Department of Forest Products Technology

SO_2-ethanol-water (SEW) fractionation of lignocellulosics

Mikhail Iakovlev

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Mikhail Iakovlev

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Abstract

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Abstract

This study deals with SO_2-ethanol-water (SEW) fractionation as a potential method for a Lignocellulosic Biorefinery to achieve high yield separation of the three important components of biomass; cellulose, hemicelluloses and lignin. Representatives of all principal biomass species were successfully treated by SEW fractionation at similar rates. The kinetics of delignification, polysaccharides removal and cellulose hydrolysis at different temperatures and SO_2 concentrations are described and interpreted from the viewpoint of acid-catalysed degradation of the biomass polymers. The fractionation pattern is compared to that of commercial acid sulfite cooking.

The kinetics of delignification, hemicelluloses removal and cellulose hydrolysis during SEW fractionation each follow a two phase behaviour. The delignification is first order in lignin and SO_2. The observed lignin sulfonation and delignification patterns can be explained using Hägglund's consecutive fast sulfonation-slow hydrolysis scheme.

During the initial phase of fractionation, the hemicelluloses removal and cellulose hydrolysis rates are related to the delignification rate, while in the following bulk phase the former two processes proceed independently from the latter. It is proposed that during the initial phase the hemicelluloses are removed together with lignin in the form of lignocarbohydrate complexes, while cellulose is protected by lignin from hydrolytic attack leading to a lower hydrolysis rate. Most hemicellulose side units as well as acetyl groups are cleaved during the first phase, while the glucomannan and xylan backbone polymers are removed at a considerably lower rate in the second (bulk) phase following first order kinetics in the residual polysaccharides. The observed polysaccharides dissolution behaviour can be interpreted in terms of low glucomannan stabilisation by crystallisation on cellulose at the applied conditions. Minimal cellulose dissolution occurs during fractionation, but the cellulose degree of polymerisation decreases by hydrolysis following zero-order kinetics.

The products include cellulosic fibres and a spent liquor containing lignin and hydrolysed hemicellulose sugars, the latter present up to 50% in monomeric form. The investigated overall and carbohydrate material balances show no carbohydrate losses as further supported by very low amounts of formed oxidation and dehydration products. The properties of the fibre products are evaluated and their potential applications are discussed.

The amount of sulfur bound to lignin is 2-3 times lower than that in acid sulfite cooking, and accounts for less than 1.1% on wood. The rest of SO_2 (95-97%) can be fully recovered by distillation.

Keywords Biomass, Biorefinery, Fractionation of softwoods, SO_2-ethanol-water fractionation

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PREFACE

This study was carried out during the years 2007-2011 at the Department of Forest Products Technology of Helsinki University of Technology now upgraded to Aalto University, and financed by the Finnish Funding Agency for Technology and Innovation (Tekes) through the FiDiPro program. In this short preface I am happy to express my gratitude to the people I had pleasure to work with during these years.

I will start by going back to autumn 2006 when a just-started postgraduate student from Russian (or perhaps 2nd generation Soviet) province wanted to experience Europe and was given a hand (or hands) by Tapani and Adriaan with great help of (and the whole idea coming from) Sergey. During that autumn I got my first experience with e-mails when I received them from Kristiina (I used my mom's address). My replies to her were carefully composed and translated to English together with Lida. Kristiina found me a beautiful apartment in Otaniemi where I stayed for more than 3 years. The 1st of February 2007, the day of my arrival to Finland, is the most memorable day! Helsinki trams vanishing in the strong snowfall seen from my bus window, and the first footprints in the virgin Otaniemi snow… The first days in Finland resembled a famous trilogy "Barbarians arrive to Rome" but I received a great care from (and Rome was saved by) Tapani, Riitta, Kristiina, Sergey, Alexey and Gary (my first office mate). I would like to especially thank Tapani for his support and input in my education over these years! I am also thankful to my parents who found strength to kick me out, although they did not want me to go away.

Soon Adriaan arrived to Finland. He became truly a glaring guiding star on my path. He dedicated *all* his time (i.e. 100%) to support me and other students (compare this to the official 40% of his *working* time in Finland). In addition to always immediately responding to hundreds of my e-mails (on average within 20 minutes), we had countless hours of most fruitful discussions (carefully summarised on the following pages of this book). After each of such discussions

somehow my self-esteem was always raised (with the reference level being normally quite low), and the aroused feeling of a forthcoming breakthrough was a major driving force during these years (although it still remains forthcoming).

So when Adriaan arrived in March 2007, he told me that instead of the originally planned black liquor gasification project we were going to explore SO_2-ETHANOL pulping and I immediately agreed, although neither I, nor he had any knowledge of the process (in addition, I had not yet smelled SO_2 which turned out to significantly modify the pleasant flavour of ethanol). But before I started the first cooks, I moved to the 3rd floor of the old PUU1 to the same office with Katri, and we have since been sharing offices most of these years. I must announce that she is the softest-hearted person on Earth and the best possible neighbour for me as we are 100% compatible! (Ooo…kei!) I received enormous support from Katri and Eero (who often came to our office primarily to see Katri, I guess) via everyday communication absorbing best western traditions through them. Special thanks go to Eero whose superfluent intelligence irreversibly covered me (among others)!

Returning to my work, I was lucky to get Terho who constructed the SO_2-bubbling system and even found an old SO_2 cylinder (probably from the times when sulfite industry was still alive in Finland). Later he provided a lot of assistance with the cookings. When the system was in place we performed the first cooks with Timo (I had never seen anything more black and indecent than those first pulps). He later became my first co-author. I have to thank Timo for teaching me everything what I can do now in the lab – cooking, kappa, visco, sugars, and many other tricks. During the next 4 years I was mostly occupied with these things (although the last year I also started to read a little).

Since I already started to talk about my co-authors, I now want to go on here with this selection criteria (structuring of this preface was a very hard task as well as composing it facing the submission dead-line being already behind). I am much obliged to Herbert who always set a very high scientific standard and was *at the same time* (!) sincerely interested in our research. Also his invaluable fundamental pulping, bleaching and cellulose chemistry courses as well as his great book contributed to this thesis a lot. I want to thank him in a separate sentence for bringing to our lab such important pieces of cooking and analytical equipment, including HPLC, HPAEC, GPC (the next will be GC, right?).

In 2010 after 2 years of sad staring at the screen trying to understand what tensile strength actually means, I decided to ask Eero (another Eero than above)

to help me with the interpretation as he was my lecturer in Paper physics course. Thanks to his expertise the last paper was published!

Niko came in early autumn 2007, and my old friend Lida arrived in February 2009. They are those who are generally referred to as “a bit more than friends”. That implies not only helping me with all graphs, computer programs, and other millions of applied life problems, which alone was quite crucial, for example, to finish this thesis. What actually this implies, I cannot put in words. They surprisingly always believed in me. I am not going to describe here the core friendship issues from fuzzy mornings and “acting like we are normal” afternoons to adventurous evenings and even worse nights at work, home, on the roads and at the destinations… but thank you so much!

I am indebted to Tiina for thousands of small talks and her very warm care of my well-being! For example, she helped me so much during the whole digestion process of this thesis! Laura (or Läypä) and Elli were also the major elements of my support and never refused to help me, although I was often “niin rude” to them (and to others: sorry, everybody!). Delphine, thank you for bringing the immensely special French atmosphere which I always enjoyed! Miro, thank you for your help (including getting illegal answers for the exam questions) and those awfully funny stories with which you made many of my days (sorry, others for too loud laughing, but blame Miro, please)!

Another circle of my communication was formed by my colleagues within Adriaan’s research group – Evangelos, Hanna, Minna and Vahid (alphabetic order). Especially tight ties we had (and have) with Minna and Evangelos who started in 2009 to continue developing the SEW process. Actually the advantages of this amazing process were falling on our heads one after another (except for those first black pulps) and we are rosily looking to the future! Thank you all for many nice moments!

I am happy that I had an opportunity to work with Marc, an extremely optimistic and mood-raising person! In the first months of HPAEC we spent a lot of nice time there, in the chromatography room (I quitted some time ago, but he seems to be still addicted to this analysis).

The members of the lunch+coffee group (Marc, Kaarlo, Vahid, Eero, Lasse + others mentioned above and below) are thanked for the most relaxing hour (or sometimes 1.5 hours, but never more than 2 hours)! Substantial part of the discussions was normally devoted to the different opinions on Finnish weather,

debates on whose pulp is better (including sometimes scientific reasoning), comments on the quality of coffee fluctuating within certain limits, etc.

I bless Tuomas for his friendship resulted, however, mostly in benefits for me, for example, obtaining an apartment for 2008-2009, and getting the driver's license! (In relation to this, other thanks are due to Niko who taught me driving!)

I am endlessly thankful to Kati for the non-stop supply of the literature and the feeling of library being like home!

I am truly grateful to Mao for everything she has done for me which resulted in so easy life!

I would like to thank Andrej (Åbo Akademi) for the invaluable knowledge on acid methanolysis he shared so generously with me!

Thousands thanks (per person) go to:
Maarit – for her huge help with measuring sugars!
Myrtel – for dozens of sulfate and sulfite determinations!
Mikaela – for establishing the HPAEC method for sugars and huge support!
Aila, Anu, Heikki, Marja and Risu – for their most generous assistance in the labs! Risu also for her support of animal rights which I greatly appreciate!
Rita – for supplying chemicals and for obtaining the Schöniger flask!
Raimo – for lending us another Schöniger flask (we still have to return it to him)!
Pena – for keeping my computer working!
Timo and Ari – for their kind helpfulness!
Akio, Anna, Annariikka, Anna-Stiina, 2 Anne, Anni, Antti, Christian, Elina, Hannele, Hannes, Iina, Ilari, Jaana, Jani, Janne, José, Juha, Kari, Karoliina, Kyösti, Lauri, Marcelo, Marina, Michael, Monika, Naveen, Neraj, Olesia, Olli, Orlando, Paula, Pertti, 2 Petris, Raili, Riikka, Ritva, Sole, 2 Susannas, Timo, Tuula, Ville and Zhen – for creating the pleasant research environment!

I am overwhelmingly grateful to Jean for his immortal art, especially for his 5th, always reviving me and convincing to continue the journey!

I am most happy to be blessed with my parents, grandparents, and the whole family loving me so much!

Finally, I deeply thank Finland and its people for the warmest welcome in my life!

In Espoo, 30th September 2011
Mikhail

LIST OF PUBLICATIONS

Paper I Iakovlev, M., Pääkkönen, T. and van Heiningen, A. (2009) Kinetics of SO_2-ethanol-water pulping of spruce. *Holzforschung* 63(6):779-784.

Paper II Iakovlev, M. and van Heiningen, A. (2011) SO_2-ethanol-water (SEW) pulping: I. Lignin determination in pulps and liquors. *Journal of Wood Chemistry and Technology* 31(3):233-249.

Paper III Iakovlev, M., Sixta, H. and van Heiningen, A. (2011) SO_2-ethanol-water (SEW) pulping: II. Kinetics for spruce, beech and wheat straw. *Journal of Wood Chemistry and Technology* 31(3):250-266.

Paper IV Iakovlev, M. and van Heiningen, A. (2011) Efficient fractionation of spruce by SO_2-ethanol-water (SEW) treatment: Material balances show complete recovery of carbohydrates and sulfur. *Submitted.*

Paper V Iakovlev, M. and van Heiningen, A. (2011) Kinetics of fractionation by SO_2-ethanol-water (SEW) treatment: Understanding the deconstruction of spruce wood chips. *Submitted.*

Paper VI Iakovlev, M., Hiltunen, E. and van Heiningen, A. (2010) Paper technical potential of spruce SO_2-ethanol-water (SEW) pulp compared to kraft pulp. *Nordic Pulp and Paper Research Journal* 25(4):428-433.

Author's contribution to the appended joint publications:

Papers I-VI Mikhail Iakovlev was responsible for the research plan with the co-author(s), performed the experimental work, analysed the results and wrote the manuscripts as principal author.

LIST OF ABBREVIATIONS

A_N – nucleophilic addition
AS – acid sulfite
CED – cupriethylenediamine
DP – degree of polymerisation
DP_n – number-average degree of polymerisation
DP_v – viscosity-average degree of polymerisation
DP_w – weight-average degree of polymerisation
E_N – nucleophilic elimination
FID – flame ionisation detector
GC – gas chromatography
HMF – hydroxymethylfurfural
HPAEC – high-performance anion-exchange chromatography
HPLC – high-performance liquid chromatography
IC – ion chromatography
IFBR – Integrated Forest Biorefinery
LCC – lignin-carbohydrate complex
LAFY – lignin- and ash-free yield
LFY – lignin-free yield
L/W ratio – liquor-to-wood ratio
PAD – pulse amperometric detector
RBA – relative bonded area
SEW – SO_2-ethanol-water
S_N1 and S_N2 – nucleophilic substitution, mono- and bimolecular
UV – ultraviolet

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INTRODUCTION AND OUTLINE

Two pressing global issues, climate change and limited conventional petroleum reserves, are driving the interest to use lignocellulosic biomass for production of transportation fuels. Unfortunately, two techno-economic barriers hinder commercial implementation of renewable transportation fuel production from wood and other lignocellulosic biomass. First, the capital cost per unit final product is high because the present largest wood processing facilities, as exemplified by pulp mills, are more than one order of magnitude smaller in feed stock energy feed rate than a modern oil refinery. The second barrier is the high operating cost to convert lignocellulosics into biofuels. This is caused by the natural resistance of woody biomass to decomposition, i.e. the "recalcitrance" to convert lignocellulosics into monosugars and lignin at high yield (Kumar et al. 2009).

The capital cost disadvantage may be reduced by integrating biofuels production into existing pulp/paper facilities. In such an Integrated Forest Biorefinery (IFBR) the collection of lignocellulosic biomass is combined with the existing wood procurement and delivery infrastructure, and the biomass conversion processes use available steam/power and water effluent treatment facilities (van Heiningen 2006). The scale of lignocellulosic biomass conversion may also be increased when the biomass fractionation process is "omnivorous", i.e. simultaneously treats all lignocellulosics (van Heiningen 2010).

Lignocellulosic biomass is a diverse entity which may be divided into two phyla – gymnosperms (or softwoods) and angiosperms (or hardwoods). The latter exists in two life-forms – trees and herbs, while all gymnosperms are trees. The main components of biomass (Koch 2006, p. 22, Nepenin and Nepenin 1994) are lignin (polyphenylpropane network, accounting for 18-32%), cellulose (highly crystalline linear polyglucoside, 35-50%) and hemicelluloses (mostly linear short-chain polysaccharides, 15-35%). Since these components have quite different chemical and physical properties, it is advantageous to separate them cleanly so that they can be used or converted into their most suitable products.

The forest products industry converts trees mostly into wood and fibre products. However, if new products are introduced, biofuels would be desirable considering their market size and the global need for renewable transportation fuels. In such a biorefinery, the carbohydrate fraction of lignocellulosics is partly or wholly converted to biofuels and chemicals, while lignin may be sold as a product or burned to produce energy needed for mill operation. The fractionation process used should be able to treat different phyla and life-forms of lignocellulosic biomass in order to increase the feedstock supply. The recovery of cooking chemicals should be simple to allow a smaller economical mill size. It is also beneficial if the process is flexible, i.e. if it is able to produce different products by changing the fractionation conditions. A candidate for such a process is the SO_2-Ethanol-Water (SEW) fractionation method.

In the present work an attempt is made to better understand the SEW fractionation process from the viewpoint of acid-catalysed degradation of biomass polymers. The kinetics of the fractionation reactions, i.e. delignification and carbohydrate hydrolysis, are presented with emphasis on:

- Analytical methods;
- Sulfur material balance and recovery;
- Overall and carbohydrate material balances;
- Effect of raw material: biomass species and feedstock properties;
- Effect of temperature;
- Effect of cooking liquor composition;
- Effect of liquor-to-material ratio;
- Products quality.

LITERATURE REVIEW

1 Biomass structural polymers

1.1 Lignin

Lignin is an amorphous heteropolymer built from phenylpropane (guaiacylpropane, G; syringylpropane, S; and hydroxyphenylpropane, H) structural units bound by ether and carbon-carbon bonds. The ratio G:S:H for spruce lignin is 94:1:5 (Erickson et al. 1973), while angiosperm lignins contain about equal amounts of G and S units, lignin of herbs being enriched in H units (Adler 1977). The weight-average DP, DP_w, of wood lignins was reported to be 15-100 (with somewhat lower values for hardwoods) at polydispersity index of about 3.5 (Fengel and Wegener 1989). The following major dimer units are present in lignin (the values correspond to the percentage of units involved in a particular structure for spruce lignin, Adler 1977): arylglycerol-β-aryl ether (containing β-O-4 bond), 48%; noncyclic benzyl aryl ether (α-O-4 bond), 6-8%; phenylcoumaran (both α-O-4 and β-5 bonds), 9.5-11%; diphenyl ether structure (4-O-5 bond), 9-12%; structures with α-1 and α-6 bonds, 2.5-3%; biphenyl structures (5-5 bond), 3.5-4%; 1,2-diarylpropane structures (β-1 bond), 7% (Figure 1).

Compared to gymnosperms, angiosperm lignins contain somewhat higher amounts of arylglycerol-β-aryl ether structures and lower amounts of phenylcoumaran structures. Angiosperm lignins are also less condensed which is related to the higher fraction of syringylpropane units (Adler 1977).

1.2 Hemicelluloses

The main softwood hemicelluloses are galactoglucomannan (about 20% on wood, Gal:Glc:Man = 0.1-1:1:3-4, DP_n 20-140, Figure 2) and arabino-4-O-methylglucuronoxylan (5-10% on wood, Ara:4-O-MeGlcA:Xyl = 1.3:2:10, DP_n 70-190, Figure 3). The former is a linear polymer backbone consisting of 1-4-linked β-D-glucopyranoses and β-D-mannopyranoses, acetylated at C_2 and C_3 (one acetyl group per

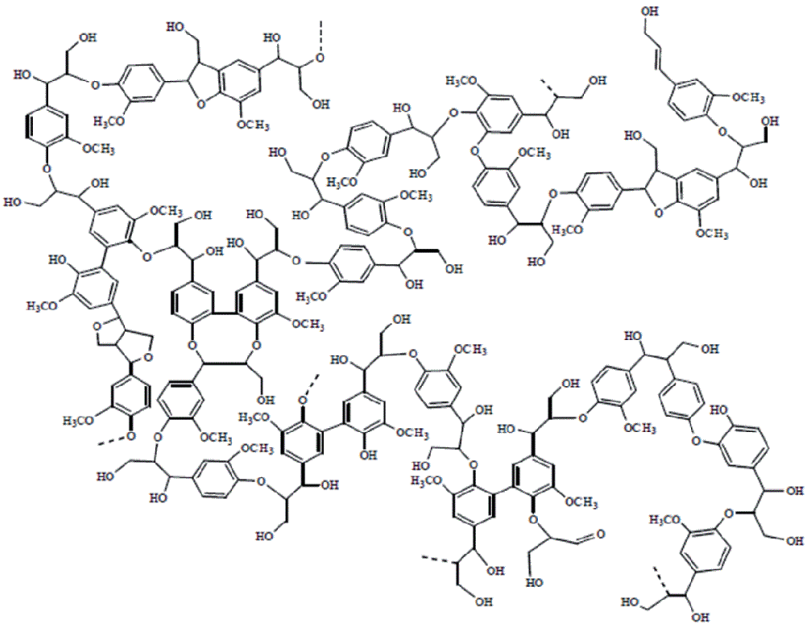

Figure 1. Softwood lignin structure (adopted from the Ljungberg Textbook on Pulp and Paper Chemistry and Technology, Book 1, p. 127).

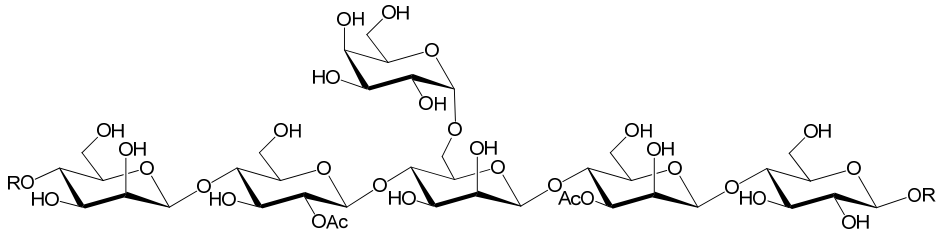

Figure 2. Softwood galactoglucomannan (adopted from Koch 2006, p. 28).

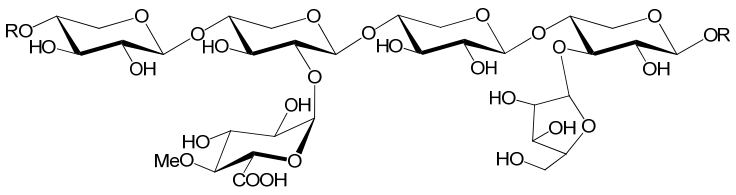

Figure 3. Softwood arabino-4-O-methylglucuronoxylan (adopted from Koch 2006, p. 28).

3-4 hexose units) and having 1-6-linked α-D-galactopyranose side units. Arabino-4-O-methylglucuronoxylan is a linear chain of 1-4-linked β-D-xylopyranoses with 1-2-linked 4-O-methyl-α-D-glucuronic acid in pyranose form and 1-3-linked α-L-arabinofuranose side units (Sjöström 1981, p. 60, 61; Fengel and Wegener 1989).

The main hardwood hemicelluloses are 4-O-methylglucuronoxylan (15-30% on wood, 4-O-MeGlcA:Xyl = 1:10, DP_n 90-220) and glucomannan (about 2-5% on wood, Glc:Man = 1:1-2, DP_n 60-70). The former is a linear polymer consisting of 1-4-linked β-D-xylopyranoses with 1-2-linked 4-O-methyl-α-D-glucuronic acid in pyranose form, acetylated at C_2 and C_3 (about 7 acetyl groups per 10 xylose units). Glucomannan is a linear chain of 1-4-linked β-D-glucopyranoses and β-D-mannopyranoses (Sjöström 1981, p. 62, 63; Fengel and Wegener 1989).

Some other polysaccharides present in both softwood and hardwood biomass are glucans (starch, callose, located, for example, in parenchyma cells), pectins (polyrhamnogalactouronides), arabinans, galactans (mostly located in the compound middle lamella, Makkonen 1967a, Fengel and Wegener 1989).

The polysaccharides composition of herbs is close to that of hardwoods, featuring high amounts of xylan. For instance various straws and reeds contain about 19-29% of pentosans and 4-7% of uronic acids, while hexosans are present in comparatively low amounts (2-3%, Nepenin and Nepenin 1994).

1.3 Cellulose

Cellulose is a linear polymer consisting of 1-4-linked β-D-glucopyranoses. It constitutes 35-50% of lignocellulosic biomass weight (Koch 2006, p. 22, Nepenin and Nepenin 1994). The DP_w of wood cellulose is high, about 7,000-15,000 (compare to DP_n of 20-220 for hemicelluloses, Fengel and Wegener 1989), and it is said that its polydispersity index is relatively low. Intra- and intermolecular hydrogen bonding is pronounced in cellulose leading to the strong self-assembly of the chains referred to as a microfibril. The degree of order between microfibrils varies leading to the existence of crystalline and amorphous regions (Sjöström 1981, p. 52).

1.4 Lignin-carbohydrate bonds

Lignin and polysaccharides are bound to each other by covalent bonds. Benzyl ether, benzyl ester and phenylglycosidic bonds were reported (Fengel and Wegener 1989). According to Lawoko et al. (2006b) all lignin in spruce is covalently bound to carbohydrates, mostly to galactoglucomannan and arabino-4-O-methylglucuronoxylan.

Eriksson and Lindgren (1977) demonstrated that lignin is bound through galactose units to the former and through arabinose and xylose units to the latter. According to Fengel and Wegener (1989) the polysaccharides are bound to lignin mostly through their side units – galactose, arabinose and 4-O-methylglucuronic acid.

2 Potential acidic biorefinery processes

2.1 General characteristics and comparison with alkaline processes

Breakdown of the biomass structural polymers is needed to achieve efficient fractionation in separate components. This applies also to solvent fractionation, although it is true that lignin is more soluble in the employed solvents than in water (McDonough 1993). Most fractionation methods employ either acidic or alkaline conditions which result in lignin and hemicelluloses depolymerisation via solvolysis reactions. Acidic conditions are provided by addition of an acid (inorganic or organic) to the cooking liquor and/or by the formation of acids, for example acetic or lignosulfonic, in the course of cooking. Addition of an acid allows decreasing the cooking temperature but often leads to serious corrosion problems, and also generally requires recovery of the catalyst for economic operation.

Most notable acidic fractionation processes include commercially practiced acid sulfite (AS) process based on sulfur(IV) compounds and so-called organosolv processes using mostly alcohol-water (for instance the Alcell process) or carboxylic acids-water (Acetosolv, Acetocell, Formacell, MILOX processes) mixtures. In addition a hybrid between AS and alcohol fractionation, i.e. the SEW process, exists and this is the subject of the present study. Alkaline processes include kraft, soda, and alkaline sulfite. The latter two were modified by addition of anthraquinone, AQ (soda-AQ and alkaline sulfite-AQ processes, respectively), and both AQ and methanol (Organocell and ASAM processes, respectively).

Acidic fractionation processes possess some significant advantages over alkaline processes. Most importantly the absence of peeling reactions at acidic conditions leads to higher carbohydrate preservation. Alkaline fractionation processes when operating at temperatures higher than 130°C, on the other hand, suffer from extensive carbohydrate degradation producing hard to recover hydroxycarboxylic acids (Carvalheiro et al. 2008). Secondly, economics require that alkaline processes have a high yield of base regeneration (above 98% except for calcium), while acidic processes do not necessarily employ a base. Furthermore, silica-rich annual plants cause serious problems due to scaling during evaporation of the spent fractionation liquor (so-called black liquor). If

high lignin-free pulp yields are desirable, then acidic processes (for instance Alcell for hardwoods; AS for softwoods) are often superior to alkaline processes (Girard 1998, p. 12, Sixta et al. 2006, p. 110). The brightness of pulp obtained at acidic conditions is higher compared to alkaline due to absence of strong chromophores such as quinones and stilbenes. Bleachability is also higher possibly because of higher reactivity and lower amount of the corresponding LCCs (Backa et al. 2004, Antonsson et al. 2003) and absence of hexenuronic acids.

Acidic processes have weaknesses as well. They often have limitations with regards to possible feed stocks. For example, softwoods pose a problem for many organosolv processes (Paszner and Cho 1989). Of those only the MILOX process (peroxyformic acid), which employs electrophilic delignification by hydroxyl cations, is capable of fractionating softwoods (Sundquist 2000). Alkaline fractionation processes generally (except for the soda process, i.e. only NaOH) are capable of delignifying both hardwoods and softwoods, although the rates for hardwoods and softwoods are substantially different (see Table 1). Another drawback of acidic processes is poorer pulp mechanical (mostly tear) strength properties compared to kraft pulps (Johansson et al. 1987).

The common products of acidic biomass fractionation processes are cellulosic fibres, dissolved carbohydrates, lignin, acetic acid, furfural and HMF. The dissolved carbohydrates are an especially important feedstock for chemical and biochemical treatment leading to various valuable products including biofuels (Magdzinski 2006, Sixta et al. 2006).

2.2 Alcohol-water processes

Alcohol-based fractionation was introduced by Kleinert and Tayenthal (1931). Among alcohols the highest efficiency of biomass fractionation is achieved with the primary alcohols (Paszner and Cho 1989). In fact, ethanol is one of the most widely used solvents for biomass fractionation. Its advantages include high availability and low toxicity, easy recovery due to its relatively low boiling point, and possibility of process integration when ethanol is also a product.

Surface tension of ethanol-water mixtures (about 30×10^{-3} N m^{-1} for 50 v/v.% ethanol-water at 20°C, Girard 1998) is close to that of pure ethanol (22.3×10^{-3} N m^{-1} at 20°C) and is much lower than that of water (72.5×10^{-3} N m^{-1} at 20°C). Ethanol-water mixtures provide fast and complete impregnation of lignocellulosics due to its transport governed by surface tension differences (so-called Marangoni effect, Sternling and Scriven 1959). Therefore the presence of ethanol eliminates the need for a separate impregnation step and decreases the overall time of fractionation. Even big fresh wood

cylinders (20×5 cm) are impregnated fast and uniformly (Kleinert 1975a). Nonetheless, drying of the wood chips reduces the delignification rate in the ethanol-water process even if the composition of the fresh liquor is adjusted to account for the lower water content in the wood chips (Kleinert 1975b, Bose and Francis 1999).

A typical ethanol-water process – the Alcell process – utilises the following conditions: ethanol-water ratio 1:1 (w/w.), temperature 190-200°C, pressure 27-35 bar, no catalyst, initial pH 6.5, final pH 2.8-3.8 (Paszner and Cho 1989, Pye and Lora 1991).

2.3 Acid sulfite (AS) and SO_2-water process

The AS process has a long industrial history and employs aqueous $SO_2/M(HSO_3)_n$ as its cooking liquor, where the cation M is calcium, sodium, magnesium or ammonium. The used amounts of SO_2 and hydrosulfites are determined by the empirically found Kaufmann diagram (Rydholm 1965, p. 467). In the present thesis SO_2 existing in the form of hydrosulfite anions is called "combined SO_2" following the central European acid sulfite industry practice (Sixta et al. 2006, p. 395). A typical composition of the cooking liquor is 20 g SO_2 L^{-1} (0.3 mol L^{-1}) as combined SO_2 and 50 g SO_2 L^{-1} (0.8 mol L^{-1}) as free SO_2, respectively (Sjöström 1981, p. 107). Cooking in SO_2-water solutions was reported in literature. According to the Kaufmann diagram the minimum SO_2 concentration for acceptable SO_2-water cooking is 12 w/w.%.

The AS process includes impregnation at about 110-120°C in order to uniformly distribute the cooking chemicals within the biomass structure. If the temperature is raised to higher values before impregnation is complete, unwanted condensation reactions take place which significantly impair delignification. The actual cooking is performed at 125-150°C (Sjöström 1981, p. 108; Sixta et al. 2006).

An important drawback of AS cooking is the very high cover-to-cover cooking times (up to 12 hours) due to the very slow (up to 6 hours) low-temperature impregnation stage (Fengel and Wegener 1989; Rydholm 1965, p. 444).

In AS cooking 10-20% of the carbohydrates are oxidised to aldonic acids (see section 3.3.2). In addition to carbohydrate-based by-products (ethanol, xylitol, acetic acid) the AS process generates lignosulfonic acids which are used in concrete admixtures, road base, oil drilling muds, etc. (Sixta et al. 2006). Sulfite pulp has poorer mechanical (tear) strength properties compared to kraft and even organosolv pulps (Johansson et al. 1987) but is suitable for specialty paper grades, tissue and dissolving pulp (Fengel and Wegener 1989).

2.4 SO_2-ethanol-water (SEW) process

SO_2-alcohol-water fractionation was introduced by Schorning (1957). He used 5.5% SO_2 in 1:1 alcohol-water (mostly methanol, but also ethanol and *n*-propanol) at 110-135°C and mostly 5 hours. Later the process was extensively studied by Ukrainian researchers: see, for example, Eliashberg et al. 1960, Primakov et al. 1961a/b, 1979, 1982, 1989. They used relatively high SO_2 concentrations (mostly 15%). In 1980-90s a few publications (Chen et al. 1990, Westmoreland and Jefcoat 1991, Puumala 1991, Pylkkänen 1992) appeared originating from the USA (mostly Michigan Technological University; MTU) and from Finland (Lappeenranta University of Technology). In these studies the SO_2 concentration was relatively low, 1-7%. In all works the following conditions were used: 30-100% ethanol/methanol in water, initial pH of about 1-1.5 at room temperature, temperature range 130-160°C (Eliashberg et al. 1960; Primakov et al. 1961a/b, 1979; Westmoreland and Jefcoat 1991). According to Puumala (1991) methanol provides a somewhat lower delignification rate than ethanol. Because of this and other advantages of ethanol (see section 2.2) it is preferred over methanol as solvent.

SEW process has many of the same advantages of the AS process compared to the kraft process: higher softwood solid residue and carbohydrate yields, lower temperatures, higher brightness and bleachability of solid residues (Primakov 1961a/b).

Yet the SEW process also has certain distinct advantages over the AS process in terms of biomass utilisation and operational efficiency. Ethanol in the cooking liquor allows fast transport of the cooking agents to the reaction sites inside the wood which eliminates the need for a separate impregnation step and decreases substantially the overall cooking duration. In addition, ethanol is known to be a better solvent for lignin and lignosulfonates than water (Primakov et al. 1979). The absence of a base in the process reduces the recovery cycle to simple distillation of ethanol and unreacted SO_2 (Iakovlev et al. 2007). Ethanol does not participate in the reactions and can be recovered almost totally (see section 4.1, Primakov 1961a). Also as will be discussed later in this thesis, absence of a base shifts the equilibrium between the sulfur(IV) inorganic compounds towards solvated sulfur dioxide and thus reduces the amount of hydrosulfite anions which are responsible for oxidation of monosaccharides to aldonic acids, a wasteful pathway present in conventional AS pulping.

3 Chemistry of acidic biomass fractionation processes

Similarly to alkaline fractionation methods, the depolymerisation reactions taking place during acidic processes are of nucleophilic nature. In fact most reactions presumably

follow the monomolecular substitution mechanism S_N1. Free-radical reactions are only possible at milder acidic conditions (McDonough 1993, Sarkanen 1990).

It has to be noted that many fractionation processes, including Alcell and AS, are operated at conditions so that the fractionation is governed by chemical reaction rather than by diffusion, as can be inferred, for instance, from the high values of the activation energies of the fractionation rates (Table 1, Rydholm and Lagergren 1959, Kleinert 1975b). Also mixing and chip thickness have no significant effect on the delignification rate in the Alcell process (Girard and van Heiningen 1997).

3.1 Lignin reactions

In this section the main lignin reactions in acidic cooking processes are reviewed, with specific attention given to alcohol organosolv (Sarkanen 1990, McDonough 1993), conventional AS (Sixta et al. 2006, Rydholm and Lagergren 1959) and SEW processes.

3.1.1 Nucleophilic substitution at α-carbon

In acidic processes delignification proceeds via monomolecular (S_N1, Figure 4, schemes 4.2 and 4.3) and bimolecular (S_N2, Figure 4, scheme 4.4) nucleophilic substitution in the propane side chain as well as via conjugate nucleophilic addition to quinone-methide (A_N, Figure 4, scheme 4.1). The S_N1 reactions include addition of a nucleophile to the benzyl cation (scheme 4.2) and non-phenolic units react (scheme 4.3) at only slightly lower rates (Sixta et al. 2006, p. 408). The substitution takes place almost exclusively at the α-carbon due to the high stability of the π-conjugated intermediates. The groups attached to the C_α of lignin – OH, OAr (e.g. α-O-4 bond) and OR (e.g. α-O-γ and α-O-carbohydrate bond) – are weak bases and poor leaving groups, so protonation is needed for accomplishing the substitution (Figure 4, 4.2-4.4) except for those phenolic units which react through quinone-methide (Figure 4, 4.1).

The S_N1 mechanism assumes formation of the intermediate to be the rate-determining step while in the S_N2 mechanism the rate-determining step is direct attack of the nucleophile on the protonated lignin unit. The nucleophiles present in the acidic fractionation systems are the solvents (water, alcohols, etc.); sulfur dioxide (hydrates and solvates) and hydrosulfite anions (in case of AS, SO_2-water and SEW processes); and the benzyl rings of other lignin units. All these components are competing for the electrophilic (protonated) lignin units in the described mechanisms. The reactions with sulfur dioxide, alcohol and water lead to substitution of OH, OAr and OR groups in lignin for sulfonic acid, alcoxyl and hydroxyl groups and are called sulfonation, alcoxylation (if

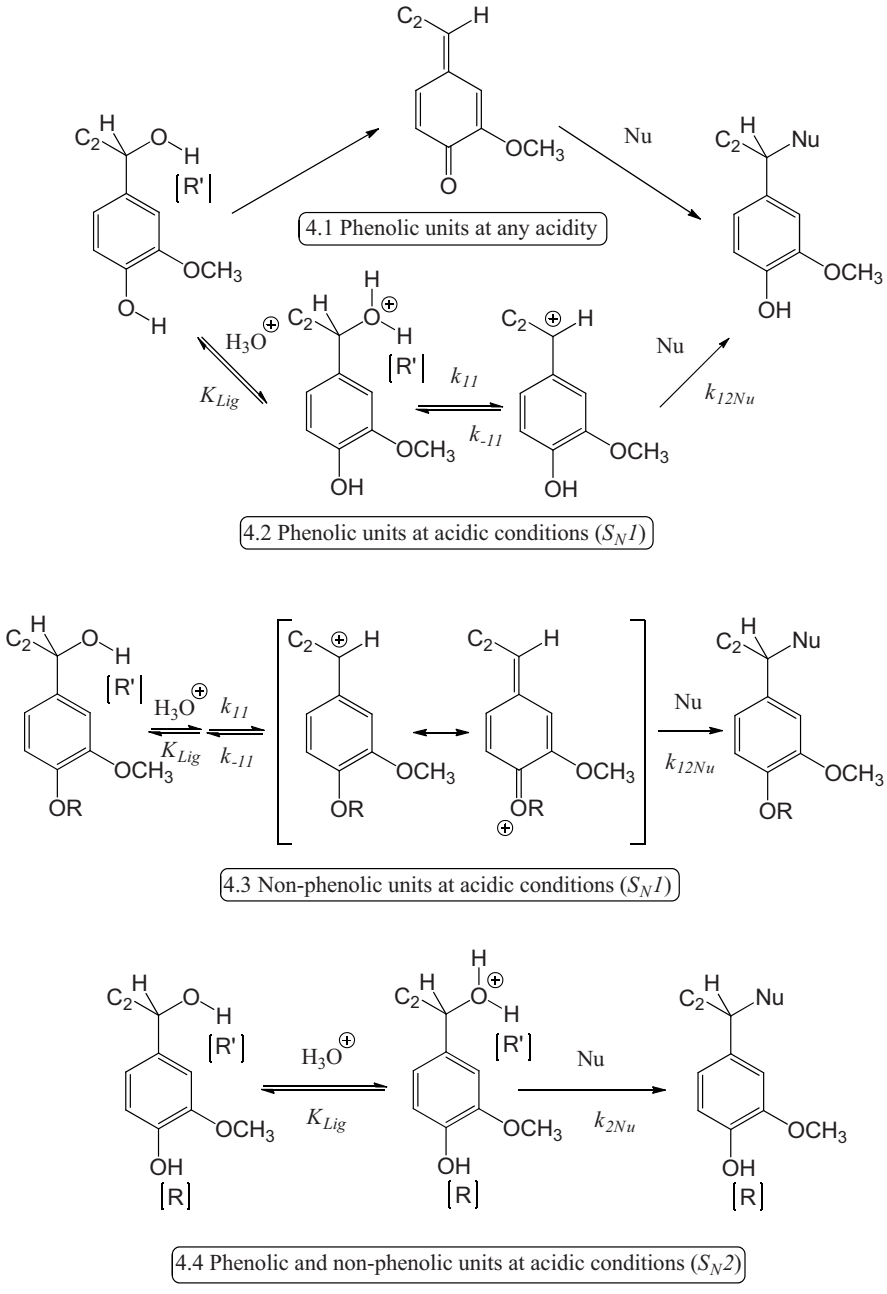

Figure 4. Lignin reactions: nucleophilic substitution at α-carbon.

hydroxyl group is substituted) and sulfitolysis, alcoholysis, hydrolysis (if aroxyl or alcoxyl group is substituted). Therefore lignin becomes soluble through fragmentation (sulfitolysis, alcoholysis and hydrolysis reactions) and hydrophilisation (sulfonation, sulfitolysis and hydrolysis reactions). The relative rates of the reactions leading to consumption of the fractionation chemicals are also most important because their recovery is required at high efficiency to assure commercial viability of the fractionation process.

The nucleophiles do however differ in their strength. For instance, SO_2 and hydrosulfite anions are certainly stronger than water and alcohols, and in the AS and SEW processes they preferentially react with lignin to form sulfonic acid groups ($pK_a \sim 1$, Vishnevskaya et al. 1981). The newly formed carbon-sulfur bond is relatively strong, so the formation of the sulfonic acid groups protects lignin from condensation reactions.

During acidic fractionation both α-O-4 and α-O-carbohydrate bonds are partly preserved at least in the solid phase (Fengel and Wegener 1989). This also applies to AS pulping where a considerable amount of cyclic α-O-4 (Gierer 1970) and α-O-carbohydrate bonds remain at the end of the cook. Spruce AS pulp contains lignin for 80% linked to carbohydrates (more to xylan than to glucomannan, Lawoko et al. 2006a). Lignin-carbohydrate ester bonds are easily cleaved in acidic conditions.

3.1.2 Sulfonation

Stereochemistry studies revealed that racemisation takes place during sulfonation of lignin model compounds suggesting an $S_{N}1$ mechanism (Gellerstedt and Gierer 1971). The nature of the sulfonating agent has been discussed extensively but no definite conclusion has been reached. In acidic systems like AS and SEW cooking liquors, the main candidates to participate in sulfonation reaction are hydrates and solvates of sulfur dioxide ($SO_2 \cdot nH_2O$, $SO_2 \cdot mC_2H_5OH$, $SO_2 \cdot xH_2O \cdot yC_2H_5OH$) and hydrosulfite anions HSO_3^-. Eliashberg et al. (1955) performed sulfonation of lignin in spruce meal by applying 10-20% SO_2 solutions in 1M hydrochloric acid at 80°C and after 15 hours obtained a sulfur content of the residual lignin corresponding to a S/C_9 ratio of about 0.24 (at 10% SO_2) and 0.36 (at 20% SO_2). This proves that sulfur dioxide species can sulfonate lignin without hydrosulfite anions. The nucleophilicity of hydrosulfite anions is higher than that of sulfur dioxide hydrates and solvates (Gierer 1970), so it can be expected that the sulfonation rate should be higher for hydrosulfite anions. However, in base-free systems, like SEW, the concentration of hydrosulfite anions is very low and the sulfonation is likely carried out mostly by SO_2. It is also assumed that SO_2 hydrates and solvates sulfonate lignin at similar rates. Cooking of spruce at 15% SO_2 and 135°C for 60-120

minutes in ethanol-water solutions over a range of ethanol concentrations, 30-85 v/v.%, resulted in a constant S/C_9 value of about 0.27 for the dissolved lignin (Tsypkina et al. 1981). However, the rates of lignin dissolution were quite different indicating that sulfonation is not a rate-limiting step. The sulfonation rates in SO_2-water and SEW liquors are of the same order of magnitude (Vishnevskaya et al. 1981). In addition Komarova et al. (1981) showed that even in 100% ethanol (at 10% SO_2) lignin is sulfonated to about the same degree as at 50% ethanol. However, the sulfonation rate is substantially lower in pure ethanol. It is explained by lower dissociation of lignosulfonic acid at higher ethanol concentration. It was also shown that in addition to sulfonic acid groups $-SO_3H$, spruce lignosulfonates contain a considerable amount of hydrosulfates $-OSO_3H$, especially at lower temperatures (Boyarskaya and Tsypkina 1970).

3.1.3 Nucleophilic α-β-elimination

During acidic treatment (for example in the Alcell process), benzyl carbocations are also known to undergo α,β-elimination (E_N) as shown in Figure 5. As a result the positive charge in the carbocation migrates to the β-carbon atom, followed by the addition of, for instance, water and β-O-4 bond cleavage (Sarkanen 1990). β-Ether cleavage is also known to occur in neutral sulfite cooking in which strong nucleophiles such as hydrosulfite and sulfite anions are present in high amounts (presumably via S_N2 substitution at the β-carbon). β-O-4 bonds are considered to be stable in AS cooking. The explanation given is that SO_2, being a moderately strong nucleophile, suppresses the α-β elimination by consuming the electrophilic sites (Fengel and Wegener 1989) but is not capable of accomplishing the substitution at the β-carbon (Gierer 1970). Nevertheless, β-O-4 bonds cleavage was recently reported for AS cooking of eucalyptus (Marques et al. 2009). In addition, the methyl-aryl ether bonds are also stable during AS cooking (Gierer 1970).

The last compound shown in Figure 5 may undergo different rearrangements and oxidation-reduction reactions producing ketones called Hibbert's ketones. The latter are however not found in the spent liquors of autocatalysed organosolv processes including Alcell (Bose and Francis 1999, McDonough 1993). Similarly, in formic acid treatment, model compounds containing β-O-4 bonds are completely consumed but the yield of the R''OH (guaiacol) is also low which is explained by intra- and intermolecular condensation (Ede et al. 1988). Formic acid is much stronger than acetic acid which explains the higher lignin condensation when using the former.

Another pathway for the cleavage of the β-ethers accompanied by the formation of formaldehyde was suggested as per Figure 6. Formaldehyde arises also from other lignin

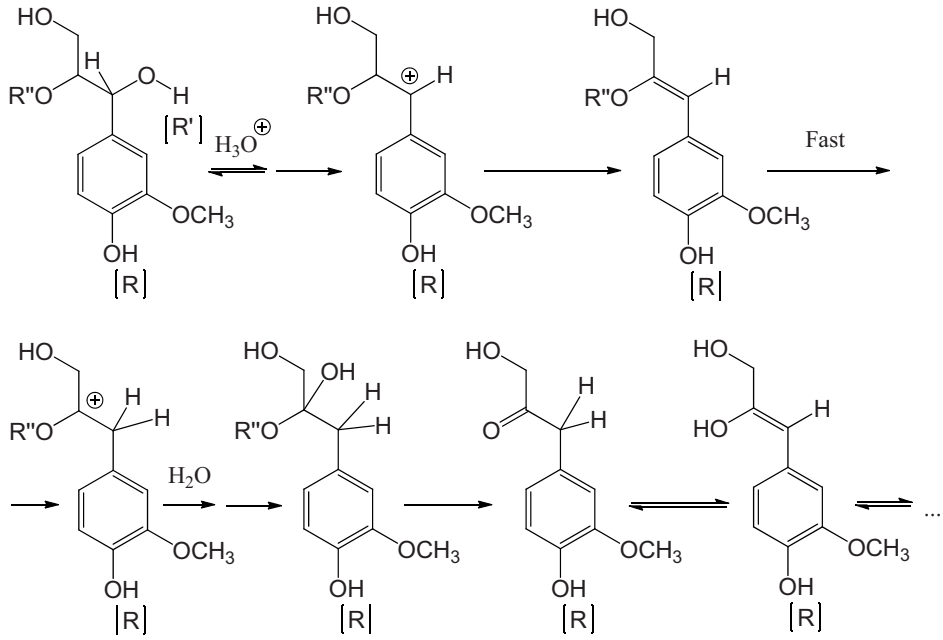

Figure 5. Lignin reactions: α,β-elimination (E_N) and β-O-4 cleavage.

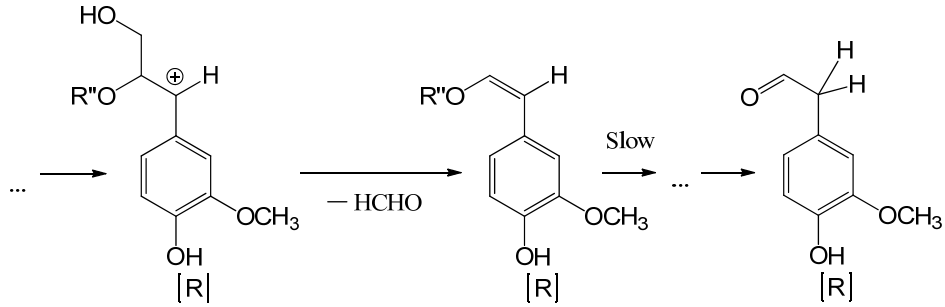

Figure 6. Lignin reactions: α,β-elimination (E_N) and formation of formaldehyde.

units (containing for instance β-5 bonds) and is known to readily form methylene cross-links between lignin units (Hoo et al. 1983). May be that is why formaldehyde was not found in the Alcell spent liquors (Girard and van Heiningen 1997). Bose and Francis (1999) found that the softwood organosolv delignification rate correlates with the content of the β-O-4 bonds in the residual lignin (at 175°C).

3.1.4 Condensation

In addition to the reactions leading to cleavage and dissolution of lignin, reactions between different lignin units, called condensation, are possible which form non-cleavable carbon-carbon bonds thereby preventing delignification.

Condensation is promoted by acidity and high temperature (Rozenberger 1961). Weak nucleophilic positions at the C_6, C_5 and C_1 sites of the lignin unit may form new carbon-carbon bonds with the C_α site to produce diphenylmethane structures (Figure 7). Polyatomic phenolic extractives, for instance hydroxystilbenes, flavonoids and tannins, may also participate in condensation reactions. It was shown (Baumeister and Edel 1980, Paszner and Cho 1989) that condensation could be the reason for the low fibre liberation point in Alcell cooking of softwoods.

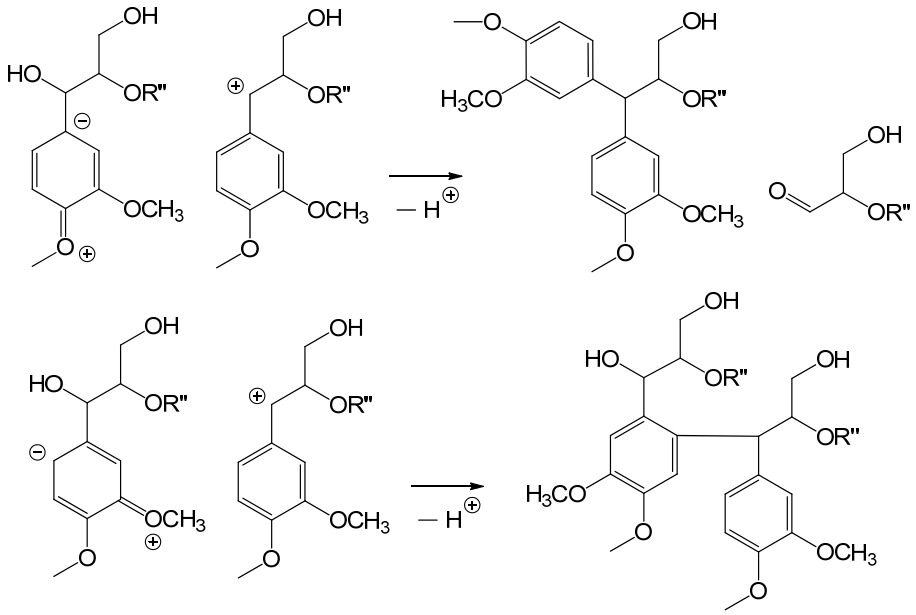

Figure 7. Condensation of lignin: formation of α-1 and α-6 bonds (adopted from Sixta et al. 2006, p. 415).

3.1.5 Homolytic reactions

It was suggested that at the mild acidic conditions and high temperatures of many organosolv processes free-radical reactions are possible. Homolysis of β-O-4 bonds proceeds through formation of quinone-methide intermediate structures (Figure 8) and

can lead to the formation of a β-5 bond (Sarkanen 1990). This pathway is not available for the non-phenolic units which leads to different reactivities for phenolic and non-phenolic units in high temperature processes (for example, in Alcell and Acetocell processes). At AS and SEW conditions (low pH and temperature) these reactions may not be significant.

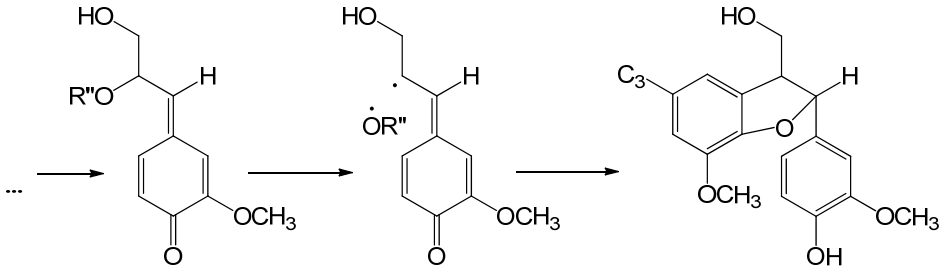

Figure 8. Lignin reactions: quinone-methide formation and homolysis of the β-O-4 bond.

3.2 Delignification kinetics

3.2.1 Kinetics of organosolv delignification

As mentioned earlier, the acid-catalysed reactions are numerous and parallel. The overall rate of delignification assuming minimal condensation is expressed as follows (using quasi-equilibrium and quasi-stationary approaches):

$$-\frac{d[Lig]}{dt} = k_{11}[LigH^{\oplus}] + \sum_{Nu} k_{2Nu}[LigH^{\oplus}][Nu],$$

$$-\frac{d[Lig]}{dt} = \frac{\sum_{Nu} k_{11}k_{12Nu}K'_{Lig}[Lig][H_3O^{\oplus}][Nu]}{k_{-11}[HL] + \sum_{Nu} k_{12Nu}[Nu]} + \sum_{Nu} k_{2Nu}K'_{Lig}[Lig][H_3O^{\oplus}][Nu], \quad (1)$$

where $K'_{Lig} = K_{Lig}\frac{\chi_{Lig}\chi_{H_3O^{\oplus}}}{\chi_{LigH^{\oplus}}}$, $K_{Lig} = \frac{\chi_{LigH^{\oplus}}[LigH^{\oplus}]}{\chi_{Lig}\chi_{H_3O^{\oplus}}[Lig][H_3O^{\oplus}]}$,

K_{Lig} – equilibrium constant of lignin protonation; χ_i – activity coefficients; k_{11} – reaction rate for the first stage of the S_N1 reactions (see Figure 4); k_{12Nu} – reaction rate for the second stage of the S_N1 reactions; k_{2Nu} – reaction rates for the S_N2 reactions; [*Lig*] – lignin "concentration", g/100 g original biomass; [$LigH^{\oplus}$] – protonated lignin

"concentration", g/100 g original biomass; [*Nu*] – concentration of the nucleophiles: SO_2, HSO_3^-, H_2O, alcohols, etc.; [$H_3O^{\oplus}$] – hydroxonium cation concentration; L – leaving group.

Lignin model compounds subjected to acidic treatment in organic solvents indeed follow first order behaviour both in the model compound and in the acidic catalyst in agreement with equation (1) (Meshgini and Sarkanen 1989). The main part of lignin removal in organosolv cooking (so-called bulk delignification) is also first order in lignin but the dependence on the catalyst (hydroxonium cation) concentration has a sigmoid shape. In addition to the bulk delignification, also initial and residual phases are observed with higher and lower rates compared to the bulk phase, respectively. It was noted that the transition between the bulk and residual phases occurs at a lower lignin content at higher temperatures (Sarkanen 1990, Girard 1998).

The cleavage of α-ether linkages in lignin is suggested as rate-governing (i.e. the fastest parallel) step in acidic delignification as it was found to proceed 2 orders of magnitude faster than the cleavage of β-ethers at moderate temperatures. It is also supported by the fact that the observed activation energy values for most organosolv processes (see for example Kleinert 1975b, Table 1) are the same as for the hydrolysis of model α-ethers – 80-120 kJ mol^{-1} (Meshgini and Sarkanen 1989). These values are considerably lower than that of the acid-catalysed β-ether cleavage of close to 150 kJ mol^{-1} (Sarkanen 1990). The high difference in the activation energy values suggests however that the difference between the rate constants for the α- and β-ether cleavage strongly depends on temperature. Bose and Francis (1999) showed that at 175°C β-O-4 bond cleavage governs the extent of delignification.

3.2.2 Kinetics of AS, SO_2-water and SEW delignification

Kinetics of AS delignification

The parallel delignification reactions approach (see Figure 4) was considered also for AS and SEW cooking by, for instance, Rydholm and Lagergren (1959) and Vishnevskaya et al. (1981). The former suggested that both sulfitolysis and hydrolysis determine the delignification rate in AS cooking, while the latter argued that hydrolysis is the fastest parallel reaction and therefore rate-determining both in AS and SEW cooking. Nonetheless, it had become obvious that in processes involving sulfur(IV) compounds lignin can neither be dissolved solely by sulfonation nor solely by hydrolysis and therefore the concept of the consecutive reactions was introduced. Hägglund (1951, p. 415) proposed his famous two stage mechanism of sulfonation followed by hydrolysis

with the rate-limiting (i.e. the slowest) step being the latter. Häggroth et al. (1953) suggested that both reactions could be rate-limiting depending on acidity and SO_2 concentration (at high acidity and low SO_2 it is sulfonation, while at low acidity it is hydrolysis). Rydholm and Lagergren (1959) suggested that hydrolysis can be accompanied by sulfitolysis. However they favoured the parallel reaction concept. There is evidence that in order to dissolve lignin, sulfonation has to proceed together with hydrolysis. Lignin presulfonated in a separate step, cannot be dissolved by subsequent acid hydrolysis as efficiently as by SO_2-water treatment (Rydholm 1965, p. 490). Due to the complexity of the systems involved, the question about the delignification rate-limiting step is still unresolved. It is however accepted that sulfonation is somewhat faster than hydrolysis (Sixta et al. 2006, p. 408).

The sulfur content of the solid phase was followed for AS cooking (Rydholm and Lagergren 1959). The lignin sulfonation occurs in 2 phases. In the first phase, which largely corresponds to the impregnation stage, the sulfur content of the solid phase increases and reaches a maximum of 0.7-1.0% based on wood. During the second phase occurring during actual cooking, the sulfur content in the solid phase drops to almost zero due to lignin dissolution. On the other hand, the S/OCH_3 ratio in the solid phase increases during the entire cook, except at the very last stage of cooking. The maximum reached is about 0.3-0.4 S/OCH_3 and therefore it has been stated that in order to achieve sufficient hydrophilicity, lignin must be sulfonated to about 0.3 S/OCH_3 (Rydholm 1965, p. 488-490). However, Häggroth et al. (1953) and Rydholm and Lagergren (1959) showed that part of the lignin in the solid residues can be dissolved by separate hydrolysis in mineral acid, and as a result the ratio S/OCH_3 drops to 0.05-0.15 indicating that this is the minimum level at which dissolution is possible in water. It also suggests that hydrolysis is slower than sulfonation/sulfitolysis in acid sulfite cooking. However, it was also shown that most of the lignin is hydrolysable after cooking at very high L/W ratios contrary to cooking at an L/W ratio of 4 L kg^{-1} (Rydholm and Lagergren 1959).

The sulfur content of the lignin dissolved during AS cooking corresponds to 0.3-0.5 S/OCH_3. In the liquid phase sulfonation/sulfitolysis continues and the sulfur content of lignin increases slowly to 0.7 S/OCH_3 and in some cases reaches even 1.0 S/OCH_3 (Rydholm and Lagergren 1959, Sjöström et al. 1962). In SEW cooking of spruce and larch the molar ratio in the dissolved lignin is considerably lower, 0.15-0.31 S/C_9 (Primakov 1961a, Vishnevskaya et al. 1981). Dissolved SEW lignin from poplar showed an S/C_9 ratio of 0.43 (Kushko and Primakov 1984).

Acidity effect in AS delignification. Donnan effect

The rate of the chemical reactions involved in the dissolution of lignin, including sulfonation and hydrolysis, depends on the acidity (according to equation 1), the latter being governed by the first dissociation stage of sulfurous acid and by the generated lignosulfonic acid. The importance of acidity is demonstrated by bisulfite cooking which has a lower acidity and proceeds at a slower rate than AS cooking. In order to compensate for the lower acidity, higher temperatures (150-170°C) are used in bisulfite cooking (Fengel and Wegener 1989).

The theoretical hydroxonium ions concentration in the acid sulfite cooking liquor at cooking temperature is about 1-2 mmol/L as was verified by actual measurements (Hagberg and Schöön 1973). Nevertheless, the actual acidity in the solid phase may be higher than that in the liquid phase due to the Donnan equilibrium effect caused by the presence of the sulfonic acid groups within the cell-wall "bound" liquid. Rydholm (1965, p. 477) showed that concentration of the sulfonic acid groups in AS bound liquid is about 0.2-0.4M assuming a fibre density of 1.0 g mL^{-1}, while the concentration in the "free" liquid at a L/W ratio of 6 L kg^{-1} is about 0.1M.

The affinity of sulfonated wood fibres is much higher towards the metal (Na^+, Mg^{2+}, Ca^{2+}) or ammonium NH_4^+ cations, generally used in acid sulfite cooking, than to hydroxonium ions H_3O^+. This leads to preferential binding of these cations and thus to a decrease in acidity inside the fibres compared to SO_2-water cooking (Fiehn 1964, Rydholm 1965, p. 477). According to Rydholm and Lagergren (1959) the acidity of the AS bound liquid with sodium as base is 10 times higher than in the free liquid phase (about 0.2 vs. 0.02M at room temperature), while for calcium they are about equal (in the order of 0.01M at room temperature). The latter results from the fact that the affinity of calcium to the fibre phase is much higher (about an order of magnitude) than that of sodium. Thus it could be expected that the acidity of the solid phase should be very different when cooking using these bases. However, the rate difference is very small suggesting that hydrolysis is not a limiting step and that the Donnan equilibrium effect is not important in acid sulfite cooking (Rydholm and Lagergren 1959). In any case, the effect is only of significance at the beginning of AS cooking when there is a high amount of sulfonated lignin in the solid phase.

Formal kinetics of AS and SEW delignification

Kinetics of AS cooking was a subject of extensive research in the past. The rate of AS cooking was found to be proportional to the product $[H_3O^+][HSO_3^-]$ which is proportional to $[SO_2]_{free}$ (Rydholm and Lagergren 1959, Richards and van Heiningen

2004). In AS cooking at constant total charge of SO_2 a higher hydrosulfite anions concentration (or combined SO_2) leads to lower acidity and therefore to lower rates. On the other hand, at constant combined SO_2 a higher free SO_2 leads to a higher delignification rate (Sixta et al. 2006, p. 459-460).

Activation energy values for delignification determined by different authors vary considerably: 67(in the beginning)-92(at the end) (Goldfinger 1941), 105 (at ionic strength of 0.5 mol L^{-1}, Hagberg and Schöön 1973) and 88 (Richards and van Heiningen 2004) kJ mol^{-1}.

According to Richards and van Heiningen (2004) the kinetics of AS delignification can be described by the following equation:

$$-\frac{d[Lig]}{dt} = k_0 \exp\left(-\frac{E_A}{RT}\right)[Lig][SO_2]_{free} = k_{Lig}[Lig][SO_2]_{free} = k_{Lig,obs}[Lig], \quad (2)$$

where k_0 = (4.0±0.2)×10^9 L mol^{-1} min^{-1}, E_A = 87.8 kJ mol^{-1}, $k_{Lig,obs} = k_{Lig}[SO_2]_{free}$.

Increasing SO_2 concentration at 135°C leads also to faster SEW delignification (Eliashberg et al. 1960, Primakov 1961a). Schorning (1957) warned that temperatures higher than 130°C at 5.5% SO_2 lead to slower delignification (beech) due to increased condensation. Nonetheless, Eliashberg et al. (1960) and Primakov (1961a) showed that increasing temperature at least up to 155°C at 5-15% SO_2 leads to considerably faster delignification (larch). Interestingly, the activation energy even increases from 93 kJ mol^{-1} at 15% SO_2 to 115 kJ mol^{-1} at 5% SO_2.

SO_2-Water delignification

The literature data concerning SO_2-water cooking is summarised below. In order to accomplish SO_2-water cooking, sulfonation should be promoted while condensation should be minimised. Since acidity changes with the square root of SO_2 concentration and the activation energy of condensation is higher than that of sulfonation, there are two ways to successfully achieve SO_2-water cooking: 1. by increasing SO_2 concentration and 2. by decreasing temperature. At low SO_2 concentrations few α-carbon atoms in lignin become sulfonated and many participate in condensation reactions due to high acidity arisen from the lignosulfonic groups (Rozenberger 1961).

A long impregnation stage at low temperature (lower than practiced for AS cooking, i.e. lower than 100-110°C, because the acidity is higher in the case of SO_2-water) is needed to avoid condensation. Only at very high SO_2 concentrations (higher than 20%) it is possible to eliminate the low-temperature impregnation stage. At 30% SO_2, 145°C and around 30 bar it was possible to cook hardwoods in 1 hour and softwoods in 2 hours (Wells et al. 1969).

Eliashberg et al. (1960) successfully cooked spruce in 15% SO_2-water using a stepwise increase in temperature over 5.5-7 h to produce a bright pulp without rejects. They adopted the following conditions: 2 hours at 60°C, 2 hours increase to 100°C, 1 hour at 100°C, 1 hour increase to 125°C, 2 hours at 125°C.

Successful cooking of spruce in SO_2-water was reported also at 14% SO_2 (Nikitin et al. 1968). A pulp with kappa number about 40 and yield 53% was obtained as follows: 1 hour heating to 100°C, 4 hours at 100°C, 30 minutes heating to 120°C, 1.5 hours at 120°C (H-factor 14 using E_A of 107 kJ mol^{-1}). The rate is comparable to that of AS delignification (Richards and van Heiningen 2004).

In vapour-phase SO_2-water cooking (Mamers and Grave 1974) it was possible to cook eucalyptus at 90-110°C (at 120°C condensation led to so-called "black cooks"). A pulp with kappa number of 70 and 52% yield was obtained after only 1 hour cooking at 110°C of fresh chips (no water was added) with SO_2 (pressure 32 bar, H-factor 2.5!). The extremely high rate is explained by the very high lignosulfonic acid concentration, while the high excess of SO_2 prevented condensation. The sulfur content of lignin retained in the solid residues was close to that of AS cooking, and the dissolved lignin had a lower sulfur content (about 1-2% on wood) than that in AS cooking of eucalyptus (about 2.5% on wood).

3.2.3 Effect of ethanol concentration on delignification

The effect of ethanol concentration on Alcell and SEW delignification is shown on Figures 9-11. At high ethanol concentrations the acidity is too low to initiate the cooking process, while at low ethanol concentrations the acidity is too high which leads to pronounced carbohydrates hydrolysis and lignin condensation (Sierra-Alvarez and Tjeerdsma 1995, Eliashberg et al. 1960, Primakov 1961a). The data indicates that cooking liquors with very high or very low ethanol concentration do not allow effective fractionation in terms of delignification, while medium concentrations liquors perform considerably better. Therefore the ethanol percentage for the present work was selected as 55 v/v.%.

3.2.4 Comparison of delignification rates for Alcell, SEW and kraft processes

Delignification in the Alcell (occurs in two phases, Kleinert 1974), SEW (two phases, bulk and residual, Primakov 1961a/b) and kraft (three phases, initial, bulk and residual, Sixta et al. 2006, p. 200) processes follow pseudo-first order kinetics in lignin. In the Alcell process

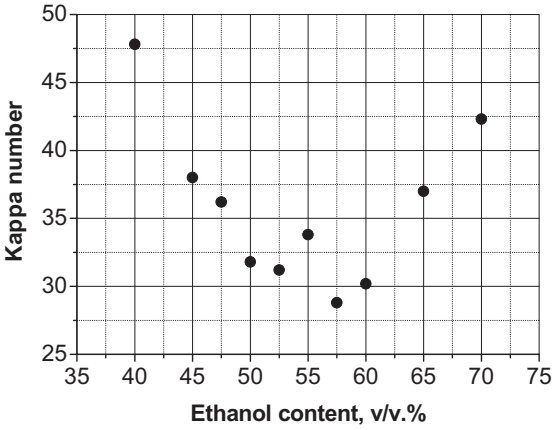

Figure 9. The ethanol concentration effect on ethanol-water delignification of juvenile poplar (195°C, 210 minutes; Sierra-Alvarez and Tjeerdsma 1995).

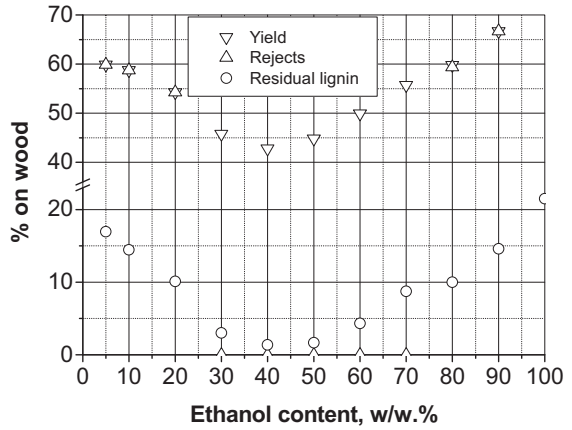

Figure 10. The ethanol concentration effect on SEW delignification of spruce (15% SO_2, 145°C, 15 minutes; Eliashberg et al. 1960).

the transition between the two phases occurs mostly in the region of 10-20% (on wood) residual lignin. This relatively high value leads to disagreements in the identification of the bulk phase. Girard (1998) and Kleinert (1974, 1975, Table 1) consider the first and the second phase for kinetic analysis, respectively. In the kraft and SEW processes the bulk phase covers most of the lignin removal, and the kinetics data for this phase are provided in Table 1.

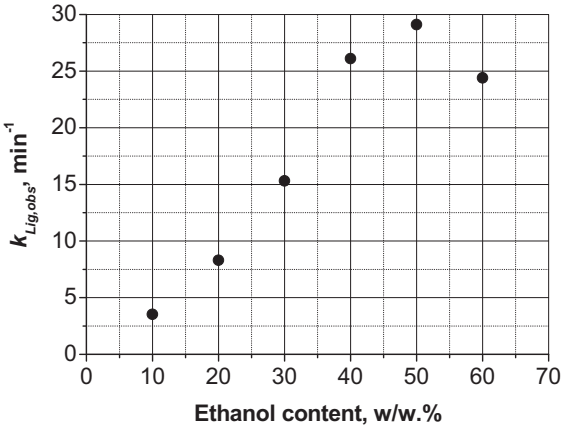

Figure 11. The ethanol concentration effect on SEW delignification rate constant, $k_{Lig,obs}$, of larch (15% SO_2, 135°C; Primakov 1961a).

Table 1. Comparison of Alcell, SEW and kraft fractionation kinetics: bulk delignification.

Process	Alcell	SEW	Kraft
Liquor composition	42.4 w/w.%[a], 50 v/v.%[b,c] ethanol-water	15% SO_2 in 50 w/w.% ethanol-water	active alkali 50 g NaOH L^{-1}, sulfidity 30%
Liquor-to-wood ratio, L kg^{-1}	10	6	10
Temperature, °C	185	135	150
Rate constant for hardwoods, 10^{-3} min^{-1}	**30** (poplar)[a] **29** (eucalyptus)[b] **28** (birch)[c]	**51** (birch)[d] **71** (aspen)[d]	**1.1** (maple)[f], **2.5** (madrona)[f]
Rate constant for softwoods, 10^{-3} min^{-1}	**15** (spruce)[a]	**48** (spruce)[d] **29** (larch)[e]	**0.47** (Western true fir and Western hemlock)[f]
E_A for hardwoods, kJ mol^{-1}	**108** (eucalyptus)[b] **85** (birch)[c]	–	**117** (birch)[g]
E_A for softwoods, kJ mol^{-1}	**118** (spruce)[a]	**93** (larch)[e]	**150** (pine)[g]

[a] Kleinert 1975b, air-dried wood; [b] Curvelo et al. 1995; [c] Girard 1998; [d] calculated from Primakov 1961b; [e] calculated from Primakov 1961a; [f] Chang and Sarkanen 1973; [g] Sixta et al. 2006, p. 190.

It can be seen that the delignification rate constants are of the same order of magnitude for Alcell at 185°C, SEW at 135°C (Table 1) and kraft at 170°C (the latter is about 40×10^{-3} min^{-1}, Sixta et al. 2006, p. 204).

3.2.5 Effect of biomass species on delignification

It is known that in most fractionation processes hardwoods are delignified faster than softwoods (Table 1). The following reasons were suggested for this phenomenon in acidic processes (McDonough 1993, Sjöström 1981):

– higher content of non-cyclic α-ether structures in hardwoods compared to softwoods;

– higher reactivity of β-ether linkages in hardwoods compared to softwoods;

– higher condensation rates for guaiacyl carbocations compared to syringyl carbocations (although on the other hand, syringyl rings are more reactive nucleophiles than guaiacyl);

– lower DP of hardwood lignin.

The delignification of softwoods by the Alcell process is about twice as slow as that of hardwoods which is similar to that found for the Kraft process. Paszner and Cho (1989) and Baumeister and Edel (1980) found that middle lamella of softwoods are delignified during the first stages of Alcell cooking, but subsequently the high acid concentration and temperature lead to condensation and reprecipitation of the solvolysis lignin products. This lignin is not removed until substantial amounts of hemicelluloses are dissolved and the cell wall accessibility is increased by the creation of connected macropores. In fact, pulps with bleachable kappa numbers were not obtained from softwoods using ethanol-water fractionation. Hardwood open cell-wall structure generally allows avoiding this problem but some hardwood species, including oaks, eucalyptus and alder, as well as herbs are more resistant to ethanol-water fractionation than other species (Sarkanen 1990, Aziz and Sarkanen 1989).

However in another study of catalysed ethanol-water pulping of softwoods little or no condensation was found (at high L/W ratio of 14 L kg^{-1}, Bose and Francis 1999).

In the kraft process the rate is found to be proportional to the OCH_3/C_9 ratio which varies considerably between different species. This is related to the fact that at the higher ratio lignin is less condensed and also the condensation reactions are less pronounced during cooking (Chang and Sarkanen 1973).

It appears from the ammonium AS cooking data provided by Rydholm and Lagergren (1959) that spruce is delignified to the same extent as birch at somewhat higher H-factors. However, it is hard to make an exact comparison between the different

species based on this data. Some species including larch, pine and Douglas fir are less suitable for AS delignification due to condensation of phenolic extractives with lignin (Sixta et al. 2006, p. 395).

It can be seen from Table 1 that the SEW delignification rates for birch and spruce are very similar. Aspen is delignified somewhat faster while larch somewhat slower.

SEW process can be called omnivorous as it successfully delignifies many different species including the following: Spruce[1,3,5], Red pine[1], Jack pine[1], Loblolly pine[1], Balsam fir[1], Douglas fir[1], Larch[2,3,5], Birch[1,3], Beech[6], Aspen[1,3], Poplar[4,6], Sugar maple[1] (Puumala 1991[1], Primakov 1961a[2], Primakov 1961b[3], Primakov et al. 1979[4], Eliashberg et al. 1960[5], Shorning 1957[6]).

3.3 Carbohydrate reactions

3.3.1 Chemistry and kinetics of hydrolysis

The main reaction of the biomass polysaccharides in acidic fractionation processes is their solvolytic depolymerisation. The hydrolysis of glycosidic bonds follows an $S_{N}1$ mechanism via protonation of either the exocyclic or ring oxygen with the rate-determining step being heterolysis of either the C_1-$O_{exocyclic}$ or C_1-O_{ring} bond, respectively (Sixta et al. 2006, p. 416). The last step is the fast reaction with a nucleophile. The first mechanism is shown in Figure 12. The reaction rate is governed primarily by the chemical structure of the polysaccharides (conformational and inductive effects, Feather and Harris 1965, Marchessault and Rånby 1959). For instance, the relative rates of acid hydrolysis of methylpyranosides of the common biomass monosaccharides β-D-glucose, β-D-mannose, α-D-galactose, β-D-xylose and α-D-glucuronic acid are 1.0, 3.0, 2.7, 4.8 and 0.2, respectively (Feather and Harris 1965). In addition to the chemical structure effects, the hydrolysis rates of biomass polysaccharides depend considerably on their morphology. The latter is especially important for the heterogeneous cellulose hydrolysis which is 1-2 orders of magnitude slower than hydrolysis of model compounds due to the highly-ordered cellulose structure (Fengel and Wegener 1989).

It is noted that the glycosidic bond at a non-reducing end is hydrolysed slightly faster than the other glycosidic bonds in a polysaccharide which is attributed to steric effects (Feather and Harris 1967). This may explain the fact that the amount of formed monosaccharides is higher than calculated based on uniform cleavage (Sjöström 1981, p. 43).

The rate of the hydrolytic reactions is also increased by acidity and temperature.

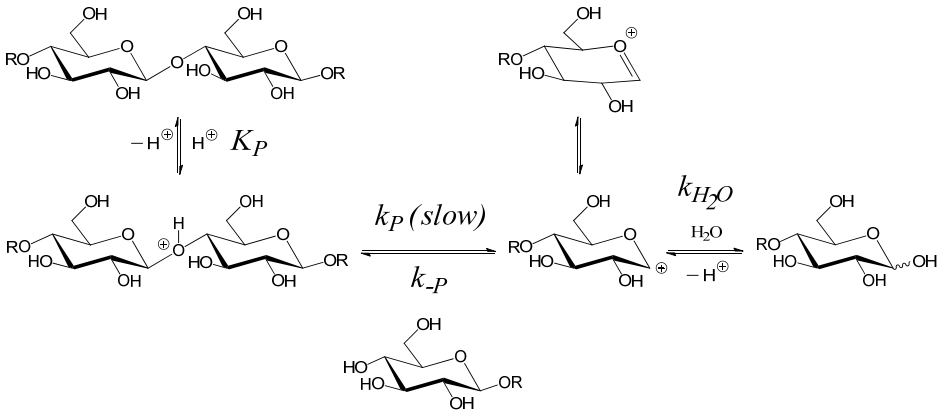

Figure 12. Acid hydrolysis of polysaccharides (Sixta et al. 2006, p. 416).

In SEW fractionation the nucleophiles most likely to participate in the hydrolysis reaction are water, ethanol and other carbohydrates producing reducing end units, ethylglycosides and new dimer structures, respectively. Therefore the rate of the polysaccharides hydrolysis could be given:

$$-\frac{d[P]}{dt}=\frac{k_P k_{H_2O} K'_P [P][H_3O^{\oplus}][H_2O]+k_P k_{EtOH} K'_P [P][H_3O^{\oplus}][EtOH]}{k_{-P}[NRHP]+k_{H_2O}[H_2O]+k_{EtOH}[EtOH]}, \qquad (3)$$

where the rate and equilibrium constants are analogous to those for S_{N1} reactions of lignin; $[P]$ – polysaccharides yield, g/100 g biomass; NRHP – the non-reducing hydrolysis product.

The relative rates of hydrolysis and ethanolysis are unknown but at constant ethanol/water ratio, assuming constant activity coefficients, the rate should only depend on the product $[P][H_3O^+]$. The unknown hydroxonium anion concentration also can be incorporated in the rate constant assuming it to be constant during the fractionation, i.e.:

$$-\frac{d[P]}{dt}=k'_P [P][H_3O^{\oplus}]=k_{P,obs}[P], \qquad (4)$$

where k'_P and $k_{P,obs}$ – the composite rate constants. Later in this thesis equation (4) will be applied to hemicelluloses removal and the rate constant $k_{P,obs}$ will be given as k_{Hemi} (equation 21).

3.3.2 Hemicellulose reactions

The hemicellulose chemistry during acidic fractionation was thoroughly investigated for the acid sulfite process, and the following literature review is based on this knowledge.

Removal of the acetyl groups and the side units

At acidic conditions acetyl groups are cleaved (acid-catalysed hydrolysis of esters, S_N2) from softwood galactoglucomannan (Sjöström 1981, p. 117) and hardwood 4-O-methylglucuronoxylan (Öhrn and Croon 1960, Annergren and Croon 1961, Meier 1962), although quantitative deacetylation does not happen contrary to that found at alkaline conditions. The formed acetic acid provides the acidic conditions for so-called autocatalysed fractionation processes.

The arabinosidic bond is the most acid labile bond in hemicelluloses, and arabinose appears in softwood acid sulfite cooking liquor before the temperature has risen to 100°C (Sundman 1950). This is in line with the fact that furanoses are much more reactive towards acid hydrolysis compared to pyranoses due to the increased ring strain in the former (Shafizadeh 1963). Galactose is also removed rapidly from galactoglucomannan, although some galactose is found in the pulps after long cooking times (Makkonen 1967b). This galactose may arise from compression wood galactans.

Glucomannan hydrolysis and stabilisation

In glucomannan the mannosidic bonds are hydrolysed faster than glucosidic bonds, which agrees with the relative acid hydrolysis rates of model glycosides. It is found that glucomannan of pine becomes more glucosidic as sulfite cooking proceeds (Makkonen 1967a).

There are strong indications that glucomannan undergoes secondary crystallisation along the cellulose crystallites after deacetylation and removal of the side units. According to Annergren and Rydholm (1959), the following conditions are required to achieve efficient adsorption of glucomannan on cellulose and therefore its stabilisation against acid hydrolysis: 1. Successful H-bonding to cellulose, and for this purpose galactose side units and acetyl groups should be removed, while a decrease in glucomannan DP should be avoided; 2. Glucomannan has to diffuse through the cell-wall towards cellulose and therefore appropriate conditions including sufficient time and hydrophilicity of the cell-wall should prevail.

This is supported by high glucomannan yields in two-stage (first – neutral or slightly alkaline, second – acidic) sulfite pulping (Annergren and Rydholm 1959,

Makkonen 1967a). In the first stage galactose units and acetyl groups are cleaved from galactoglucomannan while hydrolysis is very limited. Lignin becomes sulfonated and the glucomannan is able to diffuse through the hydrophilised cell-wall during the first stage, and its subsequent crystallisation on cellulose leads to considerably higher stability in the second cooking stage.

Also in single stage acid sulfite cooking Rusten (1962) found that it is mostly the mannan yield which contributes to the higher solid residue yield at lower temperature and higher pH (at 120°C and pH 2 and at 140°C and pH 4 the mannose yields are substantially higher than at pH 2, 140-170°C and pH 1 and 140°C). He explains the phenomenon also by higher stabilisation of glucomannan at lower temperature and higher pH.

Xylan hydrolysis and stabilisation

The presence of uronic acid as a glycone at the C_2 of xylose activates the glycosidic bond at C_4, but stabilises that at C_2 due to the inductive effect of a carboxylic group (Marchessault and Rånby 1959), and it also stabilises the glycosidic bond at C_1 due to steric hindrance (Sjöström 1981, p. 42). As a consequence the Xyl-to-4-O-MeGlcA ratio in isolated birch xylan decreases during AS cooking (Meier 1962). This is explained by slower hydrolysis of the bonds in the aldotriouronic acid unit 4-O-MeGlcA-(1→2)-Xyl-(1→4)-Xyl compared to Xyl-(1→4)-Xyl bonds in xylan. On the other hand, during heterogeneous hydrolysis of xylan in birch wood the dissolution rate is also determined by the solubility of the hydrolysis products. In this case the presence of 4-O-MeGlcA increases the solubility and now the ratio Xyl-to-4-O-MeGlcA in the solid residue increases (Meier 1962, Janson and Sjöström 1964).

Annergren and Rydholm (1959) argue that crystallisation of xylan is less favoured than that of glucomannan due to presence of uronic acid side units, and in case of softwood by the longer diffusion paths (xylan is mostly located in the middle between cellulose microfibrils closely associated with more linear lignin, while glucomannan located adjacent to the microfibrils is associated with more branched lignin; Salmén and Olsson 1998, Lawoko 2005).

It is often stated that xylan is more sensitive to acid hydrolysis than glucomannan and therefore the relative yield loss of the xylan-rich hardwoods is higher than that of softwoods (Rydholm 1965, p. 540, Sixta et al. 2006, p. 110). However, isolated galactoglucomannan is hydrolysed faster than 4-O-methylglucuronoxylan (Lawoko 2006a). This indicates again the importance of glucomannan stabilisation in the presence of cellulose.

Activation energy of polysaccharides hydrolysis

The activation energy values for homogeneous hydrolysis of both cellulose and different hemicelluloses varies within about 105-145 kJ mol^{-1}. The values found for heterogeneous hydrolysis of these polymers also correspond roughly to the same range (Rusten 1962). For instance, according to Sixta (2009), the activation energy value for xylan heterogeneous hydrolysis is 125 kJ mol^{-1}. Hemicelluloses removal during acid sulfite cooking of spruce had a 117 kJ mol^{-1} (at ionic strength of 0.5 mol L^{-1}, Hagberg and Schöön 1973). Goldfinger (1941), however, determined the activation energy for hemicelluloses removal to be 88 kJ mol^{-1}.

Dehydration and Oxidation Reactions

Monosaccharides also participate in a number of reactions, most importantly dehydration and oxidation. The products of these reactions can condense with each other and with lignin. It is known that these reactions are also dependent on acidity and temperature. High acidity promotes dehydration, while oxidation takes place at lower acidity (Sixta et al. 2006, p. 419, Slávik 1961).

Dehydration leads to the formation of anhydrosaccharides and then furfural (Figure 13) and hydroxymethylfurfural (HMF, Figure 14). The latter is rather unstable and decomposes to form formic and levulinic acids (Rydholm 1965, p. 520). In addition to these, many other aromatic compounds were identified after acidic treatment of carbohydrates (Figure 15).

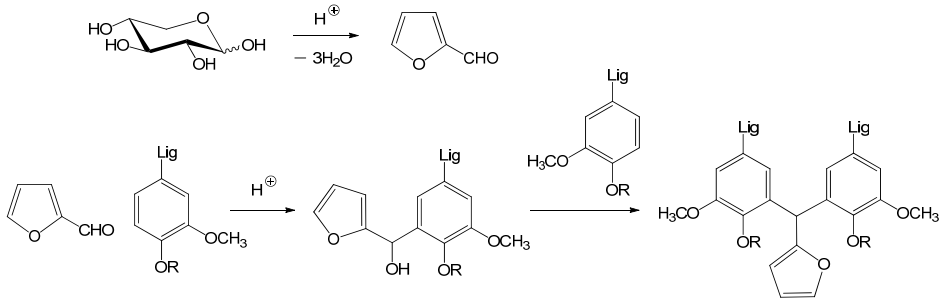

Figure 13. Degradation of pentoses under acidic conditions and condensation of the formed furfural with lignin units (adopted from Sixta et al. 2006, p. 420).

The oxidation of monosaccharides by hydrosulfite anions to form aldonic acids is a pronounced monosaccharide degradation pathway during conventional acid sulfite cooking (Figure 16). Up to 50% arabinose, 40% galactose, 15-25% xylose, 9-11% mannose

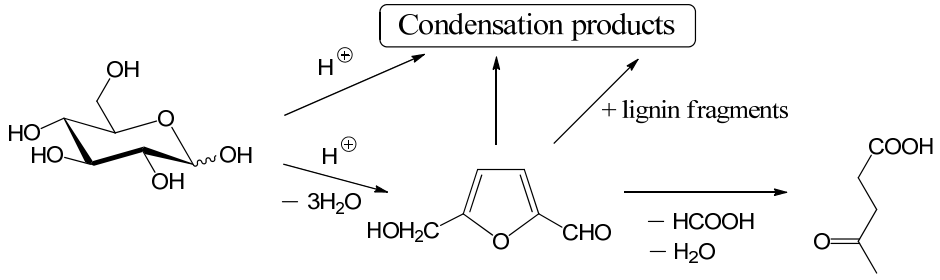

Figure 14. Degradation of hexoses under acidic conditions and condensation of HMF with lignin units (adopted from Sixta et al. 2006, p. 420).

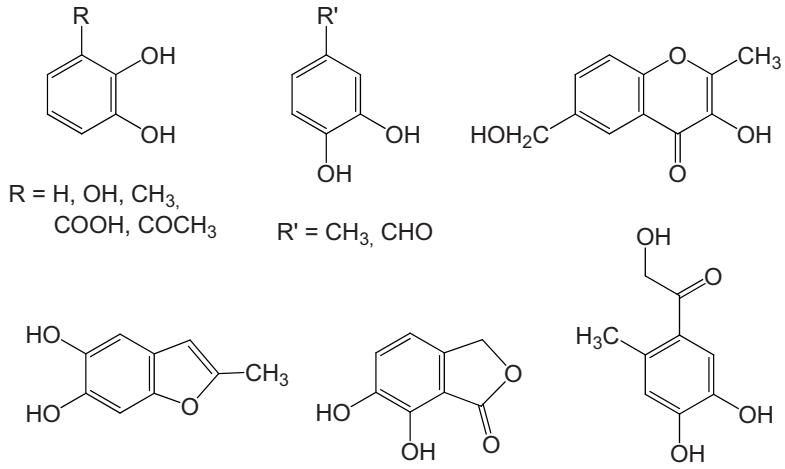

Figure 15. Aromatic compounds formed from dehydration of sugars under acidic conditions (Popoff and Theander 1976, Sixta et al. 2006, p. 420).

and 12% glucose is converted to aldonic acids in acid sulfite cooking (Pfister and Sjöström 1977). The oxidation is said to proceed faster for pentoses than for hexoses (Samuelson and Simonson 1962), and can also take place at the reducing ends of dissolved polysaccharides (Larsson and Samuelson 1969). The reaction is pronounced from the very beginning of the cook but slows down towards the end when the concentration of the hydrosulfite anions decreases (Sixta et al. 2006, p. 445-447). The formation of the aldonic acids depends on pH which governs the hydrosulfite anions concentration in the liquor through the pK_a of dissolved SO_2 (3.2 at 135°C, Rydholm 1965, p. 456). Slávik (1961) reports the absence of oxidation in a model experiment with

24 g L^{-1} SO_2 with no base and 10 g L^{-1} glucose (pH 1.4, 150°C), while at 30 g L^{-1} SO_2, 8 g L^{-1} NaOH and 10 g L^{-1} glucose (pH 1.8, 150°C) the oxidation can already be observed.

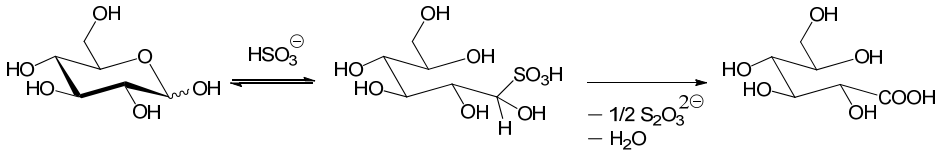

Figure 16. Oxidation of monosaccharides by hydrosulfite anions (adopted from Sixta et al. 2006, p. 423).

Other Reactions

Sulfonation of glucose and xylose by sulfite anions was reported in neutral solutions (Lindberg et al. 1964, Hardell and Theander 1971). However, only minor amounts of monosaccharides are sulfonated in acid sulfite cooking (Sjöström 1981, p. 118).

One of the most important reactions of uronic acids in acidic conditions is decarboxylation (Anderson et al. 1961). Near-stoichiometric amounts of carbon dioxide are liberated in this reaction but no corresponding pentoses are formed (D-xylose from D-glucuronic acid, L-arabinose from D-galacturonic acid). Instead, 5-formyl-2-furoic, furfural and 2,3-dihydroxy-2-cyclopenten-1-one (reductic acid) and insoluble "humins" are generated (Feather and Harris 1966). The reaction is known to be very pronounced during water prehydrolysis (Tunc and van Heiningen 2008, Leschinsky et al. 2009). However, during two stage sulfite cooking of birch no decarboxylation of 4-O-methylglucuronic acid was observed (Janson and Sjöström 1964). Another reaction path for 4-O-methylglucuronic acid is demethylation which was, however, shown to be of minor importance in two-stage sulfite cooking of spruce (Larsson and Samuelson 1969).

3.3.3 Cellulose hydrolysis

Glycosidic bonds in cellulose are randomly hydrolysed in acid conditions, although much slower than in hemicelluloses due to the high crystallinity of cellulose. As a result the average DP of cellulose decreases. However, because the DP of the degraded cellulose chains is still of the order of 1,000 (AS cooking, Makkonen 1967b), cellulose is often retained in high (or full) yield in the solid residue during acidic fractionation. Higher cellulose yields of the acidic processes (for example, Alcell, Kleinert 1974; and AS, Sixta

et al. 2006, p. 110) compared to alkaline processes is related mostly to the absence of peeling-off reactions in the former.

When subjected to heterogeneous acid hydrolysis cellulose exhibits a very fast initial hydrolysis rate which is attributed to the presence of so-called “weak links”. The latter could be explained by the inductive effects due to electrophilic substituents (e.g. carboxylic groups) being randomly present in wood cellulose in small amounts. These links are hydrolysed 100 times faster than normal glycosidic bonds in cellulose (Marchessault and Rånby 1959). Another explanation for the existence of such highly reactive bonds is physical strains at the folds of cellulosic microfibrils (Sixta 2009). In the second stage slower hydrolysis of the “regular” glycosidic bonds in the amorphous regions takes place. After the amorphous cellulose is hydrolysed, the cellulose hydrolysis enters a third and very slow stage at which the DP is approaching the so-called levelling-off DP value. Battista et al. (1956) report viscosity-average levelling-off DP values for cotton, 200-250, and for unbleached sulfite wood pulps, 250-400, both measured after hydrolysis in 2.50M hydrochloric acid for 15 minutes at 105°C. These values likely correspond to the length of the cellulose crystallites.

In acidic fractionation of biomass the most relevant stage of cellulose hydrolysis is the second. Similar equations as (3) and (4) are valid for cellulose, but the measure for cellulose solvolysis is the decrease in the number of non-cleaved glycosidic bonds instead of the decrease in yield:

$$-\frac{dn}{dt} = k'_{Cel}(T)n[H_3O^+] = k'_{Cel,obs}(T)n\,, \tag{5}$$

where n – the number of glycosidic bonds in all cellulose chains, k'_{Cel} and $k'_{Cel,obs}$ – real and composite cellulose hydrolytic cleavage rate constants.

The number of glycosidic bonds in one cellulose chain is equal to the number of glucose units in this chain minus one, so for M cellulose chains the number of glycosidic bonds, n, is (Emsley and Stevens 1994):

$$n = N - M = N\left(1 - \frac{1}{DP_n}\right), \tag{6}$$

where N – total number of glucose units in cellulose; M – number of cellulose chains; DP_n – number-average DP of cellulose.

By inserting (6) in (5) and integration of (5) we get the following equation:

$$-\ln\left(1-\frac{1}{DP_n}\right)=k'_{Cel,obs}(T)t+\frac{1}{DP_{n,0}}, \tag{7}$$

where $DP_{n,o}$ – cellulose DP in original biomass.

Since DP_n » 1, the cellulose hydrolysis kinetics simplify to a zero order expression:

$$\frac{1}{DP_n}=k'_{Cel,obs}(T)t+\frac{1}{DP_{n,0}} \tag{8}$$

Cellulose DP by viscosimetry

The cellulose DP can be calculated from the intrinsic viscosity of pulp solutions in various solvents. The method of viscosimetry has long been used for determining DP of cellulose. However, it has to be noted that in the past the intrinsic viscosity was often measured based on calibrations obtained with nitrated cellulose which has a lower DP than the starting cellulose since nitration also hydrolyses cellulose (Cael et al. 1983). Evans and Wallis (1989) obtained a correlation between the viscosity of cellulose tricarbanilates in cupriethylenediamine CED and their DP was determined by light scattering, i.e. an absolute method. Da Silva Perez further modified the correlation by correcting for the presence of hemicelluloses (da Silva Perez and van Heiningen 2002):

$$DP_v=\left(\frac{1{,}65[\eta]-116[Hemi]_{pulp}}{[Cel]_{pulp}}\right)^{1.111}, \tag{9}$$

where $[\eta]$ – intrinsic viscosity of pulps in CED, mL g^{-1}; $[Hemi]_{pulp}$ – hemicelluloses content of pulp, unit fraction; $[Cel]_{pulp}$ – cellulose content of pulp, unit fraction.

The equation provides the viscosity-average cellulose DP, DP_v, which is close to the weight-average DP, DP_w (Rusten 1962) value. Assuming a constant polydispersity index, $P = DP_w/DP_n$, the obtained values of DP_w can be used in the equations (6)-(8):

$$\frac{1}{DP_w}=\frac{k'_{Cel,obs}(T)}{P}t+\frac{1}{DP_{w,0}}=k_{Cel,obs}(T)t+\frac{1}{DP_{w,0}} \tag{10}$$

Later in this thesis DP_v is given as DP, i.e. without the subscript, while the $k_{Cel,obs}$ is shortened to k_{Cel}.

Activation energy of cellulose hydrolysis

Homogeneous cellulose hydrolysis has an activation energy of 124 kJ mol^{-1} (in sulfuric acid, Freudenberg and Blomquist 1935) or 130-150 kJ mol^{-1} (in phosphoric acid, Marchessault and Rånby 1959). The activation energy for cellulose hydrolysis in acid sulfite cooking was found to be close to 117-126 kJ mol^{-1} (by measuring viscosity of nitrated spruce cellulose in acetone, Rusten 1962) and 176 kJ mol^{-1} for beech cellulose (Fischer and Schmidt 1991). Harris and Kline (1949) determined the activation energy for the heterogeneous hydrolysis of Douglas fir cellulose by aqueous SO_2 at 0.75-5.6% as 145 kJ mol^{-1}. According to Sixta (2009), heterogeneous cellulose hydrolysis activation energies range from 160 to 180 kJ mol^{-1}.

3.4 Relative rates of the fractionation reactions: delignification and hemicelluloses removal selectivity

The possibility to change the relative rates of fractionation reactions allows obtaining products of different composition, which is important from a practical point of view. The AS cooking selectivity is primarily affected by liquor composition and temperature.

3.4.1 Delignification selectivity

The selectivity of delignification in the AS process (both with respect to hemicelluloses removal and cellulose hydrolysis) is improved by an increase in hydrosulfite anion concentration or by an increase in total SO_2 at a given level of hydrosulfite anion concentration (Sixta et al. 2006, p. 460-461). The former effect is demonstrated by the equation (Sixta et al. 2006, p. 437):

$$\frac{d[Lig]}{d[P]} = \frac{k_{Lig}[H_3O^+][HSO_3^-]}{K_{a1}k'_P[H_3O^+]} = \frac{k_{Lig}}{K_{a1}k'_P}[HSO_3^-], \qquad (11)$$

where $[HSO_3^-]$ – hydrosulfite anion concentration, K_{a1} – the first ionisation constant for sulfurous acid ($SO_2 \cdot H_2O$).

Higher delignification selectivity is also obtained at lower temperatures.

Girard (1998) proposed that Alcell delignification of birch is governed by dissolution of xylan. The residual xylan-residual lignin relationship for the Alcell pulps was reasonably linear, independent of ethanol concentration (50-60 v/v.%) and temperature (175-195°C).

3.4.2 Cellulose hydrolysis-hemicelluloses removal selectivity

In AS pulping at the same cellulose DP more hemicelluloses are retained at higher hydrosulfite anion concentration and lower total SO_2 concentration, although the influence of the cooking liquor composition is very limited on the cellulose hydrolysis-hemicelluloses removal selectivity (Rusten 1962, Sixta et al. 2006, p. 461-462).

There is no agreement in the literature about the effect of temperature on the cellulose hydrolysis-hemicelluloses removal selectivity in AS cooking. Ogait (1958) found a linear correlation between cuprammonium viscosity and yield of bleached sulfite pulp independent of temperature and liquor composition. But, according to Rusten (1962) the apparent activation energy value for hemicelluloses hydrolysis is higher than that for cellulose hydrolysis. Indeed, Ulfsparre (in Rusten 1962) showed that at a particular DP the hemicellulose retention increases with decreasing temperature. On the other hand, according to Sixta et al. 2006 (p. 462-463) at the same DP value a higher hemicelluloses retention is achieved at higher temperature.

4 Cooking chemicals mass balances and recovery

4.1 Ethanol balance and recovery in Alcell and SEW processes

Ethanol and SO_2 need to be fully recovered in Alcell and SEW-based Biorefinery processes, and thus possible reactions leading to their consumption are of concern. For ethanol one of the possible reactions is ethoxylation/ethanolysis of lignin and carbohydrates. No ethoxyl groups were found in the lignin isolated from the Alcell spent liquor (Kleinert 1974). Primakov (1961a) determined the alcoxyl content of lignin dissolved in SEW spent cooking liquor of larch, 0.43-0.45 mol alcoxyls/100 g lignin (at 15% SO_2, 135°C and 105 minutes, 145°C and 55 minutes, and 155°C and 35 minutes), which is about equal to the amount of methoxyl groups in native larch lignin. Therefore it can be concluded that ethanol does not ethoxylate lignin at cooking temperature or that the ethoxyls are split off when the temperature is lowered. Although there are a variety of other pathways for ethanol consumption at acidic conditions, for instance, dehydration to diethyl ether, oxidation to acetaldehyde, formation of acetals, ethylglycosides, ethylacetate, sulfurous acid esters, it was shown by Kleinert (1974) and Primakov (1961a) that ethanol can be quantitatively recovered from Alcell and SEW spent liquors by distillation. For instance Primakov (1961a) was able to recover 99.2% ethanol straight after the SEW cooking and 98.9% from spent and wash liquors. This is further evidence that ethanol is not consumed during Alcell and SEW fractionation. The presence of water in the liquor explains suppression of the ethanol dehydration reaction.

4.2 Sulfur mass balance and recovery in AS and SEW processes

4.2.1 AS process

The main reaction leading to consumption of SO_2 in AS cooking is sulfonation which leads to a sulfur content of the residual and dissolved lignin of 0.3-0.4 and 0.5-0.7 S/C_9, respectively. It corresponds to about 2-4 g sulfur/100 g wood (Rydholm 1965, p. 489-490). In addition to lignin sulfonation SO_2 is consumed in carbohydrate oxidation reactions (Figure 17). The consumption is initiated by the reduction of hydrosulfite anions by the carbohydrate reducing ends. The arisen thiosulfate anions may also lead to lignin condensation by forming sulfur bridges especially at the end of a cook (Sixta et al. 2006). In addition, hydrosulfite anions are known to oxidise pinene to cymene and formic acid to carbon dioxide (Regestad and Samuelson 1958). For magnesium AS cooking of beech, the amounts of sulfur bound to dissolved organics, existing in the form of sulfate and thiosulfate anions are 3.7, 0.20-0.23 and <0.01 g/100 g wood, respectively (Sixta et al. 2006, p. 437).

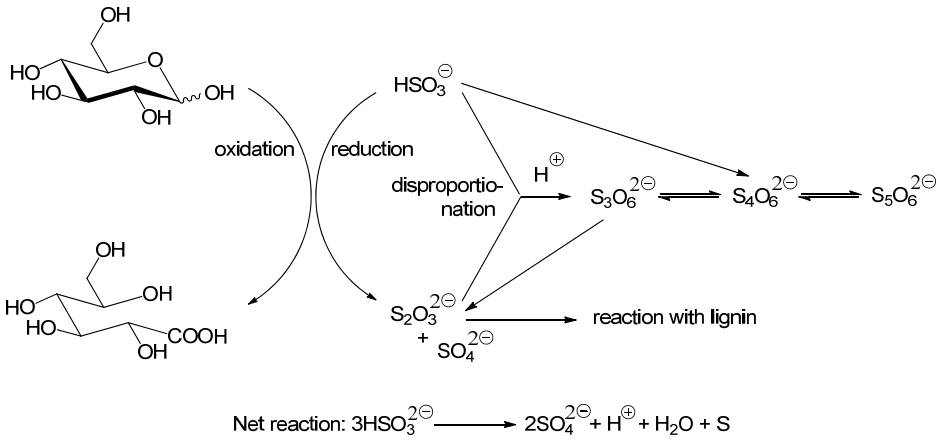

Figure 17. Inorganic side reactions in acid sulfite cooking (adopted from Sixta et al. 2006, p. 423).

In addition to the listed pathways of SO_2 consumption, part of SO_2 becomes "loosely-bound" to some components of the spent liquor. It represents SO_2 existing in the form of α-hydroxysulfonates formed in a nucleophilic addition (A_N) reaction of hydrosulfite anions to carbonyl groups of lignin, carbohydrates and volatile aldehydes (Sjöström et al. 1962). These compounds differ in stability: the sulfur dioxide bound to lignin is easily liberated by mild alkaline treatment, while for example

α-hydroxymethanesulfonic acid is stable in alkaline conditions (Sjöström et al. 1962). According to Hägglund (1951, p. 429) the "loosely-bound" SO_2 can be removed by distillation provided the pH of the liquor is sufficiently low. The different relative amounts of the loosely-bound SO_2 are determined by different authors. According to Adler (1947) in case of AS dissolving pulp most SO_2 is bound to volatile aldehydes (formaldehyde, methylglyoxal, furfural) while when producing paper pulps most SO_2 is bound to lignin. Carbohydrates do not seem to contribute significantly to the loosely bound SO_2 formation. Samuelson and Westlin (1947) showed that most SO_2 is bound to low-molecular weight compounds. Sjöström et al. (1962) determined the total amount of SO_2 loosely bound to lignin as high as 0.25 S/OCH_3.

In AS processes both the non-consumed sulfur dioxide and the base need to be recovered. However, except for magnesium, no efficient recovery was developed, and even for the magnesium AS process, recovery of sulfur is not complete (about 80%; Sixta 1986).

4.2.2 SEW process

The amount of sulfur bound to dissolved lignin during SEW cooking (15% SO_2) of larch (50 w/w.% ethanol-water, 135-155°C, Primakov 1961a) and spruce (15-85 w/w.% ethanol-water, 135°C, Vishnevskaya et al. 1981) was found to be about 0.25-0.31 S/C_9, while SEW cooking of poplar resulted in 0.43 S/C_9 in the dissolved lignin (50 w/w.% ethanol-water, 135°C, Kushko and Primakov 1984). Therefore dissolved softwood SEW lignin contains about half the sulfur content as that of AS cooking. Also it is expected that the reactions shown in Figure 17 are not pronounced in SEW fractionation due to the substantially lower hydrosulfite anion concentration compared to AS cooking. Primakov (1961a) measured the amounts of sulfate and thiosulfate anions in the liquid phases from SEW cooking of larch – 0.25-0.4 and 0.06-0.25 g sulfur/100 g wood, respectively. The amount of loosely-bound SO_2 (as α-hydroxysulfonates) was found to be 1.1-1.4 g sulfur/100 g wood. The sulfur material balance showed that up to about 2-3 g sulfur/100 g wood is consumed by an unknown reaction (Primakov 1961a). Primakov et al. (1982) claim that sulfur consumption in SEW cooking is 3-4 times lower than in acid sulfite cooking although no data is provided. Also no attempt to regenerate SO_2 after SEW cooking has been reported in literature.

MATERIALS AND METHODS

Mostly air dried (dry matter content 92.9%) but also green (dry matter content 48.9%) spruce (*Picea abies*) chips and only green beech (*Fagus sylvatica*) chips (dry matter content 62.3%) were used for the fractionation experiments after screening using the screens O45; //8; //6; //4 and //2 mm and combining the fractions from the screens //4 and //2 mm. Wheat straw (*Triticum aestivum L.*, dry matter content 93.7%) was screened using the screens O13, O7, O6 and O3 mm and the fractions from the screens O6 and O7 mm were used.

The fractionation liquor preparation comprised of injecting gaseous sulfur dioxide into an ethanol-water solution, and the SO_2 concentration was determined from the increase in the weight of the solution. Deionised water and ETAX A ethanol (96.1 v/v.%) were used. In the actual cooking liquor (including the moisture inside the chips) the volume fraction of ethanol was 0.55 and the concentration of SO_2 was 3.0-27 w/w.%. The raw material (25 o.d. g chips or 13.1 o.d. g straw) and the liquor at a liquor-to-wood ratio of mostly 6 L kg^{-1} (considering the chip moisture) were placed in 220 mL bombs. The bombs were put into a silicon oil bath having temperatures 125–165°C (±1°C). At the end of the specified total elapsed time (including the equivalent heat-up time of about 8-9 minutes, see section 7), the bombs were rapidly removed from the bath and put into cold water. After cooling, the solid residue was removed from the bombs and placed into a washing sock. In most experiments after squeezing the liquid phase, the solid residue was washed 2 times with 50 mL of 40 v/v.% ethanol-water solution at 60°C and finally 2 times with 500 mL of deionised water at room temperature (see section 5).

The original biomass and the obtained solid residues were analysed for yield, total lignin, carbohydrates, acetone-soluble extractives, ash and sulfur content. The solid residues which were easily defibrated by hand, i.e. resulting in pulps, were analysed for kappa number and intrinsic viscosity in cupriethylenediamine (CED) solution. The carbohydrate content of the wood and solid residues was determined using two techniques: acid methanolysis with GC-FID detection and double stage sulfuric acid hydrolysis with HPAEC-PAD detection.

The obtained liquid phases (see Paper IV) were analysed for density, dry solids content, SO_2 (as hydrosulfite anions, by IC), sulfate anions (by IC), furfural and hydroxymethylfurfural (by HPLC), aldonic acids (by HPAEC) and sulfur content of the dry solids. The monomeric and total carbohydrate content of the liquid phases was determined again using the GC-FID and HPAEC-PAD detection. Acetic acid in the liquid phases was calculated from the difference between the acetyl content of wood and the corresponding solid residue.

For a more detailed description of the analytical procedures one is referred to the attached papers. The procedures for lignin determination in both solid and liquid phases are given in Paper II, while those for carbohydrate determination – in Paper IV. The details concerning determination of the sulfur content of both solid and liquid phases as well as regeneration of SO_2 after fractionation are also given in Paper IV, while wood meal fractionation is described in Paper V. The information about mechanical strength and optical properties of the pulps is located in Paper VI.

RESULTS AND DISCUSSION

5 Development of washing procedure for the solid residues (Paper I)

In order to investigate the fractionation kinetics it is necessary to remove all liquid containing dissolved lignin and carbohydrates from the fibres. So our first task was to establish an effective washing procedure. Since hemicelluloses are better removed with polar solvents (water) and lignin is more soluble in low-polar solvents (dioxane, ethanol, etc.) it was decided to use ethanol-water mixtures as wash liquor. Ethanol was chosen because of ease of integration with the recovery of the cooking liquor. Washing with 90% dioxane in water was also investigated to determine the maximum amount of lignin which could be removed from the pulp since this is known to be an excellent lignin solvent (Browning 1967, p. 732). Table 2 summarises the washing experiments performed on the solid residues obtained from spruce. It shows that washing with water does not remove all dissolved lignin, while washing with ethanol-water solution results in nearly the same kappa number as obtained with dioxane-water washing. There is no significant difference in solid residue kappa number when using 40 or 70 v/v.% ethanol-water solutions, and no further improvements are obtained after the second stage of washing. Thus in the subsequent experiments the solid residues were washed twice with 40% ethanol-water at 2 L kg^{-1} (based on wood) and 60°C followed by washing twice with water at 20 L kg^{-1} (based on wood) and room temperature.

It may be noted that washed SEW solid residues are mostly very bright, similarly to acid sulfite pulps.

6 Raw material properties, impregnation

6.1 Raw material particle size and impregnation (Papers I and V)

Sufficient impregnation of the raw material with cooking liquor prior to actual cooking is crucial for every cooking process. It is also often dependent on the chip size.

Table 2. Comparative washing of the spruce SEW solid residues (12% SO_2, 40 minutes at 145°C).

Solvent washing at 60°C (L/W ratio 2 L kg^{-1})		Water washing at 20°C (L/W ratio 20 L kg^{-1})	Kappa number
Solvent	Frequency		
–	–	Twice	49.4
–	–	Thrice	40.5
Water	Twice	Twice	48.1
40% Ethanol-water	Once	Twice	36.4
40% Ethanol-water	Twice	Twice	35.6
40% Ethanol-water	Thrice	Twice	35.7
70% Ethanol-water	Once	Twice	40.2
70% Ethanol-water	Twice	Twice	34.8
70% Ethanol-water	Thrice	Twice	35.6
90% Dioxane-water	Thrice	Twice	34.2

It was shown by Primakov (1961a) that SEW cooking can be accomplished successfully without a separate impregnation stage. He also demonstrated that the presence of the separate impregnation stage increases the delignification rate only slightly.

In the present work the fractionation efficiency was determined for air-dried chips of // 6-8 mm (upper limit of chips used in sulfite plants) and of // 2-4 mm cooked without a separate impregnation. It was also compared to wood meal (diameter 1.0 mm) cooking with 15 hours impregnation at 25°C. It is obvious from Table 3 that the solid residues properties are not affected by the particle size over the range 1-8 mm. It also shows that a separate impregnation stage is not needed. The fact that the fractionation rate is not affected by the particle size indicates that it is governed by chemical reaction, rather than by diffusion.

Table 3. Influence of particle size on spruce SEW fractionation (12% SO_2, 80 minutes at 135°C).

Chips thickness, mm	Solid residue properties		
	Yield, %	Kappa number	Intrinsic viscosity in CED, mL g^{-1}
1.0 mm (wood meal) [a]	53.0	34.3	–
2-4	52.2	36.1	1050
6-8	51.2	35.7	1042
6-8	51.5	36.5	–

[a] including 15 hours of impregnation at 25°C.

6.2 Raw material dry matter content (unpublished)

Dry matter content of the supplied raw material may vary due to transportation and storage, and penetration of the cooking agents inside the raw material may be affected. However, a viable fractionation process should be able to digest raw materials with a wide range of water content. Therefore, green (dry matter content 48.9%) and air-dried (dry matter content 92.8%) spruce chips were subjected to SEW fractionation applying the same conditions. The amount of water in the green chips was considered in the calculation of the fresh liquor composition and amount. Table 4 shows that both the green and air-dried chips are successfully fractionated, and the initial dry matter content has almost no effect on the properties of the resulting solid and liquid phases provided the composition and amount of the fresh liquor is corrected considering the amount of water in the chips. Therefore ethanol is able to impregnate very fast both dried and green chips. The reason for this phenomenon is the so-called Marangoni effect whereby a bulk flow (convection) occurs from fluid in a low surface area region (ethanol-water mixtures having relatively low surface tension, see section 2.2) to that in a high surface area region (cell-wall capillaries and water, Sternling and Scriven 1959, Marton and Granzow 1982).

Table 4. Influence of spruce chips dry matter content on SEW fractionation (12% SO_2, 80 minutes at 135°C).

Raw material	Green chips	Air-dried chips
Dry matter content of the raw material, %	48.9	92.8
Solid residue yield, %	50.1	51.2
Kappa number	32.0	34.1
Solid residue composition, g/100 g solid residue		
Cellulose	82.1	80.1
Hemicelluloses	11.7	12.5
Lignin	5.9	6.3
Liquid phase carbohydrates composition, g L^{-1} (as monosaccharides)		
Mannose	14.3	13.3
Xylose	6.7	6.6
Glucose	3.8	3.5
Total carbohydrates	34.4	32.6

7 Temperature and pressure profiles of the fractionation (Paper III and unpublished)

The development of temperature inside the digester during the heat-up period was followed for three cooking temperatures – 125, 135 and 145°C (Figure 18). The equivalent

heat-up period, t_{eq}, can be calculated by combining the effects of temperature, T, and duration, t, based on the activation energy value, E_A, as (Sixta et al. 2006, p. 190):

$$t_{eq} = \frac{\int_0^t \exp\left(\left(\frac{E_A}{R}\right)\left(\frac{1}{373} - \frac{1}{T_c}\right)\right)dt - \int_0^t \exp\left(\left(\frac{E_A}{R}\right)\left(\frac{1}{373} - \frac{1}{T(t)}\right)\right)dt}{\exp\left(\left(\frac{E_A}{R}\right)\left(\frac{1}{373} - \frac{1}{T_c}\right)\right)}, \quad (12)$$

where R – gas constant, R = 8.314 J mol^{-1} K^{-1}; $T(t)$ – temperature development during cooking, K; T_c – final cooking temperature, K.

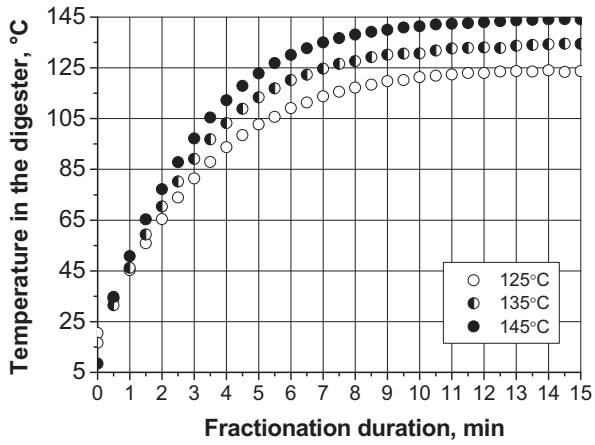

Figure 18. Heat-up period characterisation.

It was calculated that for any reaction with an activation energy in the range from about 90 to 130 kJ mol^{-1}, the equivalent heat-up period is close to 8 minutes over the range of final cooking temperatures used in the present study. For the reactions with an activation energy of 130-180 kJ mol^{-1}, the equivalent heat-up period is about 9 minutes. Most important chemical reactions occurring during hydrothermal fractionation of lignocellulosics have activation energies within these two regions.

The pressure in the digester was measured for SEW fractionation of spruce at 12% SO_2 and 135°C during 80 minutes. The pressure was constant, 12.0 bar, at the cooking temperature. At 145, 155 and 165°C the pressure was measured as 14.5, 17.5 and 19.5 bar, respectively. The values are close to those determined for 15% SO_2/50 w/w.% ethanol-

water cooking of larch (Primakov 1961a): 12.5, 15.0 and 17.5 bar at 135, 145 and 155°C, respectively.

8 Sulfur mass balance (Paper IV)

Primakov (1961a) has shown that the amount of SO_2 remaining after SEW fractionation measured as sulfite anions is considerably lower than the amount of SO_2 charged. The difference corresponded to up to 4 g sulfur/100 g wood (i.e. 8% SO_2). This fact was confirmed by us as we obtained values of about 4-6% as S on wood. Therefore it was important to find the pathway of the apparently considerable SO_2 consumption.

SO_2 reacts with lignin to form stable lignosulfonic acids which are present both in the solid and liquid phases. The sulfur content of selected solid residues varied from 0.040 to 0.095 S/C_9 (see Figure 30), and the highest amount based on wood was only 0.2 g/100 g (see Figure 29). In order to measure the sulfur content of the dissolved lignin, selected spent liquor samples were evaporated at 105°C and the dry solids were combusted using the Schoniger combustion flask method (Schöniger 1956). During evaporation all free and so-called loosely-bound SO_2 (bound to carbonyls producing α-hydroxysulfonates; Rydholm 1965, p. 520) are removed from the liquid phase and the remaining sulfur is in the form of lignosulfonic acids and inorganic anions such as sulfate and thiosulfate. However, the measured sulfate anions concentration of the liquid phases corresponded to only 0-0.2 g sulfur/100 g wood and even this small amount could be an artifact due to oxidation of a small fraction of the sulfite anions being present in >30-fold excess during the analysis. Evidence for this is that the sulfate anions are also found in the fresh original SEW liquors. We did not measure thiosulfate anions, but Primakov (1961a) showed that they are negligible. Therefore it is likely that most of the sulfur determined by the combustion of the dry solids is bound to the dissolved lignin in the form of lignosulfonic acid (Table 5). The molar ratio is about 0.15-0.26 S/C_9 which is comparable to that determined for the lignin isolated from spent softwood SEW liquor by Primakov (1961a, larch) and Vishnevskaya et al. (1981, spruce), 0.25-0.31 S/C_9, but lower than that of acid sulfite lignin, 0.5-0.7 S/C_9 (Rydholm 1965, p. 490). The lower S/C_9 ratios correspond to lower SO_2 concentrations. Nevertheless, the highest amount of the sulfur bound to dissolved SEW lignin (12% SO_2, 80 minutes) is only 1.1% on wood, i.e. much lower than 4-6% measured as the decrease in sulfite anions between the fresh and final cooking liquor after alkali addition.

Thus neither the amount of sulfur bound to lignin in the solid and liquid phases, nor the amount of sulfate and thiosulfate anions can account for the apparent consumption of sulfur. The often-stated existence of SO_2 in spent acid sulfite liquors as "loosely-bound" SO_2 formed by addition reactions of hydrosulfite is unlikely since the

concentration of hydrosulfite anions is very low. It is also known that α-hydroxysulfonates are decomposed by alkali treatment (Sjöström et al. 1962). We found that neither hot (100°C) nor cold (20°C) 1M NaOH treatment for 1 hour released any additional SO_2 from the spent SEW liquor at 12% SO_2 and 80 minutes, confirming the absence of α-hydroxysulfonates.

Table 5. Sulfur content of the dissolved SEW lignin (135°C).

[SO_2], %	Cooking duration, min	Sulfur, % on wood	S/C_9
3.0	60	0.31	0.170
	220	0.62	0.156
6.0	60	0.42	0.162
12	60	0.81	0.229
	80	0.94	0.228
	80	1.08	0.263

Therefore it was decided to investigate the recovery of SO_2 by distillation after cooking at two conditions: 3.0% SO_2/220 minutes and 12% SO_2/80 minutes. As can be seen in Table 6, the recovered SO_2 corresponded to the difference between the initially charged and consumed amounts. Thus it is shown that 95-97% of the initially charged SO_2 can readily be recovered by distillation from the liquid phase, and that the remaining 3-5% of SO_2 is mostly present as lignosulfonates. It was already reported by Hägglund (1951, p. 429) that the "loosely-bound" SO_2 can be removed by distillation provided the pH of the liquor is sufficiently low. Although the recovery of SO_2 was accomplished at 100°C and a vacuum of -900 mbar for 1.5 hour at temperature, it has not been investigated whether milder recovery conditions would be sufficient. Also we have no explanation for the apparently much higher sulfur consumption when SO_2 is measured in the liquid phase as sulfite.

Table 6. SO_2 mass balance at 135°C as % sulfur on wood (and as % on initially charged amount, in brackets).

Conditions	Initially charged SO_2	SO_2 bound to lignin in		SO_2 recovered by distillation	Total SO_2 bound to lignin and recovered
		solid residue	liquid phase		
3.0% SO_2, 220 minutes (kappa 47.2)	8.28 (100)	0.0419 (0.51)	0.62 (7.5)	7.89 (95.3)	8.55 (103.3)
12% SO_2, 80 minutes (kappa 33.5)	33.7 (100)	0.0476 (0.14)	0.94/1.08 (2.8/3.2)	32.6 (96.7)	33.6/33.7 (99.7/100.0)

9 Overall material balance (Paper IV)

The overall material balance describes the relative amounts of wood material remaining in the solid residue (i.e. solid residue yield) and that dissolved in the liquid phase (i.e. dissolved components yield, reported as corrected liquid phase dry solids content). The liquid phase dry solids content in g/100 g wood, DS_W, was calculated from the measured concentration in g L^{-1}, DS_V, using the following formulae:

$$DS_W = \frac{DS_V}{1000}\frac{L}{\rho}, \tag{13}$$

where L – amount of liquid phase, g/100 g wood; ρ – liquid phase density, g mL^{-1}.

$$L = W + w + F - Y, \tag{14}$$

where W – original weight of wood, 100 g; w – amount of water in wood, g/100 g wood; F – amount of the fresh liquor, g/100 g wood; Y – solid residue yield, g/100 g wood.

The liquid phase densities of the 3.0, 6.0 and 12% SO_2 fresh cooking liquors at 0°C are 0.924, 0.933, and 0.957 g mL^{-1}, respectively.

The solid residue and dissolved components yields are determined gravimetrically after evaporating all the liquid at 105°C overnight from the washed solid residues and liquid samples. During this treatment the fractionating chemicals, i.e. SO_2, ethanol and water, are removed from the liquid phases. However, other volatile wood-derived components may also be removed which then would lead to a loss in the overall balance. The most notable of such components is acetic acid formed from the acetyl groups of spruce galactoglucomannan. Other include methanol cleaved from pectins, formaldehyde originating from lignin, and formic acid mostly coming from sugar degradation. On the other hand, during the fractionation process the cooking chemicals may covalently bind to wood components which may lead to an overestimation of the overall balance. SO_2 binds to lignin in the form of sulfonic acid groups, while new hydroxyl and ethoxyl groups are introduced to lignin and carbohydrates originating from water and ethanol, respectively. The latter two are difficult to quantify. For calculation of the actual dissolved components yield we added acetic acid (as acetyl groups) to and subtracted water (bound to monosaccharides formed during fractionation) from the liquid phase dry solids content. The overall material balance for the samples fractionated using 12% SO_2 liquors is presented in Figure 19 as 102-104% on wood, while for the samples obtained using 3.0 and 6.0% SO_2 the sum of the solid residue and dissolved components yields is between 98 and 99% on wood. The amount of sulfur covalently bound to lignin was measured for a few conditions (Figure 29 and Table 5) and it

corresponds to 1.1-2.8 g SO_3H/100 g wood with the higher numbers found for the higher SO_2 concentrations. The final correction for the accumulated sulfur leads to the overall mass balance of 97-101%. This excellent overall material balance closure indicates either that the reactions leading to under- and overestimation compensate each other or that they are not significant. It has to be noted that formation of lignin ethyl ethers and ethyl glycosides corresponding just to 1% of the charged ethanol would have led to about 3% increase in the overall material balance. Therefore these results indicate that ethanol is not consumed appreciably by ethoxylation/ethanolysis reactions.

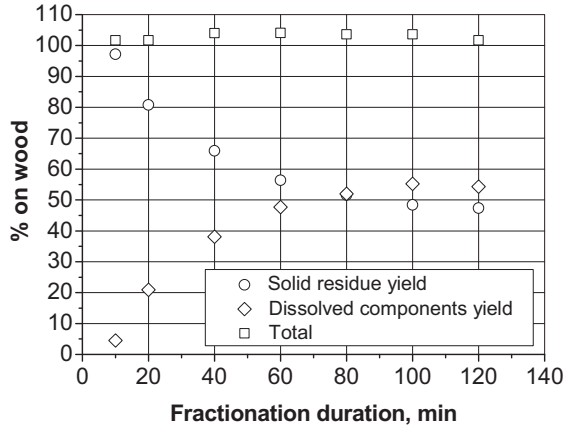

Figure 19. Overall material balance of SEW fractionation at 12% SO_2 and 135°C.

10 Solid phase composition

One of the main objectives of the work was to describe the SEW fractionation kinetics in terms of solid phase composition development – delignification and removal of polysaccharides. Therefore it is important to select reliable and fast methods for the analysis of lignin and carbohydrates in the solid phase.

10.1 Lignin content in the solid phase (Paper II)

Two methods to quantify lignin in solid phase (fibres) are commonly used. The first is a time-consuming direct method which includes two stage sulfuric acid hydrolysis (72 and 4%) and provides the total lignin content as the sum of acid-insoluble (condensed lignin called Klason lignin) and acid-soluble (measured by UV absorption) lignin. The second method is a fast indirect method called Kappa number which relies on the addition of

permanganate anions to the aromatic rings of lignin followed by degradation of the adducts (Li and Gellerstedt 1998). In this section the goal was to find out if a correlation exists between Kappa number and the total lignin content for the solid residues obtained at different SEW fractionation conditions of three species; softwood spruce, hardwood beech and wheat straw. The correlation was studied for the solid residues which have passed the defibration point, i.e. for pulps. The latter occurs at a yield of about 60% for both spruce and beech. All the studied wood pulps did not contain visible rejects. However, shives were present in the wheat straw pulps. The ash content of the pulps was measured to correct the acid insoluble precipitate for substances other than lignin. Since the ash content of wood pulps was negligible, the acid insoluble residue of the wood pulps corresponds to the Klason lignin content. However the wheat straw pulps contain a considerable amount of inorganics, mostly silica. The latter compound is not soluble in the acidic media of SEW pulping or that of Klason lignin determination. Therefore in order to obtain the Klason lignin content of the straw pulps the amount of acid-insoluble inorganics in them was subtracted from the amount of acid-insoluble residue. The acid-insoluble inorganics content of the straw pulps was taken to be equal to the 5.5% ash content (on original fibres) of all pulps cooked for more than 40 minutes.

By plotting the Klason lignin content of the pulps versus kappa number (Figure 20, Table 7) it can be concluded that the linear relationships extend over the whole range of studied Klason lignin content. In case of spruce, the raw material and pulping temperature did not influence the kappa number-Klason lignin relationship. The proportionality coefficient for the spruce Klason lignin-kappa number linear plot, 0.164, is close to that determined for spruce Na bisulfite pulps (0.158, Lorås and Löschbrandt 1961) and Ca sulfite pulps (0.165, Kyrklund and Palenius 1964).

Table 7. The linear relationship between Klason and total lignin content and kappa number values for SEW pulps obtained at 12% SO_2.

Biomass species	Relationship	Range of Klason lignin content, %
Spruce	%Lignin Klason = 0.164×Kappa – 0.14; R^2 = 0.998 %Lignin total = 0.165×Kappa + 0.63; R^2 = 0.997	1.4–12.5
Beech	%Lignin Klason = 0.152×Kappa – 0.30; R^2 = 0.996 %Lignin total = 0.193×Kappa + 0.31; R^2 = 0.999	1.1–7.7
Wheat straw	%Lignin Klason = 0.138×Kappa – 1.27; R^2 = 0.993 %Lignin total = 0.155×Kappa – 0.16; R^2 = 0.995	2.1–8.1

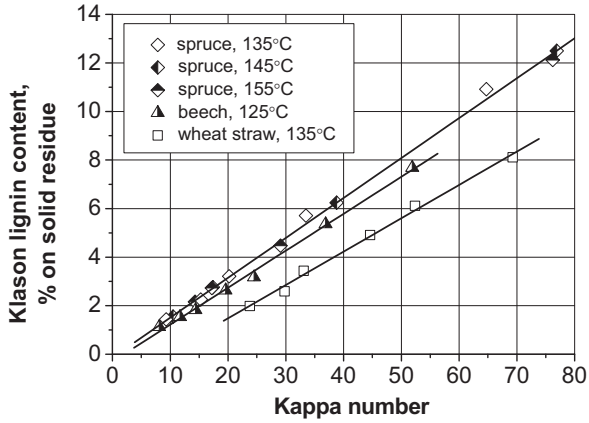

Figure 20. The relationship between ash-free Klason lignin and kappa number values for the investigated SEW pulps (12% SO_2).

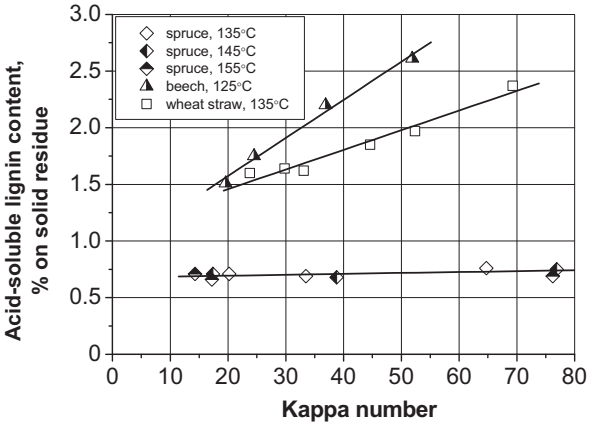

Figure 21. The relationship between acid-soluble lignin and kappa number values for the investigated SEW pulps (12% SO_2).

The acid-soluble "lignin" content of the investigated pulps obtained from spruce is about 0.7% on o.d. pulp at all cooking conditions, which is significantly lower than that reported for sulfite pulps (Lorås and Löschbrandt 1961, Kyrklund and Palenius 1964). This is likely related to the considerably lower sulfonation degree of SEW lignin compared to AS lignin. The acid-soluble content of the beech and straw SEW pulps at high kappa number (see Figure 21) are close to the values of the original species (3.5 and

2.7%, respectively) and thus are considerably higher than that of spruce. The acid-soluble lignin content of beech and wheat straw decreases linearly with kappa number until at least kappa 20 (Figure 21). The fact that the acid-soluble "lignin" amount in spruce pulps does not depend on degree of pulping suggests that the absorption of the hydrolysates at 205 nm is due to compounds other than lignin. Most likely a significant part of the adsorption is caused by carbohydrate degradation products, e.g. HMF and levulinic acid.

The total lignin content of the pulps is also plotted against kappa number. It can be seen (Figure 22, Table 7) that linear relationships are also obtained in this case, all passing through the origin within experimental accuracy, confirming that kappa number represents solely lignin. However, each tested species has a slightly different slope which is probably related to differences in lignin structure (i.e. different substituents in the benzene rings). The spruce SEW pulps exhibit a similar linear correlation for total lignin content versus kappa number as found by Lorås and Løschbrandt (1961) for both spruce Ca sulfite (the proportionality factor of 0.166-0.178) and Na bisulfite pulps (the proportionality factor of 0.166-0.173). Likewise, the total lignin content versus kappa number relationship for beech SEW pulps is close to that found by Kyrklund and Strandell (1969) for both birch and spruce sulfite pulps (proportionality factor of 0.174-0.198). The total lignin content vs. kappa number linear plot for the straw SEW pulps also contains no intercept. Therefore, the explanation given by Oreopoulou (1988) that the intercept (about 3.5-6.5) is caused by the presence of shives is unlikely but rather is

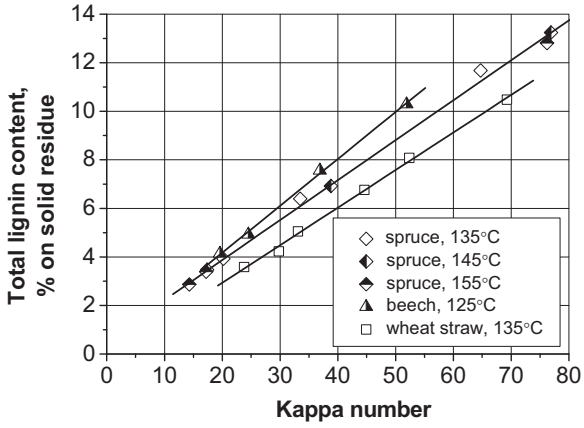

Figure 22. The relationship between total lignin and kappa number values for the investigated SEW pulps (12% SO_2).

caused by the high ash content of the straw pulps.

Overall it may be concluded that the relationship between residual lignin content and kappa number in SEW pulps is similar to that of sulfite pulps.

Since the correlation Kappa number-Total lignin content is very good, the Kappa number method was used for the determination of lignin content in the defibrated solid residues, i.e. pulps.

10.2 Comparison of the acid hydrolysis/HPAEC-PAD and acid methanolysis/ GC-FID methods for the analysis of carbohydrates content in the solid phase (Paper IV)

Carbohydrate content of the solid phases was also determined by two different analytical techniques – double-stage acid hydrolysis/HPAEC and methanolysis/GC. The comparison was made for the original spruce wood and for most of the solid residues obtained after SEW cooking of spruce at 3.0-12% SO_2 and 135°C. Figure 23 shows the amount of carbohydrates in wood and the solid residue obtained after cooking at 12% SO_2, 135°C and 80 minutes. All other solid residues exhibit the same pattern. Xylose and mannose in all the solid phases determined by methanolysis/GC constitute only 50-75% of those determined by acid hydrolysis/HPAEC. This underestimation is explained by the fact that part of glucomannan and xylan are probably crystallised onto cellulose, and methanolysis is not strong enough to access and cleave the glycosidic bonds in crystalline areas (Sundberg et al. 1996). Hydrolysis liberates glucose both from glucomannan and cellulose. From the known ratio mannose:glucose = 4.15 for softwoods (Janson 1974) it is possible to compute the amount of cellulose in the wood and solid residues as: $[Cel] = [Glc]_{tot} - [Man]/4.15$, where $[Glc]_{tot}$ – total glucan content, $[Man]$ – mannan content of the wood/solid residue. Since most of cellulose is not accessible by methanolysis, the total amount of glucose determined by the methanolysis/GC is only slightly higher than that assigned to glucomannan as determined by the acid hydrolysis/HPAEC method. This confirms that cellulose in wood is methanolysed only to a very small extent (Sundberg et al. 1996). However, in the solid residues from which most of the glucomannan is removed, the methanolysis/GC method still gives 3.5-5.5% of total glucan based on wood indicating that accessibility of cellulose increases slightly probably due to lignin removal and partial acid degradation of cellulose during fractionation.

Contrary to mannose, xylose and glucose, the methanolysis/GC method provides a higher content of arabinose (only in wood), rhamnose and galactose compared to acid hydrolysis/HPAEC. This may be explained by the fact that some of these sugars degrade during the first stage of the acid hydrolysis which is not corrected for by 4% acid hydrolysis of the standard sugar solutions used for determining the response factors.

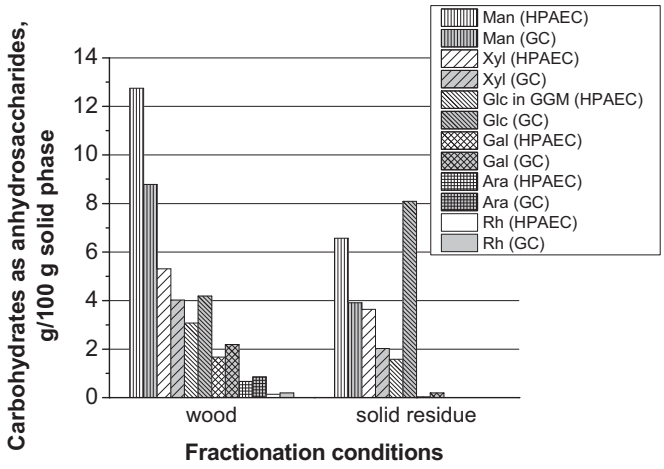

Figure 23. Comparative hemicellulose composition of the original wood and the solid residue (at 12% SO_2, 135°C, 80 minutes) by double stage acid hydrolysis/HPAEC and methanolysis/GC. The value given for glucose by HPAEC is calculated as: [*Glc*] = [*Man*]/4.15 (Janson 1974).

Arabinose is detected by neither of the methods starting from 40 minutes cooking. Most galactose (90%) is removed from the solid phase within 30 minutes cooking and only traces are detected by acid hydrolysis/HPAEC at longer times. However, the GC method gives considerably higher amounts of galactose in most of the solid residues. Small amounts of rhamnose in the solid phase are determined by both methods only up to 30 minutes of cooking.

Based on the above results and the fact that the mild conditions of the methanolysis/GC method allow determination of uronic acids simultaneously with neutral sugars, the following calculation procedure was adopted for the solid phase composition. The amounts of mannose, xylose, glucose and (in solid residues) arabinose were determined by acid hydrolysis/HPAEC while galactose, rhamnose, uronic acids and (in wood) arabinose were determined by methanolysis/GC.

10.3 Solid phase material balance (Paper IV)

The composition of the feedstocks is given in Table 8. In addition to lignin and carbohydrates lignocellulosic biomass contains various low-molecular weight organic compounds (i.e. extractives) and inorganic compounds (i.e. ash). Extractives were analysed gravimetrically after the extraction with acetone which dissolves both lipophilic

Table 8. Feedstock composition, g/100 g.

Components	Spruce		Beech		Wheat straw	
	determined	literature data*	determined	literature data*	determined	literature data**
Carbohydrates	67.8	–	71.9	–	–	61.2
Cellulose	39.9	41.7	41.9	39.4	–	34.8
Hemicelluloses	27.9	–	30.4	–	–	26.4
Galactan	2.19	2.8	0.8	1.4	–	
Glucan (in GGM)	3.07	–	0.7	–	–	C_6 2.6
Mannan	12.8	13.6	1.1	0.9	–	
Arabinan	0.85	1.2	0.7	0.7	–	
Xylan	5.31	5.6	19.5	19.0	–	C_5 19.0
Rhamnan	0.20	0.3	–	0.5	–	–
Acetyl groups	1.11	–	4.5	–	–	–
GalA	1.44	–	–	–	–	
4-O-MeGlcA	0.95	1.8	3.1	4.8	–	4.8
GlcA	0	–	–	–	–	
Lignin	27.7	27.4	26.1	24.8	20.6	(24.5)
Klason	27.4	–	22.6	–	17.9	–
Acid-soluble	0.34	–	3.48	–	2.70	–
Extractives	1.81	1.7	0.50	1.2	1.97	–
Ash	0.44	–	0.50	–	9.29	–
Silica	–	–	–	–	(5.5)	–
Sum of all components	97.7	99.4	99.0	92.7	–	–

* Koch 2006, p. 23, 29; ** Nepenin and Nepenin 1994.

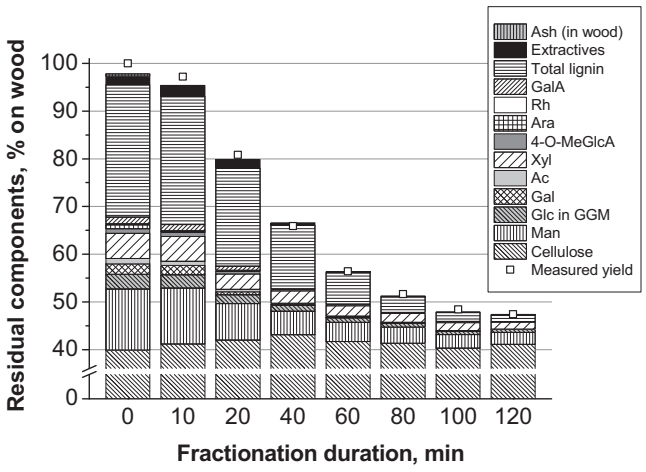

Figure 24. Solid phase material balance for SEW fractionation at 12% SO_2 and 135°C.

and hydrophilic extractives (Fengel and Wegener 1989). During SEW fractionation of spruce (1.81% extractives), beech (0.50%) and wheat straw (1.97%) most of the extractives are dissolved. The SEW fractionation medium is a polar solvent which should be capable of dissolving hydrophilic extractives (for example, lignans and flavonoids). Furthermore, the fatty acids esters will be hydrolysed and also removed. Most of the inorganics (or ash) in the wood species (about 0.5% on wood) are also removed during SEW fractionation. Wheat straw contains silica at about 5.5% on wood which is not soluble in acid and therefore remains in the solid phase. This is an advantage compared to alkaline processes where high silica containing herbs cause serious problems related to scaling during black liquor evaporation.

Solid phase material balances for the fractionation experiments using 3.0, 6.0 and 12% SO_2 liquors at 135°C were established and Figure 24 illustrates the mass balance for 12% SO_2 case. By comparing the sum of all components with the measured solid residue yield it is apparent that the solid phase material balances closure is excellent in all studied cases. The latter also confirms the accuracy of the analytical methods.

11 Wood meal fractionation (Paper V)

To better understand the chemistry of SO_2-ethanol-water (SEW) cooking it was compared to SO_2-water, acid sulfite (AS) and ethanol acid sulfite (ethanol-AS) cooking, all performed at 12% free SO_2, 135°C and 80 minutes. By using wood meal and applying 15 hour impregnation at room temperature the influence of diffusion on the rate of the processes was minimised. The composition of the solid residues is given in Table 9.

Table 9. Properties of the solid residues obtained after fractionation of wood meal: liquor-to-wood ratio 4.8 L kg^{-1}, 135°C, 80 minutes.

Cooking	Colour	Yield, %	Kappa no.	Lignin, % on wood	LFY, % on wood	Sulfur in solid residue,		Sulfur in liquid phase,		Total accumulated sulfur,	
						% on wood	S/C_9	% on wood	S/C_9	% on wood	S/C_9
SO_2-water	brownish	56.9	122	11.8	45.1	0.323	0.162	1.32	0.493	1.64	0.352
SEW	bright	53.0	34.3	3.33	49.7	0.0685	0.122	0.813	0.198	0.882	0.189
AS	extremely bright	50.9	21.5	2.13	48.8	0.125	0.349	2.57	0.598	2.70	0.579
ethanol-AS	very bright	85.6	98.0	14.4	71.2	0.812	0.335	1.34	0.597	2.15	0.461
SEW, chips*	bright	51.2-51.8	29.4-33.5	2.81-3.30	48.3-48.7	0.0476	0.086	0.94-1.08	0.23-0.26	0.99-1.13	0.21-0.24

* L/W ratio 6 L kg^{-1}

It can be seen that the solid residue and liquid phase obtained in the present SEW cooking of spruce meal has nearly the same composition and sulfur content as that obtained in SEW cooking of the chips without separate impregnation step. It again proves that impregnation is not necessary in SEW fractionation and that diffusion is not a rate-limiting factor.

11.1 Carbohydrates dissolution

SEW and AS pulps have close lignin-free yields (LFY), 49.7 and 48.8% on wood, while SO_2-water pulp LFY is lower, 45.1%. It is worth noting that no carbohydrates are dissolved during ethanol-AS cooking since the pulp LFY of 71.2% on original wood meal corresponds to the carbohydrate content of the original spruce.

LFY is determined by hydrolysis and solubility of the carbohydrates. However, before dissolution occurs the carbohydrates must be sufficiently depolymerised. Thus LFY can be considered a measure of the effective acidity of the cooking system at temperature. Highly acidic SO_2-water cooking intensively removes carbohydrates (LFY 45.1%), although the delignification rate is relatively low (lignin content 11.8% on wood). Also the LFY of low acidic ethanol-AS pulping (both base and ethanol are present) is the same as that in wood. By comparing LFY of AS (48.8%) and SEW (49.7%) pulps one can conclude that the effective acidity of these systems is very similar. However, the calculation of acidity at temperature, disregarding the effect of ethanol, gives a 7 times higher value for SEW cooking than AS (see Paper V). Thus it follows that the presence of ethanol at a 1:1 ratio in water significantly decreases the effective acidity.

11.2 Lignin sulfonation

The sulfur content of lignin in the base-free-cooked pulps (SEW and SO_2-water, 0.122 and 0.162 S/C_9, respectively) is 2-3 times lower than that in the pulps cooked in the presence of a base (AS and ethanol-AS, 0.349 and 0.335 S/C_9, respectively; note that Rydholm, 1965, p. 490, gives 0.3 as the minimum value required for lignin dissolution in AS cooking). The S/C_9 ratio in the liquid phase of the cooks with a base of about 0.60 agrees with that reported in the literature for AS cooking (Rydholm 1965, p. 490). Comparison of the S/C_9 ratio for the AS and ethanol-AS solid and liquid phases indicates that presence of ethanol has no effect on sulfonation. Since above it was shown that the effective acidity of the systems is decreasing in the order SO_2-water > AS ≈ SEW > ethanol-AS, it follows by comparing the S/C_9 ratio of AS with ethanol-AS and SEW with AS that acidity has also no direct effect on sulfonation rate. This fact favours that sulfonation takes place via quinone-methide since this reaction route takes place at any

acidity (Ivnäs and Lindberg 1961). The free SO_2 concentration was the same for all 4 experiments. Condensation cannot be used as an explanation for the lower sulfonation in SEW cooking, because SO_2-water cooking is substantially affected by condensation while the S/C_9 ratio is still higher for the SO_2-water pulp than for the SEW pulp. Rather the opposite is true, i.e. a low degree of sulfonation leads to more condensation. Another explanation is that ethanolysis may compete with sulfonation leading to a lower S/OCH_3 ratio. However, no ethoxyl groups were found in dissolved lignin of SEW cooking (Primakov 1961a). Therefore the only possible explanation for the different sulfonation rates in the base and base-free cookings is the different amounts of bound SO_2, i.e. hydrosulfite anions. In this context it is interesting to note that in the Russian literature, for example by Boyarskaya and Tsypkina (1970), hydrosulfite anions are thought to be responsible for the sulfation reaction resulting in lignin hydrosulfates $Lig\text{-}OSO_3H$ which could explain the higher sulfur content in AS and ethanol-AS cooking.

11.3 Lignin condensation

An indirect evidence for condensation is the brown colour of pulps and liquors (darker pulps correspond to darker liquors). SO_2-water pulp is very brown and has undoubtedly suffered from condensation. AS and ethanol-AS pulps are extremely bright, they are even brighter than the original wood meal. Thus it may be speculated that condensation does not take place during AS and ethanol-AS cooking. SEW pulp is just a bit darker than AS, ethanol-AS and the wood meal which suggests some lignin condensation. The reason for the occurrence of condensation in SEW cooking is seen in the lignin S/C_9 ratio: in AS (S/C_9 0.349) 3 times more α-carbons become sulfonated than in SEW (S/C_9 0.122) which protects the AS lignin from condensation despite the similar acidity in both systems.

11.4 Lignin dissolution

The rate of lignin dissolution is similar for SEW (lignin content 3.33% on wood) and AS (lignin content 2.13% on wood) cooking, although the sulfonation rates are very different (S/C_9 0.122 and 0.349 for SEW and AS solid residues, respectively). On the other hand, the lignin dissolution rates are very different for the AS and ethanol-AS cooking (lignin content 2.13 vs. 14.4 % on wood, respectively), while the sulfonation rates are almost the same (S/C_9 0.349 and 0.335). Thus there is no direct relationship between sulfonation and lignin dissolution rates. Primakov (1961a) also found a lower sulfonation degree for SEW dissolved lignin compared to that of AS cooking (S/C_9 of about 0.25 vs. 0.6) and related it to the 5-times higher solubility of lignosulfonic acid in ethanol compared to than in water. It was also shown that removing ethanol from the liquid phase leads to

precipitation of lignin (Primakov and Barbash 1989). Pylkkänen (1992) also found that 50-70% lignin precipitates after removal of ethanol from the liquid phase obtained from the SEW cooking at 3% SO_2. However, the difference in lignin solubility does not explain the poor delignification in the case of ethanol-AS cooking. Rather a more likely explanation is related to the recent finding that almost all lignin in softwood is linked to carbohydrates as lignin-carbohydrate complexes (LCCs, Lawoko et al. 2006b). Since no carbohydrates are removed during ethanol-AS cooking, part of the lignin attached to carbohydrates can only dissolve if this LCC bond is cleaved. The α-ether LCCs may be cleaved by SO_2 possibly through the quinone-methide pathway which does not require acidity. The fact that all carbohydrates are retained in the solid phase implies that the dissolved lignin is carbohydrate-free and this eliminates the dissolution path of lignin in the form of LCCs.

Absence of the straightforward correlation between S/C_9 ratio (corresponding to sulfonation/sulfitolysis) and delignification rate leads to a conclusion that the latter is determined by another chemical reaction, probably hydrolysis. Assuming hydrolysis to be the rate-determining step in Hägglund's consecutive sulfonation-hydrolysis scheme (Hägglund 1951, p. 415-418), it would be easy to explain the difference in lignin dissolution rates based on the differences in effective acidities of the liquors. The effective acidity of the systems is decreasing in the order SO_2-water > AS ≈ SEW > ethanol-AS. The lignin dissolution rate follows the same order with the exception of the SO_2-water system which is considerably affected by condensation.

The above comparison of the 4 cooking systems shows that there is a balance between sulfonation, condensation and hydrolysis reactions. There exists an optimum acidity and sulfonating ability of the pulping system at which hydrolysis is maximised and condensation is minimised. This optimum condition was found empirically for AS by varying bound and free SO_2 amounts (Rydholm 1965, p. 467; i.e. the so-called Kaufmann diagram). The same optimum exists for SO_2-water and SEW systems and was also empirically found to occur at a 1:1 ethanol-water ratio (Eliashberg et al. 1960); with a higher ratio leading to a too low acidity for efficient hydrolysis, while at a lower ratio the acidity is too high leading to significant condensation.

12 Fractionation kinetics: concentration of active cooking chemicals

Formally, to describe the kinetics of delignification and polysaccharides degradation, the activities of the cooking chemicals at cooking temperature, primarily SO_2, hydrosulfite anions and hydroxonium cations (acidity) need to be known. The system is further complicated by the presence of ethanol which affects the activity coefficients, especially that of the hydroxonium cation, and the equilibrium constants. Since the activity

coefficients are not known for the present system, the activities are approximated by concentrations.

The applied cooking liquors contain high weight percentages of SO_2 (3.0-27%). Due to the relatively high pK_{a1} value of sulfurous acid at cooking temperature (3.2 in water at 135°C, Rydholm 1965, p. 456; higher in ethanol being a weaker proton acceptor than water), the dissociated amount of SO_2 can be neglected, and the concentration of SO_2 in the fresh liquor at cooking temperature can directly be calculated from the charged amount of SO_2. As cooking proceeds SO_2 is consumed via reactions with lignin and by side reactions. However, the highest measured amount of bound sulfur corresponds to only 1.1% on wood with the rest recoverable as SO_2 (section 8). Therefore, the concentration of SO_2 in the liquid phase at a liquor-to-wood ratio of 6 L kg^{-1} was taken to be constant during cooking and equal to that in the fresh liquor.

The acidity during cooking may be estimated from the amount of strong sulfonic acids groups formed plus the acidity resulting from the dissolved SO_2 when the effect of ethanol is neglected. In the beginning of cooking the amount of SO_2 is 0.43 (3.0%), 0.87 (6.0%) and 1.79 (12%) mol L^{-1}. At 135°C according to the pK_{a1} of sulfurous acid in water, the hydroxonium cation concentration for the different SO_2 concentrations is 0.02, 0.02 and 0.03 mol L^{-1}, respectively. The amounts of lignosulfonic acids formed during cooking at these SO_2 concentrations correspond to about 0.03, 0.03 and 0.05 mol L^{-1}, respectively (section 8). These numbers suggest that the acidity of the liquid phase does not change significantly during an SEW fractionation. This is indirectly confirmed by the pH of the liquid phases measured at room temperature (using conventional glass electrode); at 3.0% SO_2 the pH changes from 1.2 to 1.0; at 6.0% from 1.1 to 1.0; at 12% from 1.1 to 0.9 (at 135°C).

It is known that the acidity in the fibre-bound liquid is different from that of the free liquid outside the fibres (Fiehn 1964) when the fibre wall contains a significant amount of ionisable groups (i.e. sulfonic acids). The importance of this so-called Donnan equilibrium was estimated as follows. Assuming full ionisation of lignosulfonic acid groups attached to the solid phase, and a density of the fibre-bound liquid of 1.0 g mL^{-1} (Rydholm 1965, p. 477), the acidity of the fibre-bound liquid phase would be about 0.06M at the beginning of cooking and decrease constantly during fractionation to about 0.02M. The acidity of the free liquid outside the fibres is calculated to be 0.02-0.05M. Therefore the acidities of the two liquid phases, neglecting the effect of ethanol, are very close. The presence of ethanol reduces the ionisation of all acids and thus would further decrease the difference in acidity between the fibre-bound and free liquid. Thus it may be concluded that the Donnan equilibrium is not important in SEW fractionation.

The hydrosulfite anion concentration is difficult to estimate in the ethanol-water mixture. The concentration of hydrosulfite anions in the SEW fractionation liquid is

roughly estimated to be about 10-40 mmol L^{-1} at 135°C (compared to 300 mmol L^{-1} for acid sulfite liquor, Sixta et al. 2006, p. 396). The estimate is made for the ethanol-free solution and is based on the sulfurous acid first ionisation stage (pK_{a1} = 3.2 at 135°C, Rydholm 1965, p. 456; acidity is controlled additionally by lignosulfonic acids).

13 Delignification kinetics

13.1 Delignification of different biomass species (Paper III)

In this work SEW fractionation of 3 biomass species was studied: spruce, beech and wheat straw representing gymnosperm trees; angiosperm trees and herbs, respectively. The decimal logarithm of the residual lignin content, % on feedstock, is plotted versus fractionation duration on Figures 25 (12% SO_2, 135°C), 26 and 27 (12% SO_2, 125-165°C), and 32 (3.0-27% SO_2, 135°C). The lignin content of the original biomass species (spruce – 27.7%, beech – 26.1%, and straw – 20.6%, Table 8) is placed at 8 minutes, which is the equivalent heat-up time for delignification (see section 7). It can be seen from Figure 25 that delignification can be divided in 2 phases. The first phase (or bulk delignification) is first order in lignin and it starts right at the equivalent heat-up time (the lines pass through the original lignin content of the feedstocks). The bulk phase lasts until lignin content of about 1.0-2.0% on wood for all fractionation experiments (except 3.0% SO_2) when the considerably slower phase, i.e. residual delignification, takes over.

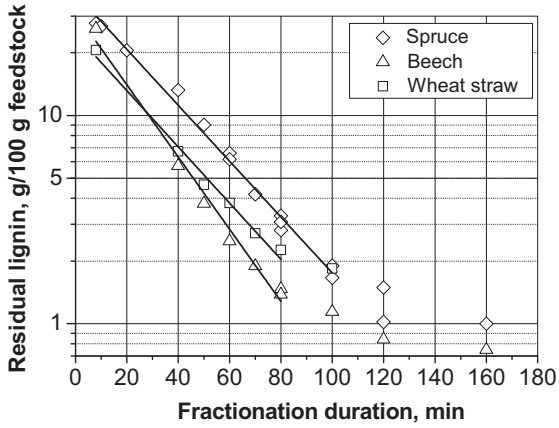

Figure 25. Delignification of different species at 12% SO_2 and 135°C: residual lignin versus fractionation duration.

The kinetics of bulk delignification can be described by the equation:

$$-\frac{d[Lig]}{dt} = k_{Lig,obs}(T)[Lig], \quad (15)$$

where $k_{Lig,obs}$ – the observed bulk delignification rate constant determined from the slopes of the lines ln([*Lig*]) = f(*t*); *T* – temperature, K; [*Lig*] – lignin content of the solid residues, % on feedstock.

The first order in lignin is in accordance with the nucleophilic substitution mechanism for the main delignification reactions, i.e. sulfonation and hydrolysis (Figure 1).

From the slopes of the *bulk* delignification linear plots, including the original lignin content at the equivalent heat-up time, the delignification rate constants were calculated for different temperatures (Table 10). Interestingly, the SEW bulk delignification rates for all species are similar at a particular temperature. For example, at 135°C the rate constant for beech is 39.9×10^{-3} min^{-1}, for spruce 30.9×10^{-3} min^{-1}, and for straw 31.1×10^{-3} min^{-1}; at 145°C – 87.6×10^{-3} min^{-1} for beech and 64.0×10^{-3} min^{-1} for spruce. The main delignification mechanism, i.e. acid-catalysed sulfonation and hydrolysis at the α-position of propane side chain present in all the phyla, explains the closeness of the rate constants.

The delignification rate of kraft pulping at 170°C (k = 0.04 min^{-1} at 1M NaOH; Sixta et al. 2006, p. 204) is comparable to that of SEW pulping at 135°C.

Table 10. SEW delignification kinetics.

[SO_2], %	Temperature, °C	Spruce		Beech	
		$k_{Lig,obs}\times10^3$, min^{-1}	$k_{Lig}\times10^3$, L mol^{-1} min^{-1}	$k_{Lig,obs}\times10^3$, min^{-1}	$k_{Lig}\times10^3$, L mol^{-1} min^{-1}
12	125	–	–	20.0	11.1
3.0	135	7.91	18.3	–	–
6.0		16.1	18.4	–	–
12		30.9	17.2	39.9	22.2
18		36.5	13.2	–	–
27		44.9	10.4	–	–
12	145	64.0	35.7	87.6	48.8
	155	135	75.0	–	–
	165	216	120	–	–
$E_{A,Lig}$, kJ mol^{-1}		106.8		102.2	
$A_{Lig,obs}$ (at 12% SO_2), min^{-1}		1.44×10^{12}		4.96×10^{11}	
A_{Lig}, L mol^{-1} min^{-1}		8.03×10^{11}		2.76×10^{11}	
a, L mol^{-1}		0.145		–	

Another aspect worth mentioning of SEW cooking of the different species is that both spruce and beech reach a bleachable grade (respectively 30 and 20 kappa number) in about the same time. Thus at 135 °C a kappa number of 20 is obtained at 70 minutes for beech while for spruce kappa number 30 is reached at 80 minutes.

For comparison the *bulk* delignification rate constants for SEW pulping (50 w/w.% ethanol-water, 15% SO_2) calculated from Primakov's data (1961b) are: spruce – 47.9×10^{-3} min^{-1} (135°C) and 90.3×10^{-3} min^{-1} (145°C), birch – 51.4×10^{-3} min^{-1} (135°C) and 112.6×10^{-3} min^{-1} (145°C). The reason for the latter somewhat higher rates than ours may be explained by the higher SO_2 and lower ethanol concentrations in the cooking liquors used by Primakov.

On the other hand the *residual* delignification proceeds slower for beech than for spruce SEW fractionation (e.g. at 145°C after 70 minutes of cooking beech SEW pulp has a kappa number of about 11, while spruce SEW pulp reaches this kappa in less than 60 minutes). After reaching a kappa number level of around 10 (lignin content based on pulp of 2.2%) the delignification of beech slows down dramatically (Figure 27) at all three temperatures. So this level of delignification would be the limit when considering producing dissolving pulp.

Formally the kinetic data also could be described as second order in lignin, i.e. $1/[Lig]$ vs. time. It should be noticed that the second order behaviour fits the data over a wider kappa number range because it covers a significant part of the residual delignification phase as well. However, this kinetic behaviour, which is meaningless from a mechanism point of view, was noted earlier also for kraft cooking kinetics (Li et al. 2002).

13.2 Temperature effect on delignification (Papers I and III)

Figures 26 and 27 show the effect of temperature on SEW delignification (at 12% SO_2) of spruce and beech, respectively. The rate increases considerably with temperature. For instance, at 165°C a pulp of kappa number 30 is obtained at 15 to 20 minutes of total cooking time.

The Arrhenius equation was applied to establish the dependence of fractionation reactions rate constants on temperature:

$$\frac{d\ln k}{dT} = \frac{E_A}{RT^2}, \text{ or } k = A\exp\left(-\frac{E_A}{RT}\right), \tag{16}$$

where k – rate constant of the particular reaction at fixed temperature; E_A – activation energy for this particular reaction, kJ mol^{-1}; R – gas constant, 8.314 J mol^{-1} K^{-1}, A – pre-exponential factor.

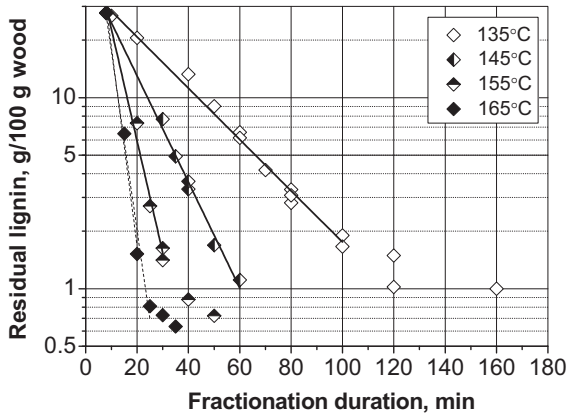

Figure 26. Temperature effect on delignification of spruce at 12% SO_2: residual lignin versus fractionation duration.

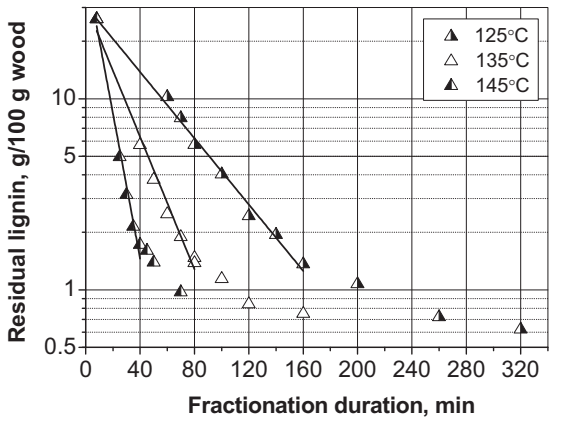

Figure 27. Temperature effect on delignification of beech at 12% SO_2: residual lignin versus fractionation duration.

By plotting the natural logarithm of the delignification rate constant versus the inverse of the temperature, activation energy values of 102 kJ mol^{-1} for beech and 108 kJ mol^{-1} for spruce bulk delignification were obtained with an excellent fit (Figure 28, Table 10). The closeness of these values again indicates the same delignification mechanism for different phyla.

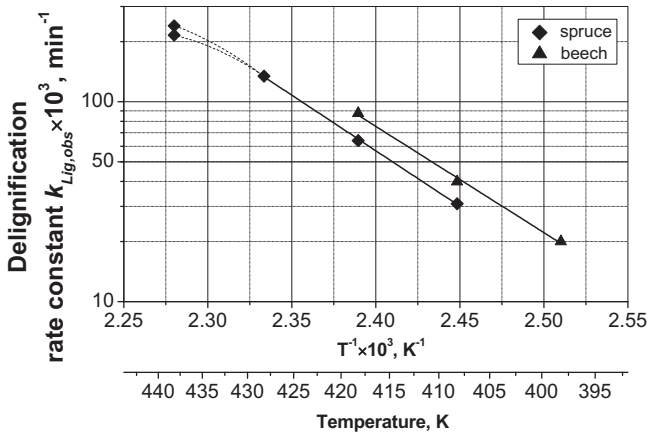

Figure 28. Temperature effect on delignification at 12% SO_2: determination of activation energy.

The activation energy values are somewhat lower than that of kraft delignification (134 kJ mol^{-1}, Vroom 1957) but close or somewhat higher than those of acid sulfite delignification (67-92 kJ mol^{-1}, Goldfinger 1941; 88 kJ mol^{-1}, Richards and van Heiningen 2004; 105 kJ mol^{-1}, Hagberg and Schöön 1973).

Considering the temperature dependence of the delignification rate, the equation (15) may be modified:

$$-\frac{d[Lig]}{dt} = A_{Lig,obs}\exp\left(-\frac{E_{A,Lig}}{RT}\right)[Lig] = k_{Lig,obs}(T)[Lig], \qquad (17)$$

where $A_{Lig,obs}$ – pre-exponential factor for the observed bulk delignification rate constant, $k_{Lig,obs}$, min^{-1}; $E_{A,Lig}$ – activation energy for the bulk delignification, kJ mol^{-1}. The value of the pre-exponential factor at 12% SO_2 is also given in Table 10.

The high values of activation energies provide further evidence that the delignification rate is governed by chemical reaction. The small deviation from perfect straight line behaviour for spruce at 165°C (438 K), Figure 28, may be related to a small effect of diffusion limitation at this high rate, or could be related to increased experimental error in the determination of the rate constant at the very short fractionation times (see Figure 26). It has to be noted also that no visual evidence of condensation was present even at 165°C when the fractionation was accomplished at 12% SO_2 (the solid residues remained bright).

13.3 Effect of SO_2 concentration on sulfonation and delignification of spruce (Paper V)

13.3.1 SO_2 concentration effect on sulfonation

In this section the change in the sulfur content of the solid (Figures 29-31) and liquid phases during bulk delignification is described and quantified.

Figures 29 and 30 show the sulfur content of the solid residues based on original wood and as S/C_9 ratio versus cooking duration, respectively. The solid phase reaches the highest sulfur content on original wood basis (about 0.2% on wood or 0.045 S/C_9 for the 12% SO_2 cooking) after only 10 minutes of cooking, i.e. at the end of the heat-up period. At this point about 97% of lignin is still retained in the solid residue. As cooking proceeds the sulfur content of the solid residues based on wood decreases due to lignin dissolution. The development over time of the sulfur content of the solid residues based on original wood shown in Figure 29 can be compared to that in AS cooking (Rydholm 1965, p. 489). The first stage is governed by sulfonation of lignin without its dissolution (i.e. during the heat-up period in SEW and taking a few hours during the impregnation of the AS process) and the second stage being lignin dissolution resulting in a rapid decrease in the sulfur content of the solid residue (durations are similar for SEW and AS).

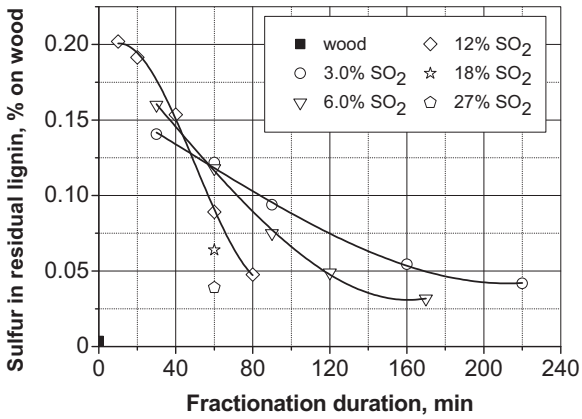

Figure 29. Development of sulfur content in residual spruce lignin, % on wood, during fractionation at different SO_2 concentrations and 135°C.

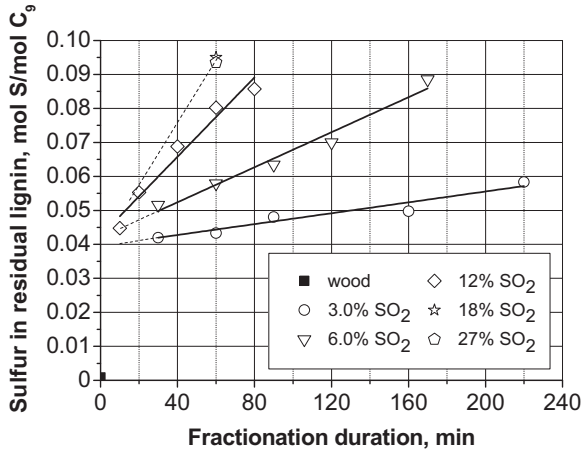

Figure 30. Development of sulfur content in residual spruce lignin, S/C_9, during fractionation at different SO_2 concentrations and 135°C.

However if the sulfur content is based on the residual lignin content (see Figure 30) then the degree of lignin sulfonation, expressed as S/C_9 ratio, gradually increases by a factor 1.5-2 over the entire cook. It is noted that the highest S/C_9 values (0.045-0.09) are considerably lower than the value of 0.3 required for lignin dissolution in AS cooking (Rydholm 1965, p. 490). Otherwise the relative development of the sulfur content over time in SEW cooking resembles that in AS cooking (Rydholm 1965, p. 489) where the S/C_9 also increases until the very last stages of the cook. Finally it can be seen in Figure 30 that the rate of increase of S/C_9 increases roughly linearly with SO_2 concentration from 3.0 to 12%: 8.00×10^{-5} (at 3.0% SO_2), 25.8×10^{-5} (at 6.0% SO_2) and 58.4×10^{-5} (at 12% SO_2) mol S/(mol $C_9\times$min). No clear increase in the rate is observed when the concentration is increased from 18 to 27% SO_2.

The dissolved lignin has a higher S/C_9 content (0.16-0.26 S/C_9) than the residual lignin, which means that higher sulfonated lignin is removed preferentially from the solid phase. Similarly, the degree of sulfonation of SEW dissolved lignin is also substantially lower than that dissolved in AS pulping (S/C_9 ratio of 0.5-0.7, Rydholm 1965, p. 490), especially at lower SO_2 concentrations. At 3.0% SO_2 the S/C_9 ratio is the same for 60 and 220 minutes of cooking, 0.16-0.17, although 12% of lignin on wood is removed between these points.

If the lignin dissolution rate would be determined by sulfonation and sulfitolysis, i.e. by the reactions leading to accumulation of sulfur in the residual lignin, then it is expected that the relationship between residual lignin sulfur content and the amount of

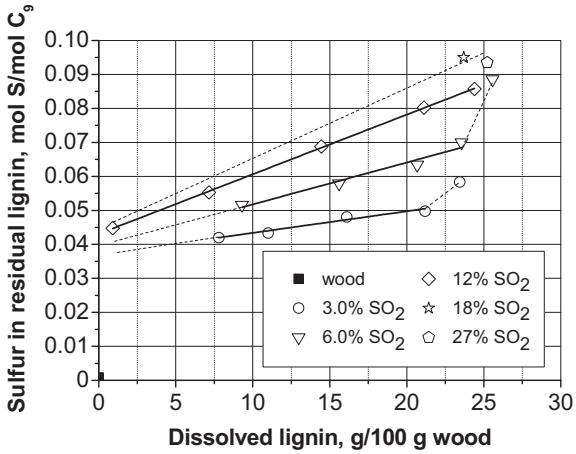

Figure 31. Sulfur content in residual spruce lignin, S/C_9, versus fractionation duration at different SO_2 concentrations and 135°C.

removed lignin would be the same when cooking at different SO_2 concentrations. However it is evident from Figure 31 that at the same lignin removal, the S/C_9 content of the residual lignin is higher at higher SO_2 concentrations. Therefore the rate of the reactions leading to sulfur accumulation in the residual lignin, i.e. sulfonation and sulfitolysis, does not determine the dissolution rate. The acidity of the liquid phases at different SO_2 concentrations is only slightly different, so hydrolysis should also proceed at similar rates in all cases. As will be shown later, the rate of delignification also increases approximately linearly with SO_2 concentration up to about 12%, and then the increase slows down at higher concentrations, similar to that seen for the rate of increase in S/C_9 ratio in Figure 30. According to Hägglund, sulfite delignification is a consecutive process of sulfonation followed by hydrolysis and dissolution of the sulfonated lignin (Hägglund 1951, p. 415-418). Thus a reasonable explanation for the higher S/C_9 ratio at higher SO_2 concentrations seen in Figure 31 is that the rate of removal of sulfonated lignin by diffusion out of the fibre walls is controlling the amount of residual lignin since the formation of sulfonated lignin in the fibre wall increases with increasing SO_2 concentration. The rate of diffusion of sulfonated residual lignin is governed by the solubility of the sulfonated lignin fragments and their slow effective diffusion coefficient in the fibre wall. Since the solubility of the lignosulfonic acids in ethanol-water is significantly higher than that of lignosulfonates in the aqueous AS liquor (Primakov et al. 1979; Primakov and Barbash 1989), this may also explain the significantly lower S/C_9 ratio of residual lignin in SEW pulp as compared to AS pulp. In the present SEW

experiments the cook is ended by rapid cooling and a final water wash. The low temperature and absence of ethanol greatly reduce the solubility and effective diffusion coefficient of the sulfonated lignin (Favis and Goring 1984, Willis and Goring 1985, 1987) and thus "lock-in" the residual sulfonated lignin in the fibre wall. Thus it appears that the rate of lignin dissolution is both controlled by the reaction of SO_2 with lignin and by the solubility and effective diffusion of sulfonated lignin in the fibre wall.

13.3.2 SO_2 concentration effect on delignification

Figure 32 and Table 10 show that the delignification rate constants, $k_{Lig,obs}$, are significantly different at different SO_2 concentrations. In fact in the region 3.0-12% the rate is proportional to SO_2 concentration. Therefore it is possible to again modify the rate expression as follows:

$$-\frac{d[Lig]}{dt} = A_{Lig}\exp\left(-\frac{E_{A,Lig}}{RT}\right)[Lig][SO_2] = k_{Lig}(T)[Lig][SO_2] = \\ = A_{Lig,obs}\exp\left(-\frac{E_{A,Lig}}{RT}\right)[Lig] = k_{Lig,obs}(T)[Lig], \tag{18}$$

where A_{Lig} – pre-exponential factor for the bulk delignification rate constant, k_{Lig}, L mol^{-1} min^{-1}; $[SO_2]$ – SO_2 concentration in the fresh liquor, mol L^{-1}.

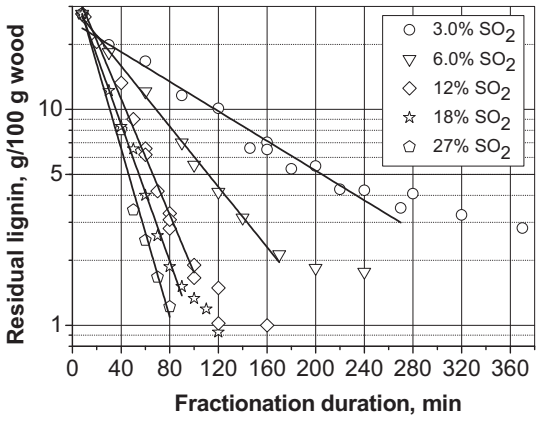

Figure 32. SO_2 concentration effect on delignification of spruce: decimal logarithm of residual lignin versus fractionation duration at 135°C.

However, when the SO_2 concentration is further increased to 18 and 27% the delignification rate increases at a slower rate. Lignin solubility cannot explain the phenomenon as the sulfonation rate also increases at a slower rate in this high SO_2 concentration region. Therefore a physicochemical explanation for a heterogeneous reaction system was considered in which the reactant (SO_2) first adsorbs on the active lignin site (α-carbon) before sulfonation takes place. The overall rate of such a process would be dependent on the amount of the available reaction sites and could be written according to the Langmuir-Hinschelwood concept as:

$$-\frac{d[Lig]}{dt} = \frac{k_{Lig}[Lig][SO_2]}{1 + a[SO_2]}, \tag{19}$$

where a – empirical constant.

By plotting the inverse of the observed delignification rate constant, $k_{Lig,obs}$, versus the inverse of SO_2 concentration (Figure 33) the value for a of 0.145 L mol^{-1} was obtained. Therefore the second term in the denominator, $a[SO_2]$, is equal to 0.06, 0.26 and 0.62 for SO_2 concentration of 3.0, 12 and 27%, respectively. Thus this Langmuir-Hinschelwood expression shows that at concentrations lower than 12% first order in SO_2 kinetics is followed while at higher than 12% the rate increases less than linearly with SO_2.

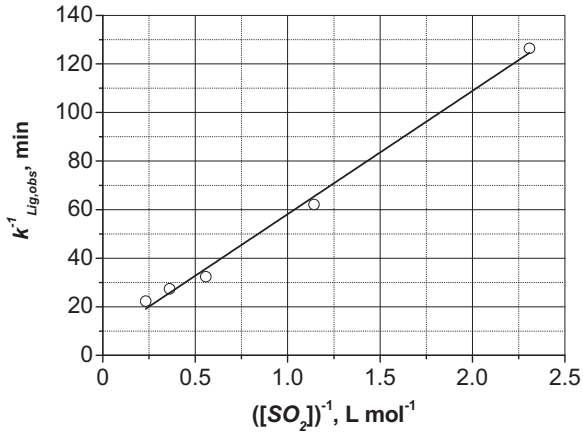

Figure 33. The inverse of the observed bulk delignification rate constant, $k_{Lig.obs}$, versus the inverse of SO_2 concentration (at 135°C).

It can be seen in Figure 32 that the end of the bulk delignification phase (and thus the beginning of residual delignification) occurs at higher lignin content when the SO_2 concentration decreases. This may be explained by more lignin condensation at the same amount of delignification when the SO_2 concentration is lower. This is supported by the observation that both the solid and liquid phases at 3.0% SO_2 have a considerably more intense brown colour than those produced at higher SO_2 concentrations. Also it can be seen that at 3.0% SO_2 it is not possible to reach a low lignin content of about 2 g/100 g original wood (which corresponds to a kappa number of about 25). The increase in the importance of condensation at lower SO_2 concentrations is understandable since condensation increases with increasing acidity and decreasing sulfonation, while delignification increases with increasing SO_2 concentration. Since the acidities are rather similar during the bulk delignification phase at the different SO_2 concentrations, it follows that the importance of condensation increases at lower SO_2 concentrations.

13.3.3 Comparison of the SEW and AS delignification kinetics (Paper V and unpublished)

According to Richards and van Heiningen (2004) the kinetics of AS delignification can be described by the following equation:

$$-\frac{d[Lig]}{dt} = k_0 \exp\left(-\frac{E_A}{RT}\right)[Lig][SO_2]_{free} = k_{Lig}[Lig][SO_2]_{free} = k_{Lig,obs}[Lig], \qquad (20)$$

where k_o = (4.0±0.8)×10⁹ L mol⁻¹ min⁻¹, E_A = 87.8 kJ mol⁻¹, $k_{obs} = k_{Lig,obs}[SO_2]_{free}$.

We applied this equation to SEW cooking. In Table 11 the values of k_{Lig} based on equation (20) and those experimentally obtained for SEW cooking are given. It is seen that the rate constant of SEW delignification, k_{Lig}, is very close to that of AS delignification at a particular free SO_2 concentration.

Table 11. Values of the delignification rate constant, k_{Lig}, calculated from Richards and van Heiningen (2004) and found experimentally for SEW cooking.

Temperature, °C	$[SO_2]$, %	Based on Richards and van Heiningen (2004), $k_{Lig}\times10^3$, L mol⁻¹ min⁻¹	Experimentally obtained for SEW cooking, $k_{Lig}\times10^3$, L mol⁻¹ min⁻¹
135	3	23±4	18.3±1.2
135	6		18.4±0.6
135	12		17.2±0.6
145	12	42±8	35.8±1.4
155	12	76±14	75±3

Further evidence that the SEW delignification rate is similar to that of AS cooking is obtained by comparison with data of Rydholm and Lagergren (1959) for spruce. The latter reports that for Ca acid sulfite cooking a pulp with kappa number of 30 was obtained at an H-factor of 86 (5.0% total SO_2, 0.96% combined SO_2), while for Na acid sulfite an H-factor 62 (5.7% total SO_2, 0.94% combined SO_2) was needed. For SEW pulp at 6.0% SO_2 a 30 kappa pulp is obtained at a similar H-factor of 53. In all cases an E_A of 107 kJ mol^{-1} was used for the H-factor calculation.

In AS pulping of beech to produce dissolving pulp with kappa number 25 an H-factor of 80 is needed (at total SO_2 0.76 mol L^{-1}, free SO_2 0.32 mol L^{-1}, L/W ratio 2.4 L kg^{-1}, cooking temperature 148°C, Sixta et al. 2006, p. 439, recalculated using E_A value of 107 kJ mol^{-1}), while in SEW fractionation (12% or 1.79 mol L^{-1} SO_2) of beech the same kappa is obtained at an H-factor of about 16. It can be seen that H_{SEW}/H_{AS} = $rate_{AS}/rate_{SEW}$ = Free $SO_{2\,AS}/SO_{2\,SEW}$, implying that the rate is proportional to the free SO_2 concentration.

Therefore the delignification rate constants seem to be similar for SEW and AS cooking at a particular free SO_2 concentration. This provides further confirmation that SO_2 is the sulfonating species. It also is indirect evidence that the bulk delignification rate constants are not affected by condensation.

14 Kinetics of polysaccharides removal

14.1 General aspects of polysaccharides removal (Papers I, III-V)

The carbohydrates are hydrolysed and removed from the solid phase at acidic SEW fractionation conditions. The carbohydrate retention is reported as a total solid residue yield or as lignin- and ash-free (LAFY) yield or a carbohydrate component yield. Information on delignification selectivity can be obtained by plotting the total solid residue yield versus kappa number, the practical measure of lignin content (Figure 34 for 12% SO_2 and 135°C; Figures 38 and 39 for 12% SO_2 and 125-165°C; Figure 45 for 3.0-27% SO_2 and 135°C). In order to explain the dissolution behaviour, the carbohydrate composition of the solid residues was followed in detail for spruce at 3.0-12% SO_2 and 135°C. Neutral carbohydrates were measured for spruce solid residues at 12% SO_2 and 135-165°C as well as for beech at 12% SO_2 and 135°C. In this section the general behaviour of polysaccharides in SEW fractionation will be described, while the effect of the different biomass species, temperature and SO_2 concentration on the hemicelluloses removal kinetics are treated separately in the subsequent sections.

Cellulose does not dissolve during SEW fractionation of spruce at all applied conditions. This is in agreement with the fact that cellulose is also mostly retained during

AS cooking (Sixta et al. 2006, p. 110). The cellulose content of all spruce SEW solid residues lies mostly between 40 and 42% on wood, and this range is caused by experimental error (according to Koch 2006, p. 23, the cellulose content of spruce is 41.7%). It is known that due to its crystallinity and high DP cellulose is hydrolysed 1-2 orders of magnitude slower than the model glycosides (Fengel and Wegener 1989). In case of beech cooking (12% SO_2, 135°C) the cellulose content drops from the initial value of 41.9% to 38.8% after 30 minutes cooking. This removal of cellulose may be explained by dissolution of low-molecular weight glucan (for instance, starch, Tunc and van Heiningen 2011). Also according to Patt et al. (2006), the cellulose content of beech is only 39.4%. The cellulose content does not change appreciably from 30 minutes to about 120 minutes cooking time. However, at high cooking durations (160 minutes at 135°C, 320 minutes at 125°C) it is obvious that cellulose losses occur with a low solid residue yield of about 36%.

Hemicelluloses removal during SEW fractionation takes place in two phases as can be observed from plots of the decimal logarithm of mannan and xylan versus time (Figures 36, 40, 41, 46, 47). During the first, relatively short, phase (called "initial" phase) about 50-75% of original mannose and xylose is removed from the solid phase (i.e. the non-linear region in the Figures), while during the second phase (called "bulk" phase) the removal is substantially slower and is first order in mannan and xylan (i.e. the linear region in the Figures). The lower removal rate of glucomannan and xylan during the second phase may be related to the morphology of this residual fraction. In effect this fraction consists of glucomannan closely associated with cellulose already in the original wood and that which is "crystallised" onto cellulose during the first phase. Also during the first phase most of the labile side units of the wood polysaccharides as well as pectins are removed (studied only for spruce).

The first-order behaviour during the second phase is consistent with S_{N1} acid hydrolysis, and the kinetics can be expressed by the modified equation (4):

$$-\frac{d[Hemi]}{dt} = k'_{Hemi}(T)[Hemi][H_3O^+] = k_{Hemi}(T)[Hemi], \qquad (21)$$

where [*Hemi*] – mannan and xylan content of the solid residue, % based on original feedstock; k'_{Hemi} and k_{Hemi} – real and composite rate constants for hemicelluloses removal.

The acidity of the fractionation system is unknown but is assumed to be constant during the fractionation (see section 12) and can be incorporated in the rate constant.

Galactoglucomannan loses 90% of its α-D-galactopyranose side units within about 30 minutes of fractionation at 135°C (3.0-12% SO_2) which is in agreement with the relatively high reactivity of the galactosidic bonds reported earlier for this polysaccharide

(Makkonen 1967b). A small amount of galactose (0.1-0.2% on wood) is found in the other solid residues by methanolysis/GC, which may represent compression wood galactan. The acetyl groups are cleaved somewhat slower from galactoglucomannan, but still about 90% of them are cleaved at the transition point between the two phases of hemicelluloses removal. About 3-5% of the original acetyl groups survive SEW fractionation at all applied conditions. This is in agreement with earlier reported behaviour of acetyl groups in acidic cooking (Sjöström 1981, p. 117). Based on the relative removal rates of mannose, galactose and acetyl groups it is obvious that the substituents are hydrolytically cleaved from the glucomannan remaining in the solid phase, although some acetyl groups could also be removed while still attached to dissolved glucomannan. No evidence of glucomannan becoming more glucosidic during cooking is found (contrary to Makkonen 1967a).

Arabinose side units are even faster removed from arabino-4-O-methylglucuronoxylan than galactose from galactoglucomannan because of the very high reactivity of the furanosidic bonds towards acid hydrolysis (Shafizadeh 1963). 70 and 100% of arabinose is dissolved during the heat-up period (i.e. 10 minutes) to 135 and 165°C (at 12% SO_2), respectively. This is similar to the arabinose behaviour in AS cooking (Sundman 1950). No arabinose remains in the solid phase after 15-30 minutes of cooking at 135-155°C. On the other hand the glucuronide bond between the xylan backbone and 4-O-Me-glucuronic acid is particularly strong as was reported earlier (Sjöström 1981, p. 42). 4-O-Methylglucuronic acid is detected in all solid residues. Glucuronic acid is detected neither in wood nor in any solid residue, indicating absence of demethylation of 4-O-MeGlcA in the solid phase. The ratio Xyl:4-O-MeGlcA equals to 8 in the original wood and gradually increases with increasing cooking duration towards ca. 13 (3.0% SO_2, 370 minutes; 6.0% SO_2, 240 minutes and 12% SO_2, 80 minutes). This is in agreement with the heterogeneous acid hydrolysis pattern of wood where the more soluble xylan fragments containing 4-O-methylglucuronic acid are preferentially dissolved, thereby increasing the ratio Xyl:4-O-MeGlcA in the xylan retaining in solid phase (Meier 1962, Janson and Sjöström 1964) even though the 4-O-methylglucuronide bond is exceptionally resistant towards acid hydrolysis.

The close relationship between the hemicelluloses removal and delignification in the first phase may be explained by their removal as LCCs. The comparatively high stability of glucomannan and 4-O-methylglucuronoxylan towards acid hydrolysis during the second phase could be explained by the fact that these fractions are not bound to lignin but closely associated with cellulose, either originally or with the association formed during the first phase. The occurrence of crystallisation of linear galactosyl-, arabinosyl- and acetyl-poor polymers onto the cellulose in the second phase has been reported in literature (Annergren and Rydholm 1959).

Finally, galacturonic acid and rhamnose coming from pectins (polyrhamnogalactouronides, Fengel and Wegener 1989) and as a dimer unit next to the reducing end of spruce xylan (Andersson et al. 1983) are efficiently dissolved during the first phase, and detected only in the solid residues cooked for 10-40 minutes (at 135°C).

14.2 Polysaccharides removal and delignification selectivity: different biomass species (Paper III)

The development of the solid residue yield during SEW fractionation of the 3 species at 12% SO_2 and 135°C is shown in Figures 34 and 35. Figure 35 shows that at constant kappa number the lignin- and ash-free yield (LAFY) is generally increasing in the order: straw < beech < spruce. However, the high ash content of the straw pulps leads to the highest conventionally measured yield for these pulps (Figure 34).

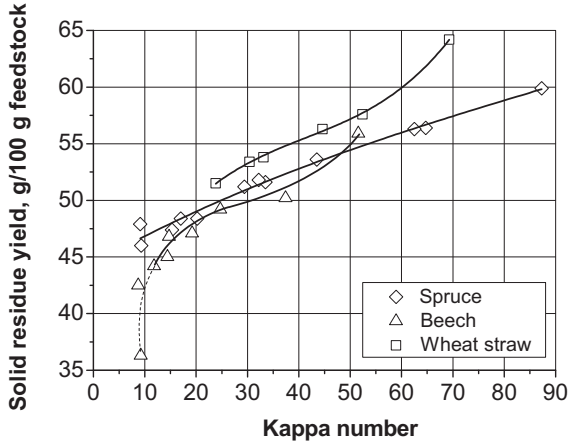

Figure 34. Polysaccharides removal from different species at 12% SO_2 and 135°C: solid residue yield versus kappa number.

The hemicellulose retention in spruce and beech as a function of cooking time is shown in Figure 36. Both species reach the transition between the first and second phases at about 40 minutes. It may be noted that beech glucomannan does not exhibit a higher removal rate in the first phase. The relative amount of xylan removed during the first phase for beech is higher than that for spruce (67 vs. 51%). Spruce loses 61% of glucomannan at the transition point. The rate constants for the hemicelluloses removal during the second phase are given in Table 12. The glucomannan removal rate is very similar for spruce and beech, while the xylan removal is faster for beech (11.6 vs. 6.91

min^{-1}). A possible explanation for the latter is the amount of stabilising 4-O-methylglucoronide side units in hardwood xylan being about halve of that of softwood xylan (Sjöström 1981, p. 61-63).

The delignification rate for beech is about 1.3 times higher than that for spruce at 135°C, which leads to lower differences in hemicellulose retention for spruce and beech at a particular lignin content (Figure 37).

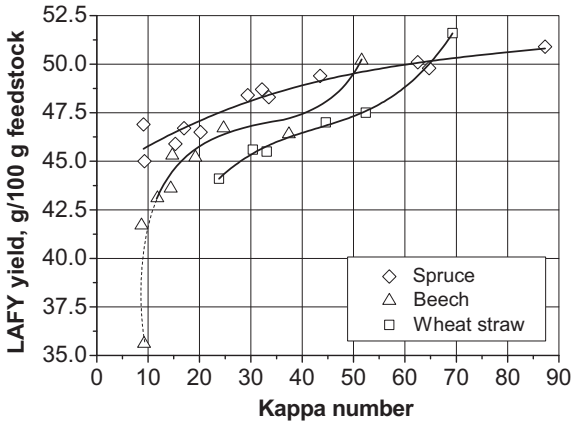

Figure 35. Polysaccharides removal from different species at 12% SO_2 and 135°C: lignin- and ash-free solid residue yield versus kappa number.

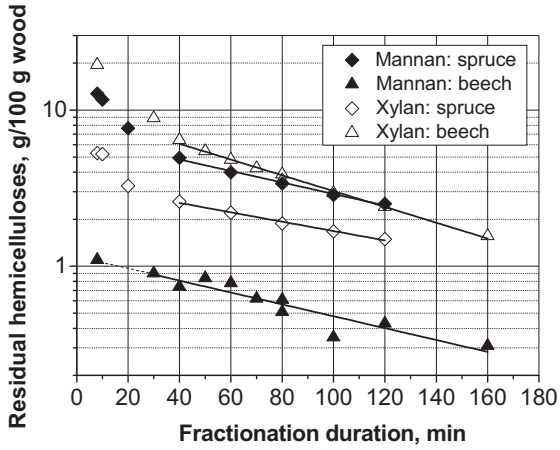

Figure 36. Polysaccharides removal from different species at 12% SO_2 and 135°C: residual hemicelluloses versus fractionation duration.

Table 12. Hemicelluloses removal kinetics.

[SO_2], %	Temperature, °C	Spruce		Beech	
		mannan	xylan	mannan	xylan
		$k_{Man}\times10^3$,	$k_{Xyl}\times10^3$,	$k_{Man}\times10^3$,	$k_{Xyl}\times10^3$,
		min^{-1}			
3.0	135	2.56	2.80	–	–
6.0		4.15	3.56	–	–
12		8.46	6.91	8.76	11.6
	145	16.4	12.7	–	–
	155	37.6	31.0	–	–
	165	72.9	60.7	–	–
$E_{A,Hemi}$, kJ mol^{-1}		108.4	110.1	–	–
A_{Hemi}, min^{-1}		6.07×10^{11}	8.09×10^{11}	–	–

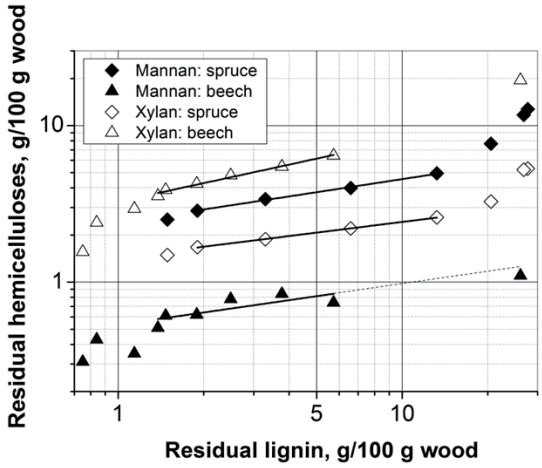

Figure 37. Polysaccharides removal from different species at 12% SO_2 and 135°C: residual hemicelluloses versus residual lignin.

Therefore, since the sum of glucomannan and 4-O-methylglucuronoxylan in spruce and beech wood is the same (21.2%), the somewhat lower beech solid residue yield can be explained by a higher xylan removal both during the first and second phases compared to the glucomannan and xylan removal for spruce. The substantially higher acetyl groups and uronic acid content of beech xylan cannot compensate for the higher xylan loss because they are also mostly removed. The higher relative xylan removal in beech compared to spruce was observed earlier for the Mg AS cooking (Sixta et al. 2006, p. 454).

The very steep yield loss observed for beech cooking at kappa number values lower than 10 (Figures 34 and 35) is related to the extremely slow residual delignification accompanied by dissolution of cellulose during this phase.

14.3 Temperature effect on polysaccharides removal and delignification selectivity (Papers I and III, unpublished)

The spruce solid residue yield is plotted versus kappa number at different temperatures in Figure 38. The yields of the spruce pulps found in the present experiments and reported by Primakov (at 15% SO_2, 50 w/w.% ethanol-water, Primakov 1961b) are almost identical at a particular lignin content. It can be seen that the yields (at levels of similar kappa numbers) are higher than those of kraft pulp (~ 46% for kappa number 30; Sixta et al. 2006, p. 289) as are the yields of softwood AS pulps. The reason for that is that glucomannan is known to be highly susceptible to alkaline peeling. In addition, the yields are somewhat lower than those in the AS process (Sixta et al. 2006, p. 110). The reasons for this will be discussed below.

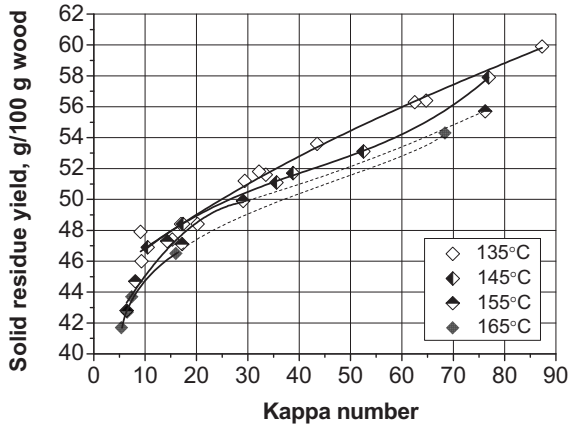

Figure 38. Temperature effect on polysaccharides removal from spruce at 12% SO_2: solid residue yield versus kappa number.

It is also clear from Figure 38 that the yield at constant kappa number decreases with increasing temperature. This trend was also observed for larch SEW cooking (15% SO_2, Primakov 1961a) as well as for common AS cooking.

The solid residue yield vs. kappa number plot for beech SEW fractionation at different temperatures is shown in Figure 39. The trend is less straightforward than that

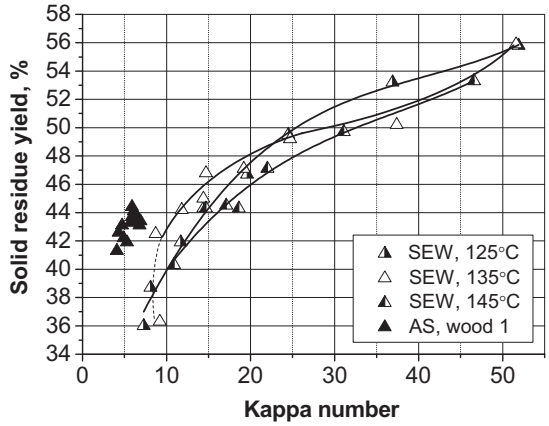

Figure 39. Temperature effect on polysaccharides removal from beech at 12% SO_2: solid residue yield versus kappa number (the conditions for Mg AS cooking: free SO_2 32 g L^{-1}, bound SO_2 25 g L^{-1}, L/W ratio 2.3 L kg^{-1}, maximum temperature 150°C, the data is provided by Professor Herbert Sixta).

of spruce, but it still shows that lower temperature leads to higher delignification selectivity. Also included in the Figure is data on industrial Mg AS cooking of beech (total SO_2 13% on wood, free SO_2 56% of the total, L/W ratio 2.3 L kg^{-1}, maximum temperature 150°C, the data is provided by Professor Herbert Sixta). It is obvious that the delignification selectivity during the residual phase at these selected conditions is poorer for SEW fractionation. The SEW yields are also lower compared to kraft at the same kappa number (50% for kappa number ~15; Sixta et al. 2006, p. 110) as are the yields of hardwood AS pulps. This is related to the fact that xylan is relatively stable against alkaline peeling, while it is quite labile to acid hydrolysis.

The reasons for the observed trends in delignification selectivity at different temperatures will be explained for spruce. In Figures 40 and 41 the xylan removal is plotted as decimal logarithm versus fractionation time. The two phases of hemicelluloses removal are clearly observed at each temperature. At higher temperatures the transition point occurs at lower cooking time and at lower residual hemicellulose content.

The rate constants for the hemicelluloses removal are given in Table 12. It is noted that at each temperature the ratio of the removal rates for glucomannan and xylan is constant, about 1.2, indicating the same temperature dependence for both. However, the opposite, i.e. xylan faster hydrolysed than glucomannan, is often observed in AS cooking (Rydholm 1965, p. 540, Sixta et al. 2006, p. 110). Also methyl-β-D-xylopyranoside is

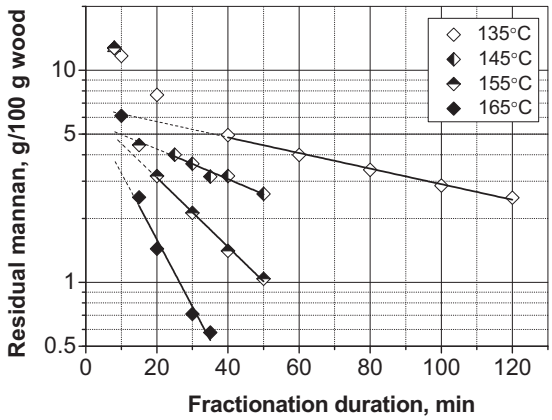

Figure 40. Temperature effect on polysaccharides removal from spruce at 12% SO_2: residual mannan versus fractionation duration.

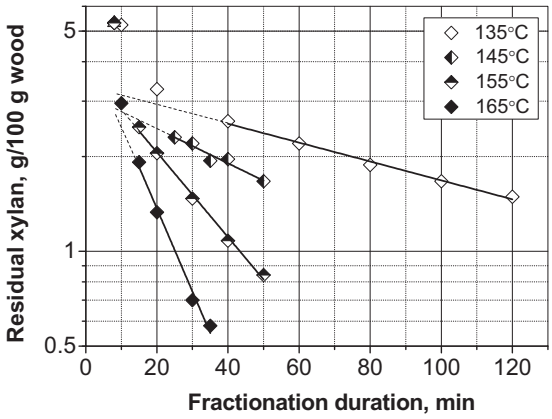

Figure 41. Temperature effect on polysaccharides removal from spruce at 12% SO_2: residual xylan versus fractionation duration.

hydrolysed 1.6 times faster than methyl-β-D-mannopyranoside (Feather and Harris 1965). However, a similar behaviour as seen in the present study was observed for spruce AS dissolving pulp (Sixta et al. 2006, p. 449). Primarily, this highlights that the hydrolysis rates of model compounds do not necessarily correspond to those of the related wood polysaccharides. The presence of 4-O-methylglucuronide side units

considerably stabilises wood xylan in both SEW and AS cooking. Regarding glucomannan it was shown that its retention is highly dependent on the conditions at the beginning of cooking. For instance, mild neutral or slightly alkaline treatment (in a two-stage sulfite cooking) leads to complete deacetylation and galactose units removal while the DP is not significantly reduced. The polymeric state of glucomannan (i.e. linear and long-chain) is said to be the most favourable for crystallisation onto cellulose fibrils and subsequent stabilisation against acid hydrolysis (Annergren and Rydholm 1959). In AS cooking the conditions in the beginning are milder due to long impregnation at low temperature compared to SEW cooking where the temperature is increased within 15 minutes to the cooking level. Therefore glucomannan stabilisation should decrease in the order: two stage sulfite > acid sulfite > SEW. On the other hand, it is said that crystallisation of xylan is hindered (Annergren and Rydholm 1959) by the presence of uronic acid side units, and for softwoods by a longer diffusion path since glucomannan is mostly associated with cellulose, while xylan is more associated with lignin (Salmen and Olsson 1998). The present results are consistent with these considerations.

By applying the Arrhenius equation (16), the activation energy values for mannan and xylan removal were obtained, 108 and 110 kJ mol^{-1}, respectively, with excellent correlation coefficients (Figure 42). These values are very close not only to each other but also to that for delignification, 107 kJ mol^{-1}. Nevertheless, the straight lines in Figures 40 and 4 1 do not intersect at the equivalent heat-up time (8 minutes) which otherwise

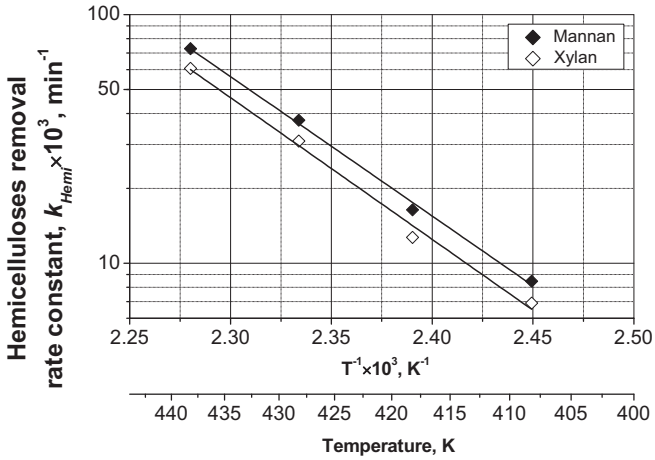

Figure 42. Temperature effect on polysaccharides removal from spruce at 12% SO_2: determination of activation energy.

would have resulted in a constant delignification selectivity at all temperatures. This is especially important for glucomannan removal (Figures 40), and leads to substantially different selectivities at different temperatures as shown in Figure 43. This phenomenon can be also related to the lower stabilisation degree of glucomannan at higher temperature. In case of xylan the difference in selectivity is smaller (Figure 44) as the

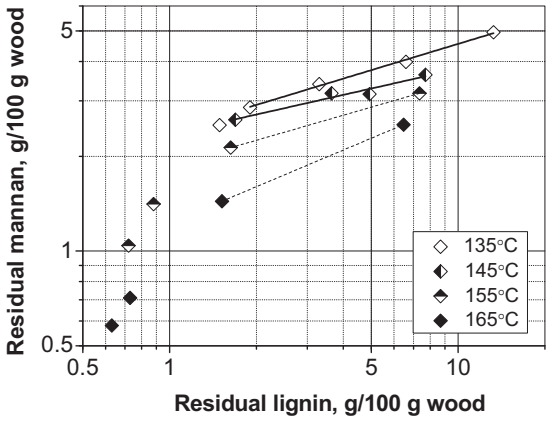

Figure 43. Temperature effect on polysaccharides removal from spruce at 12% SO_2: residual mannan versus residual lignin.

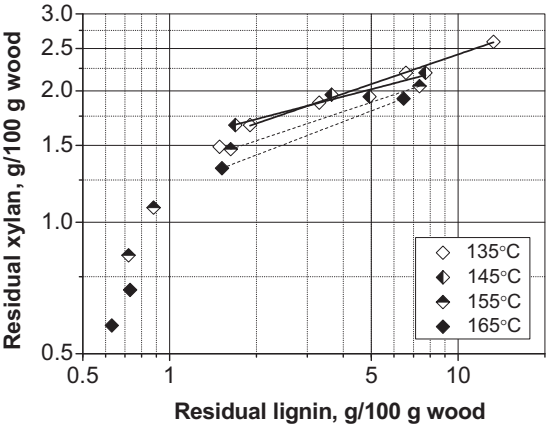

Figure 44. Temperature effect on polysaccharides removal from spruce at 12% SO_2: residual xylan versus residual lignin.

lines in Figure 41 approach each other closer at the equivalent heat-up time (8 minutes). Therefore, the delignification selectivity is better at lower temperatures mostly due to the fact that more glucomannan is preserved in the first removal phase.

This phenomenon was observed earlier for the spruce AS cooking (Rusten 1962) and was also explained by higher stabilisation of glucomannan at lower temperature due to better crystallisation on cellulose.

14.4 Effect of SO_2 concentration on polysaccharides removal and delignification selectivity (Paper V)

At a particular fractionation duration the solid residues produced at lower SO_2 concentrations have higher yields as well as higher lignin-free yields (LFY). The latter is due to higher hemicelluloses retention as cellulose is completely preserved in the solid residues. On the contrary, at a particular kappa number (Figure 45) an increasing SO_2 concentration leads to an increase in the solid residue yield due to higher hemicelluloses retention. The response of SEW delignification selectivity (with respect to hemicelluloses removal) to SO_2 concentration is similar to the response of AS delignification to free SO_2 concentration (Sixta et al. 2006, p. 461). Therefore the hemicelluloses content in the solid residue and thus also in the liquid phase may be altered by changing the SO_2 concentration.

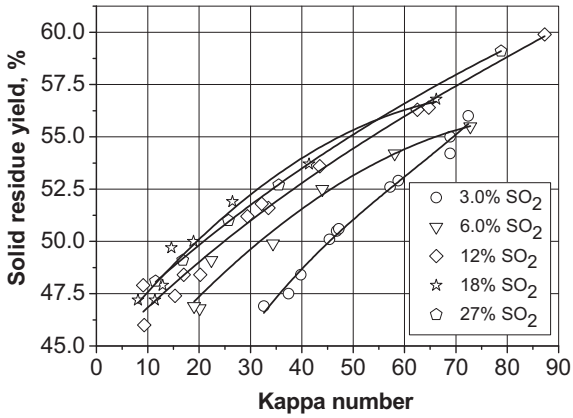

Figure 45. SO_2 concentration effect on polysaccharides removal from spruce at 135°C: solid residue yield versus kappa number.

Figures 46 and 47 show that the transition between the two phases of the glucomannan and xylan removal occurs at about 7-9% (on wood) residual lignin

corresponding to the fibre liberation point. It can be noted that the lower the SO_2 concentration in the original liquor, the longer is the first phase and the more of the hemicelluloses is removed in this phase.

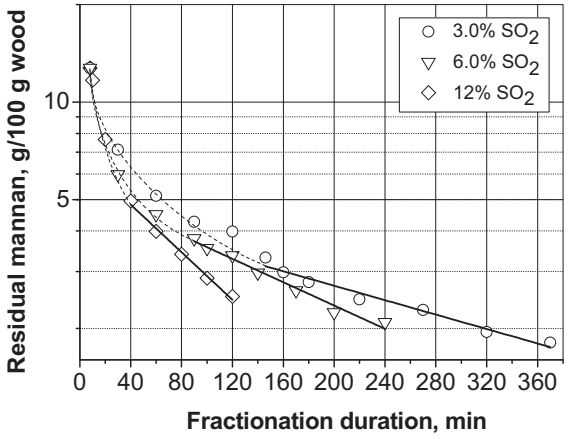

Figure 46. SO_2 concentration effect on polysaccharides removal from spruce at 135°C: residual mannan versus fractionation duration.

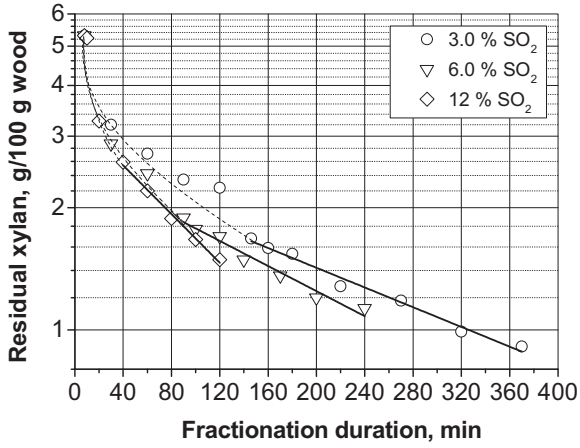

Figure 47. SO_2 concentration effect on polysaccharides removal from spruce at 135°C: residual xylan versus fractionation duration.

Although the rate constants for the second phase are substantially lower at lower SO_2 concentrations (k_{Hemi}, Table 12), more hemicelluloses are dissolved at the fibre-liberation point at lower SO_2 concentrations. Therefore, the overall effect of the SO_2 concentration on hemicellulose dissolution is smaller than that on delignification, and explains the appreciable difference in yield selectivity at different SO_2 concentrations as shown in Figure 45.

More insight in the fractionation process is obtained when the hemicellulose retention is plotted versus residual lignin content in Figure 48. In this case also two phases are observed but now both follow a linear behaviour with the slope being equal to the ratio of the rate constants $k_{Hemi}/k_{Lig,obs}$. During the initial stage (at residual lignin 27.7 to 16% on wood) the relative hemicellulose dissolution rate is obviously independent of SO_2 concentration. This may be interpreted that during this phase the hemicellulose removal is linked to delignification. Since delignification is first order in lignin from the very beginning of cooking up to the end of the bulk delignification, this suggests that delignification governs the first stage of hemicellulose dissolution whereby half or more of the mannan and xylan are dissolved. It also implies that the lignin-carbohydrate bonds are not yet cleaved substantially during this phase, and the dissolving lignin carries the hemicelluloses with it. On the other hand, the second phase of hemicellulose dissolution at a residual lignin lower than 16% on wood continues until the end of fractionation, and proceeds at lower rates relative to delignification at higher SO_2 concentrations.

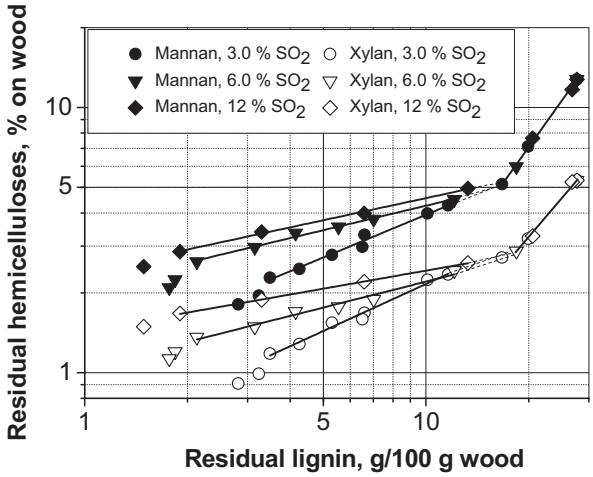

Figure 48. SO_2 concentration effect on polysaccharides removal from spruce at 135°C: residual hemicelluloses versus residual lignin.

Mannan is removed somewhat faster than xylan in the initial phase as well as during the second phase at 6.0 and 12% SO_2. It can be noted also that the ratio k_{Man}/k_{Xyl} for the second phase decreases with decreasing SO_2 concentration. The observed behaviour can be explained from the viewpoint of glucomannan stabilisation during cooking (see section 3.3.2). At lower SO_2 concentrations a part of mannan has a chance to remain longer in the fibre wall and might be protected by lignin from extensive acid hydrolysis in the same way as cellulose is protected, and thus can crystallise more efficiently.

15 Kinetics of cellulose hydrolysis

15.1 Cellulose degree of polymerisation by viscosimetry in CED

Although cellulose is mostly preserved in the solid residue, an extensive solvolytic cleavage of cellulose chains occurs. It has to be noted that cellulose degradation in SEW process correspond to the second stage of cellulose hydrolysis, i.e. hydrolysis of "normal" glycosidic bonds in amorphous regions (see section 3.3.3). A good measure of the extent of cellulose hydrolysis is intrinsic viscosity of the solid residues in CED.

It was noticed in the experiments with spruce that for kappa numbers higher than 35 the viscosity in CED is significantly reduced. The viscosity decreases possibly due to the fact that high amount of small lignin coils fill the voids between the cellulose chains in the CED solution. Therefore all solid residues with a kappa number higher than 35 were subjected to chlorite delignification prior to viscosity measurement. For the beech solid residue produced at 12% SO_2, 145°C and 30 minutes (kappa number 31.1) the intrinsic viscosity was measured both for the original and chlorite delignified solid residue and turned out to be the same in both cases (980 mL g^{-1}) which proves that chlorite delignification of SEW solid residues does not lead to degradation of cellulose, and that chlorite delignification is not needed for kappa numbers below 35.

It was also noticed that the intrinsic viscosity substantially decreases during storage of air-dried non-bleached spruce solid residues at room temperature (one year storage leads to about 30-40% decrease in intrinsic viscosity of the solid residues prepared at 3.0 and 6.0% SO_2). In the air-dried solid residues the amount of liquid is much lower than that in the solid phase during the fractionation (around 0.05 g water/g solid residue compared to the fibre saturation point of the pulps of about 1.4 g water/g solid residue). That means that the concentration of hydroxonium cations generated by lignosulfonic acids substantially increases upon drying and the high acidity promotes cellulose hydrolysis. Therefore the air-dried unbleached solid residues should not be stored for a long time prior to viscosity measurement.

In the following sections the intrinsic viscosity of the obtained solid residues is plotted versus kappa number (Figures 52, 53, 64) and versus solid residue yield (Figures 59, 60, 67). These plots are of practical importance and show the (cellulose/lignin degradation) selectivity of SEW fractionation at different conditions. However, since the intrinsic viscosity is a complex function of cellulose DP, cellulose and hemicelluloses content of the solid residues, a better measure of the degree of hydrolysis of cellulose is its DP calculated using the empirical equation (9).

15.2 Cellulose hydrolysis and delignification selectivity: different biomass species (Paper III)

Figure 49 shows that the intrinsic viscosity of spruce and beech solid residues are close at 135°C for kappa number values higher than 25, while at lower kappa numbers the viscosity of beech pulps drops faster.

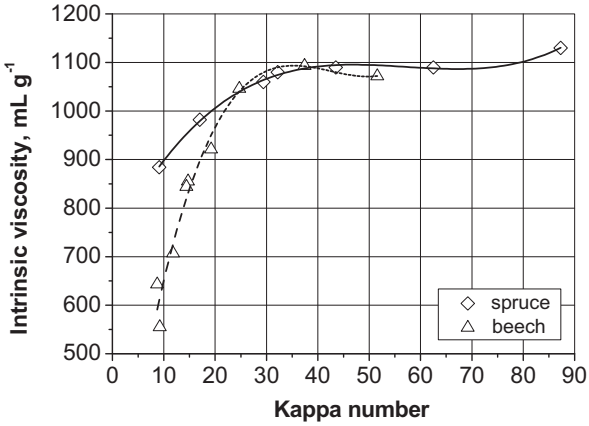

Figure 49. Cellulose hydrolysis of different species at 12% SO_2 and 135°C: solid residue intrinsic viscosity in CED versus kappa number.

The inverse of the cellulose DP was plotted versus cooking duration in Figure 50. It can be seen that the zero-order cellulose scission kinetics can be applied to the acid hydrolysis (equation 10). It is also seen that the lines intersect at a point close to the equivalent heat-up time and the DP_w of native cellulose in wood (about 10,000, Rydholm 1965, p. 108). From the slopes of the straight lines the reaction rate constants were calculated (Table 13). Their values for beech are 1.7-2.3 times higher than for spruce SEW fractionation (e.g. at 135°C the rate constant for beech is 3.28×10^{-6} min^{-1} and for spruce 1.45×10^{-6} min^{-1}; at 145°C – 7.62×10^{-6} min^{-1} for beech and 4.58×10^{-6} min^{-1} for

spruce). This may be explained by different accessibility to the amorphous cellulose regions of these two species.

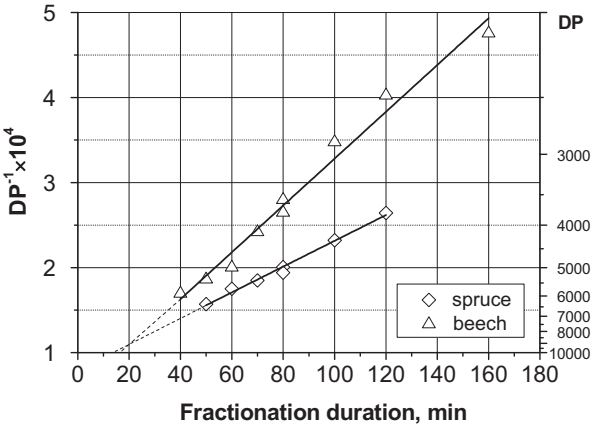

Figure 50. Cellulose hydrolysis of different species at 12% SO_2 and 135°C: inverse of DP versus kappa number.

Table 13. Cellulose hydrolysis kinetics.

[SO_2], %	Temperature, °C	spruce	beech
		k_{Cel}×10^6, min^{-1}	
12	125	–	1.04
3.0	135	1.10	–
6.0		1.29	–
12		1.51	2.75
18		1.79	–
12	145	4.76	7.80
	155	15.4	–
	165	41.2	–
$E_{A,Cel}$, kJ mol^{-1}		164.9	139.6
A_{Cel}, min^{-1}		1.91×10^{15}	2.10×10^{12}

The fact that beech cellulose appears to degrade faster than spruce cellulose, was reported earlier for Mg acid sulfite cooking (Sixta et al. 2006, p. 451-452): at an H-factor of 150 the intrinsic viscosity of beech pulp was about 600 mL g^{-1} (free SO_2 44 g L^{-1}, bound SO_2 23 g L^{-1}, L/W ratio 2.7 L kg^{-1}, 138°C), while that of the spruce pulp was about 1,100 mL g^{-1} (free SO_2 38 g L^{-1}, bound SO_2 30 g L^{-1}, L/W ratio 3.2 L kg^{-1}, 145°C). The lower rate of the spruce cellulose hydrolysis was explained by the higher lignin content of spruce.

Nonetheless, when 1/DP is plotted against decimal logarithm of lignin content (Figure 51) the differences in cellulose DP between beech and spruce are small within the bulk delignification due to the 1.3 times faster delignification for beech. On the other hand, the residual delignification is slower for beech than for spruce, and this fact together with the faster cellulose hydrolysis leads to very large differences in selectivity for these species during the residual delignification. Based on these results one can conclude that spruce is preferred over beech when SEW pulping is used for the production of dissolving pulp or specialty cellulose.

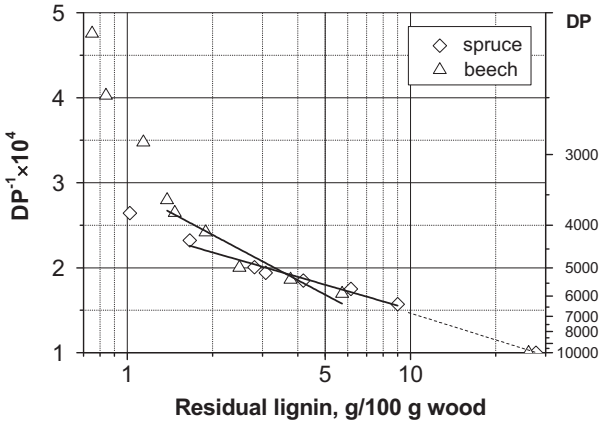

Figure 51. Cellulose hydrolysis of different species at 12% SO_2 and 135°C: inverse of DP versus lignin content.

15.3 Temperature effect on cellulose hydrolysis and delignification selectivity (Papers I and III)

The selectivity plot for spruce (Figure 52) and beech (Figure 53) at different temperatures shows that the intrinsic viscosity remains high down to kappa numbers of about 20-30, while at lower kappa number values it decreases steeply. For both spruce and beech the delignification selectivity is improved by decreasing temperature. Also the delignification selectivity is compared to the industrially established Mg AS of beech (Figure 53) and it can be seen that the selectivity of the SEW process is close to that of the AS process.

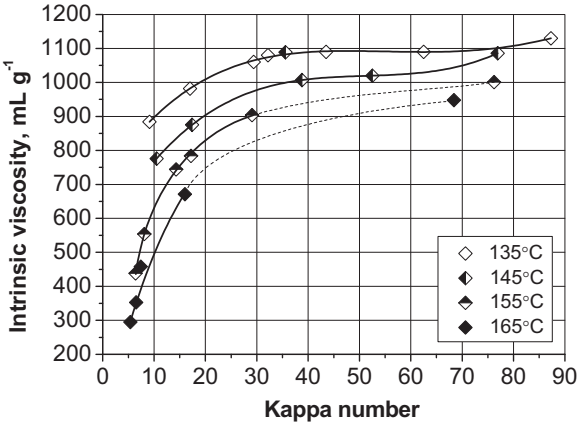

Figure 52. Temperature effect on hydrolysis of spruce cellulose at 12% SO_2: solid residue intrinsic viscosity in CED versus kappa number.

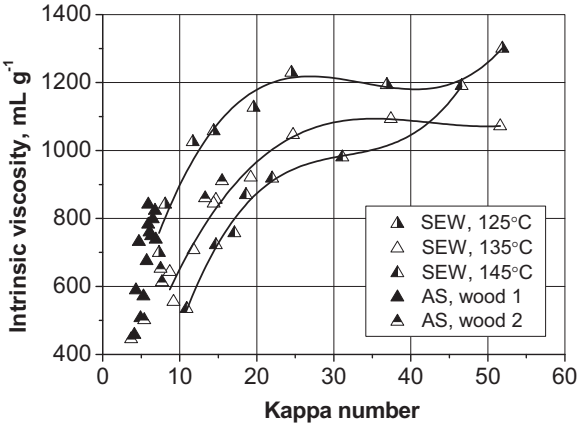

Figure 53. Temperature effect on hydrolysis of beech cellulose at 12% SO_2: solid residue intrinsic viscosity in CED versus kappa number (the conditions for Mg AS cooking: free SO_2 32 g L^{-1}, bound SO_2 25 g L^{-1}, L/W ratio 2.3 L kg^{-1}, maximum temperature 150°C, the data is provided by Professor Herbert Sixta).

The inverse of the cellulose DP versus cooking time are plotted for spruce and beech in Figures 54 and 55, respectively. The zero-order hydrolysis kinetics clearly applies at different temperatures for both species. The intersection of the lines also

corresponds to the DP_w of cellulose in native wood (around 10,000). The reaction rate constants were calculated from the slopes of the lines and are given in Table 13. It can be noted that in the case of beech cellulose hydrolysis at 125°C a certain delay period exists prior to steady-state cellulose hydrolysis which can be explained by the protective effect of lignin on cellulose hydrolysis during this initial phase (down to about 6% residual lignin on wood, corresponding to the fibre liberation point).

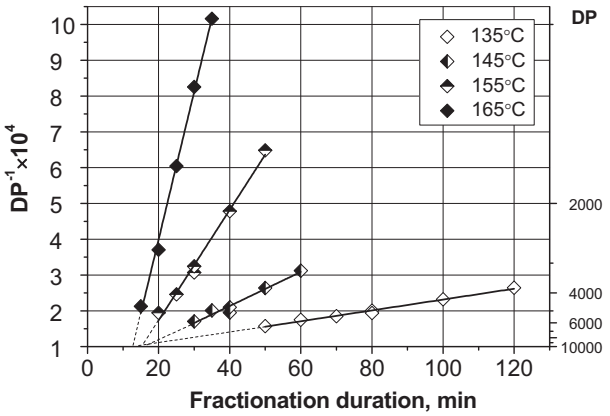

Figure 54. Temperature effect on hydrolysis of spruce cellulose at 12% SO_2: inverse of DP versus fractionation duration.

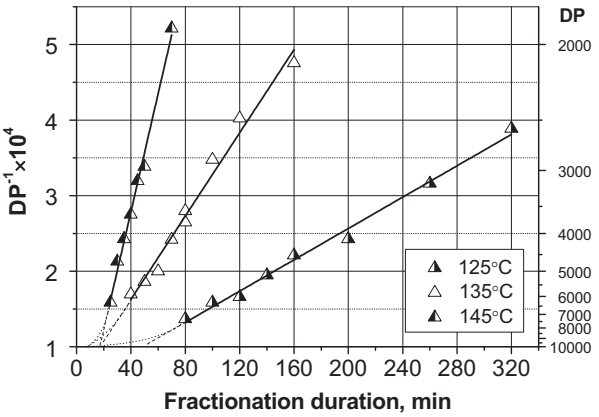

Figure 55. Temperature effect on hydrolysis of beech cellulose at 12% SO_2: inverse of DP versus fractionation duration.

Another observation is that spruce cellulose reaches a DP of about 1,000 at 165°C without any dissolution, while beech cellulose at a DP of 2,500 at 125°C suffers about 10% loss. This is possibly related to the different accessibility of cellulose in these species.

According to the Arrhenius equation (16), the activation energy of cellulose hydrolytic cleavage was calculated to be 166 and 135 kJ mol^{-1} for spruce and beech, respectively (Figure 56 and Table 13). The values are considerably different which is again likely related to different accessibility. Nevertheless, both values are higher than the activation energy values for spruce and beech delignification: 108 and 102 kJ mol^{-1}, respectively. This is in line with the observed temperature effect on selectivity (Figures 52 and 53). The activation energy value obtained for hydrolysis of Douglas fir cellulose by aqueous SO_2 at 0.75-5.6 w/w.% is 145 kJ mol^{-1} (Harris and Kline 1949).

The rates of cellulose hydrolysis relative to delignification are plotted for spruce and beech in Figures 57 and 58, respectively. The Figures further demonstrate the temperature effect on delignification selectivity.

The temperature dependence of SEW delignification selectivity with respect to cellulose hydrolysis is similar to that of AS delignification.

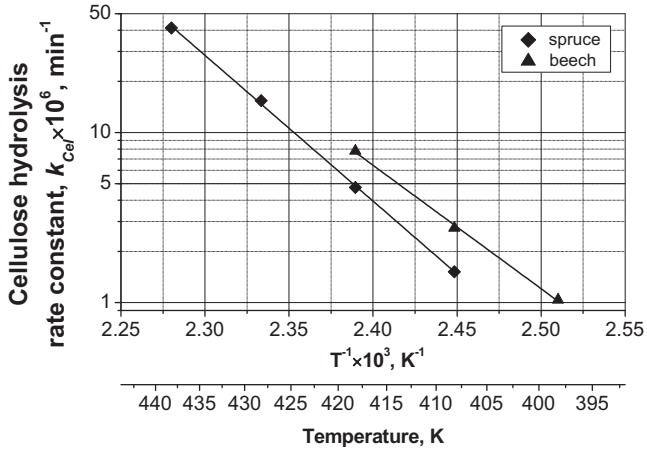

Figure 56. Temperature effect on cellulose hydrolysis at 12% SO_2: determination of activation energy.

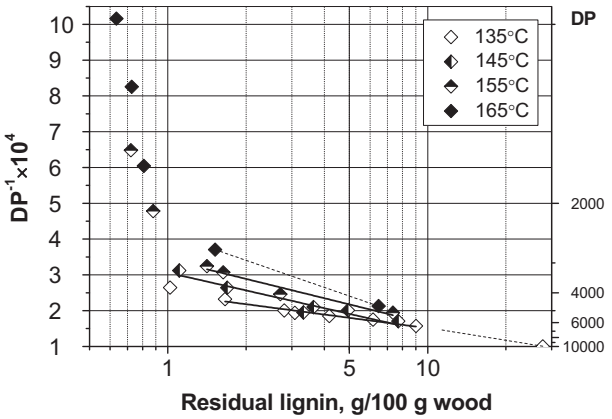

Figure 57. Temperature effect on hydrolysis of spruce cellulose at 12% SO_2: inverse of DP versus residual lignin.

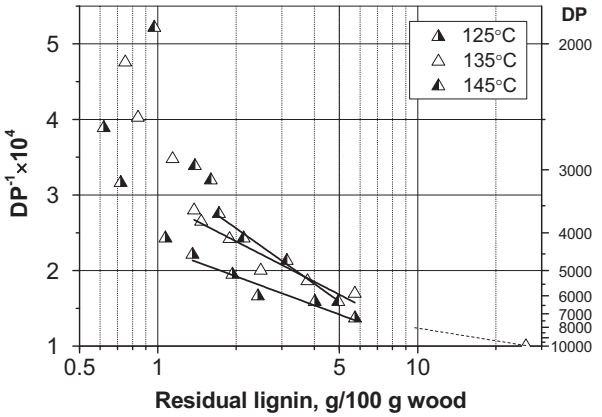

Figure 58. Temperature effect on hydrolysis of beech cellulose at 12% SO_2: inverse of DP versus residual lignin.

15.4 Temperature effect on cellulose hydrolysis-polysaccharides removal selectivity (Papers I and III)

Both cellulose and hemicelluloses hydrolysis is an acid-catalysed reaction following the same mechanism, so it is of interest to find out whether their relative rates are dependent on fractionation temperature.

Figures 59 and 60 show that at a particular yield a solid residue with mostly higher intrinsic viscosity is obtained at lower temperature both for spruce and beech. The trends are again compared to the Mg acid sulfite beech cooking on Figures 60 and 61. The behaviour is very close for SEW and AS cooking.

This phenomenon is further investigated for spruce by plotting 1/DP versus $\log_{10}([Man])$ (Figure 62) and $\log_{10}([Xyl])$ (Figure 63). The cellulose hydrolysis rate relative to glucomannan and xylan removal increases with increasing temperature as a consequence of the difference in E_A: 165 kJ mol^{-1} for cellulose hydrolysis versus 108 and 110 kJ mol^{-1} for glucomannan and xylan removal, respectively. Still since a larger amount of glucomannan is removed during the first phase (see Figure 40) at higher temperatures, the selectivity is somewhat reversed (Figure 62).

Therefore, at DP higher than 4,000 higher glucomannan retention is obtained at the same DP level which is in line with the AS cooking trend for spruce (Rusten 1962). The selectivity of glucomannan removal in the lower DP region (by extrapolation) as well as of xylan removal is the opposite and is in line with Sixta et al. 2006, p. 462-463.

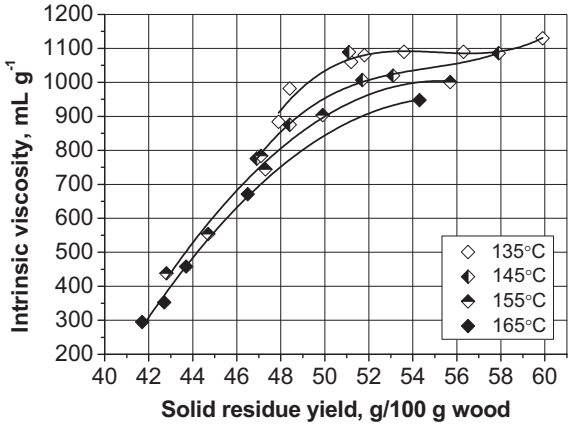

Figure 59. Temperature effect on the cellulose hydrolysis-polysaccharides removal selectivity for spruce at 12% SO_2: solid residue intrinsic viscosity in CED versus yield.

15.5 Effect of SO_2 concentration on cellulose hydrolysis and delignification selectivity (Paper V)

At a particular cooking duration the solid residues produced using lower SO_2 concentrations have higher intrinsic viscosity. However, when plotted versus kappa number (Figure 64) the trend is opposite: with decreasing SO_2 concentration the solid

Figure 60. Temperature effect on the cellulose hydrolysis-polysaccharides removal selectivity for beech at 12% SO_2: solid residue intrinsic viscosity in CED versus yield (the conditions for Mg AS cooking: free SO_2 32 g L^{-1}, bound SO_2 25 g L^{-1}, L/W ratio 2.3 L kg^{-1}, maximum temperature 150°C, the data is provided by Professor Herbert Sixta).

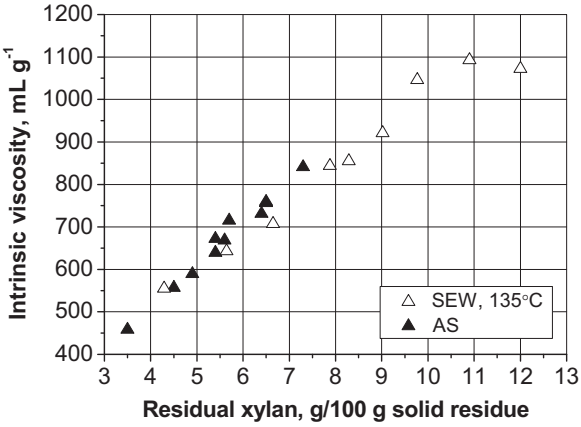

Figure 61. Cellulose hydrolysis-polysaccharides removal selectivity for beech at 12% SO_2 and 135°C: solid residue intrinsic viscosity in CED versus residual xylan (the conditions for Mg AS cooking: free SO_2 32 g L^{-1}, bound SO_2 25 g L^{-1}, L/W ratio 2.3 L kg^{-1}, maximum temperature 150°C, the data is provided by Professor Herbert Sixta).

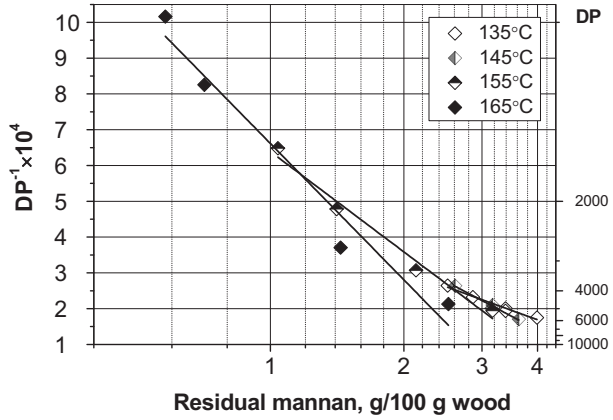

Figure 62. Temperature effect on the cellulose hydrolysis-polysaccharides removal selectivity for spruce at 12% SO_2: inverse of DP versus residual mannan.

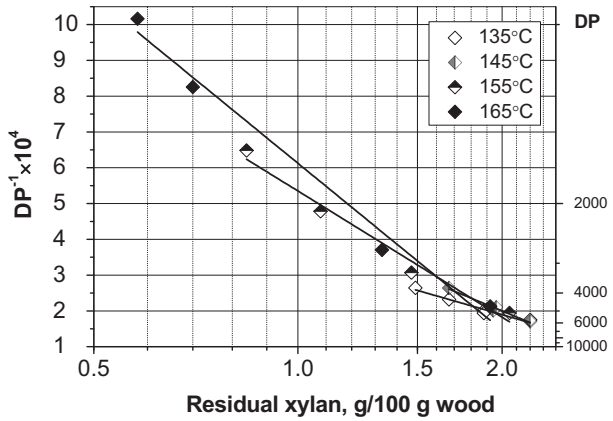

Figure 63. Temperature effect on the cellulose hydrolysis-polysaccharides removal selectivity for spruce at 12% SO_2: inverse of DP versus residual xylan.

residue viscosity drops substantially steeper. Thus the selectivity of delignification may be improved substantially by increasing the SO_2 concentration. This behaviour is similar to the selectivity response of AS delignification to the free SO_2 concentration (Sixta et al. 2006, p. 460).

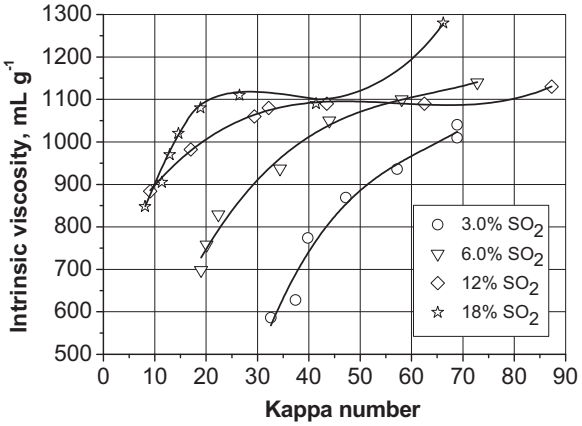

Figure 64. SO_2 concentration effect on hydrolysis of spruce cellulose at 135°C: solid residue intrinsic viscosity versus kappa number.

These trends in cellulose hydrolysis behaviour resemble those of hemicelluloses dissolution and are explained by the same facts: the acidity is similar at the different SO_2 concentrations while delignification increases nearly linearly with SO_2 concentration.

The plot of the inverse of DP versus fractionation duration is shown in Figure 65.

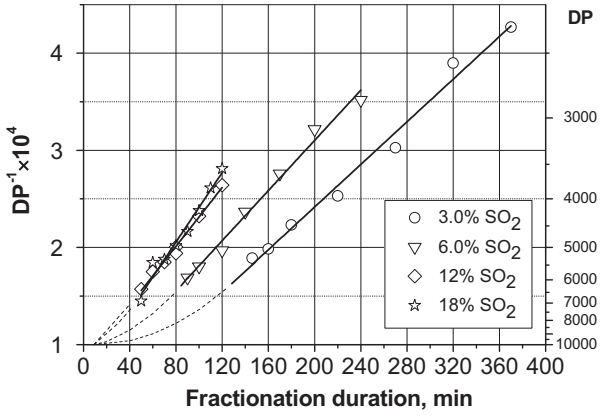

Figure 65. SO_2 concentration effect on hydrolysis of spruce cellulose at 135°C: inverse of DP versus fractionation duration.

At a particular initial SO_2 concentration the points again lie on a straight line which proves indirectly that the acidity of the solid phase does not change significantly after the fibre liberation point as discussed in section 12 and supported by the pH values measured for the liquid phases. Therefore the rate of cleavage of the cellulose chains should be proportional to the hydroxonium cations concentration as described by equation (10). Also, since the slopes of these lines (i.e. k_{Cel}, Table 13) increase only 50% when increasing the SO_2 concentration 6 times, it means that the acidities at different SO_2 concentrations are close.

The cellulose cleavage linear lines in Figure 65 corresponding to 12 and 18% SO_2 in the original liquor are almost identical and pass through the point (t = 9 minutes; DP = 10,000, Rydholm 1965, p. 108) corresponding to the cellulose DP of the original spruce wood and the equivalent heat-up time. At lower SO_2 concentrations on the other hand a certain delay period is seen prior to steady-state cellulose hydrolysis. To explain this phenomenon, the inverse of the cellulose DP is plotted in Figure 66 versus the decimal logarithm of the residual lignin. The increase in the slope at lower SO_2 concentrations corresponds to increased cellulose hydrolysis relative to delignification, i.e. diminished selectivity. It can be seen that the straight lines for the SO_2 concentrations of 3.0, 6.0 and 12 % cross at a residual lignin content of 7-8% on wood. Since the original wood contains 28% lignin, this may be interpreted that during the initial phase of delignification the lignin protects cellulose from hydrolytic attack, and the cellulose DP decreases at the same rate at all SO_2 concentrations until 7-8% on wood of residual lignin is left. Interestingly this lignin content corresponds to the fibre liberation point.

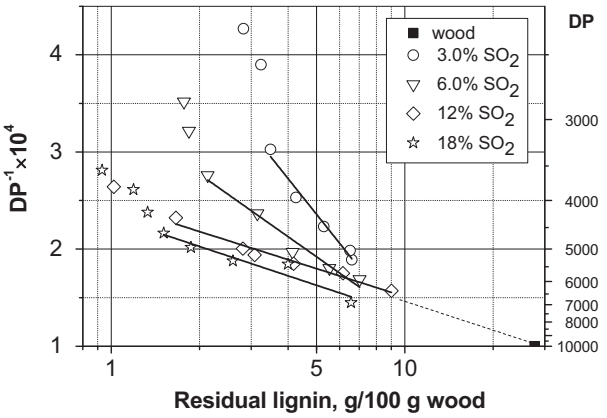

Figure 66. SO_2 concentration effect on hydrolysis of spruce cellulose at 135°C: inverse of DP versus residual lignin.

15.6 Effect of SO_2 concentration on cellulose hydrolysis-polysaccharides removal selectivity (Paper V)

In Figure 67 the viscosity of the solid residues is plotted versus yield. At lower SO_2 concentration the higher yield but lower viscosity is obtained. This graph is useful for practical purposes, rather than providing actual information about the hemicellulose removal-cellulose hydrolysis selectivity because the third component, i.e. lignin, is included in the yield. In fact, the lignin content is the major factor affecting the observed differences at different SO_2 concentrations in Figure 67. Figures 68-70 present the relationship between cellulose DP and the hemicellulose retention at different SO_2.

Since the development of cellulose DP and hemicellulose retention is more straightforward when plotted against lignin, rather than time, we will explain the observed behaviour in Figures 68-70 mostly based on the former trends. In the beginning of cooking (residual lignin 27.7-16% on wood, not shown on the Figures) the cellulose hydrolysis relative to hemicellulose removal is independent from the SO_2 concentration in the original liquor as follows from Figures 48 and 66. In the region of residual lignin of 16-7% on wood (also not shown on the Figures) cellulose hydrolysis still follows the lignin dissolution (Figure 66), while the hemicellulose removal rate relative to delignification is higher for the lower SO_2 concentrations (Figure 48). Therefore by the time when the fibre liberation point is passed (residual lignin 7-9% and cellulose DP about 6,000, Figures 68-70), hemicellulose retention is higher at higher SO_2. After the fibre liberation point, however, the reverse cellulose DP over time development is dependent only slightly on SO_2 (Figure 65) while hemicellulose retention over time is more affected by SO_2 (Figures 46, 47). Therefore at higher SO_2 the lines in Figures 68-70 have lower slope. The mannan removal changes more drastically with SO_2 than xylan removal possibly to the described stabilisation effect and this is reflected in Figures 68 and 70, where the selectivity at different SO_2 reverses at high cooking durations.

The influence of the liquor composition on the cellulose hydrolysis-hemicelluloses removal is not straightforward and would not be an important control factor which is similar to AS cooking (Sixta et al. 2006, p. 461-462). However, at higher SO_2 concentrations a somewhat lower mannan content is expected at constant DP lower than 4,000 (Figure 68).

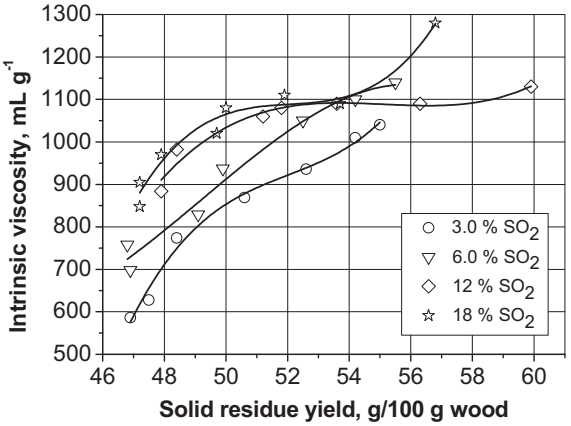

Figure 67. SO_2 concentration effect on cellulose hydrolysis-polysaccharides removal selectivity for spruce at 135°C: solid residue intrinsic viscosity versus kappa number.

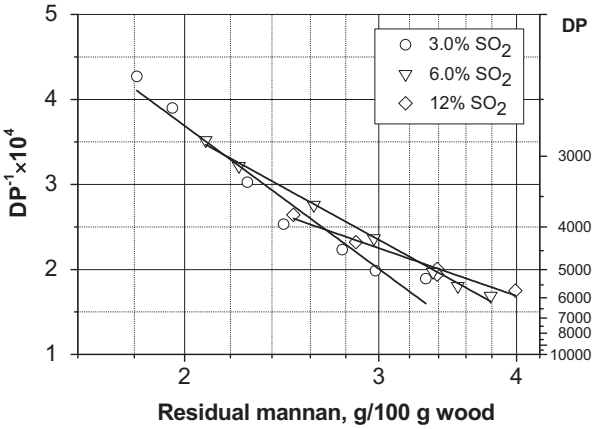

Figure 68. SO_2 concentration effect on cellulose hydrolysis-polysaccharides removal selectivity for spruce at 135°C: inverse of DP versus residual mannan.

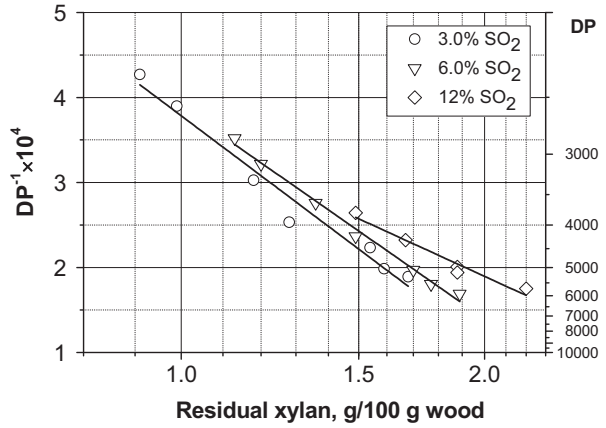

Figure 69. SO_2 concentration effect on cellulose hydrolysis-polysaccharides removal selectivity for spruce at 135°C: inverse of DP versus residual xylan.

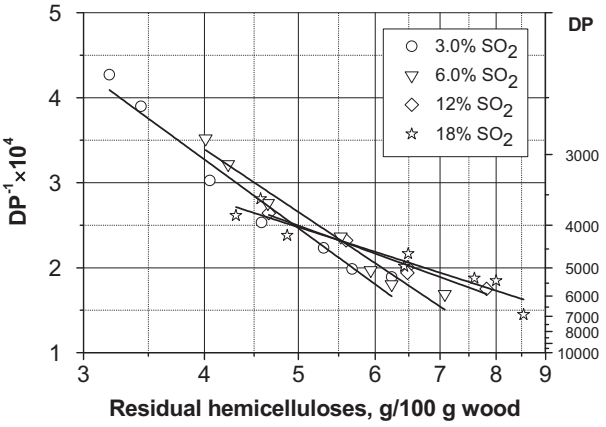

Figure 70. SO_2 concentration effect on cellulose hydrolysis-polysaccharides removal selectivity for spruce at 135°C: inverse of DP versus residual hemicelluloses.

16 Liquid phase composition and carbohydrate mass balance

16.1 Lignin content in the liquid phase by UV absorption (Paper II)

The UV spectra of diluted spent spruce SEW liquors (partly shown on Figure 71, curve *4*) are similar to typical lignin spectra (Sjöström and Haglund 1964): maximum at around 201 nm and exactly 280 nm, a shoulder at 220–235 nm, and a minimum around 260 nm. However, there are two other groups of compounds, besides lignin degradation products, which contribute significantly to the light absorbance of the spent SEW liquors – sulfur dioxide and aromatic products of carbohydrate dehydration (e.g. furfural and hydroxymethylfurfural). In order to measure the amount of lignin compounds using this method it is important to eliminate the interference from these other substances.

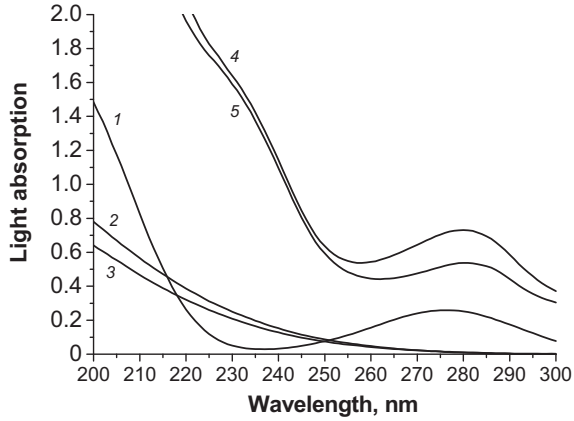

Figure 71. UV spectra (dilution with 3% H_2SO_4): *1* – 1250 times diluted fresh spruce SEW liquor (12 w/w.% SO_2); *2* – 2500 times diluted 30% hydrogen peroxide solution; *3* – the solution after mixing the fresh SEW liquor and the hydrogen peroxide solution (same dilutions as in *1* and *2*); *4* – spent SEW liquor (same composition and dilution as in *1,* 135°C, 80 minutes, kappa number 33.5); *5* – the solution after mixing the spent SEW liquor and the hydrogen peroxide solution (same dilutions as in *1* and *2*).

The light absorbance of sulfur dioxide is strong in the UV region (especially at short wavelengths) and can be observed in the spectrum of a fresh SEW liquor (12 w/w.% SO_2 in 55 v/v.% ethanol-water, diluted with 3% H_2SO_4, Figure 71, curve *1*). The same spectrum with an absorbance maximum at 276 nm was reported earlier for aqueous SO_2 solutions (Getman 1926). The maximum corresponds to the SO_2 solvates, while hydrosulfite anions absorption maximum is at 205-210 nm (Tsypkina et al. 1981). In the

present cooking experiments sulfur dioxide is charged at a very large excess, and thus is still present in the spent cooking liquors at concentrations close to the initial concentration. By comparing the curves *1* and *4* (Figure 71) it is evident that SO_2 contributes significantly to the absorption at 280 nm of the spent SEW liquor (135°C, 80 minutes, kappa number 33.5). Since the absorbance of SO_2 in solutions does not obey Beer's law (Getman 1926) it is best to convert SO_2 into a UV-transparent compound, for example by oxidation with hydrogen peroxide to sulfuric acid. After addition of a stoichiometric amount of hydrogen peroxide to a fresh SEW liquor, the absorbance of SO_2 at 280 nm disappears, indicating complete oxidation (Figure 71, curve *3*). Unfortunately, in the case of spent liquor the reduction in absorbance continues gradually after adding up to about 3 times the stoichiometric amount of H_2O_2 (Figure 71, curve *5*). However, at these conditions based on the difference between the lignin content in wood and that in pulps an average value of $\varepsilon_{280} = 19$ L g^{-1} cm^{-1} is obtained for lignin content estimation in spruce spent SEW liquors (dilution with 3% H_2SO_4, see Table 14). This value is comparable to that reported for lignosulfonates (17.5 L g^{-1} cm^{-1}, Sjöström and Haglund 1964).

Table 14. Calculation of the extinction coefficients (12% SO_2, 135°C).

Fractionation duration, min	Extinction coefficient value at 280 nm, L g^{-1} cm^{-1}	
	Dilution by 3% H_2SO_4, hydrogen peroxide applied	Dilution by 0.1M NaOH
10	30.1	32.9
20	16.4	18.2
40	17.3	19.9
60	18.3	21.9
80	18.6	22.6
100	20.0	23.2
120	19.5	23.2
Average (60–120 min)	19	23

However, a better way to avoid the interference of sulfur dioxide is to convert it to sulfite using alkali. Dilution of the fresh SEW liquor with 0.1M NaOH completely removes the interference from SO_2. Again the wavelength 280 nm was chosen, since hydroxide anions absorb greatly at 205 nm. The extinction coefficients for lignin at 280 nm were obtained (Table 14) averaged as 23 L g^{-1} cm^{-1}. The latter value is higher than 19 L g^{-1} cm^{-1} observed in 3% H_2SO_4 which is caused by ionisation of phenolic hydroxyls at higher pH (Zakis 1994). It should be emphasised that the same alkali concentration should be used to allow reliable lignin determination because the ionisation of phenolic structures is strongly dependent on pH. At alkali concentrations higher than 1M a strong increase in absorption is observed (Zakis 1994).

Furfural and hydroxymethylfurfural, belonging to the second group of the interfering compounds, have a significant light absorption in the UV region: the extinction coefficient is about 14,000 L mol^{-1} cm^{-1} at 280 nm (Chi et al. 2009). The highest amounts of these two substances in the liquid phases (see section 16.3) correspond to a 2% error in lignin determination (or less than 1% lignin based on wood) at 280 nm, i.e. within experimental error.

Nevertheless, at higher cooking temperatures and durations the concentrations of the furanic compounds may become problematic for the lignin determination. One way to avoid the influence of these compounds is to measure their concentrations using HPLC and to correct for their absorption at 280 nm. Another way is to convert them to other, UV-transparent, substances.

The removal of furfural may be accomplished by reduction with sodium borohydride in alkaline medium (0.1 M NaOH) as shown in Figure 72. Sodium borohydride reduces both furfural and sulfite anions (the evidence for the latter is the smell of H_2S and sulfur precipitation upon acidification). Our preliminary kinetics studies show that furfural reduction by sodium borohydride is a second-order reaction with a rate constant close to 250 L mol^{-1} min^{-1}. Thus for fast elimination of significant concentrations of furfural it is recommended to carry the reduction before dilution (details will be given below).

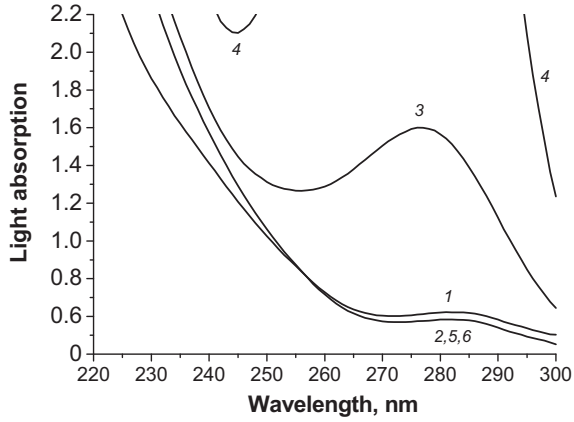

Figure 72. UV spectra of 1250 times diluted spent SEW liquors (12% SO_2, 135°C, 80 minutes) illustrating the removal of furfural interference by using sodium borohydride: *1* – the original liquor containing less than 1 μmol L^{-1} furfural, *2* – the liquor treated with sodium borohydride at 1.1 mmol L^{-1}; *3*, *4* – the liquors with addition of furfural at 70 (*3*) and 360 (*4*) μmol L^{-1}; *5*, *6* – the liquors with addition of furfural, i.e. *3* and *4*, after treatment with sodium borohydride at 1.1 mmol L^{-1}.

In the present SEW liquors with low furfural content it was found that the same decrease in the absorptivity is observed (around 6%) after addition of borohydride. This can be explained by the reduction of carbonyl groups in lignin (Zakis 1994).

Based on the kinetics of the furfural reduction, the range of absorptivities of the liquors, and the required alkalinity for $NaBH_4$ treatment, the following method for lignin determination is recommended irrespective of the level of furfural present in the SEW liquor. Take 500 μL liquor into 10 mL measuring flask and dilute with 0.1M NaOH (to neutralise the acid). Then transfer 400 μL to 25 mL measuring flask, add 100 μL of 10 g L^{-1} $NaBH_4$ in 0.1M NaOH and let react at least for 2 minutes. Then dilute to 25 mL with 0.1M NaOH and record the absorption at 280 nm (0.1M NaOH as a blank solution). Take in the account the decrease in absorptivity of lignin because of carbonyls reduction, i.e. use an extinction coefficient of 21 L g^{-1} cm^{-1}.

16.2 Comparison of the HPAEC-PAD and GC-FID methods for the analysis of total carbohydrates and monosaccharides content in the liquid phase (Paper IV)

Similar as was done for the hemicellulose content of the (residual) wood, the carbohydrate composition of the liquid phase obtained by the two analytical methods, GC and HPAEC are first compared to decide on the appropriate mass balance calculation. The amounts of total carbohydrates and monosaccharides in the liquid phase determined by the two methods are shown in Figures 73 and 74, respectively. Generally the values of total carbohydrates determined by the different methods shown in Figure 73 agree with each other mostly within 10% (relative) without any systematic difference. This relatively large error results mostly from the lower reproducibility of methanolysis/GC method estimated at 90%. However, an advantage of the methanolysis/GC method is that it allows determining uronic acids.

The relative differences between the amounts of monosaccharides shown in Figure 74 determined by the two analytical methods are larger than those in Figure 73, but again no systematic difference is found. The difference is again explained by the lower reproducibility of the GC method. The observed deficiencies in both total carbohydrates and monosaccharides analysis by GC is possibly explained by the instability of the standard alditol in the media applied. In case of monosaccharides analysis the HPAEC method is less time-consuming, but again the advantage of the GC method is that it allows determining the uronic acids, although it was not done for the present liquid samples.

It should be noted that monomeric ethylglycosides which could arise during the fractionation would not be determined by either method, but their amount would be

included in the total carbohydrate content of the liquid phase because now they would be hydrolysed/methanolysed as part of the methods.

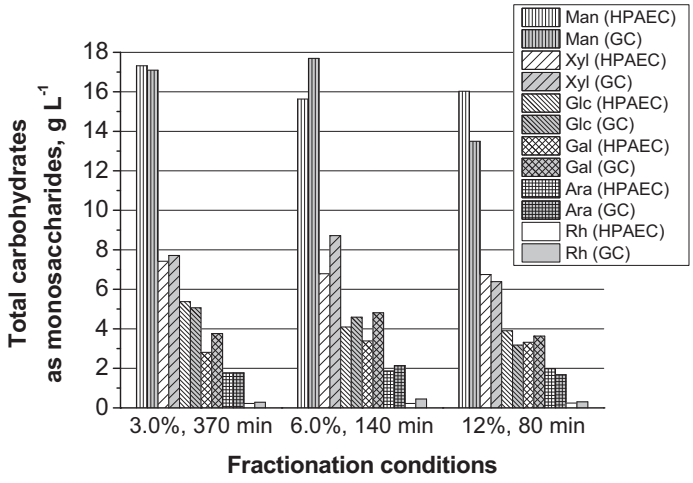

Figure 73. Comparative total carbohydrate composition of the liquid phases (at 3.0, 6.0 and 12% SO_2; 135°C) by the double stage acid hydrolysis/HPAEC and methanolysis/GC methods.

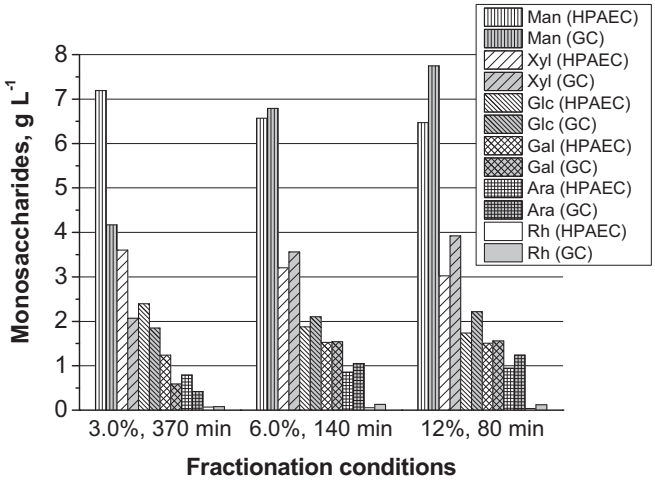

Figure 74. Comparative monosaccharide composition of the liquid phases (at 3.0, 6.0 and 12% SO_2; 135°C) by HPAEC and GC methods.

Overall for the analysis of neutral carbohydrates in the liquid phase, it is advisable to use the HPAEC technique primarily because of its higher reproducibility. The method was successfully applied in our laboratory for the total carbohydrate analysis of spruce (Sklavounos et al. 2011) and biomass (Yamamoto et al. 2011) SEW liquors. However, the methods allowing determination of uronic acids are scarce, and the GC method remains valuable for that purpose. In this work the latter method was used for both total and monomeric carbohydrates.

16.3 Carbohydrate mass balance (Paper IV)

Carbohydrates are extensively hydrolysed during the SEW cooking and high fraction of them is present in the fractionation liquid as monosaccharides. It is notable that the fraction of monosaccharides (based on total dissolved carbohydrates) is relatively constant when increasing cooking duration at a particular SO_2 concentration, but is dependent on the SO_2 concentration itself. At 3.0% SO_2 only 10-25% carbohydrates in the liquid phase exist as monosaccharides, while the amount of monosaccharides at 6.0% and 12% SO_2 are higher at 35-45% and 45-50%, respectively. The reasons for that are unknown. This can be partly related to the somewhat higher acidity of the liquid phases containing higher amounts of SO_2.

After analysis of the carbohydrate content of the residual wood and fractionation liquid samples it is now possible to establish carbohydrate total and component material balances, and determine whether carbohydrates are degraded during the SEW fractionation process (see Paper IV). The amount of carbohydrates in the liquid phase, determined as g monosaccharides L^{-1}, was recalculated on wood basis as g anhydrosaccharides/100 g wood, using an equation similar to (13). With this information the sum of the amount of each carbohydrate component in the liquid and residual wood is determined. By comparison of this sum with that present in the original wood it can be seen that none of the carbohydrates analysed, except perhaps galacturonic acid, seems to degrade during SEW fractionation (see Paper IV). No demethylation of 4-O-methylglucuronic acid is found in the liquid phase similarly to AS cooking (Larsson and Samuelson 1969). The total carbohydrate mass balance is also relatively closed (see Paper IV) confirming that no significant degradation of the carbohydrates occurs in the liquid phase, despite some variation in the results.

To verify the absence of carbohydrates losses their commonly known degradation products were also analysed: the dehydration products, furfural and HMF (see Paper IV) and oxidation products, aldonic acids. As can be seen the degradation of carbohydrates to the furanic compounds corresponds only to less than 0.6% on wood. The furanic compounds formation is dependent mostly on the duration of cooking, rather than on

the used SO_2 concentration, and therefore the highest amounts are found after durable cooking at 3% SO_2. The HMF amounts are lower than those of furfural, although the opposite would be expected for fractionation of a softwood. This may be explained by the instability of HMF which transforms into levulinic and formic acids (Girisuta et al. 2006). In the presence of ethanol HMF may also form ethoxymethylfurfural (Garves 1988). The amounts of dehydration products formed in SEW cooking are similar or lower than those in AS cooking (Sixta et al. 2006, p. 456).

The concentrations of each aldonic acid (mannonic, xylonic, arabinonic and galactonic) in the three selected liquid phases (3.0% SO_2, 370 minutes; 6.0% SO_2, 140 minutes; 12% SO_2, 80 minutes) are below 50 mg L^{-1} being the detection limit of the analytical technique. The number corresponds to less than 0.02% on wood which is strikingly low. The finding that neither dehydration to furanic compounds, nor oxidation to aldonic acids takes place to a significant effect during the SEW fractionation (contrary to AS pulping where 10 to 20% of the sugars are oxidised to aldonic acids, Sjöström 1981, p. 117) is perhaps one of the most significant results of the present study. Absence of dehydration can be explained by the relatively low fractionation temperature (135°C) and the acidity moderating effect of ethanol in the SEW process, while the absence of oxidation is related to the very low amounts of hydrosulfite anions due to the absence of a base. The concentration of hydrosulfite anions in the SEW fractionation liquid is roughly estimated to be about 10-40 mmol L^{-1} at 135°C (compared to 300 mmol L^{-1} for AS liquor, Sixta et al. 2006, p. 396, see section 12).

17 Effect of liquor-to-material ratio (unpublished)

The reduction of the liquor-to-wood ratio is most important for mill operation because of the energy and chemicals savings. In the present section the possibility to reduce the liquor-to-wood ratio below 6 L kg^{-1}, used in all other experiments, is briefly described.

Table 15 includes the properties of the solid and liquid phases obtained from the fractionation of spruce at liquor-to-wood ratio values of 6 to 1 L kg^{-1}. No difference in the fractionation rate and composition of the resulting streams is observed when decreasing the liquor-to-wood ratio to 3 L kg^{-1} indicating that the process is governed by SO_2 concentration in the liquid phase rather than by SO_2 charge. Further reduction in liquor-to-wood ratio leads to somewhat slower delignification due to SO_2 depletion and/or due to increase in the acidity because of higher lignosulfonic acid concentration. The carbohydrate retention in the solid phase is somewhat lower at lower L/W ratios, while their concentration in the liquid phase is practically constant. At a liquor-to-wood ratio of 1 L kg^{-1} delignification is significantly reduced possibly due to the pronounced

condensation favoured by high acidity and low SO_2 concentration. Dehydration reactions may be responsible for a somewhat lower carbohydrates yield in the liquid phase.

Table 15. Effect of liquor-to-wood ratio on spruce fractionation (12% SO_2, 80 minutes at 135°C).

Liquor-to-wood ratio, L kg^{-1}	6	3	2	1
SO_2 charge, % on wood	72	36	24	12
Solid residue yield, % on wood	51.5	50.0	49.8	55.4
Kappa number	33.5	34.8	44.7	n.d.
Lignin content, % on wood	3.14	3.12	3.94	9.01
LFY, % on wood	48.4	46.9	45.9	46.4
Liquid phase carbohydrates composition, g/100 g wood (as anhydrosaccharides)*				
Mannose	9.3	9.4	9.2	9.0
Xylose	4.0	4.0	4.0	3.7
Glucose	2.2	2.3	2.3	2.4
Total carbohydrates	20.5	20.6	20.4	19.5

n.d. – not defibrated solid residue; * the analysis was done in Åbo Akademi University with the help of Dr. Andrej Pranovich.

18 The mechanical strength and optical properties of spruce SEW pulp as compared to kraft pulp (Paper VI)

In this section the papermaking properties of SEW and kraft pulps of the same kappa number (about 40) are briefly compared (the yields are 53.3 and 49.3%, respectively).

The drainage resistance of the SEW pulp increases much faster during beating than that of the kraft pulp (Figure 75) indicating the lower cell-wall strength of the former. Density is also higher for the SEW pulp sheets than for kraft if plotted against number of beating revolutions (Figure 76), which indicates higher bonded area (RBA) for the SEW pulps (at the same beating energy). However, at constant drainability the density of the SEW pulp sheets is about the same as that of kraft pulp. Therefore, SEW pulp has higher beatability compared to kraft pulp.

Dry zero-span for the SEW pulp is about 150 N m g^{-1}, while for the kraft pulp it is close to 180 N m g^{-1}. Tear index of the SEW pulp is considerably lower than that of kraft pulp (Figure 77). Therefore, SEW pulp has clearly weaker fibres compared to kraft pulp.

Internal bond (Scott-bond) strength develops significantly quicker during beating for SEW pulp, while at constant sheet density Scott-bond strength is about the same for

both pulps. Therefore, SEW pulp has higher interfibre bonding at the same beating energy level, but it is similar to kraft pulp at the same sheet density.

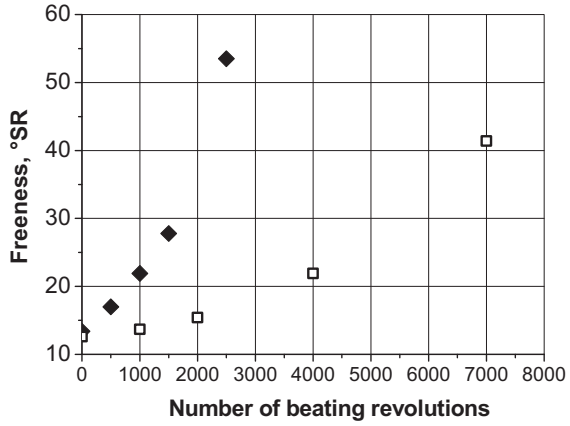

Figure 75. Freeness versus number of beating revolutions: ◆ – SEW; □ – kraft pulps.

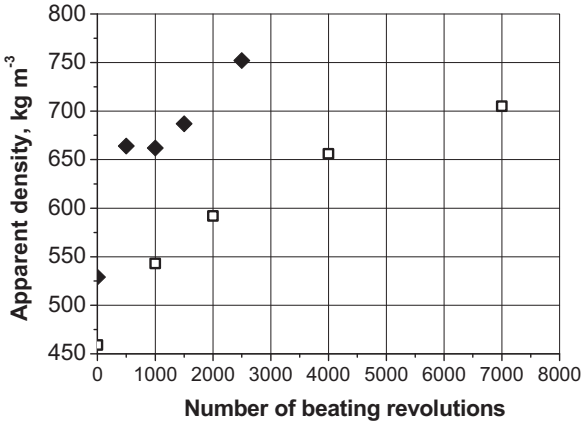

Figure 76. Apparent density versus number of beating revolutions: ◆ – SEW; □ – kraft pulps.

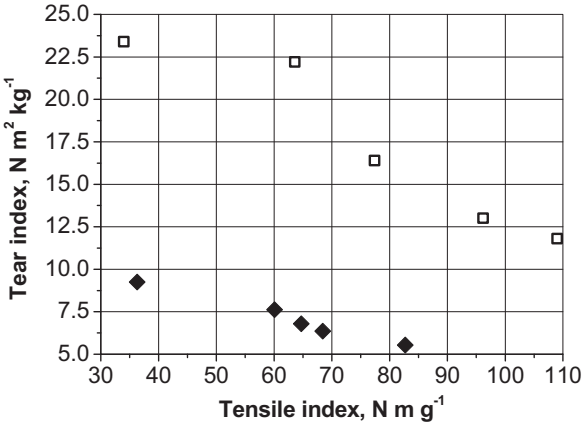

Figure 77. Tear index versus tensile index: ◆ – SEW; □ – kraft pulps.

The SEW and kraft pulp tensile index development follows the same curve if plotted versus beating duration but when it is plotted versus density, SEW pulp has poorer tensile index compared to kraft pulp (Figure 78).

The brightness of the unbeaten SEW pulp is about 47% while that of the kraft pulp is about 25%, indicating better optical properties of the former.

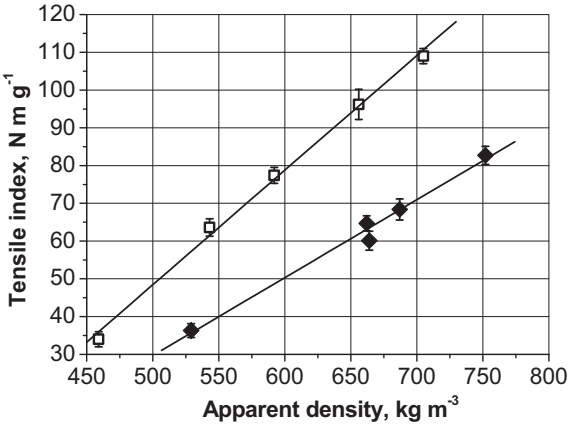

Figure 78. Tensile index versus apparent density: ◆ – SEW; □ – kraft pulps.

CONCLUSIONS

The SO_2-ethanol-water (SEW) process is shown to be an efficient fractionation method for all principal types of lignocellulosic biomass. The fractionation rate is similar for softwoods, hardwoods and annual plants which would allow production of relatively homogeneous product streams by simultaneous fractionation of different wood and agricultural biomass feedstocks. Furthermore the fractionation rate is affected neither by the raw material particle size in the range 1-8 mm, nor by its dry matter content in the range 49-93% due to very fast transport of ethanol-water solution into the cell wall governed by surface tension differences.

The kinetics of SEW delignification can be divided into 2 phases, fast bulk and slow residual. The former is first order in lignin and SO_2 with an activation energy of 107 and 102 kJ mol^{-1} for spruce and beech, respectively. The observed bulk delignification behaviour can be explained by Hägglund's consecutive sulfonation-hydrolysis scheme with the latter reaction being rate-determining. In addition lignin solubility might also play an important role. This is supported by the absence of a direct relationship between lignin sulfonation and dissolution. Lignin condensation is observed at lower SO_2 concentrations due to the lower sulfonation rate, while at 12% SO_2 and temperatures up to 165°C no apparent condensation is seen. However, condensation does not appear to affect the rate of SEW bulk delignification as the latter is similar to AS cooking at the same free SO_2 concentration. The rates of both bulk delignification and residual lignin sulfonation increase linearly from 3.0 to 12% SO_2, while at 18-27% SO_2 this increase slows down considerably possibly due to SO_2 adsorption saturation.

Hemicelluloses removal in SEW fractionation is largely similar to that in AS cooking and proceeds in 2 phases – fast initial and slow bulk dissolution. In the initial phase 50-70% of the hemicelluloses including practically all arabinose and galactose side units and most acetyl groups are removed from the solid phase. Removal of glucomannan and xylan backbone polymer chains during the first phase seems to be primarily dependent on lignin removal, and can be explained by their dissolution in the form of lignocarbohydrate complexes. In the second phase the remaining glucomannan and xylan are removed relatively slowly, which is possibly related to a morphological

effect, i.e. crystallisation onto cellulose, either already present in the wood and/or occurring during the initial fractionation phase. Glucomannan removal during the second phase is 1.2 times faster at 12% SO_2 compared to xylan removal contrary to both model compounds reactivity and general acid sulfite knowledge. This can be explained by stabilisation of xylan by the 4-O-methylglucuronic acid side chains (as in AS cooking) and by less glucomannan stabilisation due to absence of a mild impregnation stage in contrast with the AS process.

Spruce cellulose is completely retained in the solid phase, while beech cellulose tends to dissolve when treated for a long time even though its DP is not reduced as much as in the case of spruce. The cellulose hydrolysis also proceeds in 2 phases – slow initial (observed for spruce at 3.0 and 6.0% SO_2 and somewhat for beech at 125°C) and fast bulk hydrolysis. It is suggested that the lower rate of cellulose hydrolysis during the first phase is caused by barrier protection provided by lignocarbohydrate complexes.

The present results suggest that by changing the fractionation conditions (SO_2 concentration and temperature) the composition of both solid and liquid phases can be adjusted as required by product demands. Temperature and SO_2 concentration have a pronounced positive effect on the rate of all fractionation reactions; delignification, hemicelluloses removal, cellulose hydrolysis. The delignification selectivity can be improved by decreasing the temperature and increasing SO_2 concentration. The cellulose hydrolysis-hemicelluloses removal selectivity is less adjustable and straightforward in behaviour.

The carbohydrate reactions during SEW fractionation are limited mainly to useful hydrolysis reactions which proceed similarly to those of acid sulfite cooking. No wasteful carbohydrate side reactions such as dehydration and oxidation are observed during SEW fractionation. The absence of the latter is a particular advantage compared to AS pulping.

The SEW fractionation liquid at the present liquor-to-wood (L/W) ratio of 6 L kg^{-1} contains high concentrations of carbohydrates (35-40 g L^{-1}), with up to 50% of these carbohydrates in monomeric form. Evaporation of ethanol present at 55% in the fractionation liquid, combined with a more practical L/W ratio of about 3 L kg^{-1} would increase the carbohydrates concentration to well above 100 g L^{-1}. Such solution would represent a perfect feedstock for production of biofuels and bio-based chemicals.

The solid residues in the form of cellulosic fibres would be a prime feed stock for production of glucose by either acid or enzymatic hydrolysis, or could be directly used for pulp and paper products by selecting the appropriate fractionation conditions and lignocellulose feed properties.

The mechanical strength and optical properties of spruce SEW solid residues are similar to those of AS pulps. They beat easily implying lower beating energy consumption to achieve a certain density or fibre swelling level and lower investments

needed for beating equipment. They have excellent z-directional strength and good tensile strength but low tear strength. High brightness before bleaching is a clear advantage of the SEW solid residues which allows avoiding long bleaching sequences. One significant problem of SEW solid residues is their poor water removal properties which may lead to production capacity problems at fast and large paper and board machines. However, the water removal properties seem to be less crucial, for instance, in tissue production and small specialty paper machines. The high sheet density of SEW solid residues is an advantage in certain specialty papers like greaseproof and release paper. Because of the low fibre strength and low beating energy consumption, SEW solid residues could be suitable for nanocellulose production. In addition, increased fibre swelling (internal fibrillation) could also lead to easier breaking of loosened internal fibre wall structure into fibrils.

Another possible application of SEW solid residues is dissolving pulp production. It is shown that the intrinsic viscosity and yield/pentosan content development of SEW and commercial Mg AS cooking of beech are similar.

The amount of SO_2 covalently bound to lignin is about 2-3 times lower than in acid sulfite cooking which is explained by the low amount of hydrosulfite anions in the cooking liquor, and accounts for less than 0.2 and 1.1% sulfur on wood for the solid and liquid phase, respectively. No considerable oxidation to sulfate anions takes place either. It was shown that 95-97% of the charged SO_2 can be recovered from the fractionation liquid by distillation. The remaining 3-5%, being mostly bound to the dissolved lignin, may be sold as lignosulfonates or recovered as SO_2 after burning the spent liquor.

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