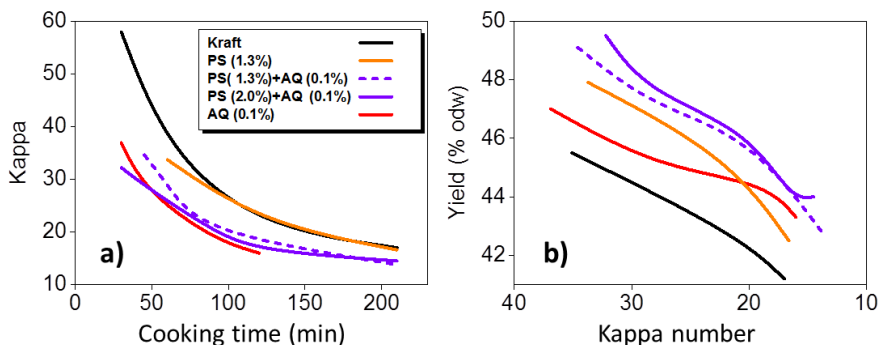
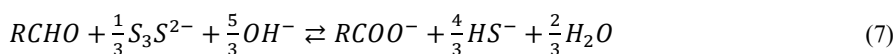


Figure 7 The effect of polysulfide (PS) and anthraquinone (AQ) on **a)** kappa reduction and **b)** pulp yield increase during kraft pulping of pine at 170°C temperature (heating from 80°C to 170°C in 90 minutes). All series at 22% odw effective alkali (EA) charge. Kraft and AQ series at 30% sulfidity, in PS experiments with 1.3% and 2.0% PS charges, the initial sulfidity before white liquor oxidation was 37 and 46%, respectively. Data extracted from Pekkala (1986).

4.3 Polysulfide Pulping (with Anthraquinone)

4.3.1 Polysaccharide Stabilization

A powerful mean to improve carbohydrate preservation is to utilize pulping additives that hinder polysaccharide degradation via peeling. Oxidation of the REG into aldonic acid end-groups practically prevents further end-wise degradation of polysaccharides. Especially the stability of GGM is improved due to its low DP and thus large amount of REGs. As a consequence of elemental sulfur addition into kraft liquor, the positive effect on pulp yield is long known (Hägglund 1946). Under alkaline conditions, elemental sulfur forms PSs (S_nS^{2-}) that can oxidize the REGs, thus rendering the polysaccharide chain less labile towards peeling reactions. The ability of PS to oxidize REGs is promoted by increasing $[OH^-]$ (Teder 1969b); end-groups are oxidized according to reaction equilibrium (7), provided the hydroxide ion concentration is sufficiently high (Sixta et al. 2006).



Even though small amount of polysulfide (S_0) is formed also in lignin fragmentation reactions with HS^- (**Scheme 4** in *Chapter 3.3.*), notable polysaccharide stabilization is not seen until additional PS charge.

Various quinonic derivatives have been recognized to improve the delignification selectivity during chemical pulping (Bach & Fiehn 1972; Heikkilä & Sjöström 1975). AQ,

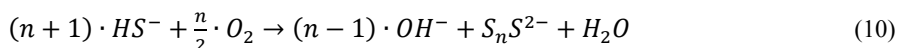
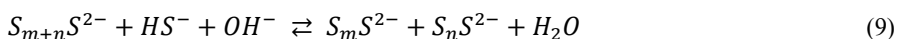
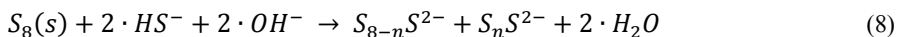
in particular, can be used with softwoods and hardwoods and is renowned for its effectiveness during soda (Holton 1977), kraft (Holton & Chapman 1977) and alkaline sulfite processes (Ingruber et al. 1982). The effect of AQ on polysaccharide stabilization is considered similar to PS; in soda and kraft conditions, the amount of aldonic acid end-groups is increased in the presence of AQ (Löwendahl & Samuelson 1977 and 1978).

4.3.2 Polysulfide Generation and Decomposition

Generation of PS

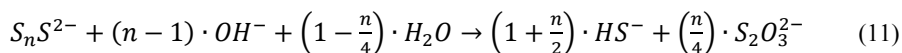
PS anions can be generated by dissolving elemental sulfur into liquor containing HS^- ions. Already at 70°C, PS anions are formed rather rapidly according to reaction (8). Further, equilibrium is formed between various PS species according to reaction (9) (Teder 1969a; Gustafsson & Teder 1969a). It has been demonstrated that the equilibrium state favoring smaller, more thermally stable PS anions (di- and trisulfides) is promoted by higher $[\text{HS}^-]$ and $[\text{OH}^-]$ (Filpponen et al. 2006; Gustafsson & Teder 1969b).

Especially in industrial applications, PS anions are generated through direct catalytic oxidation of the hydrogen sulfide ions according to reaction (10) because the PS generation is not connected to a substantial increase in alkali consumption as in the case of the dissolution of elemental sulfur (Eq. 8). Several commercial processes for white liquor oxidation are available, e.g., MOXY (Smith et al. 1975), Chiyoda (Nakamura & Ono 1988), Paprilox (Dorris 1992), and Quantum (Rudie et al. 1996); however, regardless of the commercial name, the principles are alike.



Decomposition of PS anions

The main impediment of PS is its instability at elevated temperatures. PS is thermally decomposed to hydrogen sulfide and thiosulfate according to reaction (11) (Gustafsson & Teder 1969b). While giving moderate rise to $[\text{HS}^-]$, decomposition is connected with substantial alkali consumption, as illustrated in **Figure 8**.



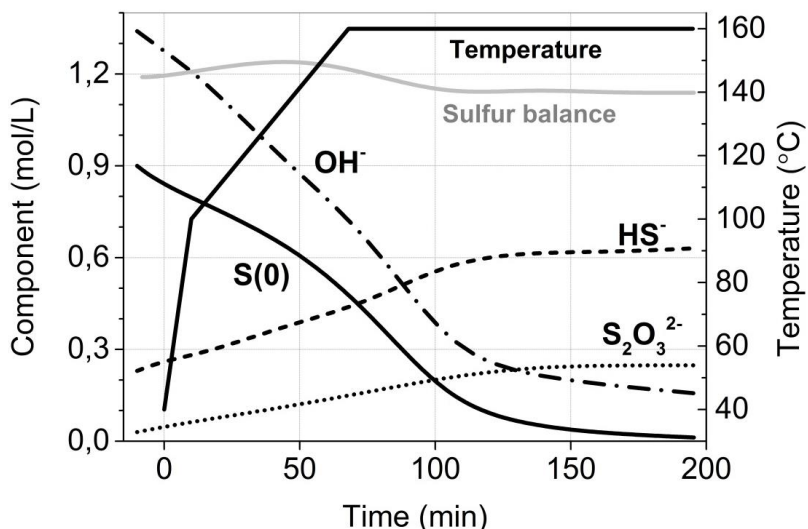


Figure 8 Polysulfide liquor composition during heating to 160°C without wood (liquor composition represents cooking at L/W ratio of 4, EA 21.5%, sulfidity 28%, and 12% odw polysulfide charge). Data extracted from Sanyer & Laundrie (1964).

Figure 9 further elucidates the effect of temperature on the rate of PS decomposition. In addition, it shows that even though hydroxide ions tend to catalyze PS decomposition at concentration levels below 0.3 M, above the given concentration limit the extent of decomposition does not increase with increasing [OH⁻]. In fact, Lindgren and Lindström (1995) demonstrated that polysulfide decomposition occurred irrespective of the concentrations of hydroxide ion, ionic strength or transition metals when wood components were not present.

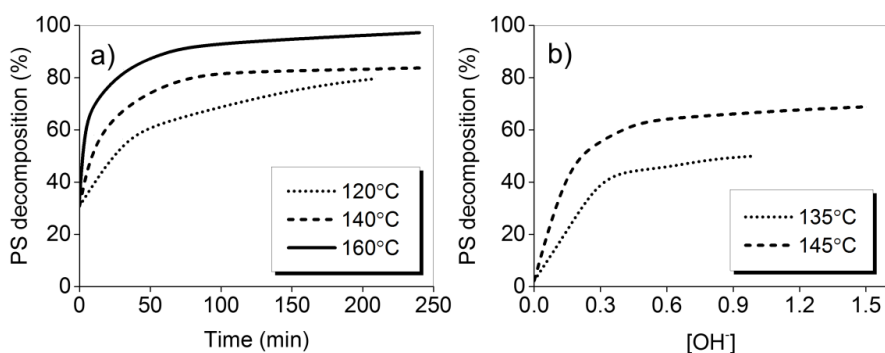


Figure 9 The effect of **a)** temperature (2.0 M [OH⁻], 30% sulfidity) and **b)** hydroxide ion concentration (after 60 minutes, 0.25 M [HS⁻]) on the polysulfide (PS) decomposition in orange liquor. Data extracted from a) Sanyer & Laundrie (1964) and b) Gustafsson et al. (2004b).

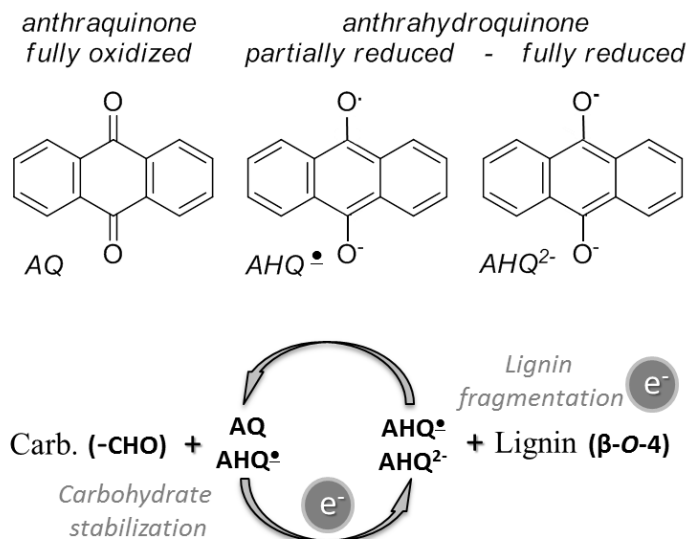
According to Lindgren and Lindström (1995), PS decomposition can be rather well predicted with a rate equation (12) in a range of 0.1-1.2 M $[\text{OH}^-]$, 0.02-0.3 M $[\text{HS}^-]$, and 150-180°C). Determined activation energy for PS decomposition was 140 kJ/mol.

$$d[S_{(0)}]/dt = -7.7 * 10^{13} e^{\frac{-E_a}{RT}} [S_{(0)}]^{1.6} [S^{2-}]^{-0.8} \quad (12)$$

where	t	time in seconds
	$[S_{(0)}]$	is the polysulfide sulfur concentration, $(\sum n[S_n S^{2-}])$
	$[S^{2-}]$	is the sulfide concentration, $([HS^-] + \sum n[S_n S^{2-}])$
	E_a	is the activation energy (140 kJ/mol)
	R	is the ideal gas constant (8.314 J/(K*mol))
	T	is the temperature in Kelvin scale

4.3.3 Anthraquinone Redox Cycle

Under alkaline conditions, three different oxidation states of AQ exists, namely fully oxidized (AQ), partially oxidized as anthrahydroquinone radical (AHQ^\bullet), and fully reduced as anthrahydroquinone (AHQ^{2-}) (Dimmel 1996). The improved delignification selectivity in AQ catalyzed pulping is generally explained by the cyclic reduction-oxidation (redox) interactions between carbohydrates and lignin (Fleming et al. 1978; Dimmel 1985), as illustrated in **Scheme 6**. According to redox cycle, AQ oxidizes the polysaccharide REG to aldonic acid end-group. Subsequently, AHQ reacts with lignin (quinone methide intermediate) and promotes the fragmentation of β -aryl ether structures, while regenerating back to AQ. Minor AQ losses occur due to side reactions with quinone methide intermediate following the formation of alkali stable components like anthrone and anthranol (Landucci & Ralph 1984). In addition, some studies imply that minor, though rather insignificant, cellulose depolymerization might be induced by AQ (Arbin et al. 1980; Vaaler et al. 2003).



Scheme 6 Redox cycle of anthraquinone.

In pulping liquor, AQ is insoluble and exists in a form of colloidal particles, whereas AHQ^\bullet and AHQ^{2-} are soluble, giving the liquor a purple/dark red color. Even though certain kraft lignin intermediates (as demonstrated by Apfeld & Dimmel 1982), as well as HS^- ions are shown to transfer AQ into partially or fully reduced AHQ species to some extent, significant rate of AQ reduction requires interactions with accessible aldehyde end-group of carbohydrate (Storgard-Envall & Dimmel 1986).

Both AHQ and HS^- promote lignin fragmentation mainly via β -aryl ether structures; the delignification kinetics of soda-AQ and kraft pulping are shown to be similar (Gierer et al. 1983). However, it is suggested that the reaction mechanism is not alike. Accordingly, various AQ species act as an electron carrier in a single electron transfer reactions (SET) (Dimmel & Schuller 1986), whereas lignin- HS^- interactions go through nucleophilic addition mechanism, which are two-electron transfer reactions (Dimmel et al. 1987).

4.3.4 Pulp Yield Increase

As emphasized above, carbohydrate preservation is improved in PS pulping as such, or in combination with anthraquinone (PSAQ). During PS pulping of softwood, the obtainable pulp yield increase depends strongly on the charge of PS, or S_0 . As exemplified in **Figure 10**, the correlation is practically linear. While producing a κ -30 pulp, the yield increase ranges between 1-4% odw, and correspond to S_0 charges of 2-8 g/L; in other words, every additional 1% odw increase in S_0 charge is connected to a pulp yield increase of approximately 1%. At optimal laboratory conditions, the above mentioned linear

correlation have been retained even up to 10% odw S_0 charges (Bouchard et al. 2004). As also shown in **Figure 10** and **Table 3**, at a given S_0 charge the yield increase with oxidized PS liquor (mill practice) is somewhat lower than with synthetic PS liquor (elemental sulfur). Even with the same S_0 charge, EA and sulfidity, synthetic PS liquor seems to be more effective in polysaccharide stabilization compared to oxidized PS liquor (Hu et al. 1998). According to Hu et al. (1998), the difference could relate to the higher reactivity of the synthetic PS liquor due to larger polysulfide anions.

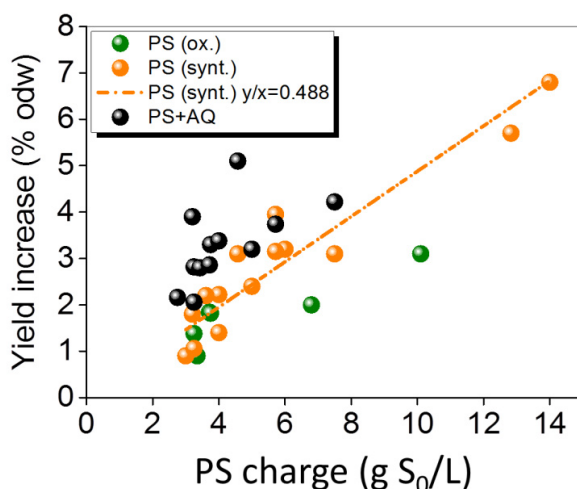


Table 3 Summary of the process conditions during polysulfide pulping of softwood. Yield values were normalized to κ -30 with a 0.2% odw yield change per $\Delta\kappa$.

Reference	Wood species	Cooking conditions				Polysulfide			AQ		Kappa		Yield increase % odw
		Method	L/W	°C	EA	sulf. %	g/L	mol/L	% odw	% odw	Calc.	Orig.	
Green & Smith (1983)	Southern pine	PS oxidized	3,5	166	15,3	30	3,3	0,10	1,2	-	30,0	32,5	0,9
Thompson et al. (1998)	Mix. softwood	PS oxidized	4	172	16,9	12	3,3	0,10	1,3	-	30,0	33,6	1,4
Pekkala (1986)	Pine	PS oxidized	3,5	170	22,0	12	3,7	0,12	1,3	-	30,0	33,7	1,8
Jiang et al. (2002)	Black spruce	PS oxidized	4	170	16,8	13	3,8	0,12	1,5	-	30,0	28,4	1,8
Pekkala (1982)	Pine	PS oxidized	3,5	170	37,8	30	6,8	0,21	2,4	-	30,0	-	2,0
Pekkala (1982)	Pine	PS oxidized	3,5	170	30,1	50	10,1	0,31	3,5	-	30,0	-	3,1
Sturgeoﬀ & Bernhardt (1998)	Mix. softwood	PS elem. sulfur	4	172	15,6	12	3,0	0,09	1,2	-	30,0	31,1	0,9
Jameel et al. (1995)	Pine	PS elem. sulfur	4	170	18,4	17	3,3	0,10	1,3	-	30,0	25,5	1,1
Hakaniemi & Teder (1997)	Pine, Spruce	PS elem. sulfur	4	170	18,5	50	4,0	0,12	1,6	-	30,0	27,4	1,4
Li et al. (1998)	Black spruce	PS elem. sulfur	5	170	25,9	15	3,2	0,10	1,6	-	30,0	-	1,8
Jameel et al. (1995)	Pine	PS elem. sulfur	4	166	18,0	20	4,0	0,12	1,6	-	30,0	31,7	2,2
Kleppe & Minja (1998)	Spruce	PS elem. sulfur	3,6	170	18,5	35	3,6	0,11	1,3	-	36,0	-	2,2
Luthe & Berry (2005)	Mix. softwood	PS elem. sulfur	3,5	170	18,3	17	5,0	0,16	1,8	-	30,0	-	2,4
Luthe et al. (2004)	Spruce (meal)	PS elem. sulfur	3,5	170	18,5	15	4,6	0,14	1,6	-	30,0	-	3,1
Olm & Tormund (2004)	Scots pine	PS elem. sulfur	5	160	17,5	25	6,0	0,19	3,0	-	30,0	30,9	3,1
Sanyer & Laundrie (1964)	Loblolly pine	PS elem. sulfur	3,5	163	20,0	34	5,7	0,18	2,0	-	30,0	-	3,2
Vaaler & Moe (2001)	Spruce	PS elem. sulfur	3,5	163	22,1	34	5,7	0,18	2,0	-	30,0	-	4,0
Vaaler & Moe (2001)	Spruce	PS elem. sulfur	2	170	15,0	48	12,8	0,40	2,6	-	30,0	28	5,7
Molin & Teder (2002)	Spruce	PS elem. sulfur	5	160	19,3	25	14,0	0,44	7,0	-	30,0	-	6,8
Sanyer & Laundrie (1964)	Loblolly pine	PS elem. sulfur	4	165	18,4	17	3,3	0,10	1,3	0,10	30,0	30,1	2,1
Jameel et al. (1995)	Pine	PSAQ elem. sulfur	4	172	14,5	12	2,8	0,09	1,1	0,07	30,0	31,3	2,2
Sturgeoﬀ & Bernhardt (1998)	Mix. softwood	PSAQ elem. sulfur	4	172	16,9	12	3,3	0,10	1,3	0,07	30,0	27,4	2,8
Thompson et al. (1998)	Mix. softwood	PSAQ elem. sulfur	4	172	16,9	12	3,3	0,10	1,3	0,07	30,0	27,4	2,8
Green & Smith (1983)	Southern pine	PSAQ oxidized	3,5	166	15,3	30	3,4	0,11	1,2	0,08	30,0	30,5	2,8
Pekkala (1986)	Pine	PSAQ elem. sulfur	3,5	170	22,0	12	3,7	0,12	1,3	0,10	30,0	34,6	2,9
Luthe & Berry (2005)	Mix. softwood	PSAQ elem. sulfur	3,5	170	18,3	17	5,0	0,16	1,8	0,05	30,0	-	3,2
Jiang et al. (2002)	Black spruce	PSAQ oxidized	4	168	16,7	14	3,8	0,12	1,5	0,05	28,3	26,3	3,3
Jameel et al. (1995)	Pine	PSAQ elem. sulfur	4	166	18,0	20	4,0	0,12	1,6	0,10	30,0	29,4	3,4
Pekkala (1986)	Pine	PSAQ elem. sulfur	3,5	170	22,0	23	5,7	0,18	2,0	0,10	30,0	32,2	3,7
Li et al. (1998)	Black spruce	PSAQ elem. sulfur	5	170	25,9	15	3,2	0,10	1,6	0,10	30,0	-	3,9
Olm & Tormund (2004)	Scots pine	PSAQ elem. sulfur	4	170	16,0	46	7,5	0,23	3,0	0,10	30,0	29,8	4,2
Luthe et al. (2004)	Spruce (meal)	PSAQ elem. sulfur	3,5	170	18,5	15	4,6	0,14	1,6	0,05	30,0	-	5,1

5 Materials and Methods

5.1 Process Description

5.1.1 Raw Material Handling

Scots pine (*Pinus sylvestris* L.) grown in southern Finland was used throughout this study. In **paper I**, chips were obtained from industrial sources, whereas **papers II-V** utilized raw material from a single tree trunk, chipped with a pilot chipper. Chips were screened according to SCAN-CM:40-01. Part of chips was readily frozen and part was milled in a Wiley mill. Wood meal that pass through 1 mm hole screen was collected, air-dried to approximately 85% dry matter content, and frozen at -18°C till further use. **Papers I-IV** utilized wood meal, whereas chips were used in **paper V**.

5.1.2 Cooking Reactors

Büchi-reactor

A 2 liter Büchi-batch reactor equipped with mechanical stirring was used in **paper I (Fig. 11a)**. Air-dried wood meal (9 g odw) was charged together with 1800 mL of cooking liquor to obtain a L/W ratio of 200. After wood and white liquor addition, the reactor was sealed and air was evacuated for 5 minutes, and then pressurized to 0.5 MPa with nitrogen gas for 5 minutes. After depressurization, the reactor was heated to cooking temperature of 80, 105 or 130°C, with a heating rate of 3.0 – 4.5°C/min. Once the cooking time was reached, cooling continued at a rate of approximately 2°C/min until the reactor temperature was around 50°C. Reactor was drained through the bottom valve, after which the pulp suspension was filtered with a tissue filter (6 µm pore size), and a BL sample was collected. Reactor was rinsed with 2 L of deionized water. The rinsing water was collected and used for pulp washing. Washed pulp was air-dried at room temperature before analyses.

Tankki-reactor (papers II-V)

A 10 liter custom-made Tankki-batch reactor was used in **papers II-V** to study the kraft pulping without and in the presence of AQ and PS, as well as the ASA pulping process (**Fig. 11b**). The same wood raw material was used in all experiments.

In **papers II-IV**, air-dried wood meal (40 g odw) was charged together with 8000 mL of cooking liquor to obtain a L/W ratio of 200. After wood and pulping liquor addition, the reactor was sealed, flushed once with nitrogen, and then pressurized to 0.5 MPa for 5 minutes. After depressurization, the reactor was heated to cooking temperature of 130 – 160°C within 20 ± 1 min, despite the target temperature. Once the cooking time was

reached, cooling was continued approximately 20 minutes, until the reactor temperature was below 90°C. Pulp suspension was removed and filtered with a tissue filter (6 µm pore size), and black liquor sample was collected. Pulp was washed with 5 L of deionized water. The rinsing water was collected and used for pulp washing. Washed pulp was air-dried at room temperature before analyses.

In **paper V**, Tankki-reactor was utilized in experiments with chips at a L/W ratio of 6. Instead of mixing, liquor was continuously re-circulated through the chips bed to ensure uniform liquor composition throughout pulping. Chips with a dry content around 35% were charged in the reactor with respective pulping liquor (400 g odw, 2400 mL pulping liquor). Heating, cooking, and cooling were similar to the above described method. After cooking, the chips were washed with 10 L of deionized water and fiberized in a wet disintegrator. Pulp was further washed with approximately 10 L of water, then centrifuged to approximately 30% dry matter content and homogenized. Dry content of the homogenized pulp was determined before further pulp analyses. Pulps were stored in cold room at 4°C.

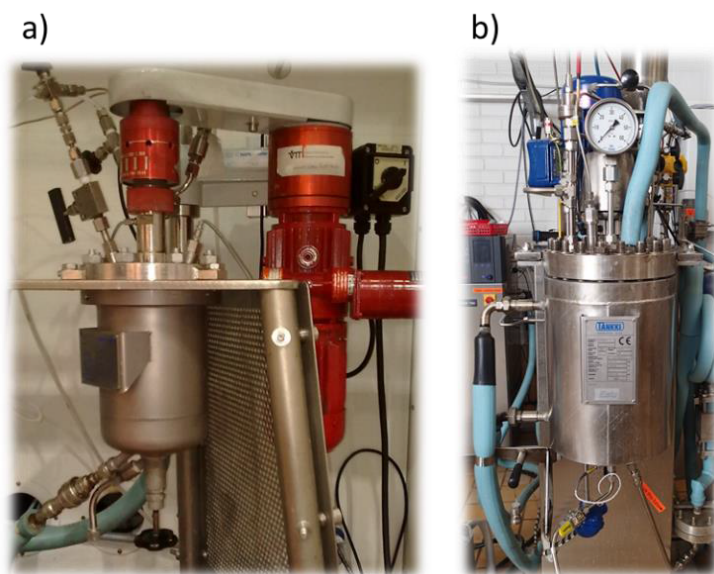


Figure 11 Batch type reactors that were used in cooking experiments: **a)** 2 L Büchi-reactor and **b)** 10 L Tankki-reactor (configurations include in reactor liquor mixing, as well as outside reactor liquor circulation).

H-factor was calculated according to Vroom (1957). Cooking time and any deviation from the target cooking temperature were corrected for isothermal conditions according to equation (13) (**papers I-V**).

$$t_T = \int_{t_{T_i}}^{t_T} \text{Exp} \left(-\frac{E_a}{R} \left[\frac{1}{T_t} - \frac{1}{T_{T_i}} \right] \right) * dt \quad (13)$$

where	t_T	the isothermal reaction time (min) at target temperature
	T_i	the initial temperature (K)
	T_t	the temperature (K) at a given time
	T_T	the target temperature (K)

5.1.3 Ultrafiltration of Black Liquor

A selected black liquor sample was extracted from chip scale experiment (**paper V**) and used in a lab-scale filtration experiment with an Amicon 8200 (200 mL cell) apparatus. Ultrafiltration set-up is presented in **Figure 12**. Polyethersulfone ultrafiltration membranes with a 10 kDa cut-off (UP010 Microdyn-Nadir) were used. The operating temperature was limited to room temperature and the pressure to 5 bar (regulated with nitrogen gas). BL feed volume was 180 mL, while the magnetic stirrer was set to 300 rpm.

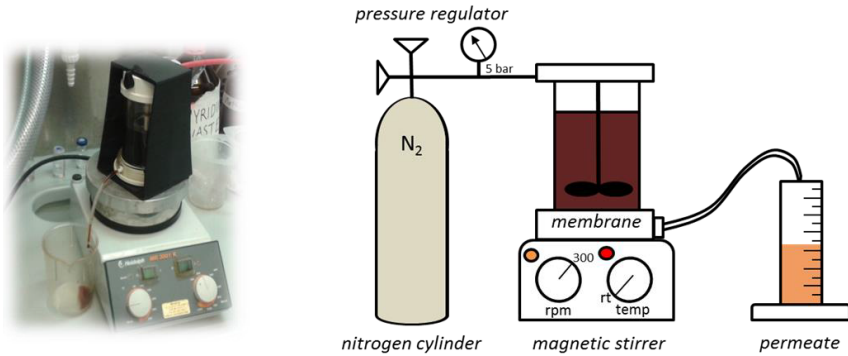


Figure 12 Filtration unit as well as a schematic illustration of the experimental set-up.

5.1.4 Oxygen Delignification

Air-bath digester

Oxygen delignification experiments (**paper V**) were carried out in a rotating air-bath digester in a 2.5 liter vessel. Prior to oxygen delignification, all pulps were chelated with ethylenediaminetetraacetic acid (EDTA). OD stage was carried out using certain fixed parameters (30 g odw pulp, 10% consistency, 0.05% Mg^{2+} and 7 bar O_2).

In addition to the above-mentioned fixed parameters, dependent on the pulping method, two different OD sequences were selected to produce a bleachable grade pulp: a conventional one-stage process (O; kappa reduction approximately from 30 to 15), and a

two-stage process with inter-stage lignin activation (OxO; kappa reduction approximately from 60 to 15). Conventional O-stage lasted for 45 minutes at 85°C and utilized a NaOH charge of 3% odw. Starting from a high-kappa pulp, conditions during the two-stage OD process were: 45 min at 85°C, 4% NaOH and 60 min at 95°C, 2% NaOH. In order to promote kappa reduction, peroxymonosulfuric acid treatment was utilized as an inter-stage treatment (2% odw act.O₂, 10% pulp consistency, pH 11, 10 min, 50°C). The source of peroxymonosulfuric acid was Oxone[®] (Sigma–Aldrich, Switzerland, CAS:70693-62-8, potassium hydrogen peroxymonosulfate sulfate, 2KHSO₅•KHSO₄•K₂SO₄). The active oxygen content in Oxone[®] was determined according to a method available online (DuPont Oxone technical attributes).

5.2 Pulp Characterization

5.2.1 Chemical Composition

Acetone-extractable material was determined gravimetrically according to SCAN 49:03. Extractive-free pulp sample was decomposed according to SCAN-CM 71:09 in a two-stage acid hydrolysis stage process. Acid hydrolysate was filtered with a glass filter to determine the amount of acid insoluble lignin (Klason lignin, KL). Monosaccharide composition was determined from the filtrate by high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) according to SCAN-CM 71:09, and acid-soluble lignin by UV spectroscopy (Shimadzu UV-2550; 205 nm) using an absorption coefficient of 110 L/(g*cm) according to Swan (1965). The polysaccharide composition was calculated from the relative amount of monosaccharides according to Janson (1970).

5.2.2 Kappa Number and Viscosity

Kappa number was determined in two ways: analytically according to permanganate consumption (SCAN-C 1:00) and numerically according to the pulp lignin content (lignin on pulp (%) = $\kappa \cdot 0.15$), following the method of Tasman (1959).

In **paper V**, due to the high kappa number, further lignin removal was necessary prior to viscosity measurement according to SCAN-CM 15:99. Based on the method presented by Wise et al. (1946), 5 min chlorite delignification pretreatment at 70°C was used to remove excess lignin from a 3 g pulp sample. During this additional delignification process, thoroughly disintegrated pulp sample was mixed in preheated liquor containing 200 mL water, 20 mL chlorine dioxide water (20 g act. Cl/L), and 2 mL of 100% acetic acid.

5.2.3 Bleachability and Handsheet Properties

As an important aspect of the overall process performance evaluation, pulp bleachability and strength properties of conventionally produced and high-yield pulps were evaluated in separate experiments. Whereas the liquor composition was identical to the one used in **paper IV**, L/W ratio was set to 50 and chips were used instead of wood meal. In addition, whereas conventional process included a single stage OD process (air-bath digester), high-yield pulp was delignified according to continuous flow-through oxygen delignification (FT-OD). A detailed description regarding the FT-OD reactor is found in a publication by Jafari et al. (2014b). Both pulps were bleached in an ECF bleaching sequence, D_0 - E_{OP} - D_1 - P , under conditions listed in **Table 4**. Bleached pulps were refined in a laboratory PFI mill at 10% consistency, and intensity levels of 1000, 3000, and 5000 revolutions. Selected strength properties of pulp and handsheet properties were measured, including pulp drainability, Schopper-Riegler number, tensile strength (ISO 1924-9), tear strength (ISO 1974), tensile stiffness (ISO 1924-2), and Scott bond (TAPPI UM 403).

Table 4 Bleaching conditions during D_0 - E_{OP} - D_1 - P sequence. All trials were performed at 10% consistency. D_0 -, D_1 - and P -stages were performed in preheated water bath in plastic bags and E_{OP} -stage in airbath digester.

	Temp (°C)	Time (min)	NaOH (% on pulp)	ClO ₂ charge (as act.Cl ⁻)	Other (% on pulp)
D_0	50	60	-	kappa factor 0.25	0.5 (H ₂ SO ₄)
E_{OP}	70	60	2	-	0.3 (H ₂ O ₂)
D_1	80	120	0.25	6*kappa (kg/t)	-
P	80	180	1.2	-	1.0 (H ₂ O ₂); 0.05 (Mg ⁺²)

5.3 Pulping Liquor

5.3.1 White and Orange Liquor

Stock solutions for sodium hydroxide and sodium sulfide were prepared by dissolving NaOH (min. 98%, VWR International) and Na₂S (60%, VWR International) into ion-exchanged water, respectively. The ion concentration of the stock solutions was determined according to SCAN-N 2:88.

Orange liquor (PS liquor) was prepared by addition of elemental sulfur into sodium sulfide solution. Before sulfur addition, sodium sulfide solution was evacuated for 5

minutes to remove dissolved oxygen. After sulfur addition, while mixing (100 rpm) the liquor was slowly heated under N₂ atmosphere to 80°C and the temperature was maintained for 70 minutes. If not instantly used (**paper V**), PS liquor was sealed in oxygen free atmosphere. The concentration of thiosulfate in the BL was analyzed with ion chromatography (Dionex ICS-1500, IONPAC AS9-HC column) according to EN ISO 10304-2 after sulfite stabilization (de Carvalho & Schwedt 2000).

AQ was provided by Kemira in a solution with 50% AQ content. All experiments were conducted with the same AQ batch that was stored in a cold room at 4°C. In cooking, the 50% AQ solution was added at the same time with wood, after which the reactor was sealed. Sealed reactor was pressurized and flushed with nitrogen in order to remove oxygen from the free vapor phase. Distinctive color of PS and fully reduced AQ liquor is shown in **Figure 13**.



Figure 13 Polysulfide (left) and anthraquinone solution (right).

5.3.2 Black Liquor Characterization

The amount of dissolved polysaccharides was evaluated according to the BL monosaccharide composition (SCAN-CM 71:09). The low-molar-mass carboxylic acids were detected with capillary electrophoresis (Beckman-Coulter, P/ACE MDQ equipped with a photo diode array UV/Vis detector) after the removal of excess -SO₄²⁻ (Niemi et al. 2011; Rovio et al. 2012). The salts were removed by Dionex Ongaard II Ba/Ag/H cartridges.

6 Results and Discussion

6.1 The Effect of Liquor Strength during Kraft Pulping

Delignification reactions, as well as carbohydrate degradation and dissolution reactions, are initiated already at low temperatures. In *Chapter 6.1*, these reactions are considered in respect to kraft liquor composition and temperature. Emphasis is put on hydroxide ion concentration $[\text{OH}^-]$ and its effect on carbohydrate preservation during initial pulping at 80 - 130°C (**paper I**), and during full delignification at up to 160°C (**paper II**). This chapter presents results that were obtained within wood meal pulping at L/W ratio of 200, and under constant sulfidity of 33%. Also, whereas sodium salt addition was not utilized in **paper I**, during experiments that are reported in **paper II**, NaCl was charged to obtain a fixed ionic strength of 2.0 M $[\text{Na}^+]$. The used cooking conditions are summarized in **Table 5**.

Table 5 The composition of kraft liquor during wood meal pulping at a L/W ratio of 200 and a sulfidity of 33%.

M $[\text{OH}^-]$	M $[\text{HS}^-]$	M $[\text{Na}^+]$	M $[\text{Cl}^-]$	Temp (°C)	paper
0.31	0.06	0.37	-	80, 105, 130	I
0.93	0.19	1.12	-	80, 105, 130	I
1.55	0.31	1.86	-	80, 105, 130	I
0.50	0.10	2.00	1.40	160	II
1.55	0.31	2.00	0.14	130, 140, 150, 160	II

6.1.1 Initial Phase of Pulping (paper I)

Certain lignin moieties do not need fragmenting to become soluble. Already at room temperature approximately 5% of the lignin could be removed, independent of $[\text{OH}^-]$ in the range of 0.31 - 1.55 M, which was in good agreement with the reported 6% for Douglas-fir (Chiang et al. 1990). Even after prolonged treatment time at 80°C, delignification degree barely exceeded 10% (**Fig. 14a**). Due to the increase in temperature, generally more lignin was removed at 105°C; however, only until 130°C and a delignification degree over 30%, delignification was found to be dependent on $[\text{OH}^-]$ and $[\text{HS}^-]$. Accordingly, pulping liquor composition did not affect the delignification rate during the initial delignification phase, which equaled to the removal of 20-30% of lignin provided that the pH was higher than the pKa value of the phenolic groups in the lignin; only at the transition phase from initial to bulk delignification the increase in $[\text{OH}^-]$ accelerated the delignification rate. These results were in agreement with those obtained by Olm & Tistad (1979).

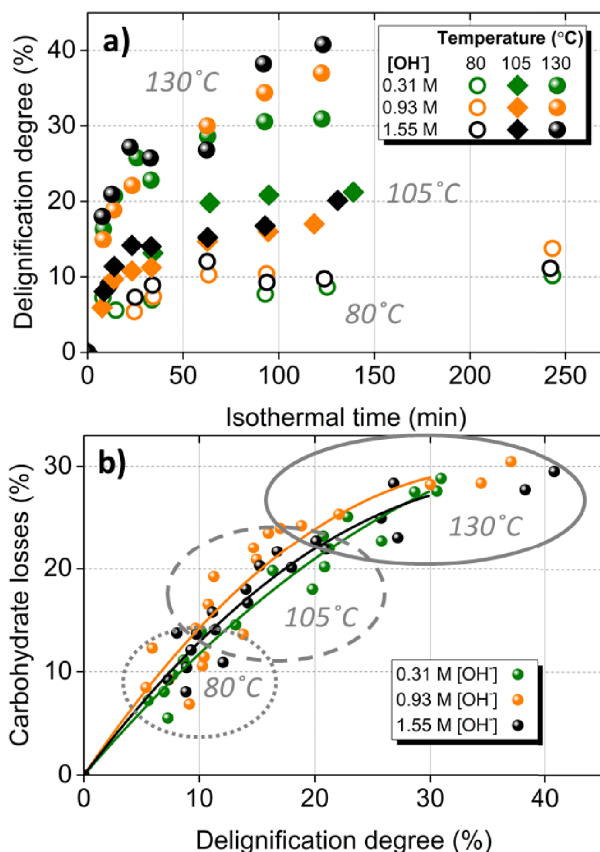


Figure 14 The effect of $[OH^-]$ (33% sulfidity) and temperature **a)** on the rate of delignification, and **b)** on carbohydrate losses during initial kraft pulping of Scots pine (wood meal; L/W ratio of 200) Solid lines represent the polynomial fit.

Initial delignification phase was characterized by poor selectivity towards lignin; carbohydrate losses exceeded 20% even before 20% lignin was removed (**Fig. 14b**). Extensive carbohydrate losses are mainly derived from GGM degradation. Recently, Pakkanen et al. (2013) demonstrated that roughly half of the GGM is lost during initial kraft pulping, resulting in extensive formation of GGM derived low-molar-mass carboxylic acids. Interestingly, most carbohydrate losses were observed at intermediate $[OH^-]$, whereas high and low $[OH^-]$ showed rather comparable results in terms of pulp yield. Based on **Figure 15**, certain GGM and AX losses took place during the initial delignification and no significant correlation to liquor alkali concentration was seen until approximately 15% delignification. During further delignification, on the other hand, the retention of GGM was favored by higher and AX by lower hydroxide ion concentration. Rather surprisingly, cellulose was least preserved under intermediate $[OH^-]$ of 0.93 M. At 1.55 M $[OH^-]$, more GGM was lost at 105°C than at 130°C (**Fig. 15**, 20% delignification

degree), therefore, especially GGM preservation was favored by more intensified conditions (in terms of temperature and hydroxide ion concentration). After 30% lignin removal at 130°C, GGM yield was increased by approximately 2.5% odw under the hydroxide ion concentration of 1.55 M compared to 0.31 M. However, no change in the pulp yield was observed as the GGM yield increase was accompanied by higher losses of AX and cellulose.

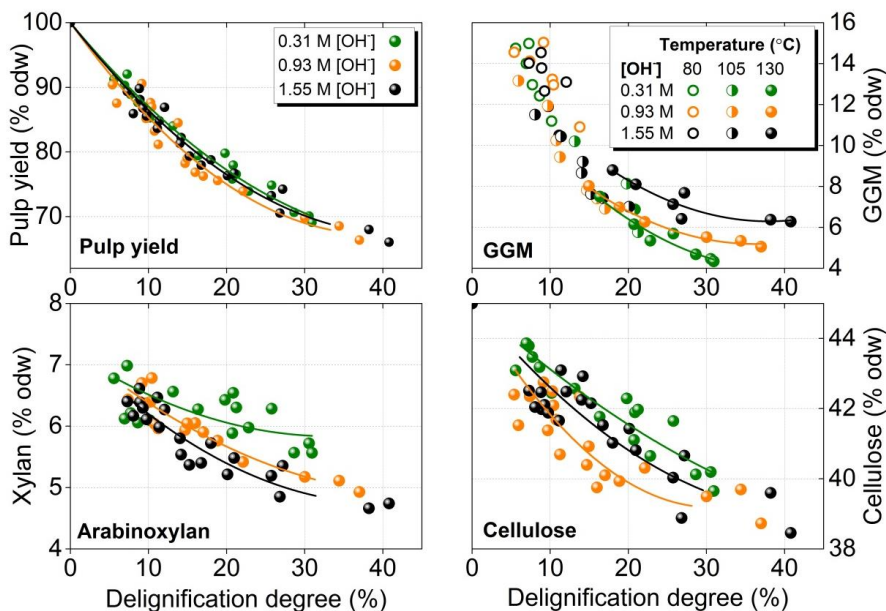


Figure 15 The effect of $[\text{OH}^-]$ (33% sulfidity) and temperature on pulp yield and pulp polysaccharide composition during initial kraft pulping of Scots pine (wood meal; L/W ratio of 200). Solid lines represent the polynomial fit.

6.1.2 Full Delignification (paper II)

Wood meal and L/W ratio of 200 were utilized to investigate the influence of kraft liquor chemical concentration on delignification and polysaccharide retention during full delignification. Two concentration levels were used, representing a constant sulfidity of 33% and a constant ionic strength:

- **Low** $[\text{OH}^-]$: 0.50 M $[\text{OH}^-]$; 0.10 M $[\text{HS}^-]$; 2.00 M $[\text{Na}^+]$
- **High** $[\text{OH}^-]$: 1.55 M $[\text{OH}^-]$; 0.31 M $[\text{HS}^-]$; 2.00 M $[\text{Na}^+]$

Initial, Bulk, and Residual Phase Delignification

During full delignification, three kinetically distinguishable regions/lignin species were revealed (**Fig. 16**). In line with the findings of **paper I**, roughly 20-25% of the initial lignin in Scots pine was easily removed, following the cleavage of α - and β -aryl ether bonds in phenolic arylpropane units (Gierer & Norén 1980). During bulk delignification the rate of delignification is decelerated as the cleavage of β -aryl ether linkages in non-phenolic arylpropane units becomes the rate limiting reaction of overall delignification (Gierer & Norén 1980). Owing to the elevated alkalinity, increasingly ionized adjacent hydroxyl groups ensure the cleavage β -aryl ether linkages in non-phenolic lignin moieties, thus promoting the rate limiting delignification reaction during bulk stage. As lignin becomes increasingly fragmented, the formation of alkali resistive inter-lignin carbon-carbon bonds is accelerated (lignin condensation); in addition, together with carbohydrate degradation products, lignin fragments might lead to the formation of lignin-carbohydrate condensation products (Gierer & Wännström 1984; Gierer et al. 1987). Due to the carbon-carbon interlinks, these condensation products are difficult to fragment under kraft conditions; therefore, characteristic to residual phase delignification kinetics, overall delignification is decelerated. In respect to pulping liquor chemical concentration, more lignin was removed at $\text{High}[\text{OH}^-]$ before the slow residual delignification kinetics transpired at 160°C (**Fig. 16**). Under $\text{Low}[\text{OH}^-]$ conditions the rate of delignification started to decelerate even before 70% of the lignin was removed. Accordingly, shorter cooking time to obtain a 80% delignification degree, or $\sim\kappa$ -60, was needed at $\text{High}[\text{OH}^-]$ conditions compared $\text{Low}[\text{OH}^-]$; the required H-factor was reduced from 1480 to 300. Especially in the delignification degree range of 40 - 80%, the influence of liquor chemical concentration on the rate of delignification was dramatic.

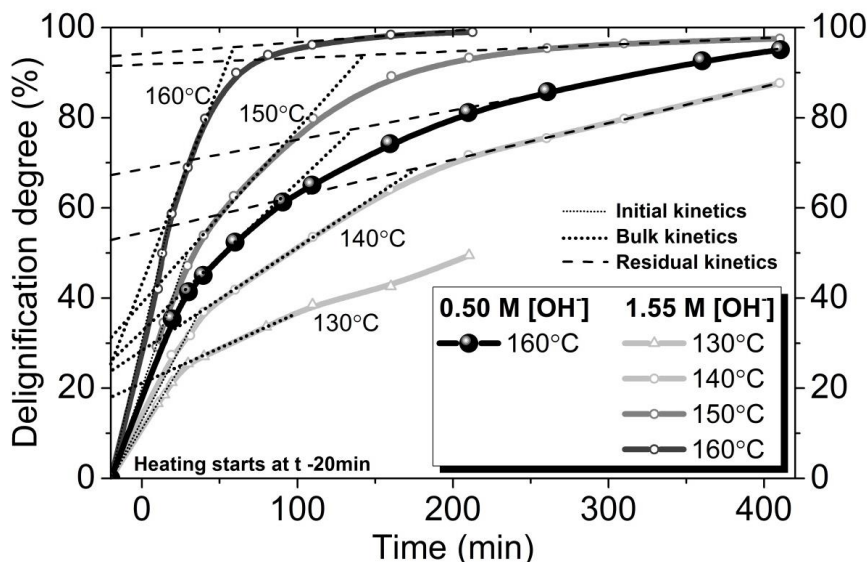


Figure 16 The effect of $[\text{OH}^-]$ (33% sulfidity) and temperature on the rate of delignification during kraft pulping of Scots pine (wood meal; L/W ratio of 200).

During the pulping at 150-160°C temperature and with 1.55 M $[\text{OH}^-]$ liquor, no significant difference in the amount of residual lignin was observed. This confirms the findings of Lindgren & Lindström (1996), who demonstrated that the effect of temperature on the amount of residual lignin is insignificant at 150-180°C with constant kraft liquor composition.

Models with a wide range of complexity have been utilized to describe delignification during kraft pulping (Nieminen & Sixta 2012). Ionized moieties create excess of negative charge in the fiber wall; therefore, according to Donnan equilibrium, the concentration of anionic pulping chemicals inside fibers is always lower compared to the ambient pulping liquor (Kuitunen et al. 2013). By utilizing the data published in **paper II**, a descriptive model that combined delignification kinetics and Donnan theory was introduced by Nieminen et al. (2014a). They estimated that approximately 25% of the total lignin reacts according to the fast initial kinetics with activation energy (E_a) of 75 kJ/mol, whereas the E_a for the bulk delignification was 138 kJ/mol. In the same study, the effect of alkali concentration on the rate of delignification was determined at 160°C; after the fast reacting lignin (~25% of the initial lignin) was dissolved, the delignification rate for the remaining lignin fraction (equivalent to bulk and residual lignin) was determined as $30.7 \cdot 10^{-3}$ 1/min for $_{\text{High}}[\text{OH}^-]$ and $7.4 \cdot 10^{-3}$ 1/min for $_{\text{Low}}[\text{OH}^-]$. Accordingly, after the depletion of easily breakable lignin inter-linkages, the rate of delignification reactions within the remaining lignin fraction proceeded roughly 4 times faster under elevated alkali condition.

Carbohydrate stabilization, dissolution, and degradation

As already demonstrated, the rapid loss of non-lignin material during initial kraft pulping was practically unavoidable, regardless of the used liquor composition. Despite the major delignification rate acceleration that followed the increase in liquor $[\text{OH}^-]$ and $[\text{HS}^-]$ during bulk delignification (**Fig. 16**), the effect of liquor alkalinity on lignin-free pulp yield was rather insignificant, varying only $\pm 1\%$ odw (**Fig. 17**). Whereas lignin-free pulp yield under $_{\text{Low}}[\text{OH}^-]$ and 160°C was practically identical to $_{\text{High}}[\text{OH}^-]$ in a temperature range of $130\text{--}150^\circ\text{C}$, at 160°C , on the other hand, the lignin-free pulp yield was slightly lower around 85% delignification degree. These results are consistent with previously reported data under comparable conditions (Bogren et al. 2007). During kraft pulping of pine chips at L/W ratio of 4, Aurell & Hartler (1965a) demonstrated that an increase in EA charge from almost 16% to 25% resulted in approximate pulp yield decrease of 1% ; in terms of pulp composition, an increase in EA charge is connected with a considerable decrease in xylan yield and a notable increase in GGM yield (Aurell & Hartler 1965b).

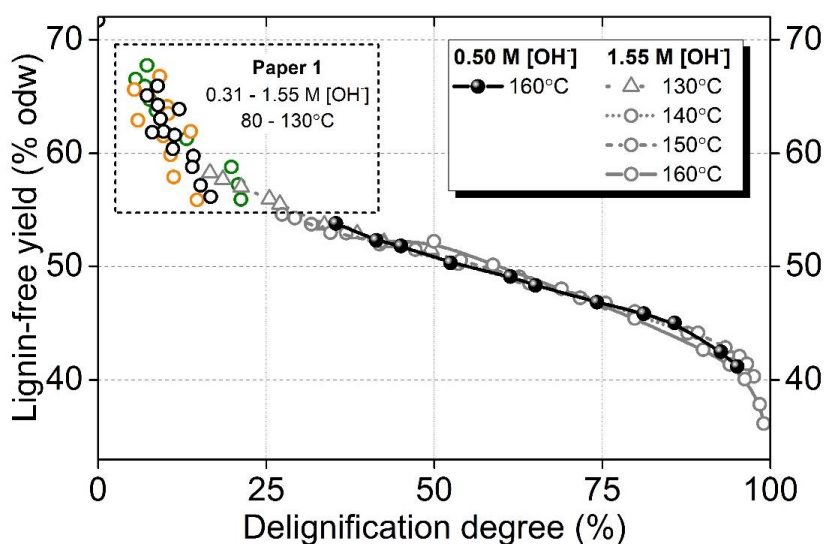


Figure 17 The effect of $[\text{OH}^-]$ (33% sulfidity) and temperature on lignin-free pulp yield during kraft pulping of Scots pine (wood meal; L/W ratio of 200). Colored symbols refer to initial pulping data (*paper I*).

Cellulose preservation was basically unaffected at 160°C by the change in liquor alkalinity, also, its dissolution was considered almost non-existent. Conversely, the effect of $[\text{OH}^-]$ on hemicellulose preservation and dissolution was notable. **Figure 18** elucidates the behavior of AX and GGM in terms of the preservation in pulp, as well as with dissolution and degradation in BL. Carbohydrate losses during heating-up mainly related to GGM. Depending on the liquor $[\text{OH}^-]$, rapid GGM losses varied between 25% and

50%; nonetheless, the residual GGM was rather resistant towards further removal. Even after 90% lignin removal, approximately one third of the initial GGM amount remained in the pulp. Recently, similar results were reported by Wigell et al. (2007), who estimated that approximately 25% of the Scots pine GGM was more resistant towards degradation under otherwise comparable soda conditions. Hansson & Hartler (1970) studied the alkaline degradation of glucomannan (isolated from chlorine holocellulose), with emphasis on peeling reactions. Following an alkaline sodium borohydride (NaBH_4) treatment at 100°C , they obtained almost 99% yield even after 120 minutes, and thus demonstrated that the rapid GGM loss under alkaline conditions is mainly caused by peeling. Compared to $\text{Low}[\text{OH}^-]$ at 160°C , GGM preservation was generally improved at $\text{High}[\text{OH}^-]$, and more pronounced at 160°C than at $130\text{--}150^\circ\text{C}$. These results further supported the theory that only sufficiently high liquor alkali concentration can rearrange REG to produce a di-anionic intermediate, and thus promote stopping reaction at the expense of peeling reaction (Lai & Sarkanen 1969). The removal of AX follows largely parallel to the lignin removal. In general, AX preservation was favored by less drastic pulping conditions; in other words, AX retention was decreased with increasing $[\text{OH}^-]$ and temperature (especially above 140°C).

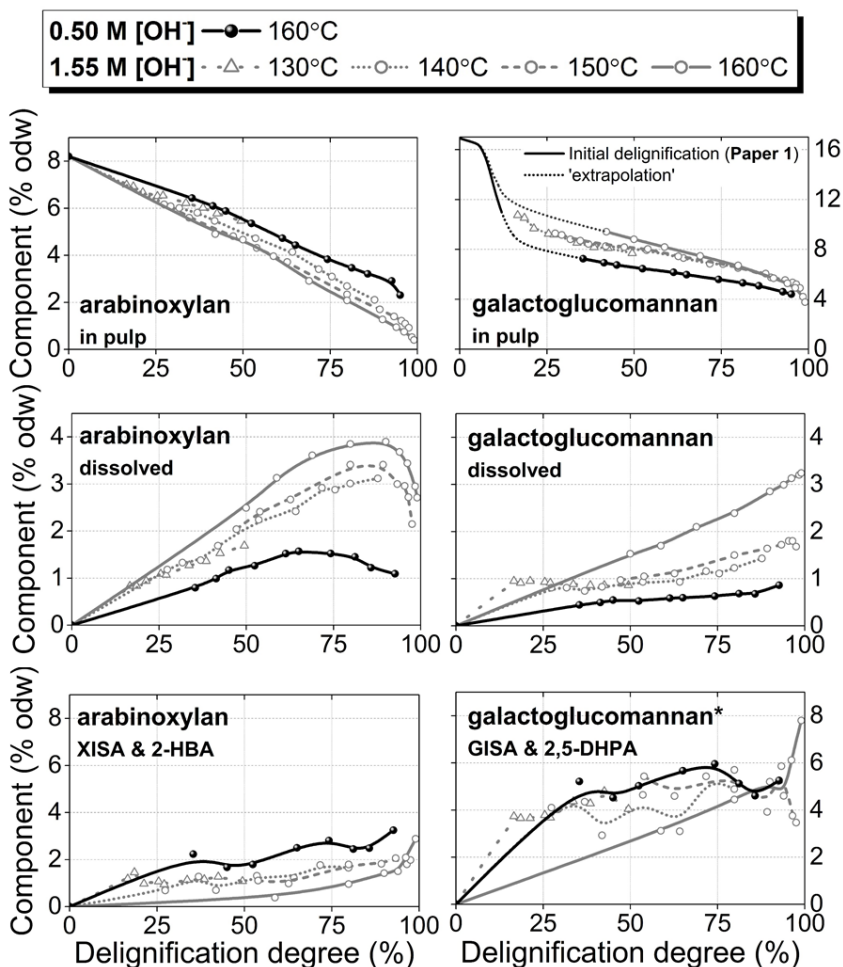


Figure 18 The effect of $[\text{OH}^-]$ (33% sulfidity) and temperature on the preservation, dissolution and degradation of Scots pine hemicelluloses during kraft pulping (wood meal; L/W ratio of 200). Main degradation products of arabinoxylan: xyloisosaccharinic acid (XISA) and 2-hydroxybutyric acid (2-HBA). Main degradation products of galactoglucomannan (* including acids from cellulose degradation): glucoisosaccharinic acid (GISA) and 2,5-dihydroxypentanoic acid (2,5-DHPA).

Due to characteristically short chain length, hemicelluloses were prone to dissolution as a polymer. In general, the amount of dissolved hemicelluloses increased with increasing liquor $[\text{OH}^-]$ and with temperature. Especially under $\text{High}[\text{OH}^-]$ conditions at 160°C , the amount of dissolved GGM and AX was high, reaching maximum values of approximately 3% and 4% odw, respectively (**Fig. 18**). Whereas the amount of dissolved GGM was found to increase continuously, the amount of dissolved AX reached a distinctive maximum value before a rapid drop was observed. At $\text{Low}[\text{OH}^-]$, the maximum

amount of dissolved AX was detected at 70-75% delignification, thus in line with previous findings by Li Jansson & Brännvall (2011). On the other hand, at $\text{High}[\text{OH}^-]$ the amount of dissolved AX increased until approximately 85% delignification. Parallel to the maximum amount of dissolved AX in BL, also the highest molecular mass for the precipitated AX was obtained (35 kDa, **paper II**), after which the molecular mass decreased significantly. It is obvious that at this stage extensive degradation of dissolved AX takes place; without a significant change in the pulp AX content, the rapid decrease in dissolved AX amount was coupled with an increase in the main AX degradation products, 2-hydroxybutyric acid (2-HBA) and xyloisosaccharinic acid (XISA). A similar AX behavior has been previously demonstrated by Saarnio & Gustafsson (1953) and Axelsson et al. (1962).

By utilizing the data on the polysaccharide composition in pulp and BL (**paper II**), a model that differentiates between the losses through primary and secondary peeling reactions was presented by Nieminen et al. (2014b). The model illustrated that substantial polysaccharide losses are initiated by alkaline hydrolysis reaction and materialized by the secondary peeling reactions; however, these reactions do not occur at a significant rate until above 140°C. In order to reduce the carbohydrate losses, they concluded that pulping temperature should not exceed 140°C.

6.2 Yield-increasing Additives (papers II-IV)

A recent thesis by Vaaler (2008) clarified the effect of oxidative methods on carbohydrate retention and pulp yield increase. It was demonstrated that under oxidative conditions, the obtainable pulp yield increase is mainly related to the preservation of GGM (hindered peeling) and in lesser extent to cellulose (mainly due to shorter cooking time). With emphasis on increasing carbohydrate retention, oxidative stabilizing methods were investigated while utilizing Scots pine wood meal and L/W ratio of 200. The behavior of polysaccharides was studied under PS, AQ, PSAQ, and ASA conditions, and compared to a conventional kraft process. In addition, the most promising high-yield pulp was further delignified in a novel flow-through oxygen delignification process and bleached in an ECF bleaching sequence to full brightness. Handsheet properties of the bleached pulp was characterized and the overall process performance was compared against a conventionally produced fully bleached laboratory pulp. In addition, the influence of liquor chemical concentration on polysaccharide behavior during oxidative conditions was evaluated, thus two hydroxide ion concentration levels were utilized (**Table 6**).

Table 6 Liquor composition during kraft, AQ, PS, PSAQ, and ASA pulping with Scots pine wood meal at L/W ratio of 200.

	Low[OH ⁻]	High[OH ⁻]	note	paper
Kraft liquor	0.50 M [OH ⁻]	1.55 M [OH ⁻]	33% sulfidity; ionic strength adjusted to	II
	0.10 M [HS ⁻]	0.31 M [HS ⁻]	2.00 M [Na ⁺] with NaCl	
	0.15 g AQ/L		AQ charged into kraft liquor	
Polysulfide liquor	PS	6 g S(0)/L	kraft liquor without NaCl addition; make-up NaOH for [OH ⁻] adjustment	IV
	PSAQ	6 g S(0)/L + 0.15 g AQ/L	AQ charged into polysulfide liquor	IV
Alkaline sulfite liquor	ASA	0.50 M [OH ⁻]	sulfite-to-hydroxide ion ratio of 0.75;	III
		0.38 M [SO ₃ ²⁻]	0.15 g AQ/L	

6.2.1 Delignification Rate and Polysaccharide Stabilization

As previously emphasized, an increase in the liquor strength is connected with an accelerated delignification. In the presence of oxidative additives, delignification was generally further promoted, and more lignin was removed before slower residual delignification kinetics started to dominate the overall delignification rate. Especially during High[OH⁻] PS and PSAQ pulping at 160°C, kappa number 30 (κ -30; 90% delignification degree) was easily reached before delignification rate started to decelerate (**Fig. 19**). Due to the rapid delignification during High[OH⁻] PS and PSAQ pulping, the temperature was decreased to 130°C in order to obtain a lignin removal rate that was comparable to reference Low[OH⁻] pulping at 160°C. The combination of High[OH⁻] and AQ, on the other hand, was interesting; the rate of delignification during kraft and AQ pulping was practically identical, and in ASA even slower than in kraft. In general, the effectiveness of AQ depended on the availability of reducing carbohydrate end-groups and β -aryl ether structures in lignin. The effect of AQ was clearly reduced in combination with elevated liquor chemical concentration. This probably related to a less dynamic lignin-polysaccharide redox cycle; in other words, higher concentration of sulfite and hydrogen sulfide anions improved the lignin fragmentation (outside the redox cycle), and higher [OH⁻] promoted GGM stopping reaction. These observations were in line with the findings of Sturgeoff & Bernhardt (1998) and Vaaler (2008), who demonstrated a less effective AQ behavior with increasing [HS⁻] in PSAQ pulping.

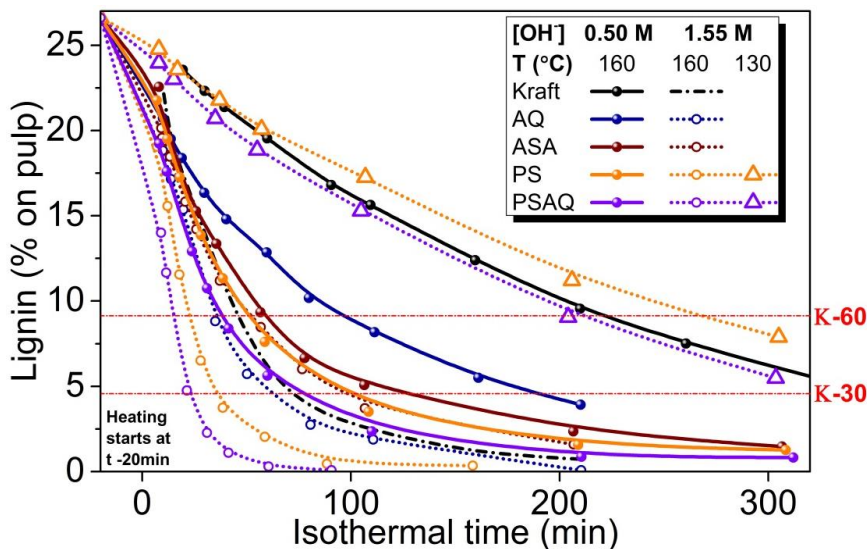


Figure 19 The effect of $[OH^-]$, temperature, and oxidative additives on delignification rate during alkaline pulping (Scots pine wood meal; L/W ratio of 200).

Compared to kraft, no additional cellulose stabilization was observed in any combination of stabilizing additives under $Low[OH^-]$ conditions, whereas under $High[OH^-]$ conditions cellulose yield was notably increased with AQ and even more with PS and PSAQ (**Fig. 20**). Somewhat surprisingly, the opposite was observed in case of GGM. Under $High[OH^-]$ conditions, the GGM yield was practically alike in pulping with AQ, PS and PSAQ, whereas at $Low[OH^-]$, and with PSAQ in particular, the additional GGM stabilization was significant. Accordingly, the effect of AQ on GGM stabilization was significantly reduced under $High[OH^-]$ conditions as compared to the $Low[OH^-]$ conditions. In the presence of oxidative additives, and especially in PSAQ, the rate of AX losses was accelerated parallel to delignification, indicating that part of the AX was removed together with lignin.

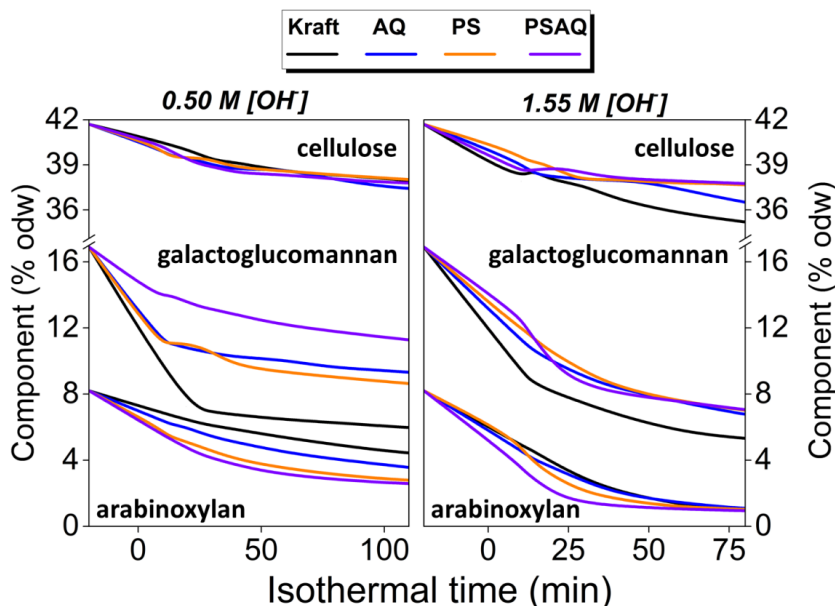


Figure 20 The effect of oxidative additives and liquor strength on polysaccharide stabilization during kraft pulping at 160°C.

6.2.2 Carbohydrate Retention in Pulp and BL at 160°C and 130°C

Pulping temperature of 160°C

In line with the general understanding, the influence of AQ, and especially that of PS, was mainly associated with improved pulp GGM stability, however, as shown in **Figure 21**, they also affect the stability of dissolved hemicelluloses. During AQ, PS, and PSAQ pulping, the amount of the main hydroxy acids was significantly reduced, and in some cases, certain acids could not be detected (**papers II-IV**). For example, no 2,5-DHPA was detected, and the amount of GISA and XISA was substantially decreased at 160°C regardless of the [OH]. Because of the hindered degradation reactions, a significant decrease in the overall hydroxy acid amount was observed; coupled with an increased pulp and BL hemicellulose amount, this indicates a reduced degradation of the dissolved polysaccharides parallel to the pulp polysaccharides. At a 90% delignification degree (κ -30), a substantial amount of hemicelluloses was found in the BL, under $\text{high}[\text{OH}]$ conditions, corresponding to roughly 50% of the initial AX, and 15-30% of the initial GGM.

Pulping temperature of 130°C

One of the most conspicuous outcomes of the temperature decrease from 160°C to 130°C, was the lower amount of dissolved hemicellulose; up to 50% less was dissolved at 130°C. Especially AX was preferably retained in pulp instead of being dissolved in the BL (**Fig.**

21). The amount of dissolved GGM was also notably decreased, nonetheless, it did not directly contribute to an enhanced GGM retention in the PS pulp, whereas in the PSAQ pulp, GGM was effectively retained. Despite the longer cooking time that was required for 80-90% delignification, due to lower temperature the retention of cellulose was moderately improved. Compared to the results at 160°C, somewhat higher amounts of GISA and XISA were detected at 130°C in the PS but not in the PSAQ BLs, thus well correlating with the improved AX and GGM preservation in the PSAQ pulp. In addition, no LA, 2-HBA or 2,5-DHPA were detected in the PS or the PSAQ BLs.

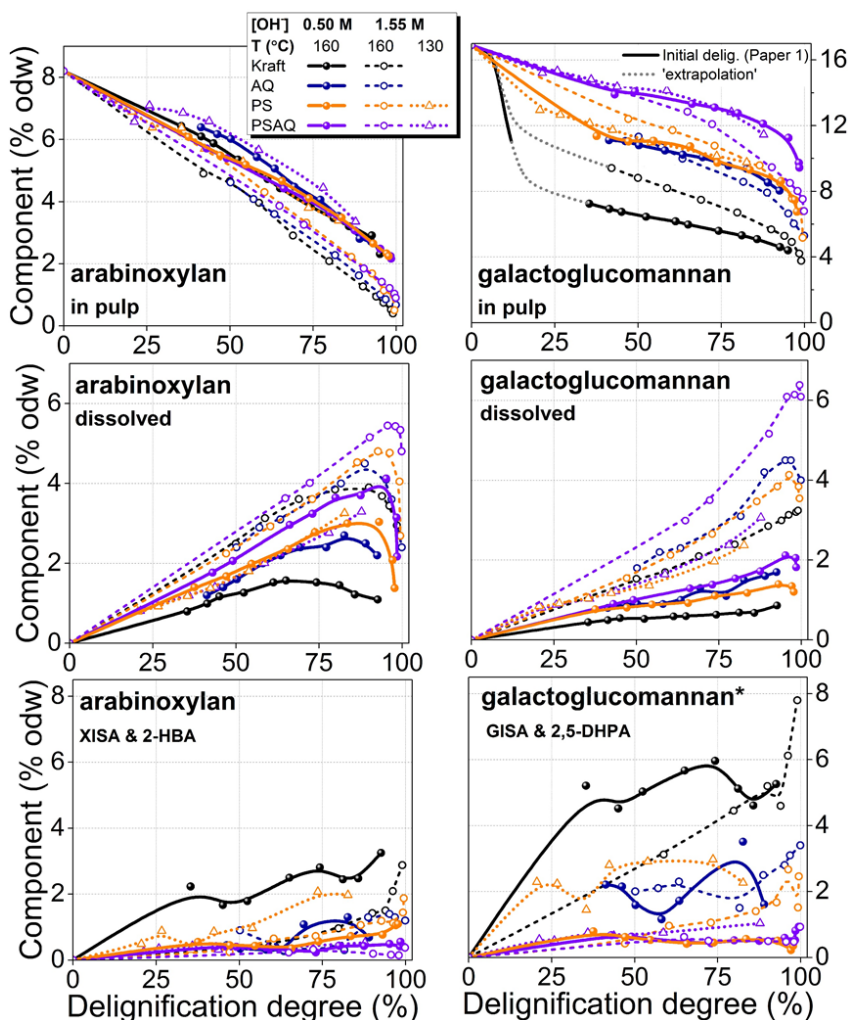


Figure 21 The behavior of Scots pine hemicelluloses in the presence of oxidative additives: anthraquinone (AQ), polysulfide (PS) and polysulfide-anthraquinone (PSAQ) pulping (wood meal at L/W ratio of 200). Main degradation products of arabinoxylan: xyloisosaccharinic acid (XISA) and 2-hydroxybutyric acid (2-HBA). Main degradation products of galactoglucomannan (* including acids from cellulose degradation): glucoisosaccharinic acid (GISA) and 2,5-dihydroxypentanoic acid (2,5-DHPA).

Pulp yield increase and the overall carbohydrate recovery

In general, oxidative methods that provide a pulp yield increase mainly via GGM stabilization tend to lose some of the yield advantage when approaching to lower kappa numbers. As reported by Minja et al. (1997) and compared to conventional kraft pulp, an additional yield increase of 4.4% odw was obtained during PSAQ pulping to κ -80, however, the yield advantage for κ -30 pulp was reduced to 2.0% odw. Therefore, even higher kappa numbers, such as κ -45 or even κ -60, are preferable in order to maintain high pulp yield. The polysaccharide composition in pulp and BL is summarized in **Figure 22** for all of the studied high-yield pulping modifications. In any single oxidant process modification at 160°C, excluding the $\text{High}[\text{OH}^-]$ AQ process, the κ -60 pulp yield was rather comparable and varied between 56.0% and 57.0% odw. In PSAQ, additional yield increase was attributed to an enhanced GGM stability. In general, a pulp yield increase was favored at lower temperature; the highest κ -60 pulp yield in PS (58.0 %) and PSAQ (61.8%) was obtained at 130°C.

Even though extensively speculated and even reported (Li et al. 1998), based on **Figure 22**, PS and AQ did not behave synergistically in terms of pulp yield increase. This supports the findings of Dimmel et al. (2003), who used model compounds to demonstrate that PS-AQ interactions are improbable under alkaline conditions. However, it should be noted that due to the diluted pulping system and small wood particle size, significant polysaccharide stabilization was obtained already in the presence of either AQ or PS.

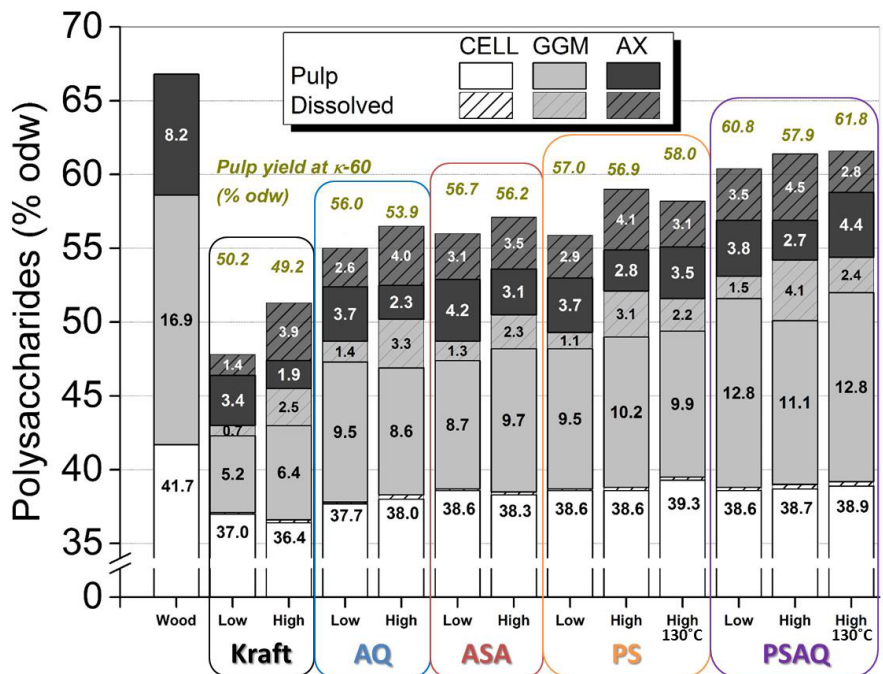


Figure 22 The amount of polysaccharides in pulp and BL during kraft, AQ, ASA, PS, and PSAQ pulping to κ -60. 'Low' and 'high' correspond to hydroxide ion concentrations of 0.50 M and 1.55 M [OH], respectively. AQ and PS charge was 0.15 g AQ/L and 6 g S₀/L, respectively. In all cases, wood meal and L/W ratio of 200 was used at 160°C (PS and PSAQ also at 130°C).

6.3 High-alkali Low-temperature Polysulfide Pulping (paper V)

6.3.1 General Considerations

The main production cost in softwood pulping is accounted by the raw material, thus an effective utilization of raw material is critical. Modified cooking and its modifications are today well adapted; however, due to the low concentration of active cooking chemicals, GGM stabilization via stopping reaction is not promoted, or the delignification rate notably accelerated. On the other hand, the combination of high $[\text{OH}^-]$ and high temperature would decrease fiber strength and pulp viscosity. Due to extensive thermal decomposition of PS around 150-170°C, its effect is practically limited to the pretreatment stage during conventional pulping processes (Lindström & Teder 1995; Brännvall et al. 2003; Gustafsson et al. 2004a and 2004b). Vaaler (2008) demonstrated that approximately 50% of the charged PS was consumed or degraded after the impregnation stage. The utilization of high-alkali pulping liquor, that would ensure a notable decrease in pulping temperature, is mainly hindered by the high residual alkali concentration of the BL; the conventional chemical recovery, including the Tomlinson recovery boiler, does not tolerate high load of inorganic material.

In this chapter, the high-alkali low-temperature polysulfide pulping concept (HALT-PS) is demonstrated with chips and a L/W of 6 (**paper V**). In order to recover unused cooking chemicals, ultrafiltration was used to purify HALT-PS BL from the dissolved polysaccharides and lignin. Due to the high brownstock kappa, further kappa reduction was obtained with a two-stage OD process, reinforced with an inter-stage oxidant treatment.

6.3.2 Pulping Liquor Composition and Residual Alkali Concentration

The most critical prerequisite in an effective HALT-PS concept is to maintain a high chemical concentration that ensures effective delignification even at lower pulping temperature. During HALT-PS pulping, the studied initial effective alkali charges at 40% sulfidity were 50, 60, 70, and 80% EA odw (2.08, 2.50, 2.92, and 3.33 M $[\text{OH}^-]$, respectively). Liquors were reinforced with PS (as elemental sulfur in a concentration of 6 g S_0 / L). The effect of chemical concentration (EA 50 – 80% odw) on carbohydrate preservation was studied at 130°C; in addition, the influence of temperature (140-160°C) was studied at EA 60%. Conventional kraft reference pulp was produced at 160°C, with a liquor composition comprising 22% EA (0.92 M $[\text{OH}^-]$) and 40% sulfidity.

At low liquor-to-wood ratios, a rapid decrease in $[\text{OH}^-]$ in the beginning of pulping was followed by a less intensive alkali consumption and a more levelled $[\text{OH}^-]$ profile. In

order to emphasize the importance of maintaining the alkali concentration, the used alkali charges were expressed according to the resulting residual alkali concentration. Corresponding to the initial effective alkali charges of 50%, 60% 70% and 80% EA, the approximate residual $[\text{OH}^-]$ was determined as 0.75, 1.0, 1.25, and 1.5 M $[\text{OH}^-]$, respectively (**Fig. 23**). As demonstrated in *chapter 6.2*, compared to reference kraft conditions at 160°C, the amount of hydroxy acids was notably reduced during high-alkali PS pulping at 130°C. Even though less alkali is consumed in neutralizing these acids, as a consequence of PS decomposition and end-group oxidation, the total alkali consumption was found to be higher compared to kraft (residual 0.1 M; initial 0.92 M). In addition, more alkali was consumed as the initial alkali charge was increased, suggesting more extensive fragmentation reactions in the liquor phase.

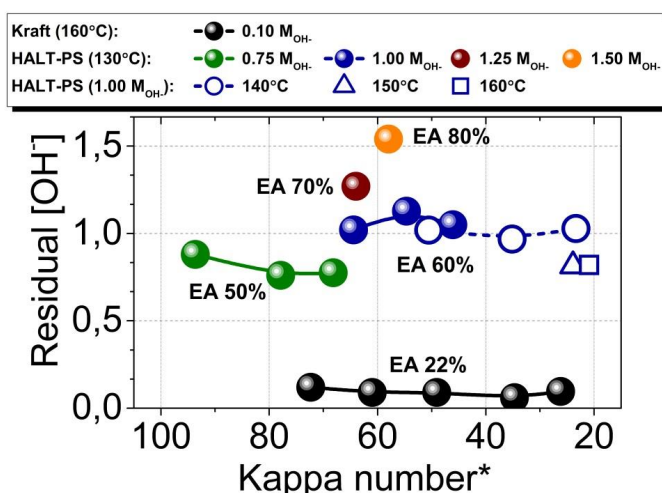


Figure 23 Residual $[\text{OH}^-]$ (mol/L) as a function of kappa number during kraft and HALT-PS pulping. Kappa number* according to pulp lignin content ($\kappa \cdot 0.15 = \text{lignin \% on pulp}$).

6.3.3 The Effect of Liquor Strength and Temperature on Delignification, Polysaccharide Stabilization, and Pulp Viscosity

Pulping under HALT-PS conditions at 130°C was connected with a substantial H-factor potential compared to the conventional kraft process; while producing a κ -60 pulp, the H-factor was reduced from approximately 1500 to 200 (**paper V**). In addition, already at 140°C the rate of delignification under HALT-PS conditions surpassed the kraft reference at 160°C (**Fig. 24**). Plotting polysaccharide yield as a function of cooking time revealed the effect of liquor strength: all carbohydrates were well preserved at 130°C provided that the residual alkali did not exceed 1.00 M $[\text{OH}^-]$. Above this concentration, additional AX and cellulose losses occurred, while GGM retained its yield.

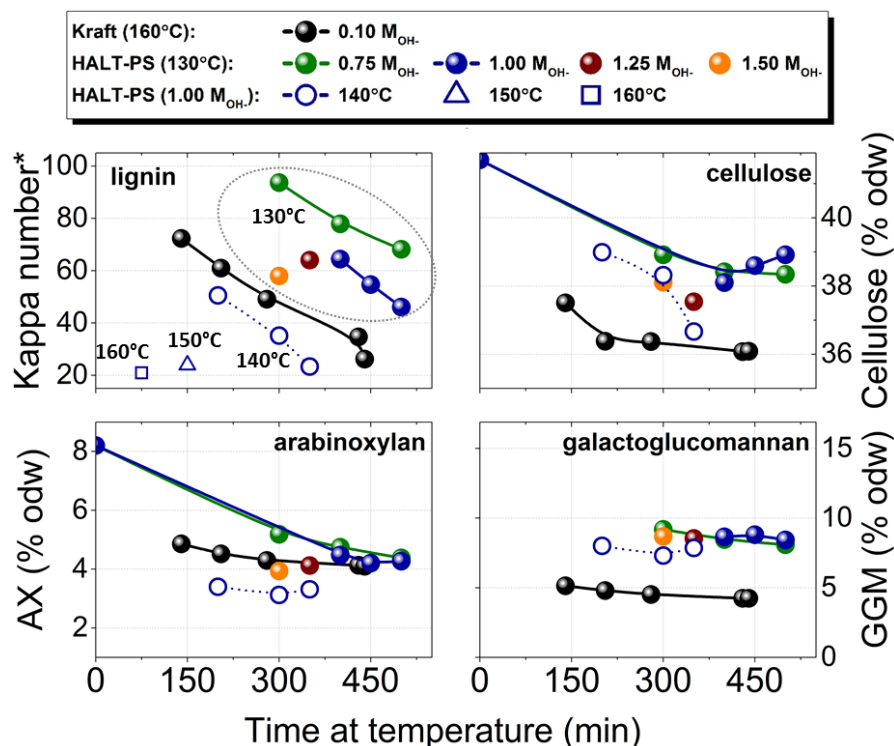


Figure 24 The effect of pulping liquor chemical concentration and temperature on delignification and polysaccharide stabilization during kraft and HALT-PS pulping.

Kappa number according to pulp lignin content ($\kappa \cdot 0.15 = \text{lignin \% on pulp}$).*

Kubes et al. (1983) concluded that owing to the increase in temperature, accelerated delignification rate does not compensate the additional viscosity losses during conventional kraft pulping. A similar observation was reported earlier by Daleski (1965). Under HALT-PS conditions, on the other hand, pulp viscosity was well maintained despite the considerably higher liquor [OH⁻] (**Fig. 25a**). Even at 140°C, pulp viscosity remained at a level comparable to the kraft reference at 160°C. Further, as illustrated in **Figure 25b**, no additional cellulose depolymerization was observed until 1.50 M residual hydroxide ion concentration. Bouchard et al. (2004) suggested that polysaccharide depolymerization is hindered in the presence of PS. However, since the conditions in HALT-PS and kraft reference were not comparable in respect to temperature or hydroxide ion concentration, it was challenging to estimate the role of PS.

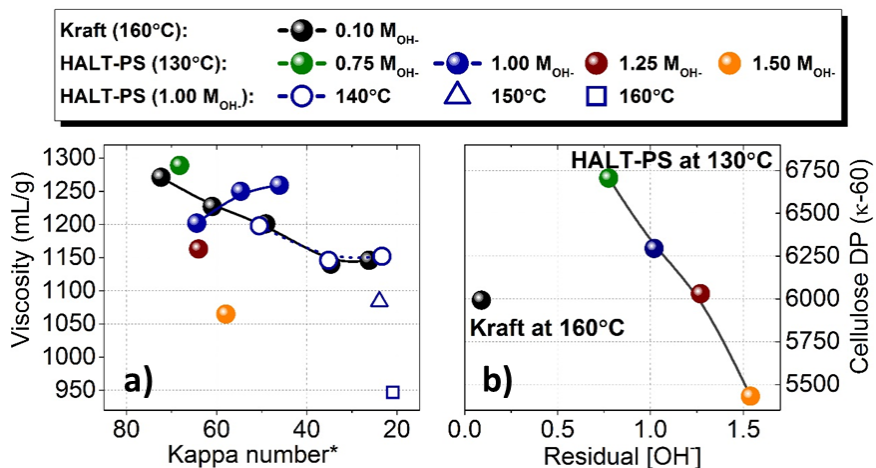


Figure 25 The effect of pulping liquor chemical concentration and temperature on **a)** pulp viscosity and **b)** cellulose degree of polymerization (κ -60 pulp) during kraft and HALT-PS pulping. Cellulose degree of polymerization is calculated according to da Silva Perez & van Heiningen (2002). Kappa number* according to pulp lignin content ($\kappa \cdot 0.15$ = lignin % on pulp).

6.3.4 Pulp Composition and Yield Increase

Compared to a conventional kraft process, the yield advantage of HALT-PS pulps was emphasized at higher kappa numbers around 50, resulting in an increased pulp yield of 7.2% odw at 130°C and of 5.2% odw at 140°C (**Fig. 26**). However, since there was no distinctive decreasing trend in the pulp yield at κ -46, results indicated that the observed yield advantage could be maintained, or even increased, at lower kappa number. Compared to the previous high-alkali PS pulping study by Brännvall et al. (2003), these results indicate that the decrease in temperature throughout cooking was one of the key prerequisites in order to preserve polysaccharides. Also, it should be noted that, even though the amount of rejects was not measured, HALT-PS chips were notably softer and thus more easily fiberized than conventionally produced kraft chips at comparable kappa number.

Compared to the kraft reference, the increase in pulp yield was attributed to an improved GGM and cellulose preservation. Whereas an $[\text{OH}^-]$ above 0.75 M was needed to obtain the highest GGM yield in respect to delignification at 130°C, a clear correlation between cellulose retention and $[\text{OH}^-]$ was not recognized (**Fig. 26**). As shown before by Meier (1961 and 1962), GGM and cellulose are mainly located in the secondary cell wall and especially in the S_2 -layer. Due to the elevated alkali concentration that ensures extensive fiber swelling, controlled deacetylation of GGM (Annergren et al. 1961) at 130°C could

result in increasingly parallel orientation of GGM with cellulose microfibrils (Stevanic & Salmén 2009). Consequently, improved GGM and cellulose stability towards degradation might be (at least partly) due to more cohesive GGM-cellulose entities.

Despite the scale-up, the effect of $[\text{OH}^-]$ and temperature on the preservation of cellulose, GGM, and AX in pulp was well in line with the results presented in *chapter 6.2* (wood meal; L/W ratio of 200). The dissolution of GGM, on the other hand, was dramatically reduced in chip scale, whereas AX content (% on wood) in the BL was only moderately decreased. Increase in temperature to 140°C did not result in additional GGM dissolution, whereas dissolved AX amount was increased.

Following the increase in temperature from 130°C to 140°C, especially AX suffered from additional losses. At comparable kappa number around κ -50, additional GGM and AX losses were approximately 0.5 and 1% odw, respectively. Also the cellulose yield loss was promoted by higher temperature, nevertheless, not until below κ -40. As supported by **Figure 26**, the additional AX loss mainly relates to dissolution, whereas GGM and cellulose losses were caused by degradation; in both cases, however, an accelerated rate of alkaline hydrolysis reactions might be the initiator of more extensive polysaccharide removal at 140°C (and especially at 150°C and 160°C). Nevertheless, as the dissolved xylan is able to redeposit onto the fiber surface (Yllner & Enström 1956; Axelsson et al. 1962; Vaaler 2008; Ribe et al. 2010), the pulp AX content was practically constant regardless of further lignin removal (**Fig. 26**). Similar behavior was not observed during wood meal pulping at diluted cooking process.

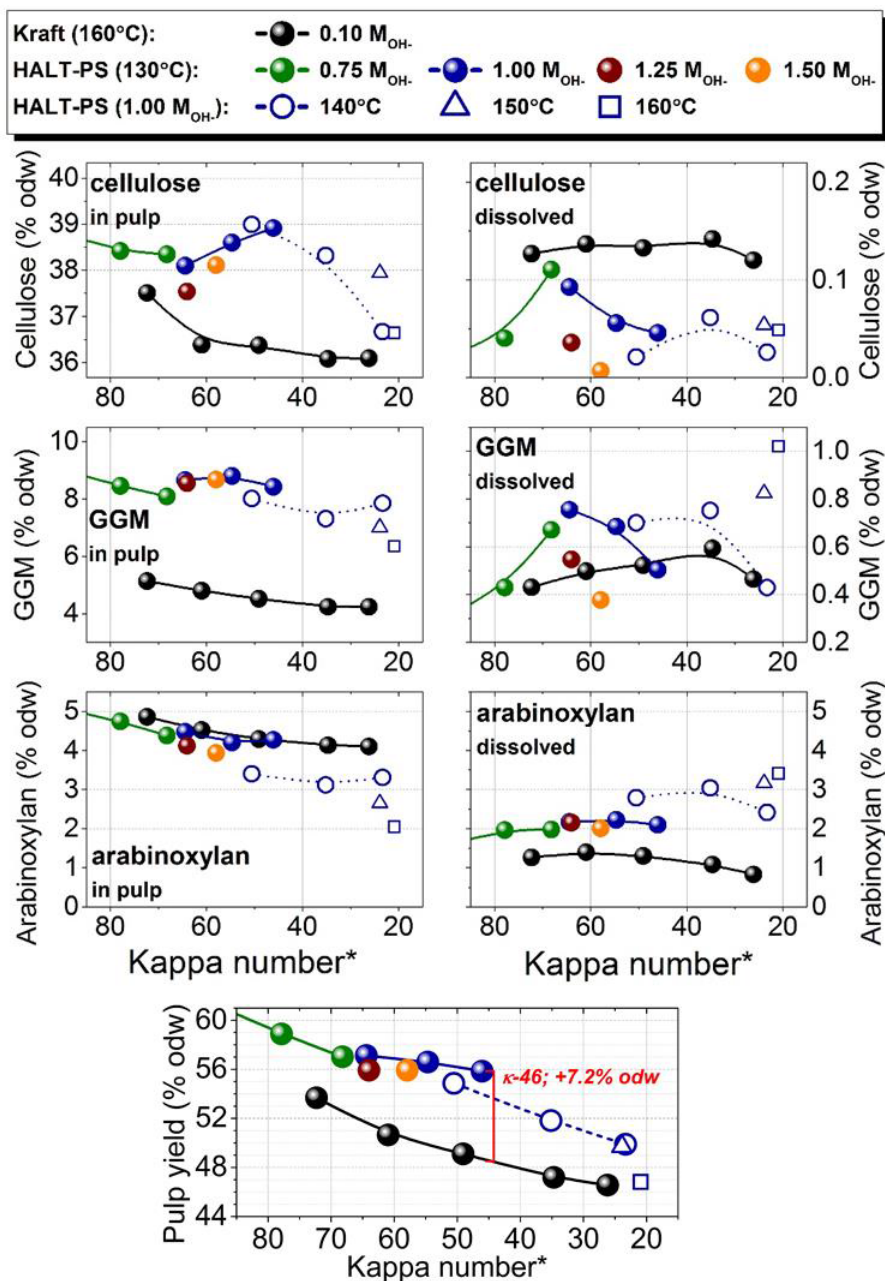


Figure 26 Polysaccharide compositions in pulp and black liquor, as well as pulp yield as a function of kappa number during kraft and HALT-PS pulping. Kappa number* according to pulp lignin content ($\kappa^*0.15 = \text{lignin \% on pulp}$).

6.3.5 Fractionation of HALT-PS Black Liquor and Alkali Recovery

Major challenge in industrial high-alkali-profile pulping process is the management of unused alkali. Due to the high residual alkali concentration, additional BL processing is mandatory, and preferably without any significant cooling. Utilization of separation and fractionation techniques to treat BL also possesses advantages; parallel to alkali recovery, it enables the recovery of side products with added value (Mesfun et al. 2014). Further lignin treatment with precipitation (Alekhina et al. 2015) or according to molar mass (Sevastyanova et al. 2014) results in lignin fractions with various functionality properties depending on the requirements of the end-products. Polymeric membranes generally tolerate high alkali concentrations, however, are limited to temperatures below 100°C (Schlesinger et al. 2006). Ceramic membranes, on the other hand, have been used to separate dissolved lignin and carbohydrates from softwood BL even at 145°C (Wallberg & Jönsson 2006). The performance and economic feasibility of ceramic membranes have been recently reported by Arkell et al. (2013 and 2014) and Jönsson & Wallberg (2009). Whereas the separation of unused cooking chemicals is practically impossible in ultrafiltration due to their low molar mass, lignin and hemicellulose retention is increased with denser membranes (Wallberg & Jönsson 2003; Jönsson et al. 2008). As a downside of dense membranes, higher operation temperature and pressure are required to compensate for the reduced transmembrane flux (Keyoumu et al. 2004).

Emphasis of the high alkali BL treatment was to remove dissolved wood components in order to recycle alkali rich lye outside the conventional recovery cycle. Operational parameters in laboratory filtration set-up were limited to room temperature and a pressure of 0.5 MPa, and thus do not represent industrial conditions. Also, due to the slow transmembrane flux even with 10 kDa cut-off membrane, a volume reduction was limited to approximately 70%. According to the described ultrafiltration set-up, lignin recovery in the primary retentate was approximately 68% while the polysaccharide retention was over 90% (**Fig. 27**). As expected, no distinctive difference in $[\text{OH}^-]$ between retentate and permeate was observed, which implies that the main residual alkali fraction was found in the primary permeate. Diafiltration was recently used by Wallberg et al. (2003) to further purify the lignin and the hemicellulose concentrate in softwood BL retentate from low-molar-mass inorganic substances. Diafiltration was used in this study to decrease the residual alkali concentration to a level suitable for the recovery boiler; accordingly, the primary retentate was diluted and subsequently ultrafiltered. Even though not performed in this study, further treatment of both permeate streams with denser membranes and/or size-exclusion chromatography (Hellstén et al. 2013) would result in a purified lye suitable for pulping/oxygen delignification phase (primary permeate) and alkaline extraction stage in bleaching (secondary permeate).

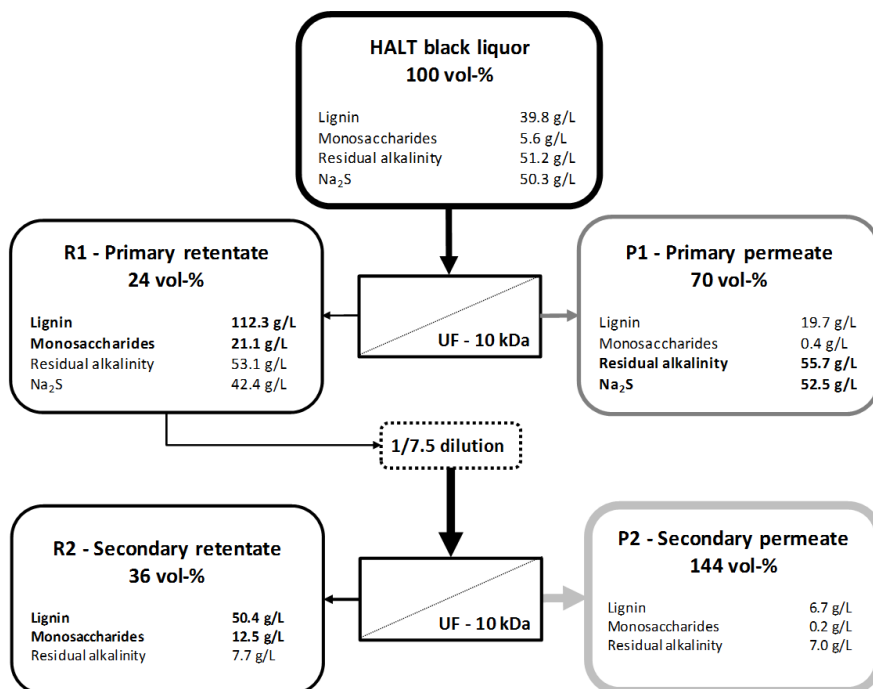


Figure 27 Fractionation of HALT-PS black liquor with membrane cut-off of 10 kDa (UF = ultrafiltration, UP010 Microdyn-Nadir membrane).

6.3.6 Two-stage Oxygen Delignification of High-kappa Pulp

In case of high-yield and high-kappa pulp, there is a pronounced demand for a selective and effective removal of residual lignin prior to the bleaching. Oxygen delignification process is generally considered to preserve pulp yield better compared to pulping. Nevertheless, whereas a typical two-stage oxygen delignification (OO) process is capable of 50-65% kappa reduction for a low κ -number brownstock softwood pulp (κ -25 to 30) (Sixta 2006), they generally lack the performance to obtain 50% (or above) kappa reduction for a high-kappa pulp without significantly impairing the viscosity or yield. The decrease in oxygen delignification efficiency is not due to depletion of free phenolic hydroxyl groups, but rather relate to the resistant, practically unreactive condensed phenolic moieties, such as 5,5-biphenyl structures, that are formed and accumulated in the residual lignin (Akim et al. 2001).

To promote delignification during extended OO process, a wide range of activators and catalysts have been summarized by Suchy & Argyropoulos (2002). In a recent study by Jafari et al. (2014a), starting from a high-kappa pine pulp, a kappa reduction of 70% was obtained during two-stage OD process including an inter-stage peroxymonosulfuric acid

treatment at alkaline conditions (OxO). Following the procedure presented by Jafari et al. (2014a), OxO sequence was applied to HALT-PS pulp (450 min at 60% EA and 130°C; **paper V** and *chapter 6.4.3*), whereas a single stage OD (O) was utilized for the conventional kraft pulp. Both pulps were treated with a chelant prior to OD in order to remove metal ions. During peroxymonosulfuric acid treatment, the solution pH was maintained around pH 11 by a continuous addition of NaOH. During the treatment pulp brightness increased significantly (based on visual inspection), indicating the removal of color producing lignin chromophores. **Table 7** presents the composition of conventional kraft and HALT-PS pulps during respective oxygen delignification sequence. Despite a rather high final kappa number after OxO, the kappa reduction was 66% and the selectivity in respect to lignin removal/polysaccharide retention was excellent.

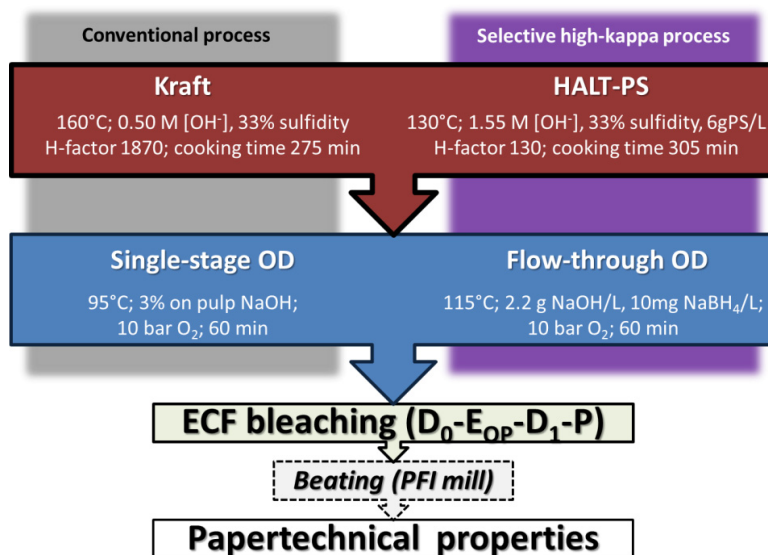
In OxO delignification sequence, the overall polysaccharide losses were rather insignificant, and mainly attributed to AX. However, even though the cellulose yield was practically unaffected, viscosity losses after peroxymonosulfuric acid treatment indicate severe cellulose depolymerization. Extensive viscosity losses were presumably due to too high peroxymonosulfuric acid charge (2% act. O₂ based on wood), as also the kappa reduction in this stage was extremely high. In addition, as was emphasized by Allison & McGrouther (1995), the complete removal of metal ions is of great importance in order to prevent cellulose depolymerization. Despite the non-optimized OxO sequence, the results presented in **Table 7** demonstrate that the yield advantage obtained during HALT-PS pulping was persistent and thus transferrable to bleachable grade pulp. According to HALT-PS concept followed by high-kappa OxO delignification sequence, the bleachable grade pulp yield was increased roughly by 6.5% odw compared to that of conventional kraft and single stage OD process. Even though certain means to enhance OD process with high initial-kappa pulp was demonstrated, the results should be addressed cautiously and further work is certainly required.

Table 7 Pulp properties during conventional kraft (Conv. Kraft) and single stage oxygen delignification process (O), as well as during HALT-PS and OxO process. CELL refers to cellulose, GGM to galactoglucomannan, and AX to arabinoxylan.

		Kappa number*	Viscosity (mL/g)	Yield (% odw)	CELL (% odw)	GGM (% odw)	AX (% odw)
Conv. Kraft	(440 min, 160°C)	26.2	1145	46.6	36.1	4.2	4.1
O	(45 min, 85°C, 3% NaOH)	13.5	1105	45.5	36.1	4.2	4.0
HALT-PS	(450 min, 130°C)	54.7	1250	56.9	38.6	8.8	4.2
O	(45 min, 85°C, 4% NaOH)	37.3	1260	54.9	38.7	8.7	4.0
OX	(10 min, 50°C, 2% act.O ₂)	21.3	985	53.5	38.8	8.5	3.8
OXO	(60 min, 95°C, 2% NaOH)	18.7	945	52.7	38.6	8.5	3.5

6.3.7 Handsheet Properties of Fully Bleached High-yield Pulp

This chapter demonstrates two different approaches to produce fully bleached pulp: conventional and high-yield process. In addition, the most important strength properties are presented. As a reference, Scots pine chips were cooked under kraft conditions to approximate κ -30 and delignified in one-stage oxygen delignification process (air-bath digester). The high-yield pulping approach, on the other hand, was terminated already at around κ -60, and performed according to the HALT-PS process. Both kraft and HALT-PS pulping were executed at L/W ratio of 50, and with liquor composition analogous to the one used in **papers II and IV**, and presented in *chapters 6.1 and 6.2*. In order to provide selective delignification and to reduce the pulp strength losses during extended oxygen delignification, key prerequisites include: effective removal of dissolved lignin, sufficient amount of available oxygen, and utilization of low and constant liquor alkali concentration. The continuous FT-OD fulfills all of the above-mentioned requirements, and was thus used to delignify the high-yield $\sim\kappa$ -60 pulp. Also a small charge of sodium borohydrate (NaBH_4) was added into alkali liquor saturated with oxygen to further preserve pulp viscosity. A detailed description regarding the FT-OD reactor has been recently published by Jafari et al. (2014b) and Jafari (2015). Both bleachable grade pulps were bleached in a conventional ECF bleaching sequence ($\text{D}_0\text{-E}_{\text{OP}}\text{-D}_1\text{-P}$). The process conditions during pulping and OD stage are presented in **Scheme 7**.



Scheme 7 Schematic illustration of the conventional and high-kappa delignification process approaches. Different to **paper IV**, the cooking process was performed with chips and at L/W ratio of 50 (instead of wood meal and L/W ratio of 200).

Both conventional and high-yield pulping attained full brightness (>89% ISO brightness). Jiang et al. (2002) demonstrated that the yield advantage obtained in PS (κ-28) and PSAQ (κ-26) pulping of softwood can be maintained or even improved throughout oxygen delignification (OD) and ECF bleaching sequence. As shown in **Table 8**, also with a high-kappa pulp the improved pulp yield (and viscosity) was effectively preserved through FT-OD and ECF bleaching; the yield of fully bleached pulp was 5.0% odw higher as compared in the conventional approach. The yield increase was mainly attributed to GGM, and in minor extent to AX and cellulose.

Table 8 Properties of brownstock, bleachable grade and fully bleached pulp during conventional and high-yield pulping approach. Cellulose degree of polymerization (DP) determined according to da Silva Perez & van Heiningen (2002).

	Conventional	High-yield
Brownstock pulp		
<i>Kappa number</i>	27	61
<i>Hemicelluloses (% on pulp)</i>	16.6	23.8
<i>Yield (% odw)</i>	46.1	57.0
Bleachable grade pulp		
<i>Kappa number</i>	12	16
<i>Hemicelluloses (% on pulp)</i>	17.0	24.0
<i>Viscosity</i>	995	955
<i>Cellulose DP</i>	4560	4790
<i>Yield (% odw)</i>	44.3	50.7
Fully bleached pulp		
<i>Hemicelluloses (% on pulp)</i>	17.6	25.1
<i>Viscosity</i>	765	805
<i>Cellulose DP</i>	3400	3980
<i>Cellulose (% odw)</i>	35.3	35.8
<i>Galactoglucomannan (% odw)</i>	4.5	8.6
<i>Arabinoxylan (% odw)</i>	3.1	3.5
<i>Yield (% odw)</i>	43.2	48.2

Both fully bleached pulps that are presented in **Table 8** were refined in a laboratory PFI mill at 10% consistency and three intensity levels, 1000, 3000, and 5000 revolutions; the development of handsheet properties in respect to refining intensity is shown in **Figure 28**. Conventional and high-yield approach represents two very different pulp types in terms of GGM content. As especially GGM is closely connected with the cellulose microfibrils (Åkerholm & Salmén 2001), its amount can alter the fibril localization of cellulose (Atalla et al. 1993). The removal of hemicelluloses ensures aggregation of individual cellulose fibrils, and thus leads to a more compact fiber structure (Duchesne et al. 2003); therefore, pulps with higher hemicellulose content are generally more easy to

beat, and less susceptible to fiber wall compression during beating (Vaaler 2008). Due to the significantly higher hemicellulose-to-cellulose ratio in HALT-PS pulp, higher tensile and lower tear index was measured at a given intensity level, thus confirming the findings of Molin & Teder (2002) and Çöpür (2007). Also, HALT-PS pulp had a significantly higher z-directional strength (Scott bond; 5000 revolution intensity level too strong to measure).

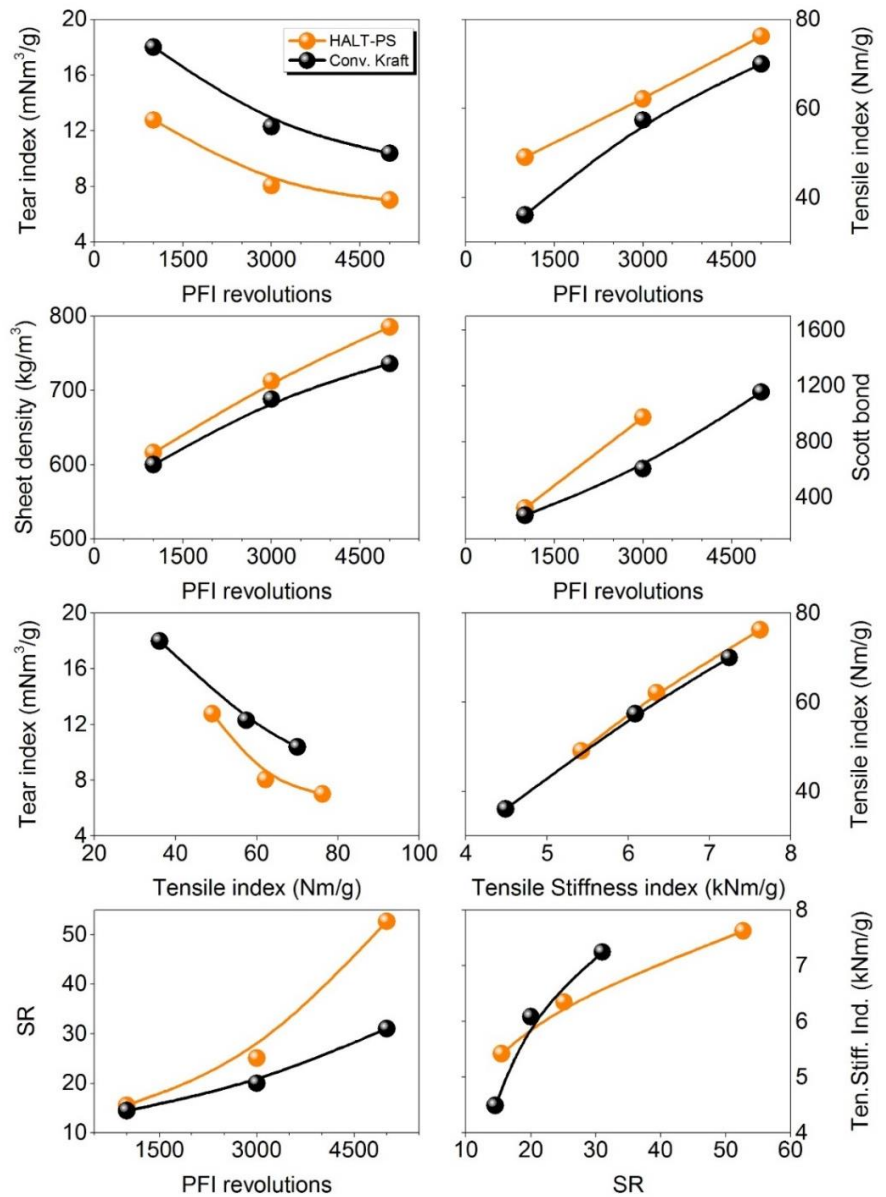


Figure 28 Handsheet properties of fully bleached Scots pine pulp produced according to conventional kraft (Conv. Kraft) and the high-alkali low-temperature polysulfide pulping (HALT-PS) concept. Three refining steps: 1000, 3000, and 5000 revolutions.

6.4 Industrial HALT-PS Pulping

6.4.1 General Outlook

In a modern Nordic softwood pulp mill more than 50% of the total production costs are connected to wood raw material (Kangas et al. 2014); therefore, an increase in pulp yield is an exceptionally explicit motivator to adapt novel pulping applications. Like Metsä Fibre Joutseno mill (implemented PS pulping in 2013), existing pulp mills are retrofitted to meet the requirements of intensive competition. Recent patent applications underline the rising interest in an up-to-date PS pulping technology. In a patent by Jiang (2009) (International Paper Company), all alkali and PS is charged into the first cooking stage operated at lower temperature. After which, part of the liquor is extracted and reintroduced in the later high temperature cooking stage, thus following the concept of modified cooking and more leveled alkali concentration. In a patent by Lindström & Wilgotson (2013) (Metso Paper Sweden AB), it was demonstrated that improved polysaccharide stability could be obtained in extended PS pretreatment stage, characterized by high alkali and PS concentration, and low temperature. Finally, in a patent by Turunen & Kovasin (2012) (Metsä Fibre Oy), the emphasis was put on decreasing the cooking temperature, and the cooking stage was obtained by moderate heating of the initially applied PS liquor. In a summary, the importance of low temperature and prolonged retention time during PS treatment has been well acknowledged in the recent research and development activities.

6.4.2 Possibilities and Challenges

The embodiment of the HALT-PS concept is not the high PS charge, but strongly alkaline pulping liquor that provides fast delignification even at lower pulping temperatures. The proposed HALT-PS process has several advantages, however, before commercial realization certain areas require advanced and novel process implementation. Some of the key advantages and future challenges are listed below.

Advantages

- Increased pulp production in respect to a given wood intake.
- Decrease in cooking temperature due to accelerated delignification rate.
- Improved papermaking properties due to higher hemicellulose content. In addition, less refining energy demand to obtain a certain pulp strength level.
- Recovery of the valuable components present in the BL.

Challenges

- Alkali recovery: in order to separate inorganic cooking components from dissolved organic material, effective BL treatment outside the conventional recovery cycle is mandatory.
- High brownstock kappa number (κ -40 to 60) places demanding requirements for the subsequent oxygen delignification process: kappa reduction of up to 75% is required.

In high-alkali concept pulping, the main motivation in additional BL treatment is to recover the unused alkali. In general, ultra- and nanofiltration can be used to separate the high-molar-mass components (lignin and oligosaccharides) from low-molar-mass components (cooking chemicals and hydroxy acids). Parallel to the BL treatment with ultra-/nanofiltration, further flexibility into alkali management could be obtained with black liquor gasification technology (BLG) (Lindström 2007; Naqvi et al. 2010). Even though the BLG technology is not yet feasible at industrial scale, most likely it will be the foundation of the next generation alkaline pulping process (Sixta 2006).

Due to the low heating value of carbohydrate derived organics in BL (oligosaccharides and hydroxy acids), isolation, purification, and processing of these components into products of added value, such as biodegradable plastics, is intriguing. Lignin, on the other hand, is characterized by a notably higher heat value. Even though kraft lignin is already used in numerous higher-value products (Vishtal & Kraslawski 2011), due to the sheer volume of the produced kraft lignin, its future exploitation will most likely balance between the production of energy and the production of high value biomaterial, which are however, produced in small amounts.

6.4.3 Economic Case Study

In respect to conventional kraft process (***Case I***), **Table 9** presents an approximation for the change in revenue for the HALT-PS based pulping process (***Case II*** and ***Case III***) while producing Nordic bleached softwood kraft pulp (NBSK). The purpose of the simplified process evaluation was to demonstrate the potential, and also the sensitivity, of the proposed HALT-PS process. Without extensive modeling, evaluation was mainly based on the increase in the brownstock pulping yield and on the additional costs attributed to BL purification. Also, yield losses after brownstock pulping are considered equivalent in all cases, and the retrofit of oxygen delignification or bleaching are not considered.

Table 9 Conventional kraft reference process (*Case I*), and a rough estimation for the change in revenue in HALT-PS-based pulping process (*Case II* and *Case III*). Pulp yield is based on the results presented in *paper V* and **Figure 26**. Produced black liquor amount correspond to pulping at L/W ratio of 4.

<u>Unit prices and auxiliary values</u>	Case I	Case II	Case III
NBSK: 620 €/adt	Kraft reference	Decreased wood consumption	Increased pulp production
Wood cost (50% dry content): 50 €/m ³			
Electricity: 0.05 €/kWh			
Pulping			
Pulp yield at kappa number 45 (% on wood)	49	56	56
Pulp production (adt/year)	600 000	600 000	685 700
Wood consumption (million-m ³ /year)	2.4	2.1	2.4
Decreased wood consumption (M€/year)	-	15.3	0
Increased pulp production (M€/year)	-	0	53.1
Decreased pulping temperature (M€/year)	-	7,5	8.6
Additional revenue/savings (M€/year)		22.8	61.7
Black liquor treatment	<i>not considered</i>		
Produced black liquor amount (m ³ /hour)	628	549	628
Annual running costs (M€/year)*	17.6	15.4	17.6
By-products			
Crude tall oil and electricity (€/adt)**	65	52	52
Lignin (€/adt)	0	***	***
Hemicelluloses (€/adt)	0	***	***
Revenues from by-products (M€/year)	39.0	31.2	35.7
Total (M€/year)	0	-0.4	40.8

* Arkell et al. (2014) - Up-scaled from a cost estimate for BL treatment at feed flow of 100m³/h.

** Kangas et al. (2014) - Reference model of a modern Nordic softwood kraft mill.

*** The price of lignin and hemicellulose depends on its properties.

One of the most important HALT-PS concept attributes (and requirements) is the decrease in pulping temperature. Following the decrease in temperature from 160-170°C (*Case I*) to 130-140°C (*Cases II* and *III*), the heat demand in pulping is reduced by approximately 250 kWh/adt. Depending on the amount of annual pulp production, the thermic potential accumulates notable improvement to mill's economy. In *Case II*, the pulp production is maintained to a level of *Case I*, however, due to the more selective pulping the savings are related to the decreased wood consumption. In *Case III*, increased pulp yield is directly transferred to increased pulp production. Based on **Table 9**, it is evident that without any process bottlenecks the increase in pulping yield should be utilized to increase the annual pulp production. It also indicates that the additional costs that relate to BL treatment are well covered by the higher pulp yield and the thermic potential. In fact, the revenue/savings from pulping (yield increase + thermic potential)

surpassed the cost of BL treatment when the yield increase was higher than 3.8% in *Case II* and 1.3% in *Case III*.

The by-product portfolio of a conventional softwood kraft mill is scarce, nonetheless critical for mill's economy. Essentially, crude tall oil (CTO) and energy are sold in addition to pulp. A downside of any process that increases pulping yield is that the power production and in lesser extent also the CTO production is reduced as more polysaccharides are retained in pulp and less wood is required in pulping. Owing to the substantial yield increase in *Cases II and III*, the revenues related to CTO and electricity were estimated to decrease by 30% in respect to *Case I*. It should be noted that the separation and purification of the dissolved lignin and hemicelluloses as a part of the BL treatment could generate additional revenues compared to the conventional kraft process. The price range of these by-products is wide, and dependent on the by-product functionality properties and purity, therefore, these were not included in the economic assessment.

7 Concluding Remarks

7.1 Present study

The main disadvantage during conventional kraft pulping processes is the extensive loss of carbohydrates that occur parallel to lignin removal. In order to reduce carbohydrate losses while producing a bleachable-grade pulp, this work investigated different aspects that have an influence on the behavior of Scots pine carbohydrates and delignification. In particular, the effect of liquor composition and temperature during kraft pulping was emphasized. In addition, proven carbohydrate stabilizing pulping enhancers, PS and AQ, were utilized as a part of the yield-increasing strategy.

The concentration of the active (OH^- , HS^- , and SO_3^{2-}), and to a certain extent also inactive (Na^+ - and other cations and anions), chemicals in the pulping liquor have a pronounced influence on pulping reactions. At a given temperature of 160°C (corresponding to a conventional kraft pulping temperature), increases in $[\text{OH}^-]$ from 0.50 M to 1.55 M at 33% sulfidity resulted in an accelerated delignification rate and improved GGM preservation. Pulp yield, on the other hand, was practically unchanged, mainly due to additional AX dissolution. In general, lower pulping temperatures reduce the extent of alkaline hydrolysis reactions, and hence also the losses via secondary peeling reactions. However, it was shown that the effect of pulping temperature on carbohydrate preservation was rather insignificant in a range of 130 - 160°C . Due to less-extensive AX dissolution, the pulp yield was approximately 0.5% higher at 130 - 150°C compared to 160°C , whereas no significant difference in GGM or cellulose preservation was observed.

PS and AQ are well-known for improving the retention of pulp carbohydrates during conventional kraft pulping conditions; however, illustration of the carbohydrate behavior (including stabilization, dissolution, and degradation) has been lacking. Based on comprehensive pulp and BL characterization, the effect of PS and AQ on carbohydrate reactions was investigated, with a special emphasis on the influence of liquor alkalinity and temperature. In general, compared to conventional kraft pulping at 160°C the carbohydrate preservation in pulp was significantly improved in the presence of PS or AQ, and even further with PSAQ. Simultaneously, the amount of dissolved polysaccharides was somewhat increased, and the amount of detected hydroxy acids in BL was substantially reduced. This indicated that carbohydrate degradation reactions can be effectively hindered by means of direct end-group oxidation in both solid and liquid phases. One of the key findings revealed that by utilizing high-alkali PS pulping liquor, the rate of delignification at 130°C was at a level of kraft reference at 160°C (wood meal,

and L/W ratio of 200); as a consequence of temperature decrease from 160°C to 130°C, AX and cellulose preservation was improved.

Alkali concentration of the pulping liquor of conventional softwood kraft processes is low, especially toward the end of the cook; therefore, a high pulping temperature is required to promote delignification reactions. PS pulping below 140°C enabled the stabilization of softwood polysaccharides and thus promoted the increase of pulp yield. However, in combination with low alkali concentrations, such a process would require a significant prolongation of the pulping time. Based on the above-described insight on the effect of selectivity enhancers and pulping conditions in a selective pulping approach, a high-alkali low-temperature PS pulping (HALT-PS) was outlined and demonstrated. With effective alkali addition 50–60% on wood, a high alkali profile was maintained throughout the pulping phase, and the delignification was effective even at 130°C. It was demonstrated that pulping according to the HALT-PS concept at 130°C produced a κ -46 pulp, with a 7.2% odw higher yield compared to conventional kraft processes at the same kappa number. Approximately two-thirds of the yield increase was attributed to improved GGM retention and the rest to cellulose. In HALT-PS pulping, the rate of depolymerization reactions via alkaline hydrolysis was decreased, and thus viscosity was well-preserved or even improved compared to reference kraft pulp.

A preliminary oxygen delignification and bleachability study revealed that the produced high-yield pulp with a kappa number of 50–60 is receptive to reinforced delignification: pulp yield advantage and fiber strength was well-maintained in fully bleached pulp. In addition to the critical factor of maintaining a good pulp strength and high pulp yield, one of the main challenges in the proposed HALT-PS process is the recovery of unused alkali. An additional BL treatment step is mandatory due to the high residual alkali concentration. In order to recover the residual cooking chemicals, a lab-scale demonstration confirmed the viability of the membrane filtration process as a measure of support for conventional chemical recovery.

7.2 Future Outlook

Yet another step toward a bio-based economy was taken in December 2015, as the first global initiative to limit potentially catastrophic climate change was agreed to in Paris. Pulp mills are essentially biorefineries, which are currently operating below their full potential. BL in particular is an underutilized source of biomaterial. More complete utilization of raw material in terms of recoverable side-products would be of great importance to mills' economies.

PS pulping, though known for more than half a century, has recently gained more attention, triggered by increasing wood costs. PS pulping is an attractive mill-proven solution for increasing pulp yield and quality, especially with softwood. Compared to conventional kraft processes, it was demonstrated that PS containing high-alkali-concentration pulping liquor enables cooking below 140°C without prolonged cooking time or risking additional pulp viscosity loss. Consequently, a substantial pulp yield increase was obtained due to improved GGM and cellulose stability.

Before the above-described pulping process becomes commercially attractive, a creative concept for the recovery and re-use of residual cooking chemicals needs to be developed. Most likely, such a chemical recovery concept would include membrane filtration, being already a rather well-established technique to quantitatively separate and recover the dissolved high-molar-mass organics, such as hemicelluloses and fragmented lignin. Parallel to the more intensive utilization of membrane separation as a part of chemical and side-product recovery, the next-generation pulp mill, or biorefinery, is most likely based on BLG technology that ensures a more flexible cooking process. Such a biorefinery, however, needs at least another decade to mature.

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Structural changes in the pulp, paper, and board markets have created a demand for a radical renewal of the pulping industry. There is a great need for identification and implementation of more effective techniques for the production of pulp, and for the recovery and separation of high added-value wood by-products. This doctoral dissertation describes the key areas on the possibilities to increase the efficiency of chemical pulping of softwood. This work demonstrates a pulp production method that promotes carbohydrate stability and increases the pulp yield substantially compared to conventional applications. It also displays a black liquor purification method for the recovery of dissolved hemicelluloses and lignin, as an essential part of the high-alkali black liquor chemical recovery.



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